Field Emission
Scanning Probe Lithography
on Molecular Resist

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Abstract

Patterning at single digit nanoscale constitutes the main technological bottleneck in next generation fabrication of nanoelectronics (e.g. quantum based devices), nanophotonics, nanobiotechnology, nanomaterials and nano-electro-mechanical systems (NEMS). In order to overcome the limits of classic well established Gaussian electron beam lithography (EBL) a novel lithographic concept based on low energy electron exposure $< 100\ eV$ is explored in this research. In particular, a Fowler-Nordheim field emission process at the foremost front of a scanning proximal probe tip is utilized. This so-named field emission scanning probe lithography (FE-SPL) is applied for spatially confined exposure of molecular type resist materials.

In fact, the combination of:

1. **Active scanning probes**, which provide a closed loop lithographic functionality;

2. The direct application of **electron energies, which are close to the lithographic relevant excitation**, enabling an efficient and spatially confined exposure process in ambient conditions; and

3. **Molecular resist** materials, e.g. calixarene, which feature a well-defined monodisperse low molecular weight system,

provides a unique combination investigated hereinafter for nanolithographic purposes.

For the first time a comprehensive insight including all involved lithographic phenomena, processes and interactions is gained. Due to the different exposure conditions in FE-SPL, (i) low energy electron exposure features a higher sensitivity and resolution capability using this kind of low molecular weight resist system, (ii) proximity effects are effectively suppressed, and (iii) novel unique lithographic reaction schemes utilizing a direct ablation of resist are enabled. In consequence, as a function of exposure conditions, mask-less patterning in both tones, negative tone by crosslinking and positive tone by direct ablation, is demonstrated. Furthermore, the superposition of both interactions gives features in self-aligned fashion.

In this work the basic lithographically applicable phenomena are experimentally investigated as function of exposure parameters, conditions and molecular resist material systems. The experimental results are supported by respective simulations and exposure models. The combined effort has established the patterning of single features with $< 5\ nm$ line width, $8\ nm$ single dots and dense features with $7\ nm$ half-pitch (hp). Challenging aspects regarding the applicability, throughput issues and pattern transfer are investigated and solved by development of tailored methods and strategies. In this context, a novel complementary mix-and-match scheme was invented. In fact, FE-SPL provides promising novel capabilities reaching far beyond a simple down-scaled EBL system.
Zusammenfassung


Die unikale Eigenschaftskombination von:

1. aktiven Rastersonden, welche eine direkte Abbildungs-Rückkopplung erlauben;
2. die direkte Anwendung von Elektronen mit Energien nahe den lithographisch relevanten Anregungen, welche einen effizienteren und räumlich begrenzten Belichtungsprozess bei gleichzeitig normalen Umgebungsbedingungen ermöglichen; und
3. Molekulare (Glass)resistsysteme, z. Bsp. Calixarene, welche ein wohldefiniertes monodisperses System mit niedrigem Molekulargewicht darstellen,
bietet dabei neue vielversprechende Möglichkeiten, welche im Rahmen dieser Arbeit gezielt für eine Nanofabrikation erforscht wurden.

Im Rahmen dieser Arbeit ist erstmalig ein umfängliches Bild der komplex zusammenhängenden Wechselwirkungen und Reaktionen erarbeitet worden. Dabei sind die lithographisch nutzbaren Phänomene sowohl als Funktion der Belichtungsparameter, -bedingungen, und des Resistmaterials experimentell untersucht, als auch durch Modelle und Simulationen beschrieben worden. Als Folge der veränderten Belichtungsbedingungen in der Feldemissions-Rastersondenlithographie (FE-SPL) konnte erstmals gezeigt werden, dass (i) die Belichtung mit niederenergetischen Elektronen in diesen Resistsystemen eine höhere Sensitivität und Auflösung ermöglichen, (ii) Proximity-Effekte effektiv unterdrückt werden, und (iii) das neuartige lithographisch nutzbare Reaktionstypen, z. Bsp. in Form einer direkten Entfernung von Resistmaterial, auslösbar sind. Einstellbar über die Belichtungsbedingungen sind damit sowohl das maskenlose Schreiben im Negativ in Form einer Vernetzung als auch im positivem „Tone“ in Form einer ablavitiven Reaktion möglich. Darüber hinaus zeigt die experimentell beobachtete und modellbasiert-erklärte Überlagerung beider Reaktionstypen neuartige selbstausgerichtete Strukturformen, z. Bsp. in Form von Doppellinien- oder Domustrukturen.

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1 Towards a Single Nanometer Manufacturing Technology

Historically, advances in nanotechnology, which covers also the realization of visionary novel nanoelectronic device concepts, rely mainly on breakthrough developments in micro- and nanofabrication technologies. Within the last five decades most of the predictions made by Richard P. Feynman in his famous after-dinner talk, „There’s a plenty of room at the bottom: an invitation to enter a new field of physics“ in 1959 [1], have been fulfilled. However, despite immense worldwide research efforts, state-of-the-art as well as next generation technologies (NGL) are still struggling to reproducibly fabricate features at 20 nm and below. In this context, novel nanofabrication technologies, which are able to effectively address the single nanometer digit regime (< 10 nm), would provide the opportunity to transform quantum mechanical effects from currently parasitic side effects (occurring in conventional CMOS technology) into the fundamental mechanism of an upcoming beyond-CMOS technology era. Moreover, single-digit nanometer manufacturing (SNM) technology will enable the realization of concepts and visions beyond our current imagination.

1.1 Fabrication at Single-Digit Nano Scale: An Enabling Technology

Within the last five decades the continuous scaling down of silicon field-effect transistors (MOSFET’s) has been the driving force in the semiconductor industry. The long-term scaling trend, which turned into a „self-fulfilling prophecy”, was described first by Intel co-founder Gordon Moore. He predicted in 1965 that the number of transistors on a silicon chip would double every two years. This general trend has driven the entire industry’s main requirements for each new chip generation. The scaling as well as the economics behind it has produced the triumphal march of integrated circuits (ICs), ensuring that every new chip generation has increased performance at lower cost per transistor. Nowadays, ICs are part of our everyday life. The industry’s commitment to Moore’s Law has forced the development of novel technologies in order to sustain that trend. In this context, the industry moves to smaller gate lengths (critical dimension (CD) features) with each new chip generation. Although the demise of Moore’s Law has been predicted repeatedly over the last few decades, it is still valid in 2016. At present, the CD of MOSFET’s ranges from ∼ 35 – 45 nm, and it is expected that the CMOS technology can remain viable down to the 10 nm scale [2, 3]. Scaling below 10 nm introduces significant difficulties in controlling the device current. Moreover, the strong influence of parasitic quantum mechanical effects such as electron tunneling hampers the device performance dramatically. The ITRS forecast [4] assumes that the microelectronic industry is approaching the end of silicon planar CMOS technology scaling sometime in the near future and possibly not later than 2018 [5]. In the near-term, a transition from non-planar finFET (fin field-effect transistor) devices towards Si nanowire devices with fully-surrounding gates are most likely [5]. However, in the long-term, radically new concepts are required in order to extend Moore’s Law into the future. In such a kind of technological leap quantum mechanical effects
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are most likely taking over as the core of novel device concepts, e.g. in single electron [5, 6, 7, 8], quantum dot [5] or spin-based devices [9]. Here, quantum effects such as quantized excitations, Coulomb blockade, single electron tunneling, electron spin effects, etc., are utilized in a well-defined way. Since only single electrons are applied for processing operations the technology is much more efficient and significantly faster. These devices, unlike classical transistors, inherently tend to improve in performance with reduction in size [2, 5]. Thus, as present CMOS devices approach technological and physical limits at the sub-10 nm scale, a ‘beyond-CMOS’ information-processing technology paradigm shift is expected. The most promising concepts therefore are evaluated in the „Emerging Research Devices (ERD)” section of the „Technology Roadmap for Nanoelectronics” [4].

Returning to the status quo, we are not limited in knowledge or visions for beyond-CMOS devices. In point of fact we are limited in fabrication of the required single-digit nano features. State-of-the-art fabrication technologies are faced with immense technological and economical challenges when proceeding to single nanometer dimensions. Currently, especially the capabilities of lithographic technologies (1.2) are by far not meeting the requirements with respect to resolution, alignment accuracy as well as critical dimension and process control, which are essentially required for a single nanometer manufacturing rise. In this context, despite the fact that the theory behind single electron transistors (SET) has been well known since the late 80’s [6, 7], the lack of adequate manufacturing methods has hampered the reproducible fabrication of room-temperature operational SET so far. Thus, a successful quantum-effect based on the beyond-CMOS paradigm shift essentially requires new lithographic as well as pattern transfer technologies embodying sub-10 nm feature size control and placement capabilities. To face the associated challenges, several research projects are currently underway, e.g. the large scale EU-project „single nanometer manufacturing for beyond CMOS devices (SNM)”, which was initiated by us in 2012 (ref. 1.4, [10]), or the $3 billion „7 nm and beyond” project of IBM [11].

In summary, the capability of a lithographic technology achieving single nanometer scale control [12] is opening entirely new horizons in nanodevice fabrication. Thereby, the development of respective nanofabrication technologies incorporating lithography and pattern transfer constitutes one of the main enablers for a range of ground-breaking and innovative device concepts within nanoelectronics, NEMS, nanophotonics and bio-nanotechnology.

1.2 Next Generation Lithography - Technological Breakthroughs required

The simplicity and high throughput capability of photolithographic techniques have paved the route of semiconductor manufacturing to its status quo as the most significant global technological development of the 20th century. Photolithography is not only the core technology in manufacturing, but also the most delicate and expensive process in semiconductor fabs. In particular, lithography is responsible for more than 35% of total chip manufacturing costs [13, 14].

In photolithography, photons are applied for transfer of geometric patterns from a photomask to a photosensitive thin film, called photoresist. This film is typically spin-coated on top of a substrate surface. As a result of the photon-triggered chemical reaction within the resist film the solubility is changed and rendered visible by a subsequent wet development step. Fundamental limitations exist due to the wave-nature of light, described by optical diffraction and interference effects. With every new chip generation (manufacturing node) immense efforts have been undertaken in order to push the resolution to consistently smaller feature sizes. Based on Rayleigh’s criteria, which defines the minimum
printable feature size ($MFS$) in projection lithography [14]:

$$MFS = \frac{k_1 \lambda}{NA}$$ (1.1)

with $\lambda$ the exposure wavelength, $NA$ the numerical aperture of the projection system and $k_1$ the technological value ($0.5 - 0.8$), the technology is progressing gradually towards lower exposure wavelength and increased numerical aperture of the exposure system. Linked with is that the depth of focus ($DoF$), described by:

$$DoF = \frac{k_2 \lambda}{(NA)^2}$$ (1.2)

is decreased. This has initiated the development of thinner resist films and chemical mechanical planarization (CMP) methods. In addition, a variety of tricky resolution enhancement methods like off-axis illumination, immersion lithography, phase-shift masks, optical proximity correction, etc. [15], have been developed in order to boost photolithography beyond diffraction limits. Nowadays, state-of-the-art lithography in semiconductor manufacturing is carried out by projection steppers, exposure wavelengths of $\lambda = 193$ nm (ArF laser source) and water immersion featuring $NA = 1.35$ [4]. The minimum feature size in single exposure is limited to $MFS = 40$ nm, defined as half-pitch (hp) [4]. By using self-aligned double patterning (SADP) [16, 17], combined with complementary lithographic techniques (ref. 6.2 and [14, 18]), smaller feature sizes than 40 nm are already in the production launch phase. Thus, by multiple patterning the shift towards smaller exposure wavelengths has been postponed.

However, with every progressive node increased efforts are required. In addition to resolution, the requirements concerning process control for critical dimensions (CD) and line edge/width roughness (LER/LWR) are getting tightened. For example, the international roadmap (ITRS, [4]) defines for the targeted 8 nm hp microprocessor gate level a CD control of 0.8 nm 3 sigma. Taking into account a multi-level lithography, an overlay registration and alignment capability of 1.9 nm (3 sigma) is demanded [4]. Beyond technological obstacles the upcoming technology must be economically viable in terms of throughput and cost. In case this is not within reach further scaling will be discontinued. Unfortunately, a trade-off between resolution, process control and throughput, valid for all common lithographic techniques (ref. section 2.3.1), is a given. Further on, practical applicability in terms of pattern transfer capability by standard methods, e.g. by plasma etching or metal lift-off, has to be established. For example, single atom-by-atom manipulation has already been demonstrated more than 25 years ago [19], but till today no applications have been developed. In summary, the next generation of lithographic methods has to be evaluated against those key points in order to lead successfully towards a sub-10 nm nanofabrication technology.

In general, the technological and economical limits of optical photolithography seem to be within reach. As stated by the ITRS, version 2013 [4]: „difficult challenges are ahead”. For near term nodes, multiple patterning (MP) and extreme ultraviolet lithography (EUVL: $\lambda = 13.5$ nm) seem to be the most promising candidates being followed by industry. However, their deployment is associated with the question of whether the remaining challenges regarding overlay, CD control and cycle times in case of MP as well as the source power, resist performance and mask infrastructure in case of EUVL can be solved in an economically meaningful way. Nevertheless, the cost for exposure tools itself continues to escalate, for example $0.25$ million in 1970 [20] compared to $50$ million for an EUVL system today [21]. Thus, also economics (ref.: [22, 23]) and the immense initial costs will prevent EUVL from getting widespread use apart from high volume manufacturing (HVM). Vast challenges are also remaining in directed self-assembly (DSA) and nanoimprint lithography (NIL) methods, mainly determined by their vulnerability to defects and the lack of sufficient process control (ref. [4]).

Also mask-less writing methods, which are applied for mask/template fabrication, research purposes as
well as for low-volume manufacturing, have to meet the tougher requirements of upcoming nodes. Since invention of the first direct write electron beam lithography (EBL) system in 1960 by Moellenstedt and Speidel [24], EBL has evolved to become the most common technique for mask-less patterning. Here, a focused beam of high energy electrons (10 – 200 keV) is applied to initiate lithographic applicable reactions within a resist film (ref. section 2.2). Typically, these triggered alterations of the solubility are utilized. Thus, in a subsequent wet development step the soluble resist parts are removed selectively, whereas the insoluble parts of the pattern remain on the substrate (ref. section 2.3). Nowadays, modern EBL systems allow for beam spot sizes of \( \lesssim 1 \text{nm} \). However, the minimum feature size achievable is typically 10 – 50 times larger. So far, the spatial resolution of EBL is rather limited by proximity effects, which leads through scattering events to deposition of energy far beyond the initial impact point (ref. 2.2). Furthermore, space charging effects cause a beam blur at higher currents [25, 26, 27, 28]. Besides, a multitude of other effects limit resolution in EBL and leads to problems of process control, for example resist issues (baking, nature of polymeric resist), development-related problems (resist swelling, adhesion, capillary collapse) as well as the RLS trade-off (ref. section 2.3).

Thus, sub-10 nm isolated and sub-20 nm dense patterning by EBL become a major stumbling block. To avoid these problems, process changes may be applied but these changes would not be feasible for production applications (discussed in section 2.2). Further on, as a result of the RLS trade-off (ref. 2.3) improvements in resolution and CD control result in a lower resist sensitivity. This leads in turn to unpractical high exposure doses (low throughput capability). Large efforts must be undertaken in order to increase the throughput capability of EBL by parallel beams. In particular, more than 10,000 beams are targeted for a massively parallel projection of writing pixels (review: [29]). The proof-of-concept has shown its general feasibility, but major technological challenges still remain. In conclusion, the application of such kind of systems for a sub-20 nm mask-less lithography is rather unlikely.

In the long term, for a sub-10 nm shift, fundamentally novel methods for nanofabrication are required. Here, lithography appears to be the biggest challenge. The struggle of process control, the lack of resolution as well as the ultra-low throughput capabilities likely are insurmountable barriers for nanofabrication - Technological breakthroughs are required. As of now, single nanometer lithography, for example the manipulation of atoms by STM- [19] and AFM- [30] techniques is rather in an early stage and far away from practical applicability. Thus, in long term novel lithographic systems, associated novel resist materials and lithographic methods and strategies are required. Here I show that scanning proximal probes offer new types of paths towards a high resolution lithography. Thereby, the closed loop patterning principle gives novel opportunities beyond a standard optical and charged particle lithography (section 1.3).

However, linked with the serial writing scheme the throughput is rather limited - Tennant’s law is still valid [27, 31]. In general, the technology has been stuck in the dilemma that high throughput lithography can not meet the high resolution demands, whereas ultra-high resolution requires tremendously increased patterning times. This trade-off and promising solutions, e.g. a novel complementary mix-and-match method, are discussed in section 6.2.

### 1.3 Scanning Probes: Multifunctional Nano-Tools

Scanning probes were initially developed for surface imaging [32, 33, 34]. Beyond that, their capability to confine interactions for imaging, probing of sample properties as well as for manipulation at the single nanometer scale and even smaller [19, 30], scanning probes have evolved towards the „gateway to the nanoworld“. Here, in imaging and probing modes the user is intended to minimize the tip-sample
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Figure 1.3.1: Integration of functions provided by scanning probes. The sequential series of imaging and lithography is the basis for a closed loop lithography.

interactions in order to keep the specimen unmodified. In contrast, in manipulation mode, so called scanning probe lithography (SPL), the tip-sample interactions are enhanced in order to induce well-defined changes of the specimen surface properties. The close proximity of nanoprobe and sample opens up multiple ways of spatially confined and specific interactions. The numerous lithographically useable tip-induced interactions investigated during the last two decades (ref. section 2.1) reveals the versatility and ease-of-use of SPL. In contrast to conventional lithography the minimum feature size is neither limited by the exposure wavelength nor by proximity effects. Instead, the spatial confinement of the specific physical and/or chemical interactions, induced by the nanoprobe, determines the resolution capability.

Due to the integration of imaging and lithography in a single system a unique combination of integrated functionalities is given, summarized in Fig. 1.3.1. By using the same cantilever probe for „reading“ and „writing“ at the nanoscale a so called closed loop lithography scheme is enabled. Herein, AFM based imaging prior to lithography is applied for initial inspection as well as for overlay alignment and stitching. Subsequently, a second AFM imaging step applied directly after lithography allows a “read-back” inspection of the generated features. Thereby, the read-back capability gives the possibility for an in-situ adjustment of the lithographic exposure parameters. By incorporation of a respective feedback loop a zero-defect patterning with ensured feature geometries can be achieved. In this context, feature correction mechanism can also be integrated.

The sequential read/write cycle of patterning in general allows (1) surface inspection before patterning, (2) AFM-based registration, stitching, and overlay alignment, (3) patterning by using real non-contact field-emission scanning probe lithography (FE-SPL) with variable exposure parameters, and (4) in-situ inspection after each patterning cycle. Thereby, the precision of alignment is mainly determined by the measurement accuracy of the AFM itself, which is typically in the sub-nm range. Also the patterning across surface topography without degradation of the resolution, with integrated overlay alignment and
stitching, is possible (ref. section 7.1). Remarkably, as demonstrated in section 6.2, in-situ detection and thereof derived alignment by using the latent exposure image is possible, which constitutes a unique capability among all lithographic methods. In comparison to EBL, wherein imaging already causes an exposure of the resist, in FE-SPL the imaging is accomplished via AFM mode, which means that no additional modifications of the resist layer are introduced. Thus, unique capabilities for a mix-and-match lithography, patented by us [35], as well as for step-and-repeat extension of the lithographic method is given (ref. [36, 37]). In summary, the unique set of functionalities, ease-of-use, low cost of ownership and high degree of flexibility makes scanning probes an attractive tool for nanofabrication. Further, by using an active cantilever technology, which was pioneered by the department of Prof. Rangelow during the last two decades, the ease-of-use of scanning probe systems is further enhanced. By integration of actuator and sensor into the cantilever beam itself (Fig. 1.3.1) the requirement of external cantilever drive and deflection read-out are circumvented. This leads to even more compact and integrable SPL platforms.

Despite its significant advantages, SPL is not explicitly mentioned in the ITRS roadmap [4] as a possible successor for mask-less lithography. This could be attributed to the throughput limitation, which is linked to the serial processing scheme. Up-scaling by cantilever arrays as well as a smart combination of lithographic methods could turn SPL from niche applications towards a widespread nanoscale fabrication technology. However, the prerequisite for this is a successful technology demonstration. In this case SPL is predestined for rapid nanoscale prototyping, mask and template fabrication as well as for highest resolution patterning within a complementary mix-and-match approach.

1.4 Thesis Background: History, SNM-Project and Collaborations

The basic concept behind field emission scanning probe lithography (FE-SPL) is based on an idea of Prof. Rangelow, which was patented by him in 2005 [38, 39]. In the related early stage investigation the direct removal effect in calixarene resist, triggered by a biased nanoprobe, was first observed. However, during that time the lithographic effects were not the main focus of research. Thus, further investigations have not been performed. During that time, as described in the patent application [38, 39], it was supposed that single molecules, as a whole, are pulled out in consequence of the applied electric field, one after another. However, neither the specific interaction and associated dependencies were investigated, nor was there a targeted lithographic system developed. In fact, there was no evidence to indicate which specific effects are provoked by the biased nanoprobe. Only the general functionality was known, without any deeper understanding. Starting here, with novel lithographic applications in mind, my PhD work focuses on this open research topic. In contrast to the initial patent application, in the frame of this work quite different explanations and a variety of other phenomena are found, which shed a different light on the basic probe-resist-sample interactions than previously thought.

In 2009 I joined the research group of Prof. Rangelow, the Department of Micro- and Nanoelectronic Systems at TU Ilmenau. As a first proof-of-concept, in the frame of my master thesis work (2010-2011, ref. [40]), I was able to reproduce the basic phenomena by using a reactivated open loop environmental scanning tunneling microscope (STM). However, the lack of an adequate experimental system and associated experimental methods prevented deeper investigations. Nevertheless, the basic phenomena of a direct removal reaction was demonstrated, whereby high resolution lithographic capabilities were revealed. In addition, a variety of other highly interesting effects, which could not be explained, were observed. Most of them were not published previously. My first results were presented at the EIPBN 2011 conference as well as in a first publication [40].
Driven by this initial success I decided to continue my work on that topic in the frame of a subsequent PhD thesis. With a clear vision for nanofabrication in mind, the focus was placed mainly on investigation of the underlying phenomena in order to turn the experimental method into a novel toolset for single nanometer manufacturing. Here, the main driving principle was always to enable a path towards single nanometer lithography, which would catalyze the development of incredibly novel device concepts in nanoelectronics, nanophotonics as well as for sensoric applications. By incorporation of active cantilever technology, pioneered since the 90’s by Prof. Rangelow, an ease-of-use closed loop lithography tool with a main focus on research applications was targeted.

Since funding for the particular research was required we (Prof. Rangelow and I) started in 2011 to work on a proposal for a large scale EU-FP7 project, in which the forces for nanofabrication in the fields of lithography, etching, novel 2D materials, resist chemistry and semiconductor metrology are joined by an European format. Finally, in 2012 the project „Single Nanometer Manufacturing for beyond CMOS devices“, shortly called SNM [10], was granted by the European Commission in order to address the critical challenges of sub-10 nm fabrication. In particular, the investigation and development of novel technologies for device fabrication at the single nanometer scale, reaching the theoretical limit of future nanoelectronic systems, was our main focus. This was demonstrated by fabrication of future quantum electronic devices, e.g. single electron transistor (SET) devices. To achieve this, a team of 16 partners from industry, academia and research institutes, coordinated by our department at TU Ilmenau, has formed an integrated project (IP). The research goals were defined by: (i) Pushing the limits of manufacturing down the single nanometer scale; (ii) Development of lithographic methods for nanometer-sized features with associated overlay placement accuracy and inspection for integration in novel nanoelectronic device process flows; (iii) Enabling of novel ultra-low power electronics, quantum devices and manipulation of individual electrons, so called single-electron devices; and (iv) Opening of new horizons for beyond CMOS technology by using novel cost-effective, global, nanolithographic technologies. The aim of project was to empower nanomanufacturing with a clear focus on industrial use, and to drive the rapid development of nanoscience leading to new fabrication processes and early industrial exploitation (ref. [5, 10]). The present thesis work was an integral part of this project, embedded in Work Package 1 (Tip based interactions - electric field), which I have also coordinated throughout the entire duration of the project (Jan. 2012 - March 2017).

1.5 Motivation, Aims and Structure of the Thesis

As previously concluded single-nanometer manufacturing is an enabling technology with huge impact on many fields in nanotechnology. The following thesis summarizes my work contributing to the development of a novel lithographic method suited for beyond CMOS device manufacturing: field emission scanning probe lithography, called FE-SPL. In particular, the combination of scanning probes, ultra-low energy exposure and molecular glass resist materials provides a unique system investigated hereinafter for lithographic purposes. Compared to standard electron beam lithography the FE-SPL method is characterized by the following advances:

1. Neither vacuum nor special gas environments are required. Lithography in ambient conditions is possible.
2. No complex electron optics are needed enabling a relatively easy setup.
3. The basic scanning probe system provides a closed loop scheme functionality delivering a unique set of integrated functionalities, ref. section 1.3.
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4. Ultra-low energy electrons are reducing / eliminating proximity effects and resist sensitivity should be enhanced (theory discussed in section 2.2).

Thus, exploration of this novel lithographic path is highly promising. However, in order to turn ambient FE-SPL into a viable lithographic technology several issues have to be addressed:

1. Development of a closed loop FE-SPL system and respective control and processing schemes, which are able to induce the aimed tip-resist interaction in an efficient way. Further, respective cantilever, tip, resist and sample preparation schemes have to be devised, and tailored for the specific application cases. Both tool and resist technology development constitutes one of the prerequisites for fundamental experiments.

2. Identification, investigation, understanding and in application case control of the fundamental physical/chemical processes occurring within the tip-resist-sample system. Thereby, the understanding of the fundamental dependencies constitute the backbone for a targeted lithographic application. Here, as revealed by the thesis, the induced phenomena are complex and usually a superposition of different effects are taking place.

3. In order to pattern features at nanometer scale the extreme spatially confined deposition of energy, which is responsible for confined activation of the lithographic applicable reaction, is essential. In accordance with the sampling theory, to reconstruct the patterned feature a $5 - 10$ times higher AFM imaging resolution is ideally required. In this context, tailored methods for analysis and characterization have to be established. As a result of repeated lithography-analysis cycles the influencing lithographic parameters have to be identified and their particular dependencies determined. In order to bring the lithography to application, methods for a reliable and reproducible dot, line and areal patterning have to be developed. Thereby, a sufficient critical dimension and process control is mandatory for applications.

4. In consequence of the limited throughput capability of SPL methods throughput enhancement strategies are required. Herein, mix-and-match methods utilizing a data splitting strategy are the most promising approach. Data splitting means that all small CD features are defined by FE-SPL, whereby all larger features are patterned by conventional lithographic methods.

5. In order to show practical applicability the principal integrability into typical manufacturing process flows has to be demonstrated. In this context, a lithographically defined pattern is only viable if a subsequent application of the resist feature is given. However, the pattern transfer by plasma etching and lift-off techniques are in general a challenging task since the typical resist film thicknesses range between $5 - 50 \text{ nm}$. Respective methods for successful pattern transfer has to be shown in order to achieve an integration into a beyond CMOS device process flow.

In this context, the following PhD work was aimed to address the specific points (1) - (5). However, the fabrication of functional devices, e.g. SETs, is not explicitly targeted within this work. Instead, the framework of the lithographic method should be investigated and the most promising routes identified. By application of the lithographic and pattern transfer methods developed herein, a SET device showing Coulomb diamonds at room temperature operation was demonstrated. This achievement was enabled by intense teamwork within Prof. Rangelow’s research group, by the SNM-project driven collaborative framework as well as by my particular work on this nanolithographic method, explained within the subsequent chapters. The structure of the thesis reflects the work packages discussed. The chapters of the thesis are summarized hereinafter in brief manner:

- **Chapter 1** gives an overview about state-of-the-art lithographic methods, the general trends in nanofabrication and the main challenges remaining in order to enable a manufacturing at
single-digit nano level. The general concept, the background of the concept as well as the aims of the thesis work are introduced.

- **Chapter 2** starts with a review about notable SPL methods and their basic interaction mechanisms. In order to understand the concept behind FE-SPL the underlying theoretical essentials are elaborated. In this context, the Fowler-Nordheim field emission theory from nano-tips is discussed and the theoretical differences in interactions between standard EBL and FE-SPL are derived. Lithographic fundamentals, its limitations and general influencing factors are worked out. The concept of molecular glass resist materials and its general differences to polymeric resists are introduced.

- **Chapter 3** summarizes all experimental considerations and related developments concerning a FE-SPL technology platform. This contains the development of probe technology, probe modules, sample and resist preparation as well as specific programs and models for feature analysis.

- **Chapter 4** constitutes as the main experimental chapter. Herein, the basic lithographic reactions are investigated. This chapter forms the basis for a general understanding and control of the nanoscale physical/chemical processes and mechanisms occurring within the nanoprobe - resist - and substrate system. Different lithographic interactions are identified, analyzed and assigned to different characteristic patterning regimes. For this purpose specific analysis methodologies and routines are developed. The lithographic results are investigated as a function of exposure parameters and secondary lithographic conditions. In terms of resist material influence calixarene molecular glass resist as well as novel specifically tailored resists were explored for lithographic applicability. Experimental studies regarding all basic lithographic feature types, in particular line, dot and areal exposure, are conducted.

- **Chapter 5** elaborates respective exposure models and related simulations in order to describe the experimental observations. Thereby, a Gaussian beam exposure model is derived. Also the influence of the dielectric resist layer in terms of electric field alterations and the derived field emission at the tip apex are investigated. As consequence of the close proximity of emitter and lithographic feature formation a lithographic back-coupling effect is revealed.

- **Chapter 6** focuses on the thriving combination of FE-SPL and standard Gaussian EBL. Thereby, an initial comparison of FE-SPL and EBL is targeted to discuss the different exposure mechanisms and related lithographic capabilities of both methods. Weak points of each method are identified. In this context, the throughput capability of FE-SPL is discussed and rated against other mask-less nanopatterning techniques. In order to overcome the throughput limitations a novel complementary mix-and-match lithographic method has been developed. A proof-of-concept using FE-SPL as fine patterning method for CD-features is given. As a result not only the throughput capability is significantly enhanced but also the process window and patterning possibilities are expanded beyond a single lithographic method.

- **Chapter 7** summarizes initial attempts towards a broad lithographic applicability. In particular, the lithographic capability is summarized and major examples with respect to lithographic resolution and closed loop patterning are shown. In terms of pattern transfer initial results achieved by plasma etching and lift-off are recapitulated.

- **Chapter 8** concludes the presented work and gives an outlook onto the future pathway towards a single nanometer fabrication technology.
2 Lithographic Fundamentals of a Field Emission Scanning Probe Lithography

In the following sections the theoretical fundamentals, which are required to understand the basic considerations behind field emission scanning probe lithography (FE-SPL), are elaborated. In order to get an overview about the diversity of SPL, an initial review classifies the different methods according to their underlying tip-sample interactions. The theoretical differences between classical high energy EBL, low energy EBL and ultra-low energy FE-SPL are derived. In terms of resist material importance in lithography, the concept of molecular glasses is introduced. Thereby, the theoretical fundamentals of basic electron-sample interactions are discussed comparing classical polymeric versus molecular resists. Herein, the factors for a reliable and applicable lithography are defined. Lithographic resolution fundamentals, its limiting factors as well as key determinants are introduced. Finally, the basic Fowler-Nordheim (FN) field emission theory is worked out in order to describe the emission processes occurring at proximal probe nano-tips.

2.1 Scanning Probe Lithography - A Brief Review and Classification of Fundamental Tip-Sample Interactions

Within the last three decades, starting with the invention of the Scanning Tunneling Microscope (STM) in 1981 [32, 33] and the Atomic Force Microscope (AFM) in 1986 [34], a family of powerful Scanning Probe Microscopy (SPM) systems have been evolved. Nowadays, a multitude of imaging modes (LFM, CFM, EFM, MFM, SNOM, SThM, KPFM, etc. [41]) drive the scientific progress towards nanometer scales in many cutting-edge research areas covering the fields of physics, electronics, chemistry and biology.

Originally, SPM technologies were developed to observe physical, chemical, or biological interactions at nanometer scales. All SPM systems and modes have in common that a local interaction map is generated, based on the specific interaction occurring between a sharp tip, a so-called nanoprobe, and the sample. In order to get an image the nanoprobe is mechanically moved across the specimen surface by a raster scan motion, in a line-by-line fashion. Thereby, the probe works as spatially confined sensor recording the interaction at every pixel location. Due to the close proximity of probe and sample, combined with the sharpness of the probe, the local interaction is focused only to the closest probe-sample spot, typically the foremost atoms of the probe. In consequence, information about nanometer-confined interactions, which could be mechanical, physical, electrical or chemical ones depending on the specific operation mode, are obtained. The experimental setup is realized typically by implementation of a feedback loop, which keeps the probe-sample interaction constant by modulation of the probe-sample spacing. Thus, the obtained „height image” represents a map of probe-sample spacing alterations, which are required in order to hold the tip-sample interaction at a constant value (the regulation set-point). In these terms, the various SPM techniques differ mainly in the nature of the specific interaction mechanisms utilized.
In imaging mode, modifications of the specimen surface itself are not intended. Thus, the strength of the probe-sample interaction (e.g. force, heat, exposure dose, etc.) has to be kept below the particular threshold level. In contrast, in case of a lithographic application the particular threshold value has to be exceeded in order to trigger spatially confined lithographic reactions. The general capability of SPM for lithographic purposes was already discovered during its pioneering days in 1985 [42]. Nowadays, high-resolution scanning probe-based methods provide an emerging toolset to face the critical nanomanufacturing challenges. In general, SPM techniques enable the possibility for high-resolution surface modifications, nano-object manipulation as well as target-aimed lithography in a closed loop manner (section 1.3). The close proximity between probe and sample defines a spatially extremely confined nano-region, wherein unique interactions for nanofabrication can be controlled. Summarized in Fig. 2.1.1, various sources for interactions are possible resulting in different lithographic applicable mechanisms. Within the spatially confined region surrounding the nanoprobe, material could be displaced, (chemically) modified, removed or deposited, depending on the applied primary and secondary interaction mechanisms utilized. In this context, displacement means a relocation of material without causing any chemical or physical alteration of the material itself. In contrast, modification implies a chemical change of the material, e.g. the crosslinking of resist or the anodic oxidation of Si. Removal (deposition) describes the conversion from non-volatile into volatile material parts (or the reverse process). Described below, the most significant nanolithographic interaction mechanisms are reviewed, classified according to the underlying initialization sources. Since here only mechanisms relevant for this particular work are elaborated, more general overviews are provided in ref. [43, 44, 45, 46, 47, 48, 49, 50, 51].

1) **Force-Induced Interactions**: Applying excessive mechanical forces in order to displace a material is the most simple way to create a pattern. Done in point-wise fashion indentation marks [52] are created while by static plowing using large loads the scratching of surfaces is achieved. Carved grooves result, characterized by border walls and/or material accumulations (see Fig. 2.1.1). Better results,
with improved lithographic control, were achieved by dynamic plowing methods [53, 54, 55]. Here, the force interaction is modulated by adjusting the amplitude of the cantilever oscillation. Despite the demonstration of superior resolution capabilities, e.g. 10 nm [56] and 3 nm [57], the application of mechanical methods is rather constrained. The limiting factor for a reproducible patterning is the stability of the tip apex itself, which is prone to deformation, contamination and degradation in consequence of the mechanical interactions [58]. Thus, diamond-coated tips, in combination with soft materials (e.g. polymeric resists), are preferred. In order to reduce the threshold forces during patterning, self-assembled monolayers (SAM) were applied as resists. Adsorbed SAM molecules were displaced (nanoshaving) [59, 60] or exchanged with other SAM molecules (nanografting) [49, 61]. A spatial resolution of $2 \times 4 \text{nm}^2$ island sizes and 10 nm single lines were achieved [61, 62]. However, dense patterning as well as the pattern transfer are critical aspects of that approach. So far, no functional nanostructures were demonstrated [63]. Also chemically assisted force-induced methods were tested leading to a reduction of the load forces and enhancing the achievable aspect ratios [57, 64]. Furthermore, the direct manipulation of molecular structures [65], nanoparticles and other nano-objects, is possible [43]. In this context, the ultimate lithographic resolution could be shown by manipulation of single atoms using STM- [19, 66] as well as AFM-methods [30]. Despite its ultimate resolution capability, the remaining challenges concerning the extremely slow manipulation rates, the narrow process window and, most significantly, the transformation of such fine manipulations into a stable and operational nanodevice prevents the breakthrough of atomic manipulation as a viable fabrication path [43, 45].

2) Heat- Induced Interactions: In the case of thermomechanical patterning a combined heat ($\sim 400^\circ\text{C}$) and force stimulus is applied in order to induce a local softening and displacement of polymeric material. This approach was exploited by the „Millipede“ data storage project of IBM [67, 68], wherein information was encoded by thermomechanical deformation of thin polymer films. A feature size resolution of 10 – 50 nm was demonstrated. In contrast to thermomechanical writing, where chemical modifications or depolymerization reactions are not intended [69], in thermochemical writing the thermal energy, which is emitted from the nanoprobe, is applied to initialize spatially confined chemical reactions. Typically, thermally activated decomposition processes are utilized. For example, the switching of the hydrophobic/hydrophilic properties of a polymer, with sub-15 nm resolution and tip speeds up to 1.4 mm/s, was demonstrated [70]. Also crosslinking [71] or diverse other chemical reactions [48, 72] could be released. By a so called thermo-mechano-chemical writing approach, a combined heat-force-stimulus is exploited to induce a direct removal of resist material. In this way parasitic side effects like thermal deformations or reflow of material are circumvented. Since in covalently bonded polymeric resists large energetic barriers must be overcome [73], amplification concepts [74] (one degradation unzips an entire chain) as well as molecular glass resist materials [75, 76, 77, 78] (weaker intermolecular networks, ref. section 2.3.2) were developed giving a more clean, debris-free decomposition / desorption process with 10 – 20 nm resolution capability.

3) Photon- / Ink- / Catalytic- Induced Interactions: In order to circumvent the diffraction limit, which constrains the resolution in conventional photolithography, the operation in near field regime using so called evanescent waves is possible. Here, typically the nanoaperture of a scanning near-field optical microscope (SNOM) is exploited for localized exposure of resists in near-field, which bypasses the Rayleigh resolution limit [79]. In this context, SNOM was demonstrated for exposure of photoresist films with 30 – 100 nm resolution [80, 81], for selective oxidation of SAM films with 9 nm resolution [79, 82] as well as for activation of direct ablation processes [83, 84]. In particular, the local energy
densities are extremely high, which leads in combination with the low transmission coefficients of SNOM nanoapertures to a strong heating of the tip apex. Some efforts were undertaken for throughput enhancement using flying plasmonic lenses in near field (80 nm resolution) [85], SNOM arrays (70 nm resolution) and so called beam pen arrays (100 nm resolution) [87]. However, these methods are linked with a loss in resolution capabilities.

Also the direct deposition of molecular inks, typically SAM molecules, has gained attention. The so called dip-pen nanolithography (DPN) was first demonstrated by Mirkin et al [88]. On this basis various methods have been evolved [89, 90]. Also thermal based DPN using metallic inks [91], electrostatic DPN [92] and DPN with reactive inks [93] were demonstrated. A lithographic resolution of 15 nm is achievable [90]. Furthermore, surface reactions could also be induced catalytically, without additional energy sources. Thereby, the coated nanoprobe (Pt, Au, Pd, etc.) works as a localized catalyst, for example for activation of chemical end groups of SAM molecules [94, 95, 96] or for spatially localized oxidation of graphene [97]. A resolution of 25 nm was reported [96].

4) Electric Field- / Electron- Induced Interactions: Electric field and electron induced interactions offer the greatest diversity in lithographic reaction mechanisms. In general, the mechanisms are initialized by an electric potential difference applied across the probe-sample-junction. In consequence of the close proximity of nanoprobe and sample, relatively high and nonuniform electric fields are generated, which leads in turn to a multitude of secondary physical and/or chemical processes at the nanoscale. However, due to the multitude of potential reaction paths, several secondary reactions and side effects have to be considered. In the following, the most important mechanisms are summarized:

4-a) Electrochemical Mechanisms: Since the first investigation of local anodic oxidation (LAO), carried out by Dagata et al. [98], LAO has evolved to become the most widespread type of SPL (ref. [46, 99, 100, 101, 102, 103, 104]). As commonly accepted, a liquid meniscus is induced within the probe-sample junction forming a spatially confined reaction chamber. In this chamber a multitude of electric-field driven electrochemical reactions are possible. In this case, it has been found that the LAO process is rather a general than a Si-specific process. Many different surfaces have been successfully patterned, e.g. various semiconductors [105, 106, 107], metals [108, 109, 110], dielectric films [111, 112] as well as organic monolayers (SAM) [44, 113, 114, 115]. Thereby, the key for the chemical oxidation reaction represents the spontaneous and/or field-enhanced formation of a water meniscus, which provides both the chemically reactive species (oxyanions: $O^-\text{, } OH^-$) and the spatial confinement of the oxidation reaction [100, 116]. Remarkably, derived from theoretical calculations a stable meniscus diameter, which is in equilibrium with the surrounding vapor, with minimum dimensions of $2 - 4\text{ }nm$ [117], based on the Kelvin equation, or $1.9\text{ }nm$ [118] applying Monte Carlo simulations, are predicted. The general oxidation process can be described by: (a) water meniscus formation, (b) field-induced activation of molecules within the water meniscus, and (c) oxidation of the sample surface, mediated by the in-situ generated ions. The following reaction scheme is proposed [119] at the anode (sample) side: $M + xH_2O \rightarrow MO_x + 2xH^+ + 2xe^-\text{ and cathode (tip) side: } 2xH_2 + 2xe^- \rightarrow xH_2 + 2xOH^-$. In consequence of the oxide film growth the electric field strength is decreasing which results in a self-limiting process [99]. By using LAO methods, a $4\text{ }nm$ single feature [120] and $13\text{ }nm$ lattice periodicity [121] were demonstrated.

4-b) Electric Field and Electron Induced Deposition Mechanisms: Direct deposition can be triggered either from gaseous precursor molecules, called STM-CVD, or from liquid phase, wherein typically field-induced organic liquid menisci are formed (ref. LAO). The adoption of electron beam induced deposition (EBID) processes by a ST M-based-lithography, first carried out by Silver et al. [122], was demonstrated for a multitude of different materials [123, 124, 125, 126, 127]. Thereby,
the tip-emitted low energy electrons excite the organometallic precursor molecules, followed by a decomposition process of the precursor and material deposition. The processes are carried out typically in ultra-high vacuum (UHV) conditions while the STM is operated in field emission regime. For applications, critical issues arise from the high carbon contamination of the deposited features. In this context, Garcia et al. [128] have demonstrated the creation of carbonaceous depositions (25 nm dots) directly from CO$_2$, which is present in ambient conditions. It is assumed that in a first step CO$_2$ is captured inside the nanogap by field-induced diffusion processes at extremely high electric fields of up to $\sim 30 \, \text{V/mm}$, followed by activation of the molecules and formation of carbonaceous depositions onto the positively biased sample surface.

By replacing the water meniscus in LAO with various organic liquids, for example solvents like ethanol, 2-propanol, octane and so on, the decomposition process leads directly to the deposition of carbon-based materials [116, 129, 130]. Similar to LAO, the field-induced formation and manipulation of the liquid meniscus plays a crucial role with respect to spatial confinement of the electrochemical deposition reaction. In general, the high electric field ($\sim 10 \, \text{V/mm}$) induces a nanoscale solvent-based meniscus, within the meniscus carbon-hydrogen bonds are broken, a polymerization and crosslinking of the carbon chains is released, followed finally by their deposition onto the sample surface. Martinez et al. [133] has demonstrated ultra-high resolution patterning of carbon-based structures with $2 \, \text{nm}$ resolution and $3 \, \text{nm}$ half-pitch (hp) in ambient conditions. Similar to that, also sub-30 nm germanium nanostructures at velocities of up to $100 \, \mu \text{m/s}$ were deposited from diphenylgermane (DPG) liquid precursor [134, 135]. Thereby, it is argued that electrons are injected from the tip into unoccupied molecular orbitals of the precursor, which leads in turn to fragmentation of the molecules resulting in pure Ge deposition onto the sample surface.

(4-c) Material Transfer by Field Evaporation Mechanism: The high electric fields generated within the probe-sample-junction could lead directly to atom ionization and ejection, known as field evaporation. Depending on the bias polarity and material properties, which defines the threshold value for field evaporation of negative and positive ions, the transportation of material from tip to sample surface, or vice versa, is possible [136]. In case of extreme small tip-sample gaps the bias for field evaporation is lowered to a few volts, demonstrated by formation of $5 - 10 \, \text{nm}$ metal dots deposited on Si or on thin insulator films [137, 138, 139, 140, 141, 142]. The processes behind material transfer between tip and sample are by far not fully understood. In this context, large electrostatic force effects [138] as well as field-enhanced diffusion processes [143] are discussed.

(4-d) Electric Field / Electron Induced Removal Mechanisms: Field-induced as well as current-induced desorption processes can be triggered by a biased nanoprobe, explored mainly on SAM films [144]. In the case of an electric field supported interaction mechanism it is suggested that a positive bias voltage forces a charge redistribution, which weakens the S-Au bond. In consequence, the S-Au bond dissociates if a particular threshold field strength is exceeded. Here, only positive bias voltages lead to a desorption process. In the case of a current induced desorption process the electric field only weakens the bond, but does not lead to a direct desorption. The vibrational excitations of adsorbent molecules, caused by resonant inelastic electron tunneling, subsequently induces the observed desorption process [144, 145, 146]. By employing a hydrogen monolayer as the ultimately thin resist layer, prepared in form of hydrogen-passivated Si surfaces, an electron induced hydrogen desorption process, carried out in UHV conditions, was demonstrated for patterning with atomic precision [147, 148, 149]. Since conventional pattern transfer techniques will not work here, the high reactivity of the patterned areas (unsatisfied covalent bonds) was utilized for a selective deposition of metals, oxides, semiconductors, and dopants. Despite the ultimate atomic resolution capabilities, which enabled the fabrication of the first single atom transistor [150], a plurality of practical problems concerning throughput (extreme high
exposure doses required: $50 - 5000 \, C/cm^2$), crucial sample preparation, tip technology as well as the reactive character of clean surfaces restrict their application to single laboratory experiments.

Beside the above mentioned mechanisms, the generation of nano-holes ($3 - 10 \, nm$) and grooves, without the presence of chemical solutions, observed in Au and graphite surfaces is still controversial. Possible mechanisms range from local heating [151] to electromigration [152] as well as chemical reactions [153, 154, 155], whereby the latter one is the most likely path in ambient conditions. Here, environmental water has to be taken into account. Also depolymerization processes, which leads to a direct removal of polymeric films, have been suggested [156, 157, 158].

(4-e) Material Displacement and Removal Mechanisms within Electrostatic Nanolithography: In a so called electrostatic nanolithography, proposed by Lyuksyutov et al. [156, 159, 160, 161], the following mechanisms are assumed: (i) In consequence of the current flow between probe and sample a localized joule heating of a dielectric polymer film above its glass transition temperature is triggered, which leads to a softening of the polymeric film. Bias voltages between $5 - 50 \, V$ and currents of $1 - 100 \, nA$ are applied. A minimum current of $5 - 10 \, nA$ is required to soften PMMA and PS films [160]. (ii) As a result of the the large, non-uniform electric field gradients the softened, viscoelastic polymer is polarized and attracted towards the tip apex forming raised features. Thereby, Lyuksyutov et al. assume that no chemical reactions like crosslinking, substantial polymer degradation or ablation are occurring. Raised features with lateral dimensions of $10 - 500 \, nm$ and heights of $1 - 10 \, nm$ have been reported. By increasing the bias voltages above a certain threshold, typically $50 \, V$, high breakdown currents of greater than $100 \, nA$ leads to a direct polymer ablation mechanism. A direct hole formation has been observed. Using the same methods, Jegadesan et al. [157] found that PVAA thin films require lower bias voltage thresholds.

However, the effects are controversial. The experimental base gained during my particular work points out different mechanisms involved. Thus, I do not agree with Lyuksyutov and Jegadesans theory of an electrostatic nanolithography. The reasons will be clarified throughout the experimental section (sec. 4) of this work. Later on, Xie et al. [162] investigated the charge transport during formation of conical PMMA structures and explained the observed high currents by a water-bridge-mediated ion conduction mechanism. Martin et al. [158] have interpreted the hole formation in PMMA as an electrochemical-based reaction mechanism in the presence of an ionic transport instead of thermally-related mechanisms. Xie et al. [163] suggest a nanoscale electrical discharge and transient shock-wave process causing the raised polymer structures. So far, no sufficient, consistent and coherent theory and derived experimental verification clarifies the fundamental interaction mechanisms behind these nanoscale lithographic phenomena.

(4-f) Resist Exposure Mechanisms: Ultra-low energy electrons ($E < 100 \, eV$), emitted from a scanning proximal probe tip, could be utilized in order to cause chemical reactions such as chain scission or crosslinking in a resist film [13, 26, 164, 165, 166, 167, 168, 169, 170]. A subsequent wet development step is required in order to render the associated solubility changes visible (ref. section 2.3.1). In spite of the analogies to standard EBL, the underlying mechanisms are very different, discussed in detail in the subsequent section 2.2. At present, the achieved lithographic resolutions are $\sim 30 \, nm$ for single lines in case of low speed patterning (a few $\mu m/s$) [169] and $\sim 40 \, nm$ at higher speeds ($\sim 1 \, mm/s$) [171].

Summary: Despite the great progress of SPL, and the diversity of methods derived therefrom, there is a major technological gap between demonstration, understanding and targeted application in order to address the development of single-digit nano fabrication. Perhaps the down-scaling might end up in single
atomic fabrication, which has been already demonstrated in a very early stage [19, 30, 147, 148, 149, 150]. So far, up to now there are no solutions in sight to circumvent the diverse practical problems of atomic scale manufacturing (ref. 4-d). In case of lithography in ambient conditions a theoretical resolution limit of $2 - 3 \text{ nm}$ minimum lattice periodicity ($= \text{hp}$) is predicted [133]. However, up to now no techniques having sufficient reproducibility, throughput and practical applicability exist for patterning below the $10 \text{ nm}$ scale. In this context, electric field- and electron-induced mechanisms seem to have the highest potential, which is further explored hereinafter.

2.2 A Question of Energy: From Electron Beam Lithography towards Field Emission Scanning Probe Lithography

Despite the obvious analogies between Gaussian EBL and FE-SPL, that is to say that electrons induce spatially confined lithographic interactions, major differences in terms of operation, interactions and conditions exist, derived hereinafter.

2.2.1 High versus Low Energy Electron Exposure in Gaussian EBL

In well established Gaussian EBL (Fig. 2.2.1) a beam of high energy electrons, typically $10 - 100 \text{ keV}$, is generated, accelerated and focused forming a fine beam in order to expose a resist-coated sample surface. While the primary high-energy electrons pass through the resist film into the bulk substrate of the sample, they undergo a series of elastic and inelastic scattering events. As a result, secondary electrons (SE), backscattered electrons (BSE), as well as plasmons, phonons and photons beyond the initial point of impact are generated [27, 28, 172, 173, 174, 175, 176]. The sum of all events, which contribute to the deposition of energy in the resist, defines the total interaction volume. In this way, so called proximity effects cause a broadening of the interaction volume far beyond the initial beam spot size. For example, whereas the focused beam has a spot size of typically $\leq 1 \text{ nm}$, the total interaction area triggered can be in the range of tenths of $\text{nm}$ up to several $\mu\text{m}$ [27, 28, 174, 175, 176, 177].

In order to push the resolution of EBL towards the single nano-digit scale, highly accelerated primary beams of $100 - 350 \text{ kV}$ were applied. In conjunction with ultra-thin resist layers, which are coated on top of thin membrane samples, Manfrinato et al. [175] have demonstrated the patterning of $2 \text{ nm}$ isolated and $5 \text{ nm}$ half-pitch structures. Hence, by using high energetic beams a better focusing resulted, thus forward scattering and thereof resulting SE emission were reduced. By applying a membrane substrate, backscattering-based proximity effects were suppressed. In conjunction with an ultra-thin resist film, the electron scattering volume was minimized. As a result, the total interaction volume was extremely confined leading to highest resolution ever shown in EBL. However, transferring this methodology to standard bulk samples, which are common for all practical applications, several problems arise: (1) Due to the relatively large inelastic mean free path (IMFP) of high-energy electrons [27], the beam deposits its energy rather in the bulk material of the sample than in the resist film. (2) This energetic mismatch leads to low exposure efficiencies. (3) In turn, radiation damage of the substrate as well as heating effects are more likely [172, 177]. (4) The most profound impact has long-range proximity effects, which hamper the resolution capability in case of bulk substrates, especially in terms of dense line/space patterning.

In order to overcome these drawbacks (1-4), a low energy approach gives an alternative pathway. Here, due to the reduced IMFP the electron penetration volume (lateral as well as vertical dimensions) is
There have been some attempts to effectively access the low energy exposure regime, for example by methods that have not proved particularly successful. Another approach, followed here, is given by using miniaturized EBL columns. Practically no scattering and proximity effects should occur. Yet these secondary electrons (typically 90%) point out that 90% of the SEs with energies < 400 eV travel less than 12 nm in PMMA, while SEs with energies < 200 eV travel less than 5 nm. In this context, the exposure reaction cross sections are maximum when the electron energies are close to the bond energies (typically < 10 eV). With increasing electron energies the cross sections decrease (ref. section 2.2.2). In consequence, lower energies enable a much more efficient energy transfer between incoming electrons and resist. The resist sensitivity and, linked with that, the exposure efficiency are significantly enhanced. A further indication of this general theory can be deduced from Fujita’s EBL exposure model for calixarene resists, in which he discussed the excitation efficiency as function of energy transfers to specific energy bands. Fujita pointed out that only energy losses ranging between several eV could excite the target bond reactions, which are required for a lithographically useable reaction. According to that, mainly secondary electrons (typically 1–50 eV), which diffuse through the resist with successive energy losses, are responsible for the energy transfer into the narrow excitation bands.

In addition, low energy electrons are not scattered back by the substrate, which results in a significant decrease of proximity effects. Also radiation damage and heating are effectively suppressed. In conclusion, the majority of electrons are scattered within the resist film. The key challenges of low energy EBL are the increased forward scattering of the incident beam, shot noise limitation due to the increased sensitivity, an enlarged spot size (a more effective focusing is achieved at higher energies), and charging effects as well as the limited applicable resist thicknesses.

### 2.2.2 Ultra-Low Energy Electron Exposure by FE-SPL - A Game Changer

By following this idea to its conclusion means to go to even lower electron energies for exposure. In practice, energies below 100 eV correspond to the typical electron energy range of triggered secondary electrons in case of standard EBL. According to established theories, the energy transfer between incident low energy electrons and resist should be more efficient because the applied electron energies are very close to lithographically relevant excitations, which primarily are bond scission (disassociation) processes. In addition, due to the low energy operation practically no scattering and proximity effects should occur.

There have been some attempts to effectively access the low energy exposure regime, for example by miniaturized EBL columns or retarding electron optics. However, the development of such systems, meeting a small beam spot size at these low electron energies, is challenging. Yet these methods have not proved particularly successful. Another approach, followed here, is given by using...
low energy electron emission from scanning proximal probes. The principle is schematically outlined in Fig. 2.2.1. In contrast to standard EBL, where the beam is generated, conditioned, blanked and focused relatively far away from the sample surface using a complex electron optical system in UHV conditions, in FE-SPL the situation is quite different:

1. Due to the field enhancement effect only small bias voltages are required, typically $10^{-100}$ V, in order to induce a Fowler-Nordheim field emission process at the foremost area of the tip apex (ref. section 2.4). The beam focusing is provided directly by the close proximity and the highly localized electric field itself. Thus, the need for a complex electron optics is circumvented.

2. Since the proximity is significantly smaller than the mean free path (MFP) of electrons in ambient conditions ($\approx 340 - 570$ nm [190, 191]), no vacuum conditions are required. The operation in ambient conditions enables the construction of a much simpler system.

3. Moving towards lower energies results in an enlarged de Broglie wavelength of electrons, described by:

$$\lambda_{dB} = \frac{h}{p_e} = \frac{h}{\sqrt{2m_eE_{kin}}} \tag{2.2}$$

Since the effect is minimal, e.g. $30 keV \rightarrow \lambda_{dB} = 0.007$ nm vs. $30 eV \rightarrow \lambda_{dB} = 0.224$ nm, the resolution capability is not affected by that effect.

Concluding from the current state of scientific knowledge, it could be suggested that the exposure process in the case of low energy FE-SPL is different compared to standard EBL:

(i) Inelastic Mean Free Path (IMFP): Due to the low energy operation the IMFP of the electrons is drastically reduced ranging between 1 nm and a few nanometers in the resist layer [173, 179, 180, 181, 184, 185, 192, 193]. A typical reaction depth of $1 - 3$ nm for $50 - 100$ eV electrons could be estimated [181, 194, 195]. The exact IMFP depends on the energy of the electrons as well as on the chemical compounds and structure of the resist layer. Thus, a higher spatial confinement of the deposited energy
in lateral dimension should be achievable [27].

However, due to the minimized IMFP at lower energies the direct penetration depth of the incident electrons is limited to the uppermost few nanometers of the resist surface. For example, a 50 nm thick resist film cannot be exposed completely by a 1 keV electron beam [179]. In consequence, in the case of FE-SPL the IMFP is smaller than the typical resist film thickness. In contrast, in standard EBL the IMFP of the incident primary electrons is much larger than the resist thickness. A conclusion therefrom would be that the low energy electrons are not able to penetrate the entire resist thickness. Thus, in case of standard EBL this would lead to a partial resist film exposure.

Indeed, in the case of FE-SPL it has to be considered that the space between electron emitter (tip apex) and resist-coated sample surface is not field-free. While in EBL the approximation of continuously decelerated electrons describes the primary beam adequately (continuous slowing down approximation), in FE-SPL the primary electrons are gaining again energy from the electric field after having energy losses as a result of scattering events (ref. [13, 26, 27, 165, 166, 168, 169, 170, 193, 196]). In this context, in FE-SPL resist films thicker than the IMFP are fully exposable.

(ii) Cross-sections: The exposure yield is a convolution of electron energy spectrum and the exposure cross-sections of the respective lithographic reactions. The exposure cross-sections $\sigma_e$, e.g. for triggering of a dissociation process, can be calculated by Vriens law [181, 197, 198, 199]:

$$\sigma_{e-HE} \approx \frac{1}{(4\pi\epsilon_0)^2} \cdot \frac{5}{3} \cdot \frac{\pi e^4}{E_e} \cdot \frac{1}{\epsilon_b}, \{E_e \gg \epsilon_b\}$$

$$\sigma_{e-LE} \approx \frac{1}{(4\pi\epsilon_0)^2} \cdot \frac{\pi e^4}{E_e + 2\epsilon_b} \cdot \left( \frac{5}{3\epsilon_b} - \frac{1}{E_e} - \frac{2\epsilon_b}{3E_e^2} + \frac{\ln(\epsilon_b) - \ln(E_e)}{E_e + \epsilon_b} \right), \{otherwise\}$$

with $\epsilon_b$ the binding energy. In the case of FE-SPL Eq. 2.4 is valid. Shown in Fig. 2.2.2, the so-called exposure reaction cross-section is calculated as a function of electron energy for four different chemical compounds, which are present in calixarene molecular glass resists (ref. 2.3.3). Maximum values between 8 – 12 eV for relevant binding strengths of $C – C$ and $O – H$ chemical bonds are present. Thus, the dissociative lithographic reactions are more likely when the incident electron energy fits directly with the energies of the targeted excitations. The resist sensitivity is enhanced. With increasing electron energies the cross-sections decrease [181]. The increased cross-sections at low energies were experimentally proven [193] for certain organic molecules, e.g. for $CH_4$ [200] and substituted benzenes [201]. Ionization seems not to be relevant since the electron-impact ionization cross-sections have maximum values at higher energetic ranges, located at 70 – 100 eV for typical organic resist compounds [202].

(iii) Indications by previous investigations: By initial investigations of scanning probe-based resist exposure experiments, carried out in the early days of STM/AFM development, there is support for the expectation that different lithographic mechanisms than in EBL are likely. In this context, it is reported that in case of FE-SPL higher exposure doses are required compared to EBL [13, 26, 167, 168, 169, 193, 196]. This is in contradiction with the previous conclusion (ii). In addition, the concept of chemical amplification (ref. section 2.3.1) seems not to work in ultra-low energy electron exposure, pointed out by [26, 167, 193]. Furthermore, Rangelow et al. have demonstrated the first positive tone behavior of calixarene by exposure with low energy electrons in 2003 [203] and 2006 [38], which indicates the presence of different reaction paths. However, in all cases no detailed investigations were carried out in order to gain a deeper understanding and to reveal the fundamental processes underlying the observations.
2.3 Resist Materials in Radiation-based Nanolithography

2.3.1 Resist Exposure Mechanisms, Performance Trade-Offs and Exposure Dose Definitions

In order to define the ever-shrinking feature sizes, which are linked to Moore’s law, the resist material itself plays an increasingly important role. Nowadays, the applied polymeric photoresist materials are a complex mixture incorporating a multitude of functional parts, for example a polymeric backbone, photoacid generators / photoactive components (PAG / PAC), dissolution inhibitors, different protection sites, cross-linker, and so on. In sum these components define the performance capabilities of a resist material (more details described in [28, 204, 205]). Thereby, the performance of a resist is described mainly by:

1. **Resolution** capability: The resolution defines the minimum stable lateral feature size (line width, pixel size), which could be achieved at optimum lithographic parameters. Due to proximity effects one has to differentiate between separated (isolated) and dense (nested) patterning cases.

2. **Sensitivity** and (vertical) **contrast**: In the case of EBL the radiation resist sensitivity, which is highly process-dependent, is defined as the minimum electron dose required to induce the desired chemical modification through the entire resist film (“clearing dose” [204]). For example, in the case of a positive tone resist the sensitivity is defined as exposure dose at which the entire resist is removed during the subsequent wet development step. The contrast of a resist is specified as the slope of the linear portion of the falling (positive tone resist) or rising (negative tone resist) section of the remaining resist thickness versus the logarithm of exposure dose (ref. [28, 204]). The remaining resist thickness is measured after wet development.
3. **Line edge (LER) and line width roughness (LWR):** LER and LWR describe the fluctuations (3 sigma) of the line edge and line width, respectively. High LER/LWR causes a distortion of the resolution capability.

4. **Process compatibility:** This term summarizes the process latitude, which describes the change in critical dimensions as function of an exposure dose alterations, the line width control, process reproducibility, and the process window. Furthermore, the thermal, mechanical, and chemical stability as well as the etch durability of a resist have to be considered. The plasma etching durability is a key attribute, which has significant importance especially when ultra-thin resist layers, as in our case, are applied (ref. 7.2).

**Lithographic Tones and Exposure Mechanisms:** The properties and lithographic performance of a resist are defined by the chemical constitution, structure, and physical state. The tailored design of resists enables the tuning towards specific applications, for example as resist for optical lithography, standard EBL or in our case FE-SPL. Since electrons were applied as the incident lithographic source, in the following the focus was placed on the radiation chemistry of resist materials (ref. [204, 206, 207]).

The typical radiation-induced mechanisms in the resist can be classified into (ref. [206, 207]):

(a) **Crosslinking,** which leads to an increase of the molecular weight. An increasing exposure dose leads to a decrease of the solubility;

(b) **Scission,** which results in a decrease of the molecular weight. In consequence, the solubility is increased with increasing exposure dose;

(c) **Degradation,** which means the formation of small molecular reaction products. The products could be volatile or partially trapped in the resist. This depends on the chemical composition of the resist and the volatility of the molecular fractions which are generated;

(d) **Structural changes** of the resist, which means significant changes of the material properties, for example of the viscoelasticity.

Depending on the applied resist system and the exposure conditions (exposure energy, exposure dose, environmental conditions) one of the processes (a-d) dominates. Also multiple processes (a-d) can occur simultaneously.

The induced lithographic reactions within the resist material, and the related chemistry, defines the tone of the resist. The two common tones are shown in Fig. 2.3.1. Typically, a solubility change, which is
initiated by the lithographic reaction, renders the resist in the exposed regions soluble (positive tone) or insoluble (negative tone). The solubility of the unexposed regions remains unchanged. Since the entire interaction volume determines the lithographic resolution, not only the initial beam spot size (i) and the related electron-sample interactions, including the proximity effects, (ii) are contributing, but also secondary effects have to be considered. Here, chemical reactions and the diffusion of involved reactive species (iii), as shown in Fig. 2.3.1, could lead to significant decreases of the achievable resolution.

Referring to section 2.2, the primary electron beam undergoes a series of elastic and inelastic scattering events in forward and backward directions, which leads to generation of secondary (SE) and backscattered (BSE) electrons as well as plasmons, phonons and photons \([27, 28, 172, 173, 174, 175, 176]\). According to Bethe formula \([179, 208]\), the deposition of energy occurs mainly via the induced SEs. According to O’Donnell \([206]\), in consequence of the deposited energy in the resist, primary reactions in the form of excitations and ionization are triggered. The excited and ionized species work as initial chemical reactants. Furthermore, the primary processes could lead to the generation of free radicals. Also ionic mechanisms for secondary chemical reactions \([206]\) are possible. In this context, the resolution capability of lithographic reactions is strongly dependent on the reactivity, stability, and diffusion length of generated active species. In particular, as a function of induced chemical species, specific reaction paths are enabled or hampered. The possibility of scission processes is enhanced when the formed radicals have a higher stability. For example, the PMA radical is less stable than the PMMA radical. In consequence, PMMA undergoes mainly scission processes, whereas PMA prefers crosslinking. The influence of the stability of involved radicals in FE-SPL were discussed in more detail in the work of my former master student Yana Krivoshapkina \([209]\). Thus, an enhanced diffusion constant leads to an increased broadening of the feature dimensions \([27, 206]\).

In contrast to the energy deposition in the resist, which occurs randomly, the chemical changes are not random \([206]\). Specific chemical groups, e.g. \(COOH\), \(NH_2\), \(C = C\), \(C – Hal\), are more sensitive compared to other groups, e.g. aromatic compounds. In order to enhance the sensitivity of resist materials, the previously described primary and secondary reactions are combined in such a way that a chemical amplification of the primary reactions is achieved. Typically, catalytic reactions are exploited \([27]\). This concept, first proposed by Ito, Willson, and Fréchet in 1982 \([204]\), has led to the development of chemically amplified resists (CAR). For example, in photolithography a single photochemical event induces a cascade of subsequent chemical transformations in the resist film. As a result, the application of deep-UV lithography with acceptable throughput was enabled. In general, the active species could be either ionic or radical \([210]\). Commonly, the application of photochemical acid generators (PAGs) for an acid-catalyzation reaction were applied. Various mechanisms of amplification were investigated, e.g. depolymerization, deprotection, polymerization, dehydration, condensation, and so on, discussed in detail in ref. \([204]\).

In summary, the detailed reaction mechanisms are very specific and depend on the chemical constitution of the resist, the radiation processes applied (e.g. exposure energy, exposure dose) as well as the exposure environment. In these terms it is extremely challenging to reveal the underlying lithographic mechanisms since typically multiple active species and reaction paths exist. Further details are provided in ref. \([204, 206, 207, 209, 210]\).

**Latent Image Formation:** All reaction mechanisms (a-d) have in common that during the exposure process a so called latent image of the exposure is formed. Typically, as function of the mechanism the exposed resist regions are swelled (a), shrunken (b), degraded (c), or the stiffness or adhesion (a-d) of the exposed surfaces were changed. By using AFM techniques the latent image is measurable directly after the exposure process. As demonstrated in experimental section 6.2.2, the latent images could be
applied for alignment of FE-SPL patterning processes in the frame of a mix-and-match lithographic concept.

**The Environmental Influence:** As pointed out by O’Donnell [206], the environmental conditions in which the exposure process is carried out, significantly influence the lithographic reaction mechanisms. Thus, the irradiation in ambient conditions, applied in FE-SPL, is substantially different than a vacuum exposure process, which is typical in EBL. In the case of an ambient exposure the presence of oxygen, water, and other species has to be considered. In this context, oxygen favors scission at the expense of crosslinking [206]. The formation of peroxides and other oxygen-containing structures is likely. Thereby, oxygen reacts with radicals, whereby the availability of the oxygen is defined by the local diffusion rates which results in different properties of surface and bulk resist. It is suggested that with increasing molecular weight oxidative degradation processes (ref.: [211]) are reduced [209, 211, 212]. Further, the presence of a water film at the resist-air interface as well as water absorbed within the resist film, depending on the hydrophilic and hygroscopic properties of the resist and the humidity of the environment, respectively, has to be taken into account. A significant influence of the water film is expected because the IMFP of ultra-low energy electrons in water is only \( \approx 1 \text{ nm} \), whereby the MFP ranges between \( 0.1 - 1 \text{ nm} \) (ref. [213]). Since the typical water layer thicknesses in an ambient environment is expected between one and a few nanometers, interactions within the water layer are most likely. Here, excitation and ionization, which have thresholds of \( \sim 7.4 \text{ eV} \) and \( \sim 13 \text{ eV} \), respectively, can occur. By water radiolysis [214, 215, 216] and/or ionic dissociation of the water and related reactions [46, 104, 158, 217, 218] chemically reactive species are generated. In particular, the ionic dissociation leads to \( H^+ \) and \( OH^- \) ions. The protons can react further with \( ROH \) forming \( ROH_2^- \), which contributes to crosslinking. In contrast, the hydroxides scavenge protons, which contributes to scission processes (ref. [209]). The radiolysis reaction of water, triggered by the incident radiation, generates predominantly \( OH^- \cdot \), \( H^- \cdot \), \( e^-_{aq} \) and \( H^+ \). Thereby, the \( OH^- \cdot \) and \( H^- \cdot \) radicals are much more reactive than the \( H^+ \) and \( OH^- \) ions [214, 215, 216, 218]. \( OH^- \cdot \) works also a powerful oxidizing agent. Consequently, in ambient conditions novel lithographic mechanisms, through the presence of oxygen, water, and other species are enabled which are not accessible via conventional EBL. Depending on the environmental conditions crosslinking, scission, or degradation processes could be enhanced [206]. In order to integrate this possibility in the case of FE-SPL a novel fast environmental modification system was invented and integrated, described in section 3.1.5. Initial tests, section 4.2.6, demonstrate that by modulations of the tip-surrounding local environment specific lithographic reaction paths could be amplified or suppressed.

**The Trade-Off between Resolution, LER, and Sensitivity:** In general, there is no resist which meets all requirements for nanolithographic applications, in particular highest resolution, lowest LER, and high sensitivity. Thereby, the sensitivity defines the achievable throughput capability. A high sensitivity means that only low exposure doses (\( \text{Dose} \)) are required in order to induce the respective lithographic reactions. A trade-off between resolution, sensitivity, and LER always exists. Using CAR systems it was first recognized that an increased sensitivity results in decreased resolution (\( R \)) capability and higher LER. In particular, one has determined that \( R^3 \cdot LER^2 \cdot \text{Dose} \approx \text{Constant} \) [219, 220]. Due to the amplified reaction kinetics the spatial resolution control deteriorates. In contrast, non-amplified resists have lower sensitivities but facilitate better resolution and smaller interaction volumes (ref. [27, 220]). This seems to be also valid in the case of EBL, where highest resolution was achieved typically by application of low sensitivity resist systems, e.g. inorganic or molecular resists [28]. Thereby, as discussed previously (2.2), the sensitivity increases with decreasing electron energies. Unfortunately,
linked with that the resolution capability is decreased.

In conclusion, resist systems with lower sensitivities seem to be favorable in terms of highest resolution since a better spatial confinement control is given. This is facilitated by a better local exposure dose definition without running into shot noise problems. Moreover, a multitude of further factors limits the resolution: beam spot size, scattering events, reactive species diffusion, baking temperature, delay time between baking and exposure, writing strategy, exposure dose control, development-related and solvent-induced problems, resist thickness, resist contrast, molecular weight, and adhesion of the resist to the substrate, to mention only a few [51]. In this context, a novel low molecular-weight resist class, so called molecular (glass) resist materials, were identified as promising candidates to overcome the RLS trade-off, discussed in next section 2.3.2.

**Exposure Dose Definitions in case of EBL and FE-SPL:** The point $\Phi_P$, line $\Phi_L$ and areal $\Phi_A$ exposure doses of a resist in the case of EBL and FE-SPL are defined as follows (Eq. 2.5-2.10):

1. Point exposure dose $\Phi_P [pC]$

$$\Phi_{P-EBL} = I_{\text{beam}} t_{\text{dwell}}$$

$$\Phi_{P-SPL} = I_{\text{beam}} t_{\text{dwell}} = \int I_{\text{beam}} dt$$

2. Line exposure dose $\Phi_L [nC/cm]$

$$\Phi_{L-EBL} = \frac{I_{\text{beam}} t_{\text{dwell}}}{s}$$

$$\Phi_{L-SPL} = \frac{Q}{l} = \frac{I_{\text{beam}}}{v_t} ; \Phi_{L-SPL} [nC/cm] = 10^4 \frac{I_{\text{beam}} [pA]}{v_t [nm/s]}$$

3. Areal exposure dose $\Phi_A [mC/cm^2]$

$$\Phi_{A-EBL} = \frac{I_{\text{beam}} t_{\text{dwell}}}{s^2}$$

$$\Phi_{A-SPL} = \frac{Q}{A} = \frac{I_{\text{beam}}}{l p} = \frac{I_{\text{beam}}}{v_t} \cdot \frac{1}{p}$$

with beam current $I_{\text{beam}}$, exposure (dwell) time $t_{\text{dwell}}$, exposed line length $l$, exposed area $A$, tip velocity $v_t$ in the case of FE-SPL, step size $s$ in the case of EBL and line pitch $p$. The differences between EBL and FE-SPL in terms of line and areal exposure dose calculations arises from the different patterning strategies applied. In particular, for EBL a pixel based method is typical, whereas for FE-SPL a vector based method is chosen. The implemented writing strategies are described in detail in section 3.1.4.

**2.3.2 From Polymeric towards Molecular Glass Resist Systems**

The advances in lithographic methods, reaching the 10 nm scale, reveal the intrinsic limitation of polymeric resist materials [221, 223, 224, 225, 226]. In particular, the size of the macromolecular resist blocks, outlined in Fig. 2.3.2 for polyhydroxystyrene (PSOH), are larger than the targeted feature sizes. Furthermore, the dimension of the applied macromolecules is in the same size range as the targeted resist layer thickness. Thus, the preparation of a homogeneous resist layer with low surface roughness, as well as defining features with low LER is hampered. Fluctuations of even a single molecule can be critical.
Figure 2.3.2: Size comparison between a typical polymeric resist, in particular polyhydroxystyrene (PSOH) with 50 repeating units [221], versus molecular (glass) resist types, in particular the calixarene derivatives calix[4]arene, C-methyl-1-acetoxycalix[4]arene (CMC4R) and 4-methyl-1-acetoxycalix(6)arene (4m1ac6). The polyhydroxystyrene molecule image was taken from [221], the calixarene images from [51, 222].

Moreover, nowadays the resist is a complex mixture of polymers with a range of molecular weights, different protection levels and different protection sites (ref. [224]). The chemical inhomogeneity is another intrinsic limitation factor.

Molecular glass resist (MG) materials, for example calixarene and its derivatives, Fig. 2.3.2, represent a paradigm shift compared to polymeric resists. The monodisperse nature gives a well-defined and coherent molecular structure without distribution of molecular weights. The low molecular weight molecules, with spatial extensions of typically $\lesssim 1$ nm, are expected to give significantly smaller pixel sizes combined with lower LER [221, 223, 224, 225, 226, 227]. The lack of chain entanglement and the absence of composition and size distributions favors the controllability of the overall lithographic process. In contrast to polymeric resists, which consist of repeated monomers crosslinked by strong covalent bonds, MG resists are characterized by a hierarchical binding architecture. In particular, intramolecular bonds are of covalent nature, which gives chemically stable molecules, whereas the intermolecular system consists of multiple weak non-covalent bonds. The cooperative effect of multiple weak bonds are responsible for the formation of stable resist films (ref. [228]). In case of MG resists the amorphous, so called glassy state is targeted. By using the amorphous state, where no crystallized areas and thus grain boundaries are present, a high homogeneity, uniformity, and isotropic resist properties are ensured. Due to the high thermal and chemical stability of the single MG resist molecules, the possibility of alternative solvent-free thin film preparation techniques is enabled, investigated in section 3.2.2.

Initial efforts have been made to exploit the innovative properties of MG resist in EUV lithography ($\lambda = 13.4 \text{ nm}$) [221, 224, 229, 230, 231, 232], in standard EBL (mostly applied as demo-system as a substitute for EUVL) [28, 233, 223, 231, 234] and thermal SPL [75]. Different core molecules were deployed, for example calixarenes [183, 182, 199, 233, 235, 236, 237, 238], fullerenes [239, 240, 241, 242, 243], dendrimers [244, 245], benzenes [246, 247], truxenes [248], or triphenylene derivatives [249, 250], to mention only a few. By using calixarene and its derivatives highest resolution capabilities at the 10 nm scale has been demonstrated [182, 233, 227, 251]. But in spite of the impressive results, the RLS trade-off is still valid. Since these kind of MGs are non-amplified systems, the lack of an adequate sensitivity hampers useful applications. As early as 1960 Charlesbury [252] wrote that a decreasing molecular weight results naturally in a decreased areal sensitivity since the number of required crosslinking
Calixarenes | Resorcinarenes
---|---
(i): tert.-Butylcalix[4]arene [237]; (ii-iii) cone configuration of (i) [237, 255] | (i) Resorcinarene [237]; (ii-iii) cone configuration of (i) [256]

<table>
<thead>
<tr>
<th>Applied: 4m1ac68</th>
<th>Applied: CMC4R</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 6/8 )</td>
<td>( n = 4 )</td>
</tr>
<tr>
<td>( R_u = CH_3 )</td>
<td>( R_u = R_l = / )</td>
</tr>
<tr>
<td>( R_l = O_2CH_3 )</td>
<td>( Z = CH_3 )</td>
</tr>
<tr>
<td>Film property: hydrophobic</td>
<td>Film property: hydrophilic</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Basic unit: tert-butylphenol</th>
<th>Basic unit: resorcinol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base catalyzed cyclization (only with formaldehyde)</td>
<td>Acid catalyzed cyclization (possible with various aldehydes, with exception of formaldehyde)</td>
</tr>
<tr>
<td>Different ring sizes ([n]), commonly 4, 6, 8 phenolic units, with high yields possible</td>
<td>Only tetramer calix[4]resorcinarene possible, caused by intermolecular H-bonds [257]</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of applied calixarene and resorcinarene molecules (\( n \): repeating units; \( R_u \): upper rim modification; \( R_l \): lower rim modification; \( Z \): inter-rim modification). The table is based on [199, 236, 237, 256, 257, 258, 259].

Reactions for a defined voxel size, in order to render a gel state of the resist, is increased. This is confirmed also by ref. [233, 227]. Furthermore, solvent-related problems such as swelling induced instabilities and capillary forces during wet development limits the achievable minimum feature size [253, 254].

### 2.3.3 Calixarene-based Molecular Glass Resists for FE-SPL

**Calixarenes - Chemical Chameleons:** Calixarene and its derivatives, of which resorcinarene also counts, are small, bowl/cup shaped macrocyclic oligomers with dimensions of 0.5 – 1 nm. Calixarene and its derivatives belongs to the group of metacyclophanes. Summarized in table 2.1, calixarenes consist of phenolic units, whereby the basic repeating unit in resorcinarene is resorcinol. Due to their unique properties calixarenes have received widespread attention far beyond their initial applications in supramolecular and host–guest chemistry [260, 261, 262]. A unique composition of benzene groups, which participate in \( \Pi - \Pi \) interactions, and hydroxyl groups, which are responsible for intra- and intermolecular hydrogen bonding interactions, are available. In consequence of the free rotatability around the \( \sigma \)-bond of the methylene bridge, many conformations are possible (ref.: [257]), which differ in location of the \( OH \)-groups with respect to the molecular plane. Through stabilization by optimally arranged intramolecular hydrogen bond interactions the cone configuration for calixarenes [237] and the rccc-isomer for resorcinarenes [257] are the most stable configurations (table 2.1). However, in the case when calixarene molecules are prepared on surfaces, or dissolved in a solvent, the conformation...
could be different. The spatially defined hydrophobic cavities could be tailored to different sizes by changing the number \([n]\) of phenol/resorcin base units (smallest entity: \(n = 4\)). This enables the selective and reversible trapping of ions and neutral molecules within the cavity through formation of so-called host-guest interactions [256, 261, 262, 263]. The development of a one-step cyclization process, pioneered by Gutsche [261, 262, 264], has opened an easy synthesis with high yields. Due to the multiple functionalization capabilities in the upper and lower rims, a widespread applicability is given, e.g. for separation of ions, remediation of contaminated effluents, as selectors in chromatography, bio-organic and mimetic/artificial enzymes, selective membranes, and as catalyst material (ref.: [199, 237, 257, 261, 262, 263, 265]). Calixarene derivatives were also applied as functional material in sensoric applications [266, 267, 268], as optical material for non-linear optics [269, 270] as well as low-k heat-resistive dielectric insulator material [238, 271].

**Calixarene-based Resists for Nanofabrication:** First attempts to exploit the small sized molecules in lithography was driven by researchers of NEC corporation [182, 233, 227, 235]. They have revealed that calixarenes behave in EBL as an ultra-high resolution negative tone resist. In particular, \(8 \text{nm}\) single isolated lines have been defined by EBL in chloromethyl-methoxy-calix[4]arene resist using \(50 \text{keV}\) electrons and a line dose of \(6.25 \text{nC/cm}\) [272]. More recently, a \(12.5 \text{nm}\) hp dense patterning was achieved by EUV interference lithography [273]. Despite certain analogies between calixarenes and their polymeric relative the novolak resins, the physical and chemical properties of calixarene resist systems differ strongly from those of linear phenol resins. The strong differences in chemical and thermal stability are conspicuous. While calixarenes have high melting points, e.g. for CMC4R \(T_m > 300 \text{°C}\) [274]), which gives a supreme thermostability, novolak resist systems soften already at approximately \(150 \text{°C}\) [233, 237]. In contrast to phenol resins, calixarenes feature a high heat resistivity and chemical stability. The practical applicability of calixarene resist is supported by the capability to form extremely hard and flat surfaces (5 – 10 times higher than ordinary polymeric resists [233]). Due to the strong chemical coupling of benzene rings [199, 275] an acceptable plasma etching durability results [182, 199, 233, 237, 236, 238]. In particular, in \(CF_4\) plasma a 4-times higher etch resistivity was obtained than by using PMMA resist [182]. The plasma etching durability could be further enhanced by silylation of the phenolic hydroxyl groups [199, 275]. In this context, calixarenes were handled as “prospective material for nanofabrication” [233].

Intensive investigations were carried out in order to understand the exposure mechanisms in calixarene resists. So far, the detailed mechanisms of electron beam induced crosslinking could not be unequivocally clarified. Experiments by Ruderisch [237] and Sailer [199, 236] pointed out that the aromatic system is partially broken (aliphatic bonded hydroxyl groups were found after exposure) and the oxidation state of the carbon atoms, at which originally the phenolic hydroxyl group was bound (lower rim), are raised. The spectroscopic investigations showed no defined final state. Instead, an increase of the chemical inhomogeneity was measured, which points out that multiple mechanisms are likely to be triggered. Sailer [199] suggested that a partial oxidation of the molecular structure is most likely. Also Prins et al. [276] concluded that a break-up of the arenes, followed by linking to other arenes or functional groups is the main mechanism. Laser-based dry development experiments of EBL exposed resist features, carried out by Olynick et al. [253, 254], have revealed that \(4\text{mAc}\) loses some carbonyl units during exposure while forming new \(OH\)-groups. Thus, a removal of the acetoxy groups by the electron or laser exposure is occurring. They surmise also that the formation of aromatic \(OH\) is followed by aromatic \(OH_2^+\). In this context, it is suggested that the laser-induced ablation process is promoted by an interplay between phenolic units and extended conjugation in the aromatics [253].

Also calixarene MG resists are governed by the RLS trade-off (2.3.1). Due to the small size and low
molecular weight many more crosslinks per unit volume are required [233], which results in impracticable low sensitivities. The typical areal exposure dose required to induce a gel state of the resist is several \(mc/cm^2\), which is almost 20-times higher than that for PMMA [182]. In contrast, CARs need three orders of magnitude lower doses [199, 236]. Some attempts were made to increase the sensitivity and contrast of in EBL by:

- **Chemical functionalization:** A Cl-functionalization (chloromethyl group) has resulted in a sensitivity improvement of about 10-times [182, 221, 251, 272]. Both the larger cross-section of Cl compared to H as well as the difference in binding energy between \(C−Cl\) vs. \(C−H\) is suggested to enhance the sensitivity [221]. Further sensitivity improvements were demonstrated by introduction of allyl groups [199, 236, 237], double bonds [237] or by further modifications [199, 236, 237]. In terms of resolution, the insertion of groups which facilitate the generation of chemically reactive species, e.g. epoxy groups [233], should be avoided.

- **Arene number \([n]\):** An increased arene number \([n]\) (table 2.1) has led to enhanced sensitivity [199, 236, 237, 251, 276]. This is linked with the increase of the molecular weight which reduces the required crosslinks per unit area (ref. Charlesby theory [252]).

- **Improvement of the wet development process:** In order to improve the resist contrast, ultrasonically assisted development has shown encouraging results [277]. This is mainly attributed to the enhanced development rate. As a result, \(\sim 6\,nm\) isolated lines were resolved and the exposure dose latitude was increased by 50. However, resist adhesion problems and the feature collapse are enhanced by ultrasonic development. The application of highly purified calixarenes has further improved the resist contrast [278].

- **Attempts of a dry development process:** However, to completely circumvent solvent-related problems, dry development methods were successfully applied. In particular, thermal methods [279] as well as selective laser-based development [253, 254] were tested giving acceptable results. In thermal development volatility differences are exploited. In particular, the exposed (crosslinked) areas remain on the substrate, while the unexposed regions are transferred in volatile products. The sensitivity, contrast, and resolution were mostly maintained. In case of laser-based dry development, the laser radiation is absorbed with a higher selectivity by the exposed (crosslinked) resist areas. Thus, the tone is reversed. Patterns up to \(20\,nm\) hp were resolved while the required EBL exposure dose was reduced of about 4-times.

- **Low energy electron exposure:** Derived from section 2.2, the application of lower primary electron energies in case of EBL results in an increased sensitivity and reduced backscattering proximity. A resolution limit of \(10\,nm\) was found at \(2\,keV\) energies [183]. Lower beam energies were not accessible by conventional EBL systems [183].

**Towards Calixarene MG Resists in FE-SPL:** Despite these efforts a widespread application of calixarene MG resists in lithography has not occurred yet. The EBL-based patterning at the sub-20\,nm dense level becomes rather challenging owing to proximity effects, development-related problems, and the high electron doses required in order to crosslink the calixarenes. An alternative approach is necessary, which

(a) overcomes the low sensitivities while preserving or enhancing the resolution capabilities,

(b) prevents the additional resolution-limiting problems, in particular linked with the development process (pattern collapse, adhesion, resist swelling), and
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(c) integrates the method into a CMOS or beyond-CMOS process flow. A mix-and-match compatibility with other lithographic techniques is favored.

Within the lithographic experiments carried out, calixarenes were investigated as an initial model MG resist system. With progressing work other MG resist systems were also tested 4.4. In appendix section A.2 a summary of all applied resist materials is provided, whereby in section 3.2 the applied film preparation techniques are discussed.

2.4 Fowler-Nordheim Field Emission Theory for Nanotips

2.4.1 The Different Regimes - From Tunneling towards Field Emission

The first comprehensive experimental measurements of Metal-Vacuum-Metal (MVM) tunneling, cold field emission, and the intermediate transition regime were done by Young et. al. [280]. A so called topograpfiner set-up [281] was applied, which was the predecessor of the STM. A tungsten emitter was placed very close to a platinum surface. The current-voltage characteristics were measured in UHV conditions, shown in Fig. 2.4.1. The obtained characteristics were compatible with Simmons general theory of MVM tunneling [282, 283]. Simmons derived a general single theory based on the WKB approximation, which describes the current density \( J_g \) across the entire range including the close-spaced MVM tunneling as well as field emission (ref. Fig. 2.4.2):

\[
J_g = \frac{e}{2\pi \hbar (\beta \Delta S)^2} \left\{ \tilde{\phi} \exp \left( -N \tilde{\phi}^{1/2} \right) - (\tilde{\phi} + eU_b) \exp \left[ -N \left( \tilde{\phi} + eU_b \right)^{1/2} \right] \right\}, \tag{2.11}
\]

with the mean barrier height \( \tilde{\phi} \), the potential energy of an electron between the two metal surfaces including the image potential \( \phi_i(X) \), the distances from the first surface to the place where the potential energy equals the Fermi energy near surfaces 1 and 2, respectively \( S_1 \) and \( S_2 \), the applied bias voltage \( U_b \) (voltage applied across the MVM stack), the electron mass \( m_e \), the electron charge \( e \), Planck’s constant \( \hbar \), as well as the correction factor \( \beta \). Image potentials at both surfaces are taken into account. The model approximation of Simmons, confirmed by the experiments of Young et al., shows that one of the two different quantum mechanical processes prevails as function of applied bias voltage. In particular, in the low voltage regime \( U_b \ll \phi_o/e \) MVM tunneling dominates, whereas in the high voltage regime \( U_b > \phi_o/e \) Fowler-Nordheim field emission is overwhelming. The potential energy diagrams for both processes are schematically drawn in 2.4.2.

MVM Tunneling Regime (Low Voltage Approximation): At low bias voltages \( U_b \ll \phi_o/e \), which result in typically small tip-sample spacings \( (d_{ts}) \) of \( 3 \AA < d_{ts} < 10 \AA \) in case of a constant-current (cc) mode operation, Simmons Eq. (2.11) could be reduced to [282, 283]:

\[
J_{LV} = \sqrt{2m_e} \left( \frac{e}{\hbar} \right)^2 \sqrt{\tilde{\phi}} \frac{U_b}{d_{ts}} \exp \left( -\frac{4\pi d_{ts} \sqrt{2m_e \phi}}{\hbar} \right), \tag{2.12}
\]

Thereby, the following assumptions were made: neglection of the image potential; width of the rectangular barrier does not change: \( \Delta S = d_{ts} \); \( eU_b \) is very small and \( \tilde{\phi} \) is considered to be the zero-voltage mean barrier height \( \rightarrow \tilde{\phi} \gg eU_b \). This scenario is schematically drawn in the energy diagram.
Figure 2.4.1: Measurement of MVM tunneling. Fowler-Nordheim field emission and the intermediate transition regime: a) Voltage vs. distance characteristics at a constant current density of 50 Å/cm²; b) Current vs. voltage characteristics measured with three different emitter-to-surface spacings. The graphs are adapted from [280].

Figure 2.4.2: Potential energy diagrams of a MVM structure. Two different cases are shown: (a) \( U_b \ll \phi_o/e \), low voltage approximation; (b) \( U_b > \phi_o/e \), high voltage approximation. A rectangular potential barrier is assumed (black). The deformation of the potential barrier due to an image potential is drawn schematically in green. The schematics are based on [283].
Fig. 2.4.2-(a). Since the low voltage approximation describes very well the $I - U$-characteristics of a MVM structure at low voltages, typically $U_b < 1\, V$ [284], it is used to model the operation of the STM [33, 285]. By further simplification of Eq. 2.12 the basic dependencies of the tunneling current density $J_{LV}$ are highlighted [33]:

$$J_{LV} (\text{Tunneling}) \propto U_b \exp(-d_{ts} \sqrt{\phi})$$  \hspace{1cm} (2.13)

(a) The current-voltage characteristic is linear in the MVM tunneling regime, which means that the MVM tunnel resistance has an ohmic behavior [282, 284].

(b) The tunneling current is a very sensitive (exponential) function of the tip-sample spacing, which gives the remarkable z-resolution capability of the STM. For example, the tunneling current is changing by an order of magnitude for every ångström alteration of the tip-sample spacing [33].

**Fowler-Nordheim (FN) Field Emission Regime (High Voltage Approximation):** At larger bias voltages $U_b > \phi_0/e$, which result also in increased tip-sample spacings of $d_{ts} > 10\, Å$ in cc-mode operation, the potential barrier is changed with respect to its shape (rectangular $\rightarrow$ triangular), its width $\Delta S = E^{-1} (\phi_0/e)$ and mean height $\bar{\phi} = \phi_0/2$ (in a first approximation the image potential is neglected) [282, 283]. In particular, the barrier width $\Delta S$ becomes a function of the electric field strength $E_{pp}$ in the vacuum gap (first assumption of parallel plates applied):

$$E_{pp} = U_b/d_{ts}$$  \hspace{1cm} (2.14)

This scenario is summarized in energy diagram Fig. 2.4.2-(b). Derived therefrom, Simmons Eq. 2.11 can be approximated by [282, 283, 285]:

$$J_{HV} = \frac{e^3}{8\pi \hbar} \cdot \frac{E^2}{\phi_0} \cdot \exp \left( -\frac{8\pi \sqrt{2m_e}}{3\hbar} \cdot \frac{\phi_0^{3/2}}{E} \right)$$  \hspace{1cm} (2.15)

The obtained Eq. 2.15 is equal to the so called Fowler-Nordheim (FN) field emission equation, published first by Fowler and Nordheim in 1928 [286]. They have first described the field emission current density as function of the applied electrostatic field strength $E$ and the work function of the metal $\phi$. In contrast to Eq. 2.15, Fowler and Nordheim have applied a slightly different approximation for $\bar{\phi}$, which takes the Fermi energy level $\eta$ into account [286, 287, 288]. The current density $J_{FN}$ can be finally described by:

$$J_{FN} = \frac{q}{2\pi \hbar} \cdot \frac{\sqrt{\eta/\phi_0}}{\eta + \phi_0} \cdot E^2 \cdot \exp \left( -\frac{8\pi \sqrt{2m_e}}{3\hbar} \cdot \frac{\phi_0^{3/2}}{E} \right)$$  \hspace{1cm} (2.16)

with $q$ as multiplicative factor of the electron charge [288]. In order to underline the basic dependencies of the current density $J_{FN}$ for high electric field strengths, a first approximation of Eq. 2.15 could be carried out using the Taylor series:

$$J_{FN-\text{Approx}} \propto E^2 \exp(-\frac{\phi_0^{3/2}}{E}) \propto E^2 \left( 1 - \frac{\phi_0^{3/2}}{E} \right) \sim E^2$$  \hspace{1cm} (2.17)

In contrast to the direct MVM tunneling regime, the current-voltage-characteristics do not reveal an ohmic behavior. Instead, the current density becomes strongly dependent on the applied electric field strength $E$ [281, 289]. If we assume in a first approximation a parallel plate setup, Eq. 2.14, one can simplify Eq. 2.17 to: $J_{FN} \sim U_b^2/d_{ts}^2$, which reveals the following generalized dependencies for the FN field emission regime:
(a) The current density scales in first approximation quadratically with the applied bias voltage $U_b$.
(b) The sensitivity to alterations of the tip-sample spacing $d_{ts}$ decreases in the case of the FN regime.

In cc mode operation, which means that $J_{FN} = \text{constant}$ and $E = \text{constant}$, in the absence of geometric effects one can derive that $U_b \sim d_{ts}$.

The differences between the two types of wave-mechanical tunneling effects through a barrier [290] could be derived already from the kind of the potential barrier (Fig. 2.4.2). In the case of MVM tunneling a rectangular step-like barrier is present, which changes towards a triangular shaped barrier at higher bias voltages for FN cold field emission. In consequence, in FN field emission regime the potential barrier is lowered by increasing bias voltages, which results in a strong increase of the current density [281]. In contrast to MVM tunneling, in the case of field emission operation all electronic states are available on the vacuum side of the barrier. Thus, the current is not determined by the density of states. Having a closer look onto the MVM tunneling process, only a narrow range of free electronic states on the positive electrode side are available. This limitation is responsible that in MVM tunneling the current density increases only linearly with the applied bias voltage $U_b$. Also, in MVM tunneling potential barrier changes have only a minimal effect (condition: $U_b \ll \phi_0/e$) [281].

Cold field emission is also fundamentally different from thermionic and photoemission. In the case of cold emission the electrons are not requiring extra energy in order to „jump-over” the potential barrier. Instead, the applied external electrostatic field induces such a strong deformation of the potential barrier that unexcited electrons can tunnel through it [287, 289]. The FN Eq. 2.15 and 2.16 refers strictly to the cold field emission theory (thermodynamic equilibrium at $T = 0$). However, these equations are a valid approximation as long as $\eta/kT$ is large, which is fulfilled for all ordinary temperatures [286]. Thus, at normal room temperature operation the FN cold field emission theory is applicable. [289, 291].

The exact boundary conditions between thermionic and field emission are described by Murphy and Good in [289]. The conditions are summarized for a tungsten emitter in Fig. 2.4.3.

From Tunneling towards Field Emission - The Relevance for FE-SPL: The changes in the general behavior of MVM tunneling and cold field emission, described by the low and high voltage approximation of the general equation of Simmons (2.11), respectively, are also experimentally verified (2.4.1, [280, 281]). The transition between the operation regimes occur gradually (intermediate regime). The ratio of MVM tunneling current and FN field emission current changes accordingly. For example, for $E = 0.3 V/\AA$ and $\phi_0 = 4.5 eV$ the MVM tunneling current completely dominates for $d_{ts} \leq 10 \AA$, and an important contribution is made up to $d_{ts} < 20 \AA$ [281]. In the case of FE-SPL, due to the presence of a dielectric resist layer (ref. chapter 4), higher bias voltages and thus larger tip-sample spacings are applied (mechanical tip-resist interactions are not intended). In consequence, the direct MVM tunneling current part can be neglected. Only the FN field emission part has to be considered. However, the assumptions made in FN emission theory are describing a very idealistic case [286, 290, 291, 292]. In practice many different versions of FN-type equations appear due to the fact that the original Eq. 2.15 - 2.16 have been improved, corrected and approximated many times [292].

2.4.2 Fowler-Nordheim Field Emission Theory in Practice

Boundary Conditions of the Elementary Fowler-Nordheim Field Emission Theory: The FN theory is generally employed with remarkable success, even in case the operational conditions are violating one or usually more of the approximations [288]. The basic FN emission theory, section 2.4.1, assumed an emitter with a flat planar surface, with a constant uniform local work function, and a uniform electric field outside [286, 291]. In addition, the basic Eq. (2.15, 2.16) neglect image interactions, band structure
Figure 2.4.3: Validity range of FN cold field emission equations. The upper (1) and lower (2) limits are marked. The figure is adapted from [288]. Calculation parameters: $\psi = 4.5 \text{eV}$, $\eta = 5.851 \text{eV}$. Abbrev.: RLD: Richardson-Laue-Dushman equation for thermionic emission; RT: room temperature.

The theory is also restricted in the characteristic dimensions of the emitter, which should be larger than $10 \text{nm}$ [293, 294, 295, 296, 297]. The maximum local electric field strengths should not exceed $E_L \lesssim 10 \text{V/nm}$ for $\psi \gtrsim 3.8 \text{eV}$ [289]. The limited applicability [293, 294, 295] of the FN theory is expressed by the Nordheim parameter $y_n < 1$ (ref. Eq. 2.22, with $E_L$ in $\text{V/nm}$ and $\psi$ in $\text{eV}$) [289, 298]. If the electric field strength exceeds a critical value, $E_{critical} = c^{-2} \cdot \psi^2 \propto E_{critical}[\text{V/nm}] = 0.695 \cdot \psi^2[\text{eV}]$ (the constant $c$ is defined in 2.22), field-induced ballistic electron emission (BEE) starts to dominate. Here, the top of the potential barrier is pulled down below the Fermi level, described in ref. [290, 295, 299]. However, most metal emitters, e.g. tungsten with $\psi_{\text{tungsten}} \approx 4.5 \text{eV}$, $E_{critical} \approx 14 \text{V/nm}$, would not sustain that regime. Practical problems correspond typically to $E < E_{critical}$ [295], with the exception of low work function emitters, ref. [299]. For example, the validity range of FN cold field emission theory is shown in Fig. 2.4.3 for metal emitter.

A Generalized FN Equation and Interpretation of FN-plotted Experimental Data: For ease-of-use a generalized FN equation, based on [290, 291], which includes the generalized correction factors $\xi$ and $\Upsilon$, should be introduced. The functional form of $\xi$ and $\Upsilon$ depends on the physical assumptions and mathematical approximations made [290]. The generalized FN equation gives the field emission current $I_{FN}$:

$$I_{FN} = \xi A \cdot \frac{E^2}{\psi} \cdot \exp \left( -\Upsilon \frac{\psi^{3/2}}{E} \right) \equiv \xi R_t E^2 \exp \left( \Upsilon \frac{S_t}{E} \right), \quad (2.18)$$

The field emission current density $J_{FN}$ is defined by $J_{FN} = I_{FN}/A$, with $A$ total area of emission. The values $a$ and $b$ are universal constants, given by:

$$a \equiv \frac{e^3}{8\pi \hbar} = 1.541434 \cdot 10^{-6} \text{A} \cdot \text{eV} \cdot \text{V}^{-2} ; \quad b \equiv \frac{8\pi \sqrt{2m_e} \hbar}{3e} = 6.830888 \cdot 10^9 \text{eV}^{-3/2} \cdot \text{V} \cdot \text{m}^{-1} \quad (2.19)$$

The parameters $R_t$ and $S_t$ are defined by:

$$R_t \equiv \frac{Aa}{\psi} ; \quad S_t \equiv -b\psi^{3/2}, \quad (2.20)$$

with the work function of the emitter $\psi$ and the electric field strength $E$. This notation is very helpful
In terms of a practical applicability, which is later applied for analysis of experimental data (ref. section 4.2.1). Typically, the semi-logarithmic form of Eq. 2.18 is applied:

$$\ln \left( \frac{I_{FN}}{E^2} \right) = \ln (\xi R_t) + (\Upsilon S_t) \cdot \frac{1}{E}$$  \hspace{1cm} (2.21)

In a so called FN-plot $\ln \left( \frac{I_{FN}}{E^2} \right)$ is plotted versus $1/E$. A linear relation results when FN cold field emission is the predominant emission process. Thereby, $\ln (R_t)$ and $S_t$ are the intercept and slope of the fitted linear function. Thus the work function $\psi$ of the field emitter and its emission area $A$ could be estimated. However, when the experimental data do not yield $\ln \left( \frac{I_{FN}}{E^2} \right) \propto 1/E$ other effects or emission process are influencing or dominating the process.

**The Standard FN Equation and FN Plot including an Image Potential Correction:** The elementary FN-type equations (2.15 - 2.16) seriously underestimate the local current densities by a factor of $\sim 100$ [291, 294]. Most often the approximation by Murphy and Good (MG) [289], the so called standard FN equation [290], are applied. In contrast to the original approximations by FN [286] more realistic potential barriers, which are rounded by image force effects, are considered (Fig. 2.4.2, marked in green). Therefore, the previously mentioned generalized correction factors $\xi$ and $\Upsilon$ in Eq. (2.20 and 2.21) are described by:

$$\xi \to t^{-2}(y_n) ; \ U \to v(y_n) ; \ y_n = \left( \frac{e^3}{4\pi\epsilon_0} \right)^{1/2} E^{1/2} \psi^{-1} \equiv cE^{1/2} \psi^{-1},$$  \hspace{1cm} (2.22)

with special field emission elliptic functions $v(y_n)$ and $t(y_n)$ [280, 289, 290, 291, 292], the Nordheim parameter $y_n$ and the constant $c \equiv (e^3/4\pi\epsilon_0) = 3.794687 \cdot 10^{-5} eV \cdot V^{-1/2} \cdot m^{1/2} = 1.199985 eV \cdot V^{-1/2} \cdot nm^{1/2}$. Typically, approximations for $v(y_n)$ and $t(y_n)$, especially the Spindt approximation [300]:

$$t^2(y_n) \approx 1.1 ; \ v(y_n) \approx 0.95 - y_n^2$$  \hspace{1cm} (2.23)

have been applied [13, 300, 301]. In the case of a detailed analysis and numerical calculations a more exact approximation based on series expansion, described by Forbes, can be applied [292, 294].

**2.4.3 The Electric Field Strength to Voltage Conversion Factor**

In an experimental scenario the electric field strength $E$ at the tip apex is unknown. Typically, the emission current $I_{FN}$ is measured as function of the bias voltage $U_b$. In a first approximation ([13, 290, 296, 300]) it can be assumed that the electric field strength at the emitting area of the tip is constant and related to the applied bias voltage, expressed by:

$$E = \beta U_b ,$$  \hspace{1cm} (2.24)

Thereby, $\beta$ is the so called field conversion factor [300] or field enhancement factor [13], respectively. Proximal probe tips can be approximated by an idealized smooth hemispherical shape. In that case $\beta$ is described adequately by [302]:

$$\beta = 1/(kr_{tip}),$$  \hspace{1cm} (2.25)

with the geometric factor $k$ [287, 302] and the radius of curvature of the tip $r_{tip}$. The geometric factor $k$ was analytically approximated by [302] for the far field ($d_{ts} \gg r_{tip}$) as well as for the near field ($d_{ts} < r_{tip}$) regime, shown in Fig. 2.4.4. For the far field regime a simplified form can be applied.
Figure 2.4.4: The geometric factor $k$ as function of tip-sample geometry $d_{ts}/r_{tip}$, shown for different tip geometries (b). The idealized hemispherical tip model is drawn in (a). (b) is adapted from [302].

[302]: $k \approx 1/2 \ln \left(4d_{ts}/r_{tip}\right)$. In case of $d_{ts} < 0.5 \cdot r_{tip}$ the electric field strength does not depend on the shape of the tip. Thus, the simplest planar emitter theory can be applied in order to describe the emission. However, in case of $d_{ts} \geq 0.5 \cdot r_{tip}$, which is valid for FE-SPL due to the dielectric resist layer term, the field enhancement factor $k$ depends on the overall geometry of the tip-sample system. Also small protrusions and irregularities lead to field enhancement effects in near field (lower $k$) due to their significant influence of the electric field distribution in the tip-sample gap. In addition, $k$ is a function of the applied polarity in far field regime (tip emitting or surface emitting), discussed in [302].

As suggested by Young et al. [280, 281], in the case of a constant electric field operation (experimental mode: constant current (cc) operation with modulation of $U_b$ and measurement of $d_{ts}$), the effective emission area and the electric field strength can be derived from the experimental $U_b$ versus $\log(d_{ts})$ plots. However, due to large errors involved (50% or higher), described by [302], $I_{FN}$ versus $U_b$ measurements are more common. Here, at a constant tip-sample spacing ($d_{ts} = \text{const}$.) the emission current $I_{FN}$ is measured as function of bias voltage ($U_b$) modulations. So called FN plots are obtained, discussed in section 2.4.4. In frame of the work only the most typical emitter profile, the hyperboloid tip geometry approximation, was applied (Fig. 2.4.4). Thereby, Eq. 2.25 was applied in order derive the tip radius from the estimated field enhancement factor. When the tip radius is independently known, e.g. by SEM measurements, the geometrical factor can be estimated. However, one could only calculate the maximum value of the field conversion / enhancement factor $\beta_{max}$ (on the axis) in context of a well-defined geometry [296]. In the experimental case the field conversion factor has a local distribution, which is linked with the electric field strength variations [288]. In conclusion, the transition from $J_{FN} - E$ to $I_{FN} - U_b$ by using the outlined assumptions gives only an approximation.
2.4.4 Towards the Experimental Scenario - Analysis of Voltage-based Fowler-Nordheim Plots

The integration of the field conversion factor, defined in Eq. (2.24), into the generalized FN equation, results in the derivation of the following FN-type equation:

\[ I_{FN} = \{\xi \beta^2 R_t\} U_b^2 \exp(\{\Upsilon \beta^{-1} S_t\} U_b^{-1}) \equiv R_{exp} U_b^2 \exp(S_{exp} U_b^{-1}) \]  \hspace{1cm} (2.26)

Transformation into a semi-logarithmic form gives:

\[ \ln \left( \frac{I_{FN}}{U_b^2} \right) = \frac{1}{U_b} \{\Upsilon \beta^{-1} S_t\} + \ln (\xi \beta^2 R_t) \equiv \frac{1}{U_b} S_{exp} + \ln (R_{exp}) \] \hspace{1cm} (2.27)

Thus, three unknown variables have to be determined, (a) the work function of the field emitter \( \psi \), (b) the total emission area \( A \), and (c) the field conversion / enhancement factor \( \beta \). By using only the slope \( S_{exp} \) and intercept \( \ln(R_{exp}) \) the variables are not determinable. On the one hand a variable can be independently (\( \psi, A, \beta \)) estimated, e.g. from literature, which is typically done for \( \psi \) [13]. In the particular case this could lead to significant errors. Alternatively, a method first suggested by Charbonnier and Martin [303], which eliminates the influence of \( \beta \), can be applied. Here, \( R \cdot S^2 \) are combined, which results in [290, 291, 292, 300]:

\[ R_{exp} S_{exp}^2 = \frac{A \Gamma d}{\psi} \; ; \; \Gamma = \frac{\xi \Upsilon^2 \psi^2}{d} \equiv \frac{ab^2}{d} \] \hspace{1cm} (2.29)

with the universal constant \( d = ab^2 = 7.192489 \cdot 10^{13} A \cdot eV^{-2} \cdot m^{-2} \) and the so called exact emission area extraction function \( \Gamma \) (unit in \( eV^2 \)) according to Forbes [290]. Thus, a general equation for the total emission area is obtained, which is independent on the details of the applied model [290]:

\[ A = \frac{R_{exp} S_{exp}^2}{\Gamma d} \] \hspace{1cm} (2.30)

For a practical analysis of the voltage-based FN plots (\( \ln(I_{FN}/U_b^2) \) vs. \( 1/U_b \) plotted with \( I_{FN} \) and \( U_b \) in SI units) the focus was placed on two approximations, which are both based on the MG treatment (Eq. 2.22) of the generalized FN equation:

(1) Spindt approximation [300]: The numerical approximation includes a simplified method for determination of the image potential by using \( v(y_n) \) and \( t(y_n) \), defined in 2.23. A fixed value for the exact emission area extraction function \( \Gamma \) is applied, which gives a maximum error of \( \pm 10\% \) over the entire work function range of \( \psi = 3.4 - 11.6 \, eV \). In summary, one could derive for \( R_{exp-Spindt} \) and \( S_{exp-Spindt} \) the following equations:

\[ R_{exp-Spindt} = \frac{\beta^2}{11} \cdot \frac{Aa}{\psi} \cdot \exp(e^2 b \psi^{-1/2}) = \frac{\beta^2}{11} \cdot R_t \cdot \exp(e^2 b \psi^{-1/2}) \] \hspace{1cm} (2.31)

\[ S_{exp-Spindt} = 0.95\beta^{-1}(-b \psi^{3/2}) = 0.95\beta^{-1} S_t \] \hspace{1cm} (2.32)
Applying $R \cdot S^2$ gives the following number for $\Gamma_{\text{Spindt}}$:

$$\Gamma_{\text{Spindt}} = \frac{0.95^2}{1.1} \cdot \left\{ \psi^2 \exp \left( e^2 b \psi^{-1/2} \right) \right\} \approx \frac{0.95^2}{1.1} \cdot 2250 \approx 1846 \text{ [eV]} \quad (2.33)$$

Thus, by using Eq. 2.33, included in Eq. 2.30, the total area of emission $A$ can be estimated (error due to approximations $\pm 10\%$). An a priori knowledge of the work function $\psi$ or the field conversion factor $\beta$ is not necessary.

(2) Forbes approximation [290, 292]: In contrast to Spindt, Forbes has developed a method based on an exact numerical calculation, defined in detail in [290, 292]. When the limiting values of the emitter work function and current density are known, an optimized exact emission area extraction function $\Gamma$ could be chosen from a table, provided in [290]. This procedure can be applied iteratively in order to minimize the uncertainty.

In the low current density range, in which FE-SPL is operated, the field conversion factor $\beta$ is a fixed geometrical factor and the emitter area $A$ is independent of the current density $J$ [303]. This was also confirmed by simulations done by Mayer et al. [301], which have shown that the beam diameter depends only slightly on the beam current. By using the Spindt and Forbes approximations for determination of the total emitter emission area $A$, the exact knowledge of the emitter work function $\psi$ is not necessary. However, for extraction of the field enhancement factor the work function $\psi$ is mandatory. Advantageously, for $\psi \geq 4 \text{ eV}$ the precise knowledge of $\psi$ is not necessary since a decreased influence of $\psi$ on $J_{FN}$ is present [303, 301]. In the experimental case the series resistance of the system itself can be neglected compared to the high tip-sample resistivity. Thus, the voltage across the tip-sample gap is assumed to be equal to the applied bias voltage.

In experimental work, section 4.2.1, all three models were applied, (a) the basic FN theory without image potential correction, (b) the standard FN theory with Spindt approximation of the image potential effects, and (c) the standard FN theory with Spindt approximation of the image potential effects plus Forbes iteration in order to refine the approximation. As a direct outcome from experimental data the total emitter area $A$, the field enhancement factor $\beta$ as well as the derived parameters like tip radius of curvature $r_{\text{tip}}$ (Fig. 2.4.4) for different model assumptions were estimated. When $r_{\text{tip}}$ is independently known by using SEM the geometric factor $k$ was estimated.

### 2.4.5 General Limitations of the Simplified Model and Application of Simulations

Typically, an emitter is characterized by a complicated three-dimensional structure. Thus, the electric field is not uniformly distributed around the tip apex. In the ideal case of a hemispherically shaped tip the electric field strength has a maximum exactly below the tip at the point of a minimum tip-sample spacing, shown in an electric field simulation Fig. 2.4.5. To the outer sides of the tip apex the field strength decays. Due to the variation of the electric field strength across the tip surface the field conversion factor $\beta$ (Eq. 2.24) becomes a local value distributed respectively around the emitting area. In case of an averaged value of $\beta$, a dependency from the applied bias voltage has to be taken into account [293, 296]. Thus, the assumption of a planar FN-theory, with a fixed field conversion factor and a fixed emission area, is only a simplified case of the experimental situation. More significantly, also the influence of the dielectric resist layer alters the electric field distribution in the tip-sample vicinity. This is elaborated in detail in section 5.2. Moreover, in frame of the work a back-coupling effect was found, which alters the field distribution as function of exposure time (ref. section 5.3).
Figure 2.4.5: Simulation result of a tip-sample junction showing the electric field strength (color-coded), the electron trajectories (black lines) and current density distribution on the sample surface (red curve). The simulation was carried out without a resist, a tungsten emitter with a radius of $10\, \text{nm}$ was assumed with $35\, \text{nm}$ tip-sample spacing. A bias voltage of $+50\, \text{V}$ was applied to the sample, whereby the tip was grounded. The particular simulation was conducted by S. Lenk, published in a joint work, ref. [304].

In general, a better understanding could be gained by using numerical simulations, especially when more complicated geometries are considered, e.g. in case of advanced tips or for description of the back-coupling effect. In particular, by solving the Laplace equation the local electric field strength in the defined geometrical tip-sample structure is calculated. The local current densities are derived in turn by applying the FN cold field emission theory. Thereby, the local values of the electric field strength are applied. For estimation of the total emission current density on the tip side the local emission current densities, which are estimated across the entire tip surface, are summed. In order to estimate the current density distribution at the sample surface, the trajectories of the emitted electrons were calculated by a velocity-verlet algorithm. A static electron emission model was applied. It was assumed that no scattering of the electrons are taking place. Also charging effects were neglected. The simulation underlies the same fundamental limitations of the FN cold field emission theory as discussed previously. Thus, a metallic field emitter with constant work function was estimated. Dependencies of work function modulations on the electric field [290] were neglected. The tip geometry has only an influence on the electric field distribution and on the trajectories of the electrons. Other effects are excluded [301, 304, 305]. Although these effects are not taken into account, the limitations have to be considered, e.g. thermal effects and instabilities (due to the ultra-low current operation in our case heating effects are not likely) [306, 307, 308], space charge effects, ionization and ion bombardment, the influence of adsorbates (all common contaminants on the emitter surface increases the work function) [306], voltage drops in the measurement circuit (should be negligible), leakage currents, field penetration and band-bending effects, quantum confinement associated with small apex-radius emitters [296, 297], field-related changes of the emission area or of the local work-function, statistical effects by many-emission-sites on a nanotip, environmental effects like moisture [309], to mention only the most important limiting factors [287, 288, 290, 291, 294, 296, 297, 300].

In frame of this thesis only numerical simulations applying the Comsol Multiphysics Software package, combined with the FN field emission theory, were elaborated. The results are described in chapter 5. For more detailed information about field emission simulations I would like to refer to the work of my colleague Steve Lenk [305], our publication [304] as well as the work of Mayer et al. [301].
3 Experimental Fundamentals of a FE-SPL Technology

In this chapter the experimental foundations for a field emission scanning probe lithography on molecular resist are explained. During the initial phase of this work the focus was placed on the development of lithographic tools, the lithographic processes and related analysis methods. In particular, my work had been started from a decommissioned STM-system which I had reactivated and modified. Initial results achieved with that system were published in [40, 51, 310]. In a second development phase I modified a conventional optical laser-based read-out AFM system to achieve an integrated field emission lithography functionality. Related results were published in [311]. The experience gained from these two development phases were transferred into a third and final one, where a novel Scanning Probe Lithography (SPL) platform was completely developed from scratch. In this context, the active cantilever technology of Prof. Rangelov’s research group was exploited. Due to the immense effort, this was carried out in teamwork with the MNES research group, funded by the SNM project (particular work of others has been acknowledged in the text and references are given). However, in the following sections mainly the fundamentals are explained, which have evolved primarily during the first and second phase of development. Achievements of the third development phase are published in [5, 31, 36, 37, 225, 226, 304, 312, 313, 314, 315]. Further, this chapter describes the development of the probe technology, probe modules as well as sample and resist preparation techniques. Also basic theoretical considerations, especially in context of the design rules for cantilever systems for FE-SPL, are elaborated. For evaluation of large amounts of lithographic results specific methodologies and associated models and analysis programs have been developed, described at the end of this chapter.

3.1 Experimental FE-SPL Technology

3.1.1 The Basic Technology Platform

The development of an FE-SPL platform, which enables lithography, imaging, inspection, and alignment in the single-digit nano scale, was not a straightforward and easy task. As mentioned above, the systems were developed and optimized in gradual steps. In the final development phase a complete FE-SPL technology platform was established, based on the experience gained from the previous research phases. Here, I would like to give an overview about the technological concepts and the final state of development. The intermediate optimization steps can be tracked by the publication list provided in appendix A.6.

**Concept and Construction:** In Fig. 3.1.1 the general concept of the main setup is summarized. The development status of the technology platform in year 2015 is shown in Fig. 3.1.2 (ref. [37]). The system consists of a top X-Y-Z piezo-scanner unit, on which the exchangeable probe modules (ref. 3.1.2) are mounted. Capacitive displacement sensors are integrated, which ensures a closed loop functionality.
3 Experimental Fundamentals of a FE-SPL Technology

Figure 3.1.1: Technical concept of the FE-SPL technology platform (a). The integrated feedback loops for imaging and lithography are summarized in (b). Abbreviations: amp (amplification), SP (regulation set-point), PID (proportional-integral-derivative) controller, ADC (analog-to-digital converter), DAC (digital-to-analog converter), LRF (Lithographic Review File), Topo (topographic image of the sample surface).

Figure 3.1.2: Development status of the FE-SPL technology platform in year 2015. [36, 37]
with 0.01 nm resolution in all three axes within the entire movement volume of 10x10x5 μm³. The sample is placed on an X-Y coarse positioning bottom stage. The bottom stage gives an enhanced patterning range of up to 100x100 mm², which is suited for wafer samples of up to 4 inch. Thereby, the combination of a small-range top stage and large-range bottom stage enables a step-and-repeat pattern functionality [36, 37], which is also applied in terms of mix-and-match strategies (ref. section 6.2). The positioning accuracy of the bottom stage of 10 nm resolution and 80 nm repeatability is sufficient since by integration of AFM imaging, deviations of the sample position could be corrected (ref. closed loop concept 1.3). For coarse navigation, alignment, and approach an optical microscope system is integrated. For coarse motions of the probe in the vertical (Z) direction, which are required for approach and coarse positioning in the Z-direction, the top scanner system is mounted on a precise and stiff linear translation stage. The carriage of the linear stage is positioned by a high resolution stepper motor. The mechanical design of the system (Fig. 3.1.2) was optimized in regards to short mechanical measurement loop, sufficient mechanical stability as well as the integration of all functionalities. Thus, the SPL Z-loop was designed to be short and most robust. In contrast to a previous one arm setup construction, published in [304], a cross-beam mainframe construction was chosen. The optical navigation unit is separated from the mainframe. In this way, the stiffness of the mainframe is not weakened and mechanical noise and thermal drift effects are reduced significantly. The system base and suspension beam are made of massive aluminum alloy blocks to minimize thermal drift effects. FEM methods were applied to ensure the mechanical stability. The dynamics of the top-scanner system was improved by reduction of the total mass, which has to be moved during scanning. In terms of electronic noise reduction the first amplification stage was integrated directly on the probe modules, close to the proximal probe. Additionally, special shielding layers were introduced surrounding the first stage preamplifier boards. More details of the system construction is provided in [37]. In order to decouple the technology platform from environmental interfering sources, e.g. acoustic, thermal, electronic, and vibrational noises, the system is encased from the environment and positioned onto a multi-level damping system. Within the chamber stabilized ambient conditions are ensured, typically \( T : 22 \pm 1 \degree C \) and \( r.h. : 35 \pm 5 \% \). A novel environmental modulation system was developed and installed, which gives the possibility of a fast alteration of the probe-surrounding local environment required for specific experiments (ref. section 3.1.5). The platform was calibrated by the means of a benchmark sample provided by the Dutch Metrology Institute VSL in frame of the SNM project. The measurement uncertainty for all three categories (line width, line position, and pitch measurements) are well below 1 nm, summarized in frame of the SNM benchmarking series conducted by VSL ([10]).

The Control Unit and Feedback Loops: The complete system is controlled by a FPGA mainframe, which is connected to a dedicated PC software. The highly flexible electronic mainframe of the FE-SPL platform comprises all essential blocks for an AFM functionality. The entire hard- and software for AFM is an in-house development of our research group, explained in detail in ref. [37, 304, 316]. For extension of this system towards FE-SPL, specific electronic hardware extension units, section 3.1.3, as well as a pattern generator tool, section 3.1.4, were developed and integrated. In order to control the tip-sample spacing in both operational modes, imaging and lithography, two separate feedback loops were implemented, shown schematically in Fig. 3.1.1-(b). For the imaging a standard AM (Amplitude Modulation) - AFM feedback loop is utilized. The regulation maintains a constant oscillation amplitude, at a fixed frequency, by respective adjustments of the tip-sample spacing. The PID (Proportional-Integral-Differential) regulator uses the voltage signal coming from the piezoresistive Wheatstone-bridge of the active cantilever, which is a measure of the cantilever deflection (ref. section 3.1.7). The signal coming from the piezoresistive Wheatstone bridge is preamplified, filtered, digitized, and demodulated by a lock-in amplifier.
3 Experimental Fundamentals of a FE-SPL Technology

For lithographic operation a bias voltage is applied to the sample, whereby the tip is grounded through the I-U converter unit. In the case of constant current (cc) operation the induced Fowler-Nordheim field emission current (ref. section 2.4) is held constant via adjustments of the tip–sample spacing. In that way a constant field strength at the tip apex is achieved, which leads in turn to a constant emission current. In conclusion, the current between probe and sample serves as both a regulation signal for the tip-sample spacing as well as a localized lithographic source. Thus, for FE-SPL operation a second feedback loop was implemented, which maintains a constant current between tip and sample by modulation of the vertical (Z) position of the piezostage. The current is converted into a respective voltage signal by a high precision transimpedance amplifier unit (ref. 3.1.3), and is afterward filtered, digitized, and fed into a second PID regulator, which generates a respective output voltage signal for movement of the Z-axis piezostage. In such a way the lithographic exposure dose, which is a function of the current set-point and velocity of the probe, is exactly controlled. As in every feedback loop, the PID parameters in imaging (AFM) and lithography (FE-SPL) are subject to a proper tuning determining the speed, overshoot, error, and stability of the regulation. Whereas the parameter tuning for AM-AFM is a well known practice, e.g. [317, 318, 319], in the case of FE-SPL the proper parameter sets have to be found. Thereby, in order to narrow the PID parameter range a trick was applied. By using the constant current (cc) Fowler-Nordheim field emission in imaging mode, the gains could be determined analogous to the AM-AFM operation.

In the actual control design both feedback loops, AM-AFM and FE-SPL, control the tip-sample spacing. In consequence, a simultaneous operation is not advisable. Instead, both operations can be switched dynamically (Fig. 3.1.1), which allows a sequential imaging / patterning cycle based closed loop lithography scheme 1.3. A fast switch between both operation modes is essential in order to minimize drift effects, which can occur between imaging, alignment and FE-SPL step. However, if in future a simultaneous operation is desired the feedback and system design has to be changed accordingly, discussed in ref. [13, 168]. Here, the emission current is regulated by modulation of the bias voltage, whereby the second loop maintains a constant tip-sample spacing by using AM-AFM feedback.

In conclusion, the final control design takes advantage of both feedback loops, AM-AFM and FE-SPL, control the tip-sample spacing. In order to bring the probe in close proximity to the sample surface a three-step approach process was implemented. For a coarse approach the optical microscope system was utilized. For fine approach the AM-AFM feedback loop was applied, which means that the approach stops when a pre-defined amplitude damping is reached. In a third phase approaching the last few nanometers towards the sample a current trigger (FE-SPL feedback loop) was utilized, which stops the movement of approach when a pre-defined current setpoint is reached. Since in case of a current-triggered approach extremely slow approach velocities of typically $v_{tip-Z} = 0.5 - 2 \mu m/s$ are required in order to prevent current-overshooting events, the three phase process was evaluated to be the best choice. Here, the targeted tip-sample spacing is reached within a reasonable time, but without resulting in a mechanical tip-sample crash or an overexposure of the resist.

3.1.2 The Basic System Configurations and Related Probe Modules

Due to the stepwise development of the FE-SPL system different probe modules have been evolved, summarized in Fig. 3.1. Since each system configuration has its unique pros and cons, the different probe modules were used for specific experimental investigations. The simplest system for investigating the basic electron-resist interactions is the wire-based configuration, Fig. 3.1-(iii). This probe module consists of a small holder, at which a sharpened wire, typically made from tungsten
### Table 3.1: Possible configurations of a FE-SPL system. In (i-iv) the probe modules are schematically drawn. In the table the different configurations are compared. Abbrev. applied: U (bias voltage), I (measured current).
or Pt-Ir, is attached. Since no deflection read-out and actuation for AFM imaging is integrated, this system configuration is not applicable for a closed loop patterning scheme. Nonetheless, compared to cantilever-based systems, Fig 3.1-(i-ii), the wire-based system has advantages, which makes it the module of choice for basic experimental investigations:

1. With the perpendicular probe-sample configuration, electrostatic forces are minimized. Thus, problems with alterations of the tip-sample spacing, which are caused by electrostatic bending of the cantilever (ref. 3.1.7), as well as pull-in effects (ref. 3.1.7) are circumvented. In conclusion, a significantly higher mechanical stability of experimental setup is given.

2. The probe-sample overlapping area is minimized. As a result, the entire system capacitance, which is a limiter of the feedback dynamics, is decreased significantly (ref. 3.1.7);

3. An easy tip processing scheme is enabled, e.g. by electrochemical etching. Compared to metal-coated Si tips, this method gives extremely sharp tips < 10 nm, with smooth and well-defined tip apices (ref. section 3.1.6).

Owing to its advantage (1) the wire module was applied in all cases in which tip-sample alterations were crucial, e.g. in basic Fowler-Nordheim field emission experiments (section 4.2.1 and 4.2.2). Furthermore, due to the enhanced mechanical stability (1), and the increased feedback dynamics (2), the wire-module was used for basic lithographic parameter investigations, in which the exposure parameters were modulated over a large range. For subsequent AFM imaging, an extra AFM-module was applied.

If a closed loop lithography is desired, a cantilever configuration with actuation and deflection read-out capability is required, Fig. 3.1-(i-ii). In the case of an active cantilever system, Fig. 3.1-(ii), due to integration of functions an easier system integration, higher processing speeds and a higher flexibility compared to conventional passive cantilever approaches (Fig. 3.1-i) are enabled (ref. section 3.1.7). However, as a result of the almost parallel arrangement in the case of the cantilever configuration, parasitic side effects are present during lithographic operation. In this context, in order to minimize the related electrostatic force, the electrostatic-related deflection as well as the system capacitance specific cantilever design rules have to be followed, discussed in section 3.1.7. Further, compared to the wire probes the fabrication of ultra-sharp field emission tips with smooth surfaces is challenging, e.g. in case of metal coatings the grain sizes limits the achievable tip radius.

In the shear force configuration, Fig. 3.1-(iv), the advantages of the wire probe configuration are merged with the possibility of a closed loop lithography provided by the cantilever set-up. Here, the probe is mounted perpendicular to the sample and oscillates parallel to the surface (shear force microscopy ref.: [320, 321, 322]). Thus, the parasitic side effects of cantilever probes are eliminated, and the integrated actuation and read-out of active cantilevers enables a direct AFM imaging capability. Initial experiments carried out with that configuration has confirmed their benefits. Especially the high mechanical stability is similar to that of a wire configuration. Furthermore, due to the horizontal vibration mode of the cantilever, the tip-sample spacing oscillations are minimized, e.g. in normal mode an oscillation of $\Delta d_{ts-normal mode} \approx 10 - 100 \text{ nm}$ is resulting an vertical amplitude in shear force of only $\Delta d_{ts-shear mode} \approx 0.01 - 1 \text{ nm}$. In conclusion, the shear force system configuration is well suited for a hybrid control principle, in which both tip-sample spacing and field emission current are controlled simultaneously. However, the fabrication of sharp, well-defined planar tips is the most stringent problem, which has to be solved for further applicability. So far, initial tests were carried out with ultra-small tungsten wire tips, which were mechanically attached to active cantilevers. In a subsequent electrochemical etching step, section 3.1.6, the wires were sharpened. Since this method is not suited for batch fabrication of the probes, novel tip fabrication methods are required in order to enable a breakthrough of the shear force configuration.
3.1.3 The Lithographic Extension Modules: High precision I-U Converter and Bias Amplification Units

The electronic modules, which enable the extension of every conventional scanning probe imaging system into a FE-SPL system, consists of a home-built high precision $I-U$ (transimpedance) converter and a bias amplification unit. Since the electron exposure dose directly influences the lithographic outcome (section 4.2), the field emission current has to be measured and controlled exactly (exposure dose is proportional to emission current). Thus, in order to achieve highest lithographic resolution as well as a sufficient LWR control, an ultra-low noise operation with acceptable bandwidth and resolution is targeted. As mentioned in the beginning of this chapter, in the first two development phases the first versions of the electronic hardware were designed and realized by myself, ref. [51], whereas further improvements were achieved in team with Tihomir Angelov, Lazar Chervenkov, and Tomas Hrasok.

![Schematic block diagram of the electronic extension units integrated into the system core enabling a FE-SPL process.](image)

**Figure 3.1.3:** Schematic block diagram of the electronic extension units integrated into the system core enabling a FE-SPL process. The $I-U$ converter unit consists of a (1) high voltage (over-voltage) protection; (2) transimpedance amplifier with integrated fixed filter (VG; virtual ground); (3) programmable gain instrumentation amplifier. The bias amplification unit (4) is built-up by a high voltage amplifier. The gain is adjustable by a factor of 10. A total bias voltage range of $-100 \text{ V}...+100 \text{ V}$ is given. All signals are controlled by the SPL controller with max. in-/output voltages of $\pm10 \text{ V}$ (P-LPF: programmable low pass filter; ADC: analog-to-digital converter; DAC: digital-to-analog converter).

The electronic extension units, which were integrated in the different scanning probe configurations (ref. 3.1.2), are summarized schematically in Fig. 3.1.3. For the $I-U$ converter unit design, which converts, filters, and amplifies the current signal, a two stage variant was chosen. The first stage consists of a transimpedance amplifier circuit (Fig. 3.1.3-2) with a small value compensating capacitor, which is integrated in parallel to the feedback resistor. The writing tip is connected to the virtual ground point of the transimpedance amplifier. This means that the tip is always at virtual GND level. In the second $I-U$ converter stage the first stage output signal is amplified by an instrumentation amplifier circuit (Fig. 3.1.3-3). The second stage gain is manually adjustable from 1 to 10 in order to give the best measurement range and resolution with respect to the targeted lithographic parameter range. Due to the two stage design a smaller feedback resistor is applicable, which results in a one order of magnitude
lower noise operation compared to a single stage version with a higher feedback resistor value. In order to minimize noise and crosstalk the I – U converter unit is placed as close as possible to the proximal probe. All electrical units are electrically shielded (Fig. 3.1.3-GND). Finally, the amplified signal, which serves as control signal of the current feedback loop, is routed into a programmable low pass filter, followed by an ADC (18 bit →≈ 0.08 mV resolution).

Since in FE-SPL bias voltages higher than the controller output (±10 V) are required, an external low-noise bias amplification unit (Fig. 3.1.3-4; gain factor: 10) was built and implemented. A bias voltage range extension of up to ±100 V was achieved. In case of a tip crash at higher bias voltages, the mechanical contact between tip and sample results in a decrease of the tip-sample resistivity from GΩ to a few Ω, which gives a current peak destroying tip and sample. Thus, for protection of the I – U converter unit an over-voltage protection is required (Fig. 3.1.3-1). A solution based on anti-parallel diodes, with a current limiting resistor in series, was implemented. As ultra-low leakage and low capacitance diodes the gate-to-channel diode of n-channel JFETs were applied. Due to the high tip-sample resistivity in normal operation mode the current limiting resistor of the protection circuit is negligible. The current offsets introduced are compensated electronically for each I-U converter unit and amplification stage separately.

The characteristics of the current feedback loop is summarized in Fig. 3.1.4. The I – U converter unit has an excellent linearity within the measurement range of –2 . . . + 2 nA (–4.5 . . . + 4.5 nA) for the 200 pA/V (2 nA/V) option (Fig. 3.1.4-a-b). A bandwidth of 1 kHz (Fig. 3.1.4-c) is given, which is sufficient for the targeted application. The stand-alone I – U converter unit (without bias amplification unit) is characterized by an RMS noise of 280 fA. The entire lithographic loop shows a RMS noise level of less than 0.5 pA (Fig. 3.1.4-d). Due to that low noise level of our home-built system, in comparison to other systems [168, 323, 324] 1 – 2 orders of magnitude lower current setpoints are enabled. In conclusion, a current control in the range of a few pA, at an enlarged bias voltage range, was made possible. In particular, a 2 pA current setpoint for low energy electron exposure was demonstrated. Thereby, the higher amplification option, 200 pA/V, was chosen for low dose exposure at high current measurement resolution, whereas the 2 nA/V option was applied for high current exposure tests with less crucial current control requirements.

3.1.4 Implementation of Different Writing Strategies - The Pattern Generator and Lithographic Software

The patterning of complex features at the nanoscale, with any imaginable shape and geometry, requires the precise control of the pattern generation, placement, alignment, and the lithographic processes themselves. Since the full freedom and functionality of scanning probes should be exploited, a dedicated software extension tailored for FE-SPL was developed and integrated. In particular, the pattern generator core was developed by myself, whereas the advanced functionalities as well as the user interface were implemented by my master student Matthias Budden, described in ref. [222]. The implementation of the pattern generator for the active cantilever technology platform was conducted by Alexander Reum and Ahmad Ahmad.

The pattern generator was designed in such a way that a fully automated patterning is enabled. Different writing strategies and modes as well as parameter sets are integrated. The basic functionality of the pattern generator is summarized in Fig. 3.1.5. The developed software module processes the user-defined input data (I1-I3) and compiles a lithographic command file, which is executable by the FPGA core program of the FE-SPL controller. The input data includes the: (I1) Geometry of the
3 Experimental Fundamentals of a FE-SPL Technology

Figure 3.1.4: Characterization of the lithographic extension units: (a-b) Measurement of the transfer function and linearity of the $I - U$ converter unit. In (a) the raw ADC output signal ($U_{DAC} - Current$) versus the applied bias voltage ($U_b$) is plotted. In (b) the ADC output signal is converted into the respective current signal by using the respective transfer function (TF). A high precision $1 \, \Omega$ test resistor was applied as tip-sample gap simulator. In (c) the Bode plot of the complete $I - U$ converter unit is shown. A bandwidth of $1 \, kHz$ in normal operation case is given. In table (d) the RMS noise measurement, carried out with the complete lithographic loop (controller - bias generator - bias amplification unit - $1 \, \Omega$ test resistor - $I - U$ converter unit - controller), is summarized. A RMS noise level of less than $0.5 \, pA$ is provided (measurement averaged over 20 single measurements, filter bandwidth $1 \, kHz$, 1 pole filter applied).
Figure 3.1.5: Schematic overview of the pattern generator tool. Based on the user input data (I1, I2, and I3) a lithographic command file (output = O) is generated, which is transmitted to the FPGA of the FE-SPL controller. In FPGA the command file is executable on demand.

lithographic feature; (I2) Parameter set, at which the feature should be patterned; and (I3) Placement and alignment options. Thereby, the geometric data are composed of basic predefined elements, in our case line- and dot-features. For the basic geometric types, specific writing strategies, schematically explained in Fig. 3.1.6, were implemented. Methods from common direct-write lithography, like EBL, were adopted and tailored for our specific needs and requirements. In particular, for lines a vector-based patterning routine was applied, whereas for dots diverse pixel-based modes were developed, Fig. 3.1.6 and 3.1.8. After definition of the geometry, for every feature (e.g. line #1, line #2, dot #1, etc.) the lithographic parameter set (I2) has to be specified. This includes the detailed exposure conditions like the patterning mode, the applied bias voltage, the exposure dose, the feedback loop parameters, and so on. Thereby, the specific parameter depends on the targeted writing strategy (the dependencies are discussed in experimental chapter 4). Also the placement and alignment data, which provide detailed information about the start points, the exact alignment and stitching options, the patterning sequence, and step-and-repeat functionalities (discussed in publications [36, 37]), are defined for single elements or for entire feature groups.

Vector-based Patterning Mode for Definition of Line Features: The vector routine for line geometries is the most often used and optimized routine. As drawn schematically in Fig. 3.1.6, the geometric layout (blue) is identical with the direct tip path movement path (red). Thus, the probe is moving only along the path, which should be written. In contrast to a raster-scan motion empty areas are skipped, which saves time. In the outlined example, Fig. 3.1.6, the line segment consists of 19 single lines, which are required to define the final corner feature. The following steps are executed successively in order to write the line segment feature:

1. The tip is moved in a straight line towards the start position of the line segment. Thereby, the lithographic exposure is inactive.

2. The tip is approaching towards the surface with constant velocity until the pre-defined exposure current trigger is reached. A custom-programmed approach algorithm is applied to safely engage the tip without crashing into the surface. In order to prevent overexposure events the approach parameters (setpoint, speed, and feedback loop parameters) are optimized (ref. three phase approach, section 3.1.1).

3. After the engage trigger is activated the tip moves with active exposure and lithographic feedback
loop along the computed target path defining the lateral geometry of the feature. The XYZ-movements are regulated by three additional feedback loops providing a closed loop control of the tip position (monitoring of the LVDT sensor signals is exemplified as shown in Fig 4.2.7).

4. At the end of the line segment the exposure process is deactivated, the tip is retracted and moved automatically to the next line segment.

In vector mode the pattern generator computes a closed tip path with a minimum line length (Fig. 3.1.7). The lines are summarized in line segments, Fig. 3.1.6. For computation of that routine the FPGA-software background has to be considered. In particular, the tip is moving in straight lines between successive XY-coordinates. Thus, the piezo-scanner drives from $X_{<n>}$, $Y_{<n>}$ to $X_{<n+1>}$, $Y_{<n+1>}$ in a straight line approximation. The XY coordinates are saved in the buffers of the FPGA. The FPGA software is working with a constant time spacing principle. This means that the local tip speed of the line, defined by $X_{<n>}$, $Y_{<n>}$ (start point) and $X_{<n+1>}$, $Y_{<n+1>}$ (end point), is a function of its vector length. In consequence, vector length variations would lead to respective tip speed modulations. For example, due to the constant time spacing, in case of dividing a line in half, the tip velocity is reduced by 50% of its initial value. To overcome that problem a constant velocity pattern converter software was developed, Fig. 3.1.7. The software tool converts the standard minimum XY-coordinate description of a feature (Fig. 3.1.7-a) into an equivalent XY-coordinate spacing description (Fig. 3.1.7-b). Within the equivalent XY-coordinate spacing description a global (rotatable) grid is defined, determined by the lowest common factor of all approximated lines. As a result of the equivalent vector length the tip velocity is constant over the entire line segment. A constant exposure dose patterning is achieved independently of the initial line length.

Figure 3.1.6: Writing strategies implemented in the pattern generator software. The schematic drawings show specific target layouts (blue color). The writing schemes are outlined by the tip movement path, colored in red and gray. Thereby, a gray tip movement path means that the lithographic exposure is inactive during the respective segment traveled. A red path means that the lithographic exposure is active defining the targeted feature geometry. A red dot means that a pixel is patterned at the respective X-Y-position.
Figure 3.1.7: Concept of the constant velocity converter, which is implemented in the pattern generator software module. The tip is moving from the actual XY coordinate \(<n>\) to the next coordinate \(<n+1>\) with a constant velocity. In the case of the minimum XY-coordinate description (a), which is a common description in CAD-programs, the tip velocity is a function of the vector length of the particular line. By using an equivalent XY coordinate spacing description (b), the vector length is constant resulting in a constant tip velocity over the entire line segment feature.

In experimental work both descriptions are applied. For modulation of the tip velocity within a line segment the vector length modulation was applied (e.g. published in [310], Fig. 4). In case of a constant tip velocity the equivalent XY-coordinate description was applied and a global velocity parameter was set. By changing the global velocity parameter the patterning speed was adjusted between single line segment features. Also for patterning of arbitrary areal features by using the vector mode an equivalent XY-coordinate description was applied. Here, an additional constant line spacing algorithm was implemented in order to achieve a homogeneously distributed areal exposure dose. This areal mode was developed by Matthias Budden, described in ref. [222].

**Raster-Scan Pixel-based Mode for Arbitrary Features:** The pattern is converted into a discrete pixel form as shown in Fig. 3.1.6. The tip moves in a raster-scan motion across the sample surface. The AFM feedback loop is activated in order to keep the tip-sample spacing constant. When the actual tip position in the raster scan has reached one of the target pixels, the lithographic exposure process is activated in pulsed manner. Because the probe is rastering the entire surface, this method is time-consuming and inefficient compared to the vector-mode. Despite the inefficiency for a single probe setup, due to the individual addressing of pixels, a multi-probe operation capability is given. Thus, the raster-scan pixel patterning method is more a general approach, which is necessary for cantilever array operation. In accordance with Soh et al. [13], the entire cantilever array unit is scanned in raster-motion over the sample and the exposure mode of each cantilever is activated independently, encoded in the individual pixels of the pattern (Fig. 3.1.6). Initial efforts of a single probe operation using pixel-based modes are summarized in section 4.3.2. The proof-of-concept had been conducted by an oscillating cantilever system, which modulates the tip-sample spacing and thus leads to a pulsed field emission.
Figure 3.1.8: Pixel-based writing modes applied for patterning of dot features. The modulation of the tip-sample spacing ($d_{ts}$) could be triggered either by Z-movement of the cantilever itself or by application of the piezoscanning unit. In the graphs the pixel modes are outlined by plotting the tip-sample spacing ($d_{ts}$), the bias voltage ($U$) and the measured current signal ($I$) versus time ($t$).

**Pixel-based Modes for Dot Features:** For patterning of dot features diverse pixel-based writing modes were implemented, summarized schematically in Fig. 3.1.8. The underlying principle of the modes is identical (Fig. 3.1.6). The tip moves to the target pixel location in retracted state, with inactive exposure. At the desired X-Y-position the pixel is patterned by a short exposure pulse while the tip position is fixed. Finally, the tip is stored back at retracted state. In order to initiate a short field emission pulse either the tip-sample spacing or the bias voltage could be modulated (ref. Fowler-Nordheim field emission theory, section 2.4). The implemented pixel modes are based mainly on the tip-sample modulation scheme. The tip movement in vertical (Z) direction could be triggered either by movement of the piezo-scanner unit or by the cantilever actuation itself. Thereby, the applicable method depends also on the actual system configuration 3.1.2. For example, the vertical movement by using the piezo-scanner unit is independently applicable from the system configuration, whereas for vertical motion using the cantilever itself an active cantilever technology is required (ref. [315]). For a dynamic (AC) pixel patterning the resonant cantilever oscillation is applied in order to define incremental point exposure doses when the cantilever reaches the closest tip-sample position. Here, the total exposure dose is defined by the amount of oscillations occurring at the respective pixel location. This mode was implemented in a proof-of-concept state (regulation was not optimized), summarized in section 4.3.2. Alternatively to that, also a vertically static (DC) pixel exposure mode was realized. A controlled approach brings the tip close to the surface. A trigger is applied, which stops the vertical movement when a pre-defined current threshold value is reached. Defined by the exposure dwell time, the Z-position is kept constant. A constant height (ch) mode is applied. In order to compensate drift effects, the scanner positioning closed loops are active. In ideal case, in consequence of the constant tip-sample spacing the field emission current is constant. Thus, the exposure dose increases linearly...
with exposure time. To allow basic Fowler-Nordheim field emission measurements (ref. section 4.2.1) a special DC-pixel mode was integrated, in which during the dwell time the bias voltage can be modulated respectively (up- and down-ramping).

### 3.1.5 The Fast Environmental Modification System

The environmental conditions play a significant role in all lithographic processes. Thus, the control and modification of the lithographic environment, especially in the case of ambient conditions, is essential. In particular, the lithographic environment, which is defined by the tip-surrounding gas / vapor composition (or vacuum), appears as parameter impacting the lithographic interaction. In order to operate at constant ambient conditions an environmental regulation system is applied delivering a temperature and humidity control of $22 \pm 2^\circ C$ and $35 \pm 10\% RH$. Thereby, the FE-SPL platform is kept in a completely encapsulated chamber. Due to the large probe chamber volume and the inertia of the environmental control, modifications of the lithographic environment are not practical.

The comparison of the lithographically relevant interaction volume surrounding the probe-sample gap, typically $0.1 \cdot 10^{-20} m^3$, versus the total chamber volume, approx. $0.125 m^3$, reveals that for modification of the lithographic environment only a small volume has to be addressed. Thus, an easily adaptable so called fast environmental modification system was invented [325]. In this concept, a tailored chemical environment is provided, which is changeable within a short timescale, typically $< 10$ sec. A tailored process gas flux is provided only to the region of interest, which is defined by the actual position of the writing tip. Thus, the local environment surrounding the probe is not in equilibrium with the entire chamber volume. Summarized in Fig. 3.1.9, the custom-built environmental modification system is shown. The system consists of a hollow micro-needle, mounted on a XYZ-micromanipulator stage. The manipulator stage is applied in order to position the capillary nozzle in close proximity to the tip-sample interaction area. For alignment of the process gas flux in the direction of the tip apex region the optical microscope system is utilized. Typically, an angle of $\approx 30^\circ$ between needle and sample is adjusted. Specific process gases and gas mixtures are provided on demand by the gas processing unit, Fig. 3.1.9. In frame of the experimental investigations, section 4.2.6, primarily nitrogen as well as conditioned ambient air gases were applied. A gas washing bottle (GWB) was utilized to moisturize the process gas mixture.

In summary, by the environmental modification system specific process gases are provided directly to the tip region. This enabled a tailored chemical environment for nanolithographic experiments. Due to the minimum delay times, environmental modifications were carried out during patterning of single lithographic features, e.g. as shown in experimental section 4.2.6 for long meander patterns. However, due to the miniaturized gas nozzle system the direct measurement of the chemical environment, for example the local relative humidity, is challenging. So far, such a local measurement system was not integrated. In frame of the experimental work only estimated values or trends can be given (a further project can be focused to address this issue). A further idea, which was not followed herein, is the integration of the nozzle directly into the cantilever itself. Concepts from the volcano-type probe technology of Prof. Rangelow [39] or from fluidic nanoprobes [326, 327, 328] could be adapted in order to define a surrounding gas outlet.

### 3.1.6 Optimized Tungsten Probes for a Wire Configuration Setup

In the case of operation in STM regime blunt and very corrugated tips, produced by diverse mechanical wire cutting methods [284, 329], give atomic resolution. Due to the extremely localized interaction
Figure 3.1.9: A custom-built environmental modification system for fast tailoring of the tip-surrounding local environmental. The patented system [325] consists of a hollow micro-needle, which is positioned by a XYZ-micromanipulator setup in close proximity to the tip-sample interaction area (S: temperature and humidity sensor). For exact positioning of the nozzle the optical imaging and navigation system (OINS) is applied. Specific gases or gas mixtures are provided by a gas processing unit (R: flow / pressure regulation of the respective gases; GWB unit: gas washing bottle to moisturize the process gas; CU: control unit regulating the cross valve, which defines the applied process mixture).
in MVM tunneling regime only the foremost atom / atom cluster is responsible for the tip-sample interaction [284]. In contrast, in the case of operation in field emission regime, the tip apex plays a much more crucial role. In reference to the basic FN emission theory, section 2.4, the entire tip apex shape including its radius of curvature directly affects the local electric field strengths and thus the electron emission. In consequence of the increased bias voltages and tip-sample spacing the emission is more delocalized. The ragged structure of wire cut probes, which typically give numerous tip asperities, leads to multi-tip emission processes. This was demonstrated in frame of my master thesis work, ref. [51], as well as published in [311] showing a sixfold emission from a single tip apex.

In conclusion, a more reproducible preparation method for tungsten wire probes was necessary. Electrochemical etching methods, ref. [284, 330, 331, 332, 333], deliver, in general, radial-symmetric tip shapes with a well-defined geometry and very smooth surfaces. The method is based on the anodic etching of a tungsten wire, which is inserted in an aqueous base solution. In a first step the native tungsten oxide layer is dissolved [333] $WO_3(s) + OH^-(aq) \rightarrow HWO_4^{−}(aq)$. Subsequently, the tungsten is etched: $W(s) + 2OH^−(aq) + 2H_2O(l) \rightarrow WO_2^{2−}(aq) + 3H_2(g)$, whereby the highest etching rate occurs at the meniscus. This leads to neck-shaped forms, Figs. 3.1.11 and 3.1.10. Thereby, tungsten as an emitting material was preferred due to its optimum work function ($\bar{\psi}_{\text{tungsten}} = 4.5 \text{eV}$ [284], ref. FN-theory 2.4) and the possibility to electrochemically sharpen it at the single nanometer scale. In contrast, the best Pt/Ir etching results reported in literature was $r_{\text{tip}} = 15−25 \text{nm}$ [209].

![Figure 3.1.10: Tungsten wire probes prepared by different methods, in particular: (1) Commercial available electrochemically etched tungsten wire probes [334], $r_{\text{tip}} \approx 155 \text{nm}$; (2-4) Electrochemically etched tungsten wire probes, prepared by a home-built system. (2) The tip was further sharpened by a Ga-milling process [310], $r_{\text{tip}} \approx 9 \text{nm}$ (FIB milling mask is shown as small inlet figure: red→milled ,white→not milled); (3) The tip is prepared by a one-step etching process resulting in extreme high aspect ratio tips, $r_{\text{tip}} \approx 10.5 \text{nm}$; (4) The tip is prepared by a multi-step etching process giving mechanically very stable tips with $r_{\text{tip}} \approx 7 \text{nm}$. SEM images (1-3) were taken by the author, image (4) by Y. Krivoshapkina.](image)

A first attempt was made by application of standard commercially available tungsten probes, shown
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Figure 3.1.11: Multi-step electrochemical etching process of tungsten wire probes. The optical images are taken at different retraction steps of the etching process. Scale bar for all images: 250 µm. The process was developed by Y. Krivoshapkina in frame of her master thesis work, supervised by the author (ref. [209]). The particular image series was taken by Y. Krivoshapkina.

as an example in Fig. 3.1.10-(1). Despite their good mechanical stability, due to their large tip radii, typically 100 – 500 nm, these kinds of probes are not suited for high resolution FE-SPL. Since the commercial probes are by far not sharp enough, our own electrochemical etching system and related processes were developed. This was carried out in cooperation with Y. Krivoshapkina in frame of her master thesis work. A DC-etching drop-off method in NaOH, dissolved in distilled water, was applied for etching of 99.95% polycrystalline tungsten wires (wire diameter: 250 µm). In a first series a single step etching protocol was developed. Very sharp tips with radii of ≈ 10 nm, shown in Fig. 3.1.10-(3), had been achieved.

Despite their sharpness, first patterning tests with single step etched tips revealed that significant instabilities during operation leads in the current feedback loop to current peaks and tip crashes. As found out, mentioned also in early STM-related publications [335, 336, 337], low aspect ratio tips are essential in order to give sufficient mechanical stability. In this context, the mechanical instability of high aspect ratio tips, delivered by the single step etching process, is explainable by their resonance frequency, $f_{0-rod} = \frac{\beta^2}{2\pi^2} \sqrt{\frac{E}{\pi \delta D^2 L^3}}$ (single-clamped nano-rod description [338, 339]: $\beta^2 = 3.516$; $E$: Young's modulus; $\delta$: mass density; $D$, $L$: diameter and length of the beam). The estimated resonance frequencies are in between 1 – 10 kHz, which is located in the range excitable by the piezoscanning unit (bandwidth of the open loop scanner: 10 kHz). Additionally, the high aspect ratio wires are very soft with spring constants of $\approx 0.0001 – 0.5 N/m$ ($k_{rod} = \frac{3E\pi D^4}{64L^3}$). Thus, low forces could lead easily to bending effects, which results in huge variations of the tip-sample gap. In turn, an over-regulation of the current feedback system is most likely.

In conclusion low aspect ratio tips are favorable in order to minimize flexural bending and vibrations. Furthermore, a high tip symmetry and a well-defined ultra-sharp tip apex with low surface roughness is required. For that, a multi-step electrochemical etching process was applied. Here, the diameter of the wire is step-wise reduced. The tip is retracted step-wise after certain time periods, which leads to significantly reduced aspect ratios. Thereby, the multi-step process is controlled by a stepper motor, combined with an optical microscope for process monitoring. An example is shown in Fig. 3.1.11. As a result, Fig. 3.1.10-(4), optimized aspect ratios with ultra-sharp tips were achieved. In particular, tip radii between 7 – 20 nm were routinely obtained. Additionally, for sharpening of blunt wire probes a FIB-based milling process was developed. A related sharpening result, published in [310], is shown.
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in Fig. 3.1.10-(2). Tip radii of less than 10 nm were achieved. Thereby, a simple trick, based on the incident angle dependency of the milling yield of Ga ions, ref. [340], was applied. Using a perpendicular Ga exposure (the nanowire is aligned exactly perpendicular to the incident ion beam) leads to a self-sharpening process. Using a circular mask, with a non-milled area in the center, automatically gives single spikes useable for FE-SPL. However, since FIB-sharpening is time-consuming the wire probes were mainly prepared by the multi-step electrochemical etching process.

An EDX-analysis (ref. [51]) has revealed that all electrochemically etched tips are contaminated, in particular with Na coming from the etching solution as well as with oxygen and carbon adsorbates from the atmospheric exposure. Furthermore, compared to Pt/Ir wires, which are inert in ambient conditions, tungsten tends to oxidize [284]. This means that mainly WO₃ thin films are formed on the tip surface. In this context, it is reported that additional tip treatments (annealing, field evaporation, tip crashing into the sample, etc.) are required in order to achieve a stable tunneling current for STM-measurements. In contrast, within our experiments no additional ex- or in-situ tip treatments were necessary for a stable field emission operation in ambient conditions. Due to adsorbates and other contamination, in the first time period of field emission operation slight variations of the emission current was measured, ref. section 4.2.1. In this context, the application of a short emission stabilization patterning process, in which a few lines were written at relatively high currents and bias voltages in order to condition the tip respectively, was found to be experimentally preferable.

3.1.7 Passive and Active Cantilever for FE-SPL

In contrast to tungsten wire probes, section 3.1.6, cantilever-based systems offer the possibility of a closed loop lithography scheme. With the same tool and probe, both field emission lithography and AFM-based imaging are carried out, ref. section 1.3. Thus, the exploitation of cantilever for a final FE-SPL system is targeted, especially for the scope of applications in which the AFM-based alignment capability is stringently required.

Due to the requirement of an electrostatic potential difference, which has to be applied between tip and sample in order to trigger a field emission process, an electrostatic force is induced attracting the cantilever towards the sample surface. Thus, the cantilever bending is a function of the applied bias voltage. This effect is schematically drawn in Fig. 3.1.12. When a critical voltage is exceeded, the so called parasitic electrostatic actuator effect leads to a pull-in of the cantilever. This is an unstable, not-controllable movement of the cantilever towards the sample surface resulting typically in a tip crash. In order to avoid this, particular cantilever design rules and operational conditions have to be applied, derived hereinafter.

(I) Basic Consideration: Parasitic Electrostatic Actuator Model

The basic cantilever-sample system configuration is summarized in Fig. 3.1.12. A simplified model is derived by using a capacitor plate configuration in series with a restoring spring. The attracting electrostatic force \( F_E \), which is acting in the Z-direction towards the sample surface, is determined by employing the stored energy \( W \) in the analogous capacitor model (ref.: [341]):

\[
F_E = - \frac{\partial W}{\partial z} = - \frac{\partial (1/2CU_b^2)}{\partial z} \tag{3.1}
\]

with \( C \) the analogous capacity of the entire cantilever system. The restoring force of the cantilever \( F_R \), which is working against the cantilever deformation, is describable by a linear (elastic) spring with
Figure 3.1.12: Cantilever-sample model for normal mode operation. A simplified model for description of the electrostatic actuation is derived by using a spring, which is coupled in series with a capacitor plate configuration. The dashed profile shows the biased case illustrating the parasitic electrostatic actuation effect.

Hooke’s law:

$$F_R = k_C \Delta z, \text{with } \Delta z = z_{c-o} - z$$ (3.2)

Thereby, the spring constant $k_C$ of a rectangular shaped beam is defined by [285]:

$$k_{C\text{-rectangular beam}} = \frac{EW_cT_c^3}{4L_c}$$ (3.3)

with the Young Modulus $E$ ($p+\text{ Si }<100>: 125\text{ GPa}$ [342]) and the geometric properties of the beam $W_c, T_c, L_c$, defined in Fig. 3.1.12. The system dynamics can be described adequately by:

$$m_C \frac{d^2z}{dt^2} + D_C \frac{dz}{dt} = F_E + F_R$$ (3.4)

with total mass of the cantilever $m_C$ and the damping of the cantilever $D_C$. In the static state, in which the system operation is targeted, the restoring force and the electrostatic force are equal ($-F_E = F_R$).

For description of the system behavior the total electrostatic force of the cantilever system has to be determined. Since no exact analytical descriptions exist, approximations for the different parts of the cantilever (a-b) are applied. For exact solutions FEM simulations are necessary. Since general cantilever design rules should be derived, simulations were not carried out.

(a) The Beam: Due to the long-range character of electrostatic forces, the cantilever beam itself has to be taken into account. By neglecting the cantilever-surface tilt, typically $\approx 11^\circ$, and the fringing fields, the beam capacity $C_{beam}$ could be described by a parallel plate model. Thereby, it is considered that the force acting at the end of the beam causes a higher deflection compared to forces at the base. The beam-sample spacing is also corrected by the height of the tip $h_{tip}$ [341, 343, 344, 345]. The beam capacity is specified by:

$$C_{beam} = \int_0^L \epsilon_0 \epsilon_r \cdot \frac{W_c}{h_{tip} + z} \cdot \frac{l}{L_c} dl = \frac{1}{2} \epsilon_0 \epsilon_r \cdot \frac{W_c L_c}{h_{tip} + z}$$ (3.5)

By insertion of Eq. 3.5 into Eq. 3.1 gives the electrostatic force component of the beam:

$$F_{E\text{-beam}} = \frac{1}{4} U_0^2 \epsilon_0 \epsilon_r \cdot \frac{W_c L_c}{(h_{tip} + z)^2}$$ (3.6)
(b) The Tip: A rotationally symmetric cone-shaped tip, with a round-shaped spherical tip apex at the end, is assumed (Fig. 3.1.12). The cone-shaped tip could be approximated either by a stack of rings (detailed derivation described in [343], derivation error corrected by myself):

\[ F_{E-\text{conc.-ring approx.}} = \frac{1}{2} U_b^2 \pi \epsilon_o \epsilon_r \tan^2(\theta) \left[ \ln \left( \frac{h_{\text{tip}} + z}{z} \right) - \frac{h_{\text{tip}}}{h_{\text{tip}} + z} \right] \]

(3.7)

or by a uniformly charged line model (detailed explanation of the method in ref. [346, 347]):

\[ F_{E-\text{conc.-charged line}} = \frac{\lambda_0(U_b)^2}{4 \pi \epsilon_o \epsilon_r} \ln \left( \frac{(2z + h_{\text{tip}})^2}{4z(z + h_{\text{tip}})} \right), \quad \lambda_0(U_b) \approx 4 \pi \epsilon_o \epsilon_r U_b \left[ \ln \left( \frac{1 + \cos(\theta)}{1 - \cos(\theta)} \right) \right]^{-1} \]

(3.8)

The tip apex itself could be approximated by a sphere-plane model, whereby different approximations for small and large tip-sample distances \(d_{ts} = z\) could be applied [346, 347]:

\[ r_{\text{tip}} \gg z : F_{E-\text{sp.-0}} \approx \pi \epsilon_o \epsilon_r U_b^2 \left( \frac{r_{\text{tip}}}{z} \right); \quad r_{\text{tip}} \ll z : F_{E-\text{sp.-\infty}} \approx \pi \epsilon_o \epsilon_r U_b^2 \left( \frac{r_{\text{tip}}}{z} \right)^2 \]

(3.9)

(II) Electrostatic Forces - Investigation of Different Cantilever Designs

Using the previously described models the electrostatic force components \(F_E\) for different cantilever designs could be calculated. The overall force is then calculated by summing up of the individual components coming from the cantilever beam (parallel-plate model with consideration of a beam configuration), the tip cone (complete charged line model approx.) and the spherical tip apex (sphere-plane approx.). For example, in Fig. 3.1.13-(i-iii), the electrostatic forces are calculated as function of the tip-sample spacing (\(z\)) for three different cantilever types, in particular: (i) A standard cantilever with a low aspect ratio tip (\(h_{\text{tip}} = 5 \mu m\)); (ii) A standard cantilever with a high aspect ratio tip (\(h_{\text{tip}} = 5 \mu m\)), and; (iii) An ultra-small cantilever fabricated in Prof. Rangelows department, published in [315].

Derived from Figs. 3.1.13 and 3.1.14, the induced electrostatic forces on the cantilever are in the pN-range. Thereby, the cantilever design has significant influence on the electrostatic force. The quadratic dependency of the electrostatic force as function of the bias voltage (\(F_E \sim U_b^2\)) is shown in Fig. 3.1.14-(i). Since the applied bias voltage is determined by the field emission process, this value cannot be influenced. Thus, the cantilever has to be designed and selected in such a way that the electrostatic forces and the related deflection of the cantilever is minimized. Due to the long-range character of the electrostatic force, the cantilever beam dominates at large tip-sample spacings. That is valid for all cantilever types. At smaller spacings, in particular < 10 \(\mu m\), the cantilever design becomes increasingly important. Thereby, in the case of a standard cantilever design, large tip heights (Fig. 3.1.12-\(h_{\text{tip}}\)) lead to a significant reduction of the electrostatic forces (\(F_{E-\text{beam}} \sim 1/\left|h_{\text{tip}} + z\right|^2\)). Here, with decreasing tip-sample spacings tip-induced electrostatic forces become important, shown in Fig. 3.1.13-(ii). Conversely, in case of low tip design (Fig. 3.1.13-i) the electrostatic forces, which are originated by the beam, dominate over the entire spacing range. A further strategy for reduction of the parasitic electrostatic forces is the down-scaling of the cantilever size. For example, by using the currently smallest applicable cantilever, developed in Prof. Rangelows group (ref. [315]), the minimized beam area of 4x6 \(\mu m\) results in a reduction of the electrostatic force of about one order of magnitude compared to standard cantilever types (Fig. 3.1.13-iv). A closer look at the individual electrostatic force components, Fig. 3.1.13-(ii), reveals that the influence of the tip itself takes over already at medium tip-sample spacings (\(z < 1 \mu m\)). Thus, for the ultra-small cantilever design a simple beam-based model for description of the entire electrostatic force is not appropriate. In contrast, in the
Figure 3.1.13: Electrostatic force components \( (F_E) \) as function of the tip-sample separation \( (z) \), calculated for different cantilever types. Graphs (i-iii) show the individual influence of the beam, the tip cone and the tip apex on \( F_E \). Different models were applied, summarized in the graph legends. The resist influence is neglected. The cantilever deflection calculation, given in (iv), is based on Eq. 3.4. A static case scenario is assumed. In (iv) the \( F_E \) axis in (iv) is plotted logarithmically and the cantilever deflection axis linearly.
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Figure 3.1.14: Calculation of the electrostatic force $F_E$ (i) and the resulting deflection of the cantilever (ii) as function of bias voltage $U_b$. A fixed tip-sample spacing of $z = 50 \text{ nm}$ was assumed. Three different cantilever types, introduced and defined in Fig. 3.1.13, were considered. In (i) the electrostatic forces for the stand-alone beam model ($F_{E-\text{beam}}$ - dashed lines) and the entire electrostatic force model, with summed up individual components ($F_{E-\text{sum}}$ - solid lines), are compared. In (ii), log-log-plot, the cantilever deflection is shown for the different cantilever types ($F_{E-\text{sum}}$ applied for calculation), whereby for each cantilever type a soft (dashed lines) and a stiff (solid lines) beam was considered ($T_C$ modified accordingly, ref. Eq. 3.3).

In contrast to typical electrostatic actuators [341, 344, 345], in which the suspension of the beam is fixed, in our case the cantilever is moved by the Z-piezoscanning unit. As a result, drawn schematically in Fig. 3.1.12, the suspension of the restoring force spring is moveable with respect to the capacitor plate. For example, by retraction of the cantilever - using the piezo-scanner in z-direction - the restoring force is virtually increased. This leads, if the retraction step was large enough, to a snap back of the cantilever. During lithographic operation the current feedback loop (3.1.1) ensures by modulation of the tip-sample spacing ($z = d_{ts}$) a constant field emission current. Thus, during lithography the Z-feedback regulation ($-Z_{\text{scanner}}$ in Fig. 3.1.12) compensates the electrostatically induced deflection of the cantilever. The system works in a balance of forces equal to the static case: $-F_E = F_R$. In consequence, the cantilever has during lithographic operation always a deflection equal to the total electrostatic force. During approach, with decreasing tip-sample spacing $z$, the electrostatic force increases, which leads in turn to an increment of the deflection of the cantilever beam (Fig. 3.1.13). However, the system feedback does not measure the cantilever bending. The approach stops at a particular tip-sample spacing, at which the pre-defined field emission current setpoint is reached. In conclusion, the cantilever deflection reduces the approach distance. In Figs. 3.1.13-(iv) and 3.1.14-(ii), the deflection of the cantilever beam for the three different kinds of cantilever are estimated (Eq. 3.4 and 3.3). During lithographic operation, with typical tip-sample spacings of $10 \text{ nm} \leq z \leq 100 \text{ nm}$, the deflection values for the various cantilever
Figure 3.1.15: The balance of forces during lithographic operation. The electrostatic ($F_E$) and restoring ($F_R$) forces are calculated at a typical working distance (WD) of $d_{ws} = 30 \, \text{nm}$ for two different cantilever types, in particular for (i) standard cantilever with low aspect ratio tips, and; (ii) an ultra-small cantilever. Both cantilever types are described in Figs. 3.1.13 and 3.1.14. In terms of the restoring force calculation the deflection of the cantilever at WD was considered individually for every $U_b - k_C$ combination.

Types differ considerably. The lowest deflection ($< 10 \, \text{nm}$) reveals the ultra-small cantilever type. In contrast, the standard cantilever ($k_C = 2.8 \, \text{N/m}$) has significantly higher deflections. Thereby, the tip height is a critical design value, e.g. the deflection is $\approx 220 \, \text{nm}$ in case of $h_{tip} = 5 \, \mu \text{m}$ vs. $\approx 40 \, \text{nm}$ deflection for $h_{tip} = 15 \, \mu \text{m}$.

The balance of forces during FE-SPL reveals that a defined spring constant range $k_c$ is necessary in order to operate in a stable regime, shown for two different cantilever types in Fig. 3.1.15 (i-ii). As revealed, the main problem arises from the different dependencies of the involved forces, in particular $F_E \sim 1/z^2$ versus $F_R \sim z$. In the case of a standard cantilever type, Fig. 3.1.15-(i), a spring constant of $k_C = 2.8 \, \text{N/m}$ results in a labile working point - Only a small rise of the attractive electrostatic forces leads to an uncontrollable pull-in of the cantilever. The small increase of the electrostatic force could be caused for example by a surface defect as drawn in Fig. 3.1.12. When the cantilever position has reached the metallic defect, the lithographic feedback loop needs respective time (defined by integral gain of the PID regulator) adjusting the current, respectively, by retracting the tip. Despite a fast feedback, the cantilever can be already pulled in. Exactly that effect was identified as the main problem when working with soft cantilever - The balance of forces during lithographic operation is too labile. A slight increase and the system snaps in one direction. In consequence, stiffer cantilevers are required to shift the operation range towards a stable working point. In order to increase the spring constant, the beam thickness could be increased, shown in Fig. 3.1.15- (i) and (ii) for standard and ultra-small cantilever types, respectively (i: $T_C = 1.75 \rightarrow 3.0 \rightarrow 4.5 \, \mu \text{m}$; ii: $T_C = 0.1 \rightarrow 0.25 \, \mu \text{m}$). Since even for small tip-sample spacings ($z$), e.g. in the case of a surface defect, the restoring forces are greater than the electrostatic force ($F_E < F_R$) no pull-in effect occurs. The pull-in point, which is defined by the second intersection of $F_E$ and $F_R$, has shifted closer to the surface. As targeted, the working point is stabilized. For example, the soft ultra-small cantilever version has no stable working point, whereas the stiff version is operable to $z \approx 5 \, \text{nm}$ under an initial condition of a $30 \, \text{nm}$ working distance and $U_b = 60 \, \text{V}$.

In summary, with increasing spring constant the working point is stabilized ensuring a stable lithographic operation. A side effect of a stiffer cantilever is that also the deflection of the beam at the working...
distance is lowered, shown in the table of Fig. 3.1.15. However, the alterations of the bending of the cantilever due to modulations of the tip-sample spacing $d_{ts}$ and the bias voltage $U_b$ cannot be circumvented and have to be considered in experimental section. Thus, usually for basic research, in which the tip-sample separation has to be known, wire probes were applied. However, in the pixel-based patterning mode 3.1.4 the electrostatic actuation and the switching between two different working points could be turned into a desired actuation scheme. Exactly that method was exploited in experimental section 4.3.2 for the patterning of dot-features via an oscillating cantilever system.

(IV) The Electrical Equivalent Circuit of the Cantilever-Sample System and Derived Limitations of the Lithographic Feedback Loop

In general, the cantilever-sample system can be described electrically by an equivalent RC-circuit. The time constant $\tau_{cs}$ and the related cut-off frequency $f_{cs}$ of is defined by:

$$\tau_{cs} = RC, \quad f_{cs} = \frac{1}{2\pi\tau_{cs}}$$

with the equivalent resistance $R$ and capacity $C$ of the cantilever-sample system. Thereby, $R$ is mainly defined by the field emission gap resistivity using: $R = U_b/I_{FN}$, which is located in the range of $200 \text{ G}\Omega$ up to the $10 \text{ T}\Omega$. Due to this high value any other parts of the cantilever-sample system contributing to the total resistance are negligible. The total capacitance $C$ of the cantilever-sample system is determined by summing up of the individual cantilever components. For description of the beam capacity Eq. 3.5 is applied. The cone of the cantilever is determined by the stacked-ring approximation, given by [343]:

$$C_{\text{cone-ring approx}} = 2\pi\varepsilon_0\varepsilon_r d_{ts} \tan^2(\theta) \left[ \frac{h_{\text{tip}}}{d_{ts}} \ln \left( \frac{h_{\text{tip}} + d_{ts}}{d_{ts}} \right) \right]$$

Since only the contribution of the tip apex depends on the local properties of the sample (ref.: [348]), a more detailed model was applied [348]:

$$C_{\text{apex}} = 2\pi\varepsilon_0 r_{\text{tip}} \ln \left( 1 + \frac{r_{\text{tip}}(1 - \sin \theta)}{d_{\text{gap}} + (d_{\text{resist}}/\varepsilon_{r-d})} \right)$$

including the tip-gap-resist spacing ($d_{\text{gap}}$) as well as the dielectric properties of the resist ($\varepsilon_{r-d}$). In order to achieve best regulation performance, characterized by a fast reaction time of the current feedback loop, low time constants $\tau_{cs}$ are targeted by the cantilever design. A comparison between a standard cantilever type, an ultra-small cantilever (ref. [315]) and a tungsten wire configuration is summarized in table 3.2. As supposed, compared to the wire probe configuration the cantilever setup naturally slows down the feedback (table 3.2). In case of a standard cantilever with short tips the time constant is maximum. By using a tall tip design the time constant is reduced, which leads in turn to higher cut-off frequencies. Thereby, the estimated frequency range of $400 \sim 500 \text{ Hz}$ is sufficient for lithographic applications. By exploitation of the ultra-small cantilever design the same system dynamics as in case of a tungsten wire probe configuration can be achieved.

(V) Summary of Cantilever Design Rules for FE-SPL

Based on the developed models the following design rules and selection criteria on cantilever for FE-SPL were derived (ref. Eq. 3.1 - 3.9 and Figs. 3.1.13 - 3.1.15):
Table 3.2: Comparison of different cantilever types and system configurations with respect to an electrical equivalent RC-circuit. The table contains the individual electrical capacities $C$ coming from beam, cone and apex of the cantilever. Thereby derived are the total capacity $C_{\text{sum}}$ of the system, the time constant $\tau_{cs}$ and cut-off frequency $f_{cs}$. The calculation was done for a typical lithographic parameter set. The applied cantilever dimensions are described in Fig. 3.1.13.

1. For minimization of the electrostatic force tall tip designs ($F_{E-\text{beam}} \sim 1/[h_{\text{tip}}^2 + z^2]$), with high aspect ratio tips ($\theta$↓) and small tip radius of curvature ($r_{\text{tip}}$↓), are targeted. The tip apex form and the sharpness of the tip are crucial for the field emission process itself, discussed in detail in 2.4. However, an upper limit of the aspect ratio exists, defined by the mechanical stability and resonance frequency of the tip (ref. Fig. 3.1.10-3 outlined for a tungsten wire probe).

2. The reduction of the entire cantilever size leads to a significant decrease of the electrostatic interaction area. In consequence, the time constant as well as the electrostatic force is decreased. As pointed out in Fig. 3.1.13, the tip design becomes more important. Thus, the tip aspect ratio and its shape are crucial. Additionally, as shown in Fig. 3.1.17, the intersecting area could be further decreased by a two-leg cantilever design. Alternatively, in the case of a standard cantilever design small conductive paths instead of a large-area deposited metal coating are applied, shown in Fig. 3.1.16.

3. The main design parameter to increase the stiffness of the cantilever is the lever thickness $k_C \sim T_C^3$ (Eq. 3.3), summarized in Fig. 3.1.14-(ii) for the different cantilever types. For example, the doubling of the thickness leads to a reduction of the deflection of one order of magnitude. However, with increasing stiffness the actuation efficiency and the actuation amplitude is reduced, discussed in frame of our publication ref. [315]. In this context, Wilder et. al [169] have applied an extremely stiff cantilever with $k_C = 340 \, N/m$. As revealed by the previous theoretical investigations, a minimum spring constant of $k_C > 20 \, N/m$, in the ideal case of $k_C = 40 - 80 \, N/m$, are sufficient in case of a standard cantilever with a high tip design. In the case of small cantilever $k_C > 9 \, N/m$ is sufficient. Thus, the downsizing of the cantilever size relaxes the requirements on the cantilever stiffness. The good applicability of ultra-small cantilever types was also confirmed experimentally.

4. Since an adequately fast regulation of the tip-sample spacing is required, a minimization of the cantilever-sample capacitance is targeted. Advantageously, the methods for reduction of the RC time constant are identical with that for reduction of the parasitic electrostatic force.

(VI) Active Cantilever for FE-SPL

During the past decade the cantilever itself evolved from a simple passive deflection element to a highly integrated micro-electro-mechanical system. This was pioneered by Prof. Rangelow and his research
Figure 3.1.16: Active cantilever for FE-SPL. (a) Colored SEM image showing an active cantilever system with thermal bimorph actuation (#3, red), the piezoresistive read-out (#2, green) and sharp read/write tip (#5, blue). A zoom-in of the tip is shown in SEM images (b) and (c). The tip is connected via separate metalized lines (#4, blue). Two different tip variants were fabricated, (b) metalized tips and (c) highly doped Si tips. Tip modifications, which were evaluated, are shown in SEM images (d)-(f), in particular (d) Ga-ion based re-sharpening of the tip (same method applied as for the tungsten tip wire sharpening was applied, ref. Fig. 3.1.10-2); (e) Pt-EBID deposited tip; (f) Pt-EBID deposition followed by a Ga-ion exposure. Scale bars: (a) 50 µm; (b) 2 µm; (c) 50 nm; (d) 500 nm; (e) 250 nm; (f) 200 nm. The primal active cantilevers were fabricated by Dr. Tz. Ivanov and Dr. M. Hofer. Respective tip modifications were done by the author. The results were published partially in refs. [36, 37, 304, 315].

The primal active cantilevers were fabricated by Dr. Tz. Ivanov and Dr. M. Hofer. Respective tip modifications were done by the author. The results were published partially in refs. [36, 37, 304, 315].

Active cantilever systems, Fig. 3.1.16, incorporate both mechanical actuation and deflection read-out within the beam. This so called self-actuation, self-sensing cantilever technology enables the development of compact table-top AFM and SPL systems without the requirement of external actuation and sensing components, e.g. like a piezoshacker unit and a laser-based read-out system (ref. section 3.1.2). In particular, the cantilever is driven by a thermal bimorph actuation principle [203, 316, 349]. The bimorph is defined by a sandwich structure (Si/Si$_3$N$_4$/Al). A mismatch of the thermal heat expansion coefficients of the material stack leads to a deflection of the cantilever. Thereby, the bending of the beam is adjustable by the electrical power running through the meander-shaped metallic resistor element, which is deposited on top of the cantilever. Advantageously, both static (DC) as well as dynamic (AC-resonant) deflections of the cantilever are controllable by the applied power, ref. [316, 351]:

$$P_{heater} = \frac{1}{R_{heater}} \left[ V_{DC}^2 + 2 V_{DC} V_{AC} \sin (wt) + V_{AC}^2 \sin^2 (wt) \right]$$ (3.13)

This enables the opportunity for exploitation of the static off-resonance deflection as additional actuator in the vertical (Z) direction. In particular, a DC-current through the integrated heater gives a bending of the cantilever proportional to the square of the input current [315, 350]. Depending on the cantilever design, deflections in micrometer range are achievable, demonstrated in ref. [31, 203, 315, 351]. This cantilever-based actuation scheme is beneficial especially for pixel-based patterning routines, ref. section 3.1.4, as well as for high speed AFM imaging, discussed in [352, 353]. In addition, the heating of the cantilever results in a stiffness increase, ref: [351]. A further stabilization of the lithographic working point is achieved. The deflection read-out of the cantilever bending is realized by integrated 2-DEG piezoresistive sensors. Therefore, highly p-doped Si resistors are implanted at the base of the
cantilever. An arrangement of four integrated resistors in a Wheatstone-bridge configuration minimizes the temperature influence. In order to enhance the read-out sensitivity the mechanical stress was concentrated on the cantilever base by using a centered hole with two side slots, Fig. 3.1.16. A detailed explanation is provided in refs. [203, 315, 316, 349, 350]. In summary, the deflection read-out sensitivity is comparable to that of passive systems (80 fm/Hz\(^{-1/2}\) thermomechanical noise floor, ref. [315]).

The applied active cantilevers, shown in Fig. 3.1.16, have spring constants in the range of \(k_c = 20 - 200 \text{N/m}\), tailored mainly by variation of the Si layer thickness. The read/write tip, which is located at the end of the cantilever, is connected via a small-shaped metallic line in order to minimize the electrostatic „active“ area and to achieve a better shielding of the current feedback loop. Two different cantilever tip types were fabricated (Fig. 3.1.16), a metal emitter and a highly doped (typically \(< 0.02 \Omega \text{cm}\)) Si emitter variant. For tip metallization Pt, Ti and W were applied. Cr/Au tip coatings, which were initially tested, showed a high tip wear in AFM imaging mode. Furthermore, smaller grain sizes and thus smoother surfaces can be achieved by using Pt, Ti and W coatings. Typical \(R_q\) values for \(~20 \text{nm}\) thick films, measured by AFM, are for Cr/Au layers in between \(R_q \approx 0.7 - 1.0 \text{nm}\), with typical grain sizes of \(4 - 10 \text{nm}\), whereas Pt, Ti and W gives an \(R_q \approx 0.4 - 0.7 \text{nm}\). Due to the metallic coating, and the resulting relatively large grains, the typical tip radii are limited by \(r_{tip} = 15 - 30 \text{nm}\). The tip durability during AFM imaging is a critical issue for metallic coatings. In consequence of the tip wear in imaging mode, the performance and reproducibility in lithographic mode is limited. In this context, highly doped Si tips, without metallic tip coatings, deliver a more defined and smoother tip apex with a sharper tip radius of curvature. Sub-10 \text{nm}\) tip radii are routinely fabricated by exploiting a batch-suited tip sharpening process, which is based on well-defined oxide formation, followed by a subsequent reactive ion etching (RIE) process. Respective results and processes are published in ref. [203, 315, 316]. Similar to the modification of tungsten wire probes (section 3.1.6), cantilever tips can be modified and re-sharpened by a Ga-ion based milling, Fig. 3.1.16-(d), or by application of electron beam induced deposition (EBID), Fig. 3.1.16-(e). Also a combination of both could be applied to form a sharp emitter tip (Fig. 3.1.16-f). The related processes are published in ref. [315]. Using that, enlarged aspect ratios of the tip could be achieved. However, compared to the initial highly doped Si tips, the sharpness of the tips could not be significantly enhanced. Unfortunately, high aspect ratio tips, like those shown in Fig. 3.1.16-(f), weaken the mechanical stability of the lithographic process by picking up flexural bending and vibrations (ref.: 3.1.6). Thus, commonly un-modified and un-coated highly doped Si tips are preferred for a closed loop FE-SPL. The applied active cantilevers were fabricated by bulk and surface micromachining processes, which are described and discussed in more detail in ref. [203, 315, 316, 349, 350, 351]. Slight changes of the process flow were incorporated in order to tailor the active cantilever towards the lithographic applicability, discussed in context of sub-section (V).

(VII) Passive Cantilever for FE-SPL - Ultra-Small

In the case of the passive cantilever configuration, in accordance with the design rules defined before (V), cantilevers with tall tips and large spring constants \((k_C > 40 \text{N/m})\) were applied. In addition, ultra-small passive cantilevers, which were initially designed in Prof. Rangelows group (Dr. M. Hofer and Dr. T. Ivanov) for high speed AFM applications, ref. [315, 352, 353], have proven to be suitable for FE-SPL. In particular, two types of ultra-small passive cantilevers were selected, shown in Fig. 3.1.17: (a) An ultra-small SiO\(_x\)N\(_y\) cantilever type with \(k_C = 10 - 50 \text{N/m}\), and; (b) A two-leg Si cantilever having \(k_C = 80 - 200 \text{N/m}\) \((k_C = 2 \cdot k_{\text{leg}})\).

Thereby, the ultra-small cantilever types significantly reduces the active area. The stiffness is in the targeted region in order to ensure a stable working point (Fig. 3.1.15). The high resonance frequencies,
3.2 Sample and Resist Preparation

3.2.1 Substrates Applied and the Needle-in-a-Haystack Issue

Substrates and Multilayer Sequences Applied: The utilization of a current feedback loop for FE-SPL stringently necessitates a sufficiently conductive or semi-conductive top layer sample surface. Similar to the STM operation, non-conductive substrates cannot be applied in direct fashion. Multilayer
strategies involving a conductive bottom layer circumvent this problem and give the possibility to work independently of the substrate type. In addition, with respect to a subsequent etching transfer process, section 7.2, the multilayer stack is applicable as an amplification layer.

In consequence of the large equivalent tip-sample resistance, the demands on the substrate conductivity are not as stringent as initially suggested. In particular, moderately doped Si surfaces, typically $9 \pm 15 \Omega \text{cm}$, are sufficient. Also a thin native oxide layer, typically $<3 \sim 4 \text{ nm}$ on top of the semiconducting Si substrate was never an obstacle for maintaining of the current-feedback loop during patterning. Thus, conductive coatings on top of the Si layer were not a stringent requirement. In contrary, metal coatings, even deposited at ultra-low rates ($0.1 \sim 0.2 \text{ Å/sec}$), cause a significant increase of the surface roughness ($2 \sim 5$ times increase compared to pristine Si). Furthermore, the surface morphology is altered by the formation of grain morphology, ref. section 3.2.2. For highest resolution lithography a low surface roughness is targeted. Therefore, due to the ultra-thin resist films applied, the resist has no planarization effect. Instead, the sample surface morphology and its roughness are maintained through the resist layer, shown as an example in Fig. 3.2.2 for a Cr/Au metal bottom layer. Due to the FE-SPL feedback loop the surface roughness is further transferred into the LER and LWR of the patterned nano-features. In conclusion, for highest resolution lithography metal bottom layers should be avoided. For testing purposes in the experimental section Cr/Au metal bottom layers ($5 \text{ nm}$ Cr as adhesion promoter, followed by a $10 \sim 20 \text{ nm}$ Au layer) were used.

For the most experimental part pristine Si chips were applied. The typical surface roughness of the Si chips, cleaned prior, was $0.20 \sim 0.25 \text{ nm}$. As observed, the removal of the native oxide layer, carried out with a diluted HF-dip prior resist coating, leads to better resist surface qualities. In particular, a two-times lower roughness and a lower tendency for de-wetting of the PVD-coated resist is given (ref. section 3.2.2). For device fabrication and advanced experiments so called fully depleted SOI (FD-SOI) chips were used. Due to the ultra-thin Si top layer ($12 \pm 1 \text{ nm}$, p-doped $9 \sim 15 \Omega \text{cm}$, $<100> \pm 0.5^\circ$, RMS surface roughness $0.20 \sim 0.23 \text{ nm}$) and thin BOx layer ($25 \pm 1.5 \text{ nm}$), the stack was chosen for beyond CMOS device fabrication experiments.

Pre-Structuring for Nanolithographic Experiments and Device Fabrication: In general, by using only nanolithographic methods one is faced with a so called „needle-in-a-haystack”-problem. After patterning, and different subsequent process steps, e.g. development, plasma etching, the initial places of patterning have to be found again in order to carry out further analysis processes. Without coarse alignment and navigation this turned out to be a challenging and time-consuming task. Moreover, also for a mix-and-match lithography (section 6.2.1) overlay alignment marks are necessary. Thus, for alignment and navigation, and in order to provide a basis for a beyond CMOS device fabrication scheme, a pre-structuring on wafer-level prior FE-SPL processing was applied. This means that the developed FE-SPL fine patterning method is integrated into conventional process flows. Conventional microfabrication technologies are required for bridging the gap between the macroscopic level and the single digit nano regime. In order to keep a high degree of flexibility during processing a variety of overlay alignment marks and recognition patterns were implemented in the mask design. Examples of the experimental pre-structuring is shown in Fig. 3.2.1.

An individual pre-structuring at single test chip level was carried out by FIB-milling, Fig. 3.2.1-(a). In order to have a larger amount of chips, a wafer level fabrication process was applied using conventional photolithography, with a subsequent reactive ion etching (RIE) process step, Fig. 3.2.1-(b-c). The design in (b) was targeted to provide sufficient navigation and alignment capabilities required for basic FE-SPL experiments. The red-shaded features were etched a few hundred nanometers in depth (RIE:
Figure 3.2.1: Summary of pre-patterning aimed for nanolithographic experiments and device fabrication. (a) Initial pre-structuring, carried out with focused ion beam (FIB) milling, for navigation and alignment on an individual test chip basis. (b) Pre-patterning for navigation and alignment on Si wafer basis using (test chip size of 1x1 cm²). (c) Pre-patterning of FD-SOI wafer targeted for device manufacturing and advanced nanolithographic experiments (single test chip size: 1.5x1.5 cm²). The pre-structuring in case of (b) and (c) were done by standard photolithography, followed by an RIE etching step. The contrast in (b) arises from height differences. The features are etched a few hundred nanometers in depth. In (c) the image contrast is induced mainly by the material difference. The dark appearing area is Si, whereas the bright area is SiO₂. The etching process was stopped at the BOx layer of the FD-SOI wafer (etching depth of 15 – 25 nm).
3 Experimental Fundamentals of a FE-SPL Technology

$SF_6$ and $CHF_3$. This gives a good optical height contrast, also in this case a conductive metal layer and a resist film were prepared on top (Fig. 3.2.1-b).

The pre-structuring targeted for device features advanced nanolithographic experiments is shown in Fig. 3.2.1-(c). The plasma etching process was stopped slightly after reaching the BOX layer of the FD-SOI wafer. Thus, the image contrast arises mainly for the material difference between $Si$ and $SiO_2$. The single test chip ($15\times15\ \text{mm}^2$), separated by saw dicing after processing, contains an array of $4\times4$ single test fields. Each test field has a center field (dark - $Si$), on which the device patterning or the nanolithographic experiment should be carried out. This field is surrounded by 12 contact pads, connected to the center field. Three different kinds of center field sizes were designed, giving a sufficient degree of flexibility. Since a closed current feedback loop is required for FE-SPL, a single conductive path connecting all fields with the surrounding chip frame is provided. Thus, all $4\times4$ fields are interconnected to the surrounding chip frame, at which the chip is electrically connected to the bias voltage source. For final device measurement the single fields have to be separated again by cutting the interconnections respectively. The process flows were designed in such a way that the targeted surfaces, on which the experiments and devices are carried out, are not etched. Thus, the high surface quality of the initial Si chips (RMS surface roughness of $0.20 - 0.23\ \text{nm}$) is maintained. For device fabrication the application of positive tone FE-SPL is targeted. Here, by the subsequent plasma etching process, which is stopped at the BOx layer, the final devices are fully defined. Only two process steps are required. Thus, complex device circuits and designs could be created in a much simpler way. Initial efforts towards device features are summarized in chapter 7.

3.2.2 Ultra-thin Molecular Glass Resist Films for Nanolithography

The preparation of ultra-thin resist layers, typically $5 - 50\ \text{nm}$, is a crucial task in order to achieve highest resolution lithography. Since the overall surface roughness and morphology directly propagates into the LWR/LER of the defined lines (published in [310]), the thin film preparation method has to deliver routinely ultra-smooth resist films across the entire chip area, ideally below an RMS of $< 0.5\ \text{nm}$. Furthermore, local variations of the dielectric properties of the resist, e.g. caused by variations of the resist composition, molecular order (phase) or by contamination are directly affecting the lithographic feedback loop (ref. sections 5.2 and 5.3). Thus, clustering, de-wetting, aging and pollutions of the resist have to be prevented. The amorphous (glassy) resist state of the molecular resist is targeted. This ensures high homogeneity and isotropic resist properties over the entire chip area (ref. [223, 230, 232, 354]). Crystallization, even partially, has to be suppressed by choosing the suitable derivatives and thin film preparation techniques. The investigation of the resist surface morphology and roughness after each process step, carried out by AFM, is a good measure for the general applicability of the resist. The focus of this particular work was placed on calixarene based molecular glass resists. Also specifically tailored molecular glass resists, provided by our research partner University of Bayreuth (UBT) in the frame of the SNM-project, were applied.

Thin Film Preparation Methods for MG Resist Materials: The particular thin film preparation method not only determines the applicable calixarene and molecular glass derivatives, but also defines the properties of the resist layer. The different methods are compared in table 3.3. As function of preparation technique and molecular derivative molecular ordered (crystalline) or molecular disordered (amorphous) thin films are obtained. SAM and LB methods give a monolayer thickness control, and a well-defined order of molecules on the sample surface is achieved. However, as reported in refs. [61, 62, 90, 114, 115, 361], the practical applicability is limited since the resist layers highly tend to
<table>
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<td>single layer: 1 – 2 nm</td>
<td>single &amp; multilayer up to 10 – 15 nm with monolayer accuracy</td>
<td>5 nm – several µm, in-situ thickness control by QCM monitor</td>
<td>7 – 200 nm, thickness defined by parameter and solution</td>
</tr>
<tr>
<td>References</td>
<td>[237, 355, 356, 357, 358]</td>
<td>[258, 271, 359]</td>
<td>[225, 226, 268, 355, 360]</td>
<td>[31, 40, 182, 199, 233, 236, 237, 238, 310]</td>
</tr>
</tbody>
</table>

Table 3.3: Comparison of different thin film preparation techniques applicable for calixarene-based and related molecular glass resist materials. The schematics of the preparation methods are adapted from [237, 355]. QCM: quartz crystal microbalance.

defects and to poor uniformity. Further, chemically functionalized molecules are required. Thus, a more promising approach is given by the amorphous state of molecular resists. The molecular glass resists ensure the formation of homogeneous, uniform and smooth resist films over larger areas. Depending on the properties of the targeted derivative, spin-coating or physical vapor deposition (PVD) techniques were applied. In case of PVD preparation via thermal evaporation, the thermal and chemical stability of the molecule is most important since a degradation during evaporation should be prevented. For thin film preparation via spin-coating a sufficient solubility of the molecules in a fast evaporating solvent is required.

**Spin-Coating of Calixarene-based MG Resists:** In frame of this work mainly the calixarene derivatives cmc4r (C-methylcalix[4]resorcinarene, molecular weight: 544.59 g/mol) and 4m1ac68 (4-methyl-1-acetoxy calix[6/8]arene, molecular weight: 973.14 g/mol) were applied. Both derivatives show sufficient solubility in common solvents. This enables a thin film preparation via conventional spin-coating. Respective processes were developed and optimized in order to achieve ultra-smooth, amorphous and ultra-thin resist films. The protocols are published partially by us in refs. [51, 209]). In Fig. 3.2.2 the main results are summarized.

The 4m1ac68 derivative was dissolved in monochlorobenzene (MCB). For cmc4r methyl isobutyl ketone (MIBK) was applied. Prior to spin-coating the solutions were filtered using a Teflon syringe filter with 0.2 µm pores. Intensive stirring of the solution, followed by multiple filtering, was essential in order to achieve a low defect density film. The spin-coating process was performed for 4m1ac68 with 2000 rpm for 3 s, followed by 4000 rpm for 45 s. In case of cmc4r 3000 rpm for 30 s was applied. Subsequently,
Chip & Resist | RMS roughness measured by AFM [1x1 µm area]
--- | ---
FD-SOI, without resist | 0.20 - 0.23 nm
FD-SOI & cmc4r (c) | 0.25 - 0.35 nm
FD-SOI & 4m1ac68 (d) | 0.25 - 0.35 nm
Si + Cr (5 nm) / Au (15 nm) & cmc4r (e) | 0.40 - 0.70 nm

**Figure 3.2.2:** Ultra-thin calixarene-based MG resist films prepared by spin-coating. (a) Achieved resist layer thickness versus concentration of the spin-coating solution. In the particular example the derivative cmc4r was dissolved in a MIBK solvent. The thickness of the resist films was measured by multiple angle ellipsometry (black dots; SE400-CER500 system applied, angle: 45°–75° in 5° steps, model with fixed refractive index of $n = 1.5$). The thicknesses were verified by AFM topographic measurements (red stars). The relation between resist thickness and molar concentration is fitted by a linear function type with a slope of $1.67 \pm 0.02 \text{nm} \cdot \text{l/mmol}$. The results were published in [40]. The AFM topography images (b-e) shows the resist surface morphology and roughness of $\approx 10 \text{nm}$ thick resist layers after the prebake step. In (b-c) cmc4r and (d) 4m1ac68 resist is spin-coated on top of a FD-SOI chip. In (e) cmc4r is spin-coated on top of a Cr (5 nm) / Au (15 nm) coated Si test chip. A prebake step was used to evaporate the residual solvent and to improve the resist adhesion. In particular, a hot plate at 175°C, 5 min / 90°C, 3 min for 4m1ac68 / cmc4r, respectively, was used. Thereby, the different preparation protocols arise from the different film properties. 4m1ac68 is strongly hydrophobic [275] and cmc4r is hydrophilic. The resist layer thickness is definable via concentration of the spin-coating solution. This is summarized in Fig. 3.2.2-(a) for the cmc4r derivative. The film thickness was determined by multiple angle laser beam ellipsometry, ref. [51]. Due to the linear dependency observed between concentration and thickness (Fig. 3.2.2-a), the resist film is adjustable with sufficient fidelity for lithographic applications. For example, in case of 4m1ac68 a 0.5 wt. % solution gives 12.4 nm thick films, and a 5.7 mmol/l cmc4r solution results in a $\approx 10 \text{nm}$ resist thickness.

As observed, the resist surface roughness is highly sensitive to the substrate surface roughness and to its morphology. This is shown by example in Fig. 3.2.2-(b-d) for a Si surface versus for a Cr/Au surface, Fig. 3.2.2-(e). Thereby, the grain structure of the evaporated Cr/Au metal layer is transferred into the resist layer. A doubling of the resist surface roughness compared to a Si substrates is caused. However, taking the typical dimensions of the calixarene molecules of 0.5 – 1 nm [237, 261, 262] into account, the resist films achieved by the optimized spin-coating process reveals excellent results (Fig. 3.2.2, tabular summary). No aging, recrystallization or other effects were observed. Further details about the applied processes are provided in refs. [31, 40, 310, 311, 312]. A detailed solubility study of molecular glasses and polymeric resists, which are applicable for FE-SPL, is available in ref. [209].
Physical Vapor Deposition (PVD) of MG Resists: The PVD process is provided in frame of the SNM-project by University of Bayreuth (UBT; Dr. Christian Neuber and team). The thermal evaporation offers a complete solvent-free and thus dry path for preparation of ultra-thin resist films. In this way typical spin-coating related problems are circumvented. In summary, the following advantages are given: (1) Prevention of solvent-related problems like pinhole formation, residual solvent domains or other solvent effects, which lead to inhomogeneous resist formations (ref. [225, 226]). (2) Homogeneous and uniform resist films, even across surface topographies, are provided. In contrast, spin-coating on highly pre-structured samples results in significant variations of the resist film thickness. (3) In consequence of the dry preparation no baking step is required. (4) The resist layer thicknesses are in-situ controllable by a quartz crystal microbalance (QCM). A accuracy of $\pm 2 \text{nm}$ is provided. (5) The resist thickness is not limited by the solubility of the respective derivative. For example, layer thicknesses, e.g. for cmc4r from minimum 5 nm (thinnest achieved uniform resist films) up to a few hundreds of nanometer are possible.

However, not every molecule is suitable for PVD (ref. table 3.3). A high thermal and chemical stability of the molecule is necessary in order to inhibit a degradation during thermal evaporation. The 4m1ac6(8) calixarene derivative is thermally not stable enough since the evaporation temperature ($T_{\text{PVD}} \approx 320^\circ \text{C}$) is too high compared to its decomposition temperature ($T_d \approx 334^\circ \text{C}$, ref. [275]). In contrast, the cmc4r resorcinarene derivative evaporates at lower temperatures, without initiation of a degradation process ($T_{\text{PVD}} = 250^\circ \text{C} \leftrightarrow T_d > 300^\circ \text{C}$). In addition, the tendency of the molecule for crystallization is crucial. Recrystallization has to be suppressed. As found out, a functionalization of the molecule can be introduced, shown in Fig. 3.2.3-(i), or a co-evaporation process can be applied, Fig. 3.2.3-(ii), in order to hamper the (re)crystallization tendency. In particular, low functionalized calixarene derivatives, e.g. C4a, 4tBC4a, 4tBtc4a (detailed information about the derivatives is provided in appendix section A.2 and A.4), tends to highly crystalline films (Fig. 3.2.3-(i)). In contrast, the cmc4r derivative forms amorphous, very uniform homogeneous resist films. As a result, cmc4r resist films with 5 nm thickness and a low surface roughness of 0.25 – 0.35 nm were routinely prepared via PVD. As revealed, a combined standard cleaning procedure, followed by a HF-dip removing the native oxide, improves the surface roughness of the resist film (Fig. 3.2.3-table). In addition, the HF-dip decreases the probability of de-wetting of cmc4r since the resist adhesion is increased. An additional HMDS primer is not required.

In addition to calixarene also novel synthesized MG resists were tested, summarized in section 4.4. The preparation via PVD was evaluated, summarized in Fig. 3.2.3-(ii). Initial attempts using twisted substituted carbazole biphenyls (UBT3-UBT5) showed a spinodal de-wetting (A4). Thus, this molecule class is not suited for lithographic applicability. The spiro-based MG resists UBT7-UBT9, tailored towards high glass transition temperatures, give acceptable amorphous morphologies. In order to improve the etch performance $C_{60}$ fullerenes, which have a high thermal and mechanical stability, were tried via PVD thin film preparation. Caused by the high tendency of the fullerenes to cluster and crystallize, the formation of desired thin films was not possible in direct fashion. Here, co-evaporation of $C_{60}$ with another MG resist, in particular UBT8, has revealed a highly promising alternative path. As a result a mixed $C_{60}$-MG resist films were prepared. Surprisingly, the tendency to aggregate and crystallize was fully suppressed, which leads to smooth and uniform resist films, Fig. 3.2.3-(ii). A list of all evaluated MG resist materials is provided in the appendix, section A.2. A tabular summary of the surface morphology and surface roughness of PVD prepared MG films is given in appendix section A.4. The PVD preparation results were published partially in refs. [225, 226].
RMS roughness measured by AFM [1x1 µm area]

<table>
<thead>
<tr>
<th>Chip &amp; Resist</th>
<th>RMS roughness measured by AFM [1x1 µm area]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD-SOI, without resist</td>
<td>0.20 - 0.23 nm</td>
</tr>
<tr>
<td>FD-SOI (StCl) &amp; cmc4r</td>
<td>0.35 - 0.45 nm</td>
</tr>
<tr>
<td>FD-SOI (StCl + HF-dip) &amp; cmc4r</td>
<td>0.25 - 0.35 nm</td>
</tr>
<tr>
<td>FD-SOI (StCl + HF-dip) &amp; UBT7</td>
<td>0.30 - 0.40 nm</td>
</tr>
<tr>
<td>FD-SOI (StCl + HF-dip) &amp; UBT8</td>
<td>0.30 - 0.40 nm</td>
</tr>
<tr>
<td>FD-SOI (StCl + HF-dip) &amp; UBT9</td>
<td>0.35 - 0.50 nm</td>
</tr>
<tr>
<td>FD-SOI (StCl + HF-dip) &amp; UBT8+C60</td>
<td>0.25 - 0.30 nm</td>
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</table>

**Figure 3.2.3:** Thermal PVD preparation of ultra-thin MG resist films, in particular by employing calixarene derivatives (i) and novel tailored MG resist materials, synthesized by UBT (ii). A summary table containing all tested MG resist materials is provided in appendix section A.2 and A.4. StCl: standard cleaning procedure; HF-dip: diluted hydrofluoric acid solution for removal of the native oxide layer. PVD preparation was carried out by Dr. Christian Neuber and team at University of Bayreuth. Resist film analysis was done at TU Ilmenau by Yana Krivoshapkina and the author.
3.3 AFM-based Analysis and Evaluation of Lithographic Features

The analysis of AFM images for evaluation of lithographic features is one of the most important routines applied in frame of the thesis. In order to extract the geometric values of the patterned features, a well-defined method should be applied. In this context, a feature analysis software was developed and implemented in IGOR-Pro AFM software module. The general concept of the developed analysis software module is summarized hereinafter. In addition, limitations of the AFM-based feature analysis, with respect to the investigated feature types, are elaborated.

3.3.1 Pattern Analysis Program

The analysis of the geometric pattern data, e.g. of line and dot features, as a function of applied exposure conditions constitutes as an important pillar in order to reveal insights of the particular nanolithographic method. Herein, due to the closed loop capability of the FE-SPL system (section 1.3), AFM methods were typically applied as in-situ imaging methods. From this initial AFM image source the developed software module extracts the most relevant geometric information of the pattern, e.g. the line width, the feature depth, and so on. As summarized in Table 3.4, as a function of the measured feature type, named LT-LT3 (LT = line type), different geometric values are determined by the software. Here, the AFM topographic image is sectioned and each section is analyzed individually (marked as blue shaded areas in the AFM topographic images, Fig. 3.4). On this basis a statistical mean value and a standard deviation (3σ) of the geometric data are calculated. In order to investigate large amounts of AFM data an automatized analysis routine was implemented and realized via an IgorPro program extension. This so called feature analysis program (final version: MK-V1.5) uses specific models for each lithographic feature type, which was observed during the experimental investigations, ref. section 4.1. Overall, in case of a vector-based line patterning three different line types (LT) were identified, summarized in Tab. 3.4 (note: The origin and the mechanisms behind the feature generation are discussed in the experimental sections). All types of patterns observed could be assigned to one of these three types. Thereby, LT1 defines decreased structures, e.g. trenches, whereby LT3 describes raised structures. In the case where both types are overlaid, raised and decreased features, the LT2 model is applied for geometric feature extraction. Like drawn in Table 3.4 by a blue shaded area, the analysis areas has to be defined. The software module does a sectioning of the 2D image within the analysis area, and from every section the LT-specific pre-defined geometric values are determined. In order to get a statistically representative result, a minimum of 20 single sections were taken into account. In addition, also an averaging across multiple lines, which were patterned at same conditions, was deployed. For example, in case of the corner features shown in Table 3.4 an averaging across 6 individual lines was applied. Thereby, the statistical deviation of the mean value, for example of the line width, is a measure of the stability and controllability of the lithographic process. By making use of the developed software module a huge database of patterns was effectively analyzed. All graphs of this thesis, wherein geometric feature data is used, had been originated from the analysis software. Aside from that, the analysis software was also exploited by my supervised students, Matthias Budden [222] and Yana Krivoshapkina [209, 362], in frame of their theses.

3.3.2 Tip-Sample Convolution: Measurement Limitations and Spatial Measurement Errors

AFM tips are characterized by a minimal finite dimension, expressed typically by its radius of curvature and cone half angle. In consequence, images obtained with AFM techniques represent only an
Table 3.4: Summary of line types (LT) and the feature-specific geometric parameter extraction by an in-house developed software tool. The 2D AFM topographic images and related section graphs are applied as input for the software module. Abbreviations applied: LT-line type; LHP-left highest point; RHP-right highest point; LLP-left lowest point; RLP-right lowest point; S: Section. The following geometric properties of the patterns are determined:

- **W-1**: width measured between LLP and RLP (at mean height level);
- **W-2**: width between LHP and RHP (raised height level);
- **W-3**: width at defined percentage of the height/depth value, e.g. the FWHM width of the feature is determined by the W3 function by using 50% as input value;
- **A-1**: feature depth measured from highest to lowest altitude;
- **A-2**: feature height measured from mean level to highest altitude;
- **A-3**: feature height measured from mean level to lowest altitude.

The section profiles of the shown 100 nm hp features are not convolution-corrected (ref. section 3.3.2). In order to switch lithographically between the line types (LT) only the exposure was changed: LT1 375 nC/cm; LT2 150 nC/cm; LT1 42 nC/cm. Scale bar of all AFM images: 500 nm. The underlying patterning mechanisms of patterning are explained in chapter 4.
approximation of the specimen surface. In particular, tip-induced image distortions are significant whenever the measurement specimen contains features, which are comparable to the size of the tip itself (ref. [363]). Here, the highest resolution probe tips have a radius of curvature of typically $r_{\text{tip}} = 2 - 15 \text{ nm}$ and cone half angles of $\theta_{\text{tip}} < 10^\circ$. In frame of the SNM-project, where single nano digit scale dimensions are targeted, the metrological limits are within reach. Thus, tip-induced distortion effects are of significant relevance for accurate high resolution AFM measurements. Moreover, for analysis of AFM-based data the knowledge of measurement limitations as well as the estimation of measurements errors is required.

In Fig. 3.3.1 the tip-induced distortion effects are depicted as a function the different line types (LT) observed (ref. section 3.3.1). For description of the tip a conical probe model was applied. In general, the measured AFM image (red, dashed line) represents a mathematical convolution between probe geometry and the real surface topography. Various methods were developed in order to reconstruct the real surface topography on the basis of the convoluted image using so called deconvolution or erosion operations (ref. [363, 364, 365, 366]). However, either the specimen surface or the tip shape has to be known independently from each other, e.g. by SEM measurement (note: SEM methods suffer from their own probe-specimen broadening effects) or by AFM-operation with a known tip characterizer tool. Thus, a three-dimensional nanometer resolution measurement of the tip itself is required. Even in the case where the tip shape and radius are well known, the tip may change easily by tip wear or contamination during imaging. Unfortunately, extremely sharp tips, which are required for highest resolution imaging, are more prone to these effects. Furthermore, as pointed out in Fig. 3.3.1, the inaccessible surface regions are not reconstructable. These so called „dark areas” are marked in light
blue in Fig. 3.3.1. Since a direct tip-sample interaction is not possible, no information about these areas is gained. In point of fact it is impossible to determine from the many possibilities which the true surface topography is. In consequence, for the various line types different measurement limitations arise. In case of trenches (LT1) the measurement depth is limited by the ratio of the tip geometry with respect to the real feature width. In case of raised features (LT3) the line width is broadened by the respective tip-induced measurement errors.

As a function of the sample geometry, set in relation to the tip apex geometry, different models were applied. Thereby, the location of the tip-sample interaction point is relevant for choice of the particular model. A simple geometric model for rectangular measurement objects, in conjunction with a conical probe description, was utilized. On basis of refs. [363, 364, 365, 366] the following description for LT3 and LT1 geometries were derived:

- **LT3** single feature, linear side region model (condition $A_{real} > r_{tip}$):

$$w_{meas} = 2r_{tip} + 2(A_{real} - r_{tip}) \tan(\theta_{tip}) + w_{real} \quad (3.14)$$

- **LT3** single feature, tip round end model (condition $A_{real} < r_{tip}$):

$$w_{meas} = 2r_{tip} \cos\{\arcsin[(r_{tip} - A_{real}) / r_{tip}]\} + w_{real} = 2\sqrt{r_{tip}^2 - (r_{tip} - A_{real})^2} + w_{real} \quad (3.15)$$

- **LT1** single feature, linear side region model (condition $A_{real} > 2r_{tip}$):

$$A_{meas} = \frac{1/2w_{real} - r_{tip}}{\tan(\theta_{tip})} + r_{tip} \quad (3.16)$$

- **LT1** single feature, tip round end model (condition $A_{real} < 2r_{tip}$):

$$A_{meas} = r_{tip} - \sqrt{r_{tip}^2 - 1/4w_{real}^2} \quad (3.17)$$

Therefrom, in the case of LT1 the maximum tip penetration depth as a function of the characteristic feature width is calculated, shown in Fig. 3.3.2-(i) for different tip radii and cone half angles. In terms of an LT3 type the lateral measurement error as function of feature height is estimated, Fig. 3.3.2-(ii). Thus, for LT1 feature types the tip geometry defines the maximum measurement depth. For example, by imaging a $10\, nm$ half-pitch (hp) dense pattern using a $15\, nm$, $15^\circ$ tip apex, a tip-limited measurement depth of $1\, nm$ is given. Using a $2\, nm$, $10^\circ$ tip enhances the measurement depth to $20\, nm$. In case of LT3 feature types the width measurement has to be handled with care. For example, imaging a feature with $10\, nm$ height by a $15\, nm$, $15^\circ$ tip apex produces a $30\, nm$ lateral measurement error, whereas a $2\, nm$, $10^\circ$ tip leads to a reduced measurement error of $6\, nm$. In summary, it is obvious that ultra-sharp tip apices, $r_{tip} \leq 5\, nm$, and small cone half angles, $\theta_{tip} \leq 10^\circ$, are essential in order to allow an accurate AFM metrology at nanometer scale.

For experimental practice the explained geometric models were applied effectively in order to estimate the measurement limitations and errors, respectively. However, when more complex tip and topographic shapes are involved, dedicated deconvolution algorithms are required. In this context, Villarrubia [363] has pioneered the application of mathematical morphology operations for reconstruction methods. In frame of my work a so called „blind tip reconstruction method” was implemented. Here, the outer bound of the tip geometry is estimated without a priori knowledge of the object’s real geometry (ref. [363]). In principle, this method firstly reconstructs the tip shape, whereas in a second step the
deconvolution of the AFM image is carried out. However, a variety of limitations, especially the fact that inaccessible areas could not be reconstructed (ref. Fig. 3.3.1) limits the practical applicability (a separate presentation about this topic was given, ref. \[367\]). In frame of the experimental work usually relative instead of absolute measurements within a defined lithographic test field were carried out. Thereby, the simple geometric models were applied. Furthermore, in order to minimize tip-induced differences and to enable the best comparability between the individual measurements, the imaging of a complete test series with the same tip, using a gentle parameter set (for minimization of tip wear effects), was carried out. A detailed description of the developed measurement and analysis procedures are given in sections 4.1.1 and 4.1.3.

Figure 3.3.2: Calculation of measurement limitations (i) and spatial measurement errors (ii) in the case of LT1 and LT3 feature types (section 3.3.1). The log-log plots include different tip geometric sets (tip radius of curvature $r_{\text{tip}}$ and cone half angle $\theta_{\text{tip}}$ variations). In the case of LT1 (i) the maximum measurement (penetration) depth as function of the characteristic feature opening width is given, whereas for LT3 (ii) the lateral measurement error as function of the characteristic feature height is shown.
In order to turn FE-SPL into a lithographic tool for nanofabrication, the (1) identification, (2) investigation, (3) understanding and (4) control of the fundamental nanoscale physical/chemical processes is of essential relevance. Thus, in order to enable a transfer from basic science to lithographic applications, the related mechanisms occurring between nanoprobe, resist, and sample substrate have to be controlled in a meaningful way. In frame of the basic experimental chapter the foundations therefor have been laid. In this context, the different regimes of patterning are identified and described by corresponding lithographic interactions. The fundamental effects are investigated as a function of exposure parameters and so called secondary lithographic conditions like exposure conditions, sample type and resist. As found, due to a superposition of multiple lithographic interactions the analysis was a challenging task. Specific analysis methodologies and routines had been developed in order to identify, extract, investigate and characterize the individual lithographic effects and mechanisms. The experimental investigations were carried out for basic exposure processes including line, dot and areal exposure, respectively.

4.1 Identification and Classification of the Lithographic Regimes and Allocation to Corresponding Interactions

In frame of the basic lithographic investigations a switching of the lithographic regimes as a function of exposure parameters was observed. In order to determine the origins of the particular regimes, as well as to resolve the switching trigger, novel methodologies were developed, summarized in the following sections. As a result, the observed lithographic regimes were linked to corresponding lithographic tip-sample interactions.

4.1.1 Methodology for Vector-based Line Exposure Parameter Investigations

As described in section 3.1.4, for line features a vector-based patterning routine is applied. Thereby, the lithographic parameter set, which includes the bias voltage, the current setpoint and the tip velocity (setpoint and velocity define the line exposure dose, ref. section 2.3.1), as well as secondary lithographic factors like the line pitch, the sample type, the tip and the environmental conditions affect the lithographic result. In order to enable an effective investigation process targeted exposure methodologies and related protocols were developed. In a first step specific line exposure test field layouts were programmed, Fig. 4.1.1. The typical pattern layout for exposure parameter investigations, Fig. 4.1.1-(i), consists of an array of L-shaped corner features. Each corner feature is written by using a specific parameter set. In practical use a single exposure parameter is changed row- or column-wise, respectively, in order to extract the particular dependency. For example, the exposure dose is modulated column-wise by alteration of the current setpoint and/or the tip velocity, whereas row-wise the pitch is
modulated. In such a manner complex exposure parameter screenings were conducted. In order to ensure that during exposure no secondary effects distort the parameter screening, e.g. like lithographic instabilities, tip alterations and so on, a reference test row was applied (Fig. 4.1.1-(i), red rectangle). All features of this row (#1, 6, 11, 16, 21) are patterned with the same parameter set. In consequence, the geometric and compositional data of the reference row features is a measure of reproducibility and stability of the lithographic process itself. Since the patterning is carried out column-wise, starting from #1 ⇒ #25 in serial manner, every fifth patterned feature is a reference one. As a result of this practice, the validity of a exposure test field was determined. Thus, lithographic errors could be identified, which normally would lead to a falsification of the measurement data. Moreover, also the origin of the distortion is traced. This strategy helped particularly during the initial phase of FE-SPL system development and process investigations in order to distinguish between real parameter-dependent influences and lithographic distortions, which are not related to the exposure parameter modulations.

The second layout applied, outlined in Fig. 4.1.1-(ii), is a pitch modulation test field, in which potential proximity effects were evaluated. Furthermore, the reproducibility of the lithographic process was investigated.

### 4.1.2 Different Lithographic Regimes and Corresponding Line Types Observed after Exposure

In accordance with the exposure methodology described previously (section 4.1.1), a corresponding lithographic result is shown in Fig. 4.1.2. The 5×5 L-shaped corner feature array is imaged by AFM directly after exposure. No development step in between was applied. In frame of this exposure test the line exposure dose was changed over a wide range by modulation of the tip velocity and field emission current setpoint, respectively. A stepwise increase of the exposure dose from the upper left corner
Figure 4.1.2: Investigation of a lithographic test field directly after exposure revealing the diversity of lithographic regimes and corresponding line types. The 5x5 corner feature array is imaged by AFM. Respective 2D (i) and 3D (ii) topographic images are derived. As marked in image (ii) with lines, section graphs are extracted, shown in graphs (iii-iv). In order to modulate the line exposure dose the tip velocity was changed column-wise (increase from bottom to top), whereas the field emission current was altered row-wise (increase from left to right). In total, this leads to an increase of the line exposure dose from upper left corner (lowest dose) to bottom right corner (highest dose). A constant bias voltage of 25 V and line half-pitch (hp) of 100 nm were applied. The integral gain of the current feedback loop was aligned with the tip velocity applied. As discussed in the exposure methodology section 4.1.1, the bottommost row, marked with a red rectangle, is designed as a (R)eference row. The features of the reference row were written with a constant parameter set of 35 V, 30 pA and 1.5 µm/s, which corresponds to a line dose of 200 nC/cm. Sample type: ≈ 10 nm cmc4r resist prepared by PVD on top of a pre-structured SOI-chip (no bottom layer). Probe type: electrochemically etched tungsten wire, r_{tip} ≈ 20 nm.
starting from 16.7 nC/cm to 750 nC/cm at the bottom right corner was achieved (Eq. 2.8). Other lithographic parameters were held constant - with exception of the integral feedback gain of the PID current feedback loop. This parameter has to be adjusted in accordance to the tip velocity in order to have an appropriate regulation of the surface topography. In such a manner, the tilt of the sample as well as various other sources of surface topographic changes are compensated leading to a constant tip-sample spacing. Thus, the application of higher tip velocities has demanded a faster regulation, which means the integral gain was increased respectively.

As confirmed by the reference row (R) in Fig. 4.1.2, the FE-SPL exposure process is stable and gives reproducible results. In particular, the deviations (σ) across the complete reference row (5 structures with 6 lines each were evaluated) are in (Δ)ltitude σ_A = 0.15 nm and (w)idth σ_w = 5.79 nm. In comparison, the deviations within a single corner feature of the reference row (6 single lines evaluated) are σ_A = 0.19 nm and σ_w = 5.89 nm, which is close to that of a single L-feature. Thus, local as well as global variations are in the same range. This confirms that parameter modulations have no influence on the reference features. The exposure experiment is viable. Concerning the width measurement it has to be noted that the lateral point and line count of 1024 gives in the specific case a measurement resolution of 10.35 nm. Thus, the measured width deviations are in sub-pixel range. This reference row crosscheck method was applied for all lithographic exposures carried out in order to validate the reproducibility of the particular experiment. In this manner feature alterations coming form secondary effects like tip alterations, environmental changes as well as instabilities caused by mechanical or regulation instabilities, were eliminated.

The exposure test array, Fig. 4.1.2, shows that in the case of low exposure doses the features are raised („up“-features: +). Line heights of up to ≈ 2 nm with respect to the unexposed resist surface background are measured. The application of higher exposure doses leads to a lowering of the exposed line areas („down“-features: -). So called trenches are formed. In the intermediate dose range both line types are superimposed. In particular, the center of the exposed line is lowered (-), whereas the line edges are raised (+). The line alterations as function of exposure dose is summarized in Fig. 4.1.3-(i). Thus, the diversity of features observed after exposure was the reason for introduction of different line types LT1, LT2, LT3, ref. section 3.3.1. As a result of the geometric feature analysis using our own-written program, section 3.3.1, the plots in Fig. 4.1.3-(ii) and (iii) are derived. As pointed out in Fig. 4.1.3-(ii), the line type changes from LT3 at low exposure doses to LT1 at high dose range, with LT2 as intermediate state. In order to explain that result at least two lithographic mechanisms are initialized. At low doses a growth mechanism dominates, whereas with increasing dose a direct removal mechanism is responsible. Accordingly, the LT2 feature type displays the transition between both mechanisms. As a first approximation the removal reaction has an exposure threshold of Φ_{L-removal-LT2} ≈ 100 nC/cm, measured at the transition of LT1 to LT2 (a more detailed threshold term is discussed later). The threshold for the growth reaction is located below the investigated exposure dose range (Φ_{L-growth} < 16.7 nC/cm). Linked to the threshold difference, the geometric appearance of the features could be explained by different spatial extensions of the induced lithographic reactions. In particular, at the same dose level the growth reaction has a lower spatial confinement compared to the direct removal reaction. Hence, the double line (peak) structure of LT2 as well as the fences observed in case of LT1 features (= the small protrusions at the line edges) are explainable. A detailed investigation of the respective line widths as function of lithographic parameters is provided in the next chapter 4.2.

In Fig. 4.1.3-(iii) the height/depth of different line parts are plotted in a common graph as a function of exposure dose. Thereby, the altitude is measured with respect to the unexposed resist background level. The data of each line type merges into each other, which means that a continuous transition
Figure 4.1.3: Line type as function of exposure dose, derived from the exposure test field of Fig. 4.1.2. In (i) the link between the observed lithographic regime and the line type (LT) as function of line exposure dose is given. The geometry of the three different line types were analyzed by the feature analysis program, section 3.3.1. In (ii) and (iii) excerpts of the results are shown. In (ii) the line type and regime (mainly raised features: +; mainly decreased features: -; both raised and decreased features: +/-) as function of line exposure dose (semi-logarithmic) is plotted. In (iii) the line altitude versus exposure dose (linear plot) is shown. Thereby, the line altitude is measured with respect to the unexposed resist background (mean level of background is 0, marked by a bold dashed grey line). The raised/lowered parts of the lines, broken down by the line types, are marked in (iii): LT3: line height (+); LT2: height of the fences (+), in-trench depth (-); LT1: trench depth (-), height of the fences (+).
takes place. In the case of the LT3(+) height only a slight increase with dose is present (ultra-low
dose measurements are discussed in section 4.2.3). After the onset of the direct removal mechanism a
linear function type for the line depth versus dose is given. For this the data of LT2(-) and LT1(-) are
merged (bottommost point of the trenches are measured). The slope of the linear function gives the
resist removal rate, which is in the particular case \( \approx 2\, \text{nm per } 100\, \text{nC/cm line dose increase.} \)
A full clearance of the resist layer is achieved at \( \Phi_L \approx 700\, \text{nC/cm}. \) Clearance means that the complete resist
layer is removed opening the bottom layer. Using this linear function type the threshold for the direct
removal mechanism could be refined, defined by the intersection of the linear removal function and the
feature growth function of LT3(+). Approximating the growth by a constant height of \( \approx 2.4\, \text{nm} \) gives
a removal threshold of \( \Phi_L - \text{Thr-removal-intersection} \approx 54\, \text{nC/cm}. \) Taking a closer look onto the fence
height of LT2(+) and LT1(+), shows that an increasing dose results also in a decreasing height. In the
particular case the height decrease of the fences is approx.10-times lower compared to the trench depth
function (fences linear fit: \( \approx 0.24\, \text{nm per } 100\, \text{nC/cm}. \)).

The same kind of lithographic behavior described herein was also observed for other calixarene resists
[e.g. 4m1ac6(8)], various resist thicknesses, bias voltages as well as various probes applied. Thus, it
could be suggested that this is a general behavior of FE-SPL carried out in ambient conditions (ref.
section 4.2 concerning the investigation of influencing factors). The origin and nature behind the
lithographic effects is unresolved and should be examined in context of the next sections. With
regard to standard EBL in UHV, raised latent resist features are atypical. In contrast, the crosslinking
in standard EBL leads to a shrinkage of the exposed resist areas, described in section 6.1.1. Derived
from this disagreement, the following list of questions appear: What leads to a feature grow? What
exactly is modified below the nanoprobe and what is the composition of the features generated? Which
interactions lead to the different feature types? What are the exact spatial extensions of the diverse
reactions? What are the particular dependencies? How could all these effects exploited for a lithography
processing? To answer these questions deeper investigations were carried out, covered by the next
sections.

### 4.1.3 Methodology Refinement for Analysis of the Lithographic Feature
Composition

In order to investigate the composition and internal structure of the induced features a set of experimental
process steps, combined with intermediate nano-analysis, were applied. In particular, selective as well
as non-selective removal methods were exploited to remove defined layers of the feature. After each
removal step the features were analyzed by AFM, SEM and related analysis methods. In particular, also
AFM phase contrast imaging and Nano-Auger electron spectroscopy were used. In order to substantiate
the involved lithographic interactions it should be determined if:

1. resist material is directly ablated (= removed) during the patterning process,
2. resist material is chemically modified, in particular crosslinked,
3. if the bottom layer (Si) is modified, e.g. oxidized,
4. if deposition effects on top of the resist takes place.

Furthermore, the dependencies as well as spatial localizations of the different lithographic interactions
should be investigated individually in order to be able to describe the superimposed lithographic
outcome. For his purpose the following removal procedures were utilized:

(a) Selective removal processes:

- **Resist wet development**: Selective removal of all non-crosslinked resist parts, e.g. by MIBK
  solvent for cmc4r resist or Xylene for 4m1ac68 (protocols in appendix, section A.3). All crosslinked
resist parts are left behind. The respective development protocols were evaluated first on EBL exposed samples, ref. section 6.1.1.

- **Wet etching:** Selective removal of SiO$_2$ by a 1% HF-dip or mild ammonium fluoride based etchant $10 : 3 : 100$ $NH_4F : H_2O_2 : H_2O$.

(b) Non-selective removal processes:

- **O$_2$ plasma etching:** Removal of all organic matter on to entire chip, without a spatial confinement, allowing investigations of the bottom layer (substrate).

- **AFM-based nanoscratching:** Removal of all soft matter, e.g. resist material, by using extraordinarily high contact forces within spatially defined feature areas (for that the lithographic program was slightly modified and stiff cantilever were applied with $k_c \geq 40$ N/m). By that, parts of the feature were opened reaching the bottom layer. A defined spatial localization is given.

### 4.1.4 Identification of the Lithographic Interactions in Case of Calixarene MG Resist, Coated on Top of a Silicon Surface - Local vs. Global Sectioning and Methodology Evaluation

The previously introduced analysis strategy (4.1.3) was applied in the following for two L-shaped features patterned with a different exposure dose. In particular, feature I was exposed with $200 \, nC/cm$ and feature II with $40 \, nC/cm$ while all other parameters are kept constant. A $\approx 16 - 18 \, nm$ thick cmc4r resist layer was prepared on top of a Si substrate by PVD. The AFM imaging, Fig. 4.1.4, reveals the topography of the features after distinct process steps. Therefrom, the section graphs, Fig. 4.1.5, were derived revealing detailed insights of the structure and composition. A summary of all applied process steps, numbered #1-9, is provided in Fig. 4.1.6. Here, the alteration of the line altitude with the successive processing, distinguished between original line area and locally scratched area, starting from process step #2, is plotted. The insights gained from this experiment in context of the composition of the feature are:

1. **Directly ablated / removed resist** [Figs. 4.1.4-(a), 4.1.5-(a), 4.1.6-(process step #1)]: Directly after FE-SPL exposure, as a function of exposure dose, a direct removal process is observable. This is valid for both features. Thus, feature I and II can be assigned to LT1, which means that a trench is created in the exposure center, which is surrounded by slight fences. In accordance with Fig. 4.1.3 results, with increasing dose the trench becomes deeper. In particular, for I a depth of $d_{r-r-I} \approx 4 \, nm$ is measured, whereas in case of the enhanced dose a trench depth of $d_{r-r-I} \approx 9.9 \, nm$ is generated. The increased depth is also linked with an increased trench width, particular of $w_{r-r-fII} = 67 \, nm$ for feature II ($40 \, nC/cm$) and $w_{r-r-fI} = 92 \, nm$ for feature I ($200 \, nC/cm$).

2. **Crosslinked resist** [Figs. 4.1.4-(b), 4.1.5-(c), 4.1.6-(process steps #2-4)]: The wet development step (process step #2) reveals that parts of the exposed features (4.1.5-c) are crosslinked. In consequence, these parts are insoluble by the developer and left behind after process step #2. All unmodified or not sufficiently crosslinked resist is removed during wet development (4.1.5-b). Interestingly, the geometric forms of the crosslinked lines changes significantly as function of exposure dose. At low exposure doses more crosslinked resist material is left behind compared to the high exposure dose case ($h_{r-cl}$). In both cases (I-II) a double line structure is measurable, whereby this is more dominant in feature I profile. The center of the crosslinked region seems to be removed directly by the direct ablation mechanism, or alternatively...
Figure 4.1.4: Revealing of the features composition by using AFM topographic imaging between experimental processing steps. Two different L-features (I and II), patterned at different exposure doses (I: 200 nC/cm²; II: 40 nC/cm²), were imaged: a) Directly after FE-SPL patterning [process step #1]; b) After wet development step (10 s in MIBK solvent) [process step #2]; c) After an AFM-based local scratching process utilized for opening of resist covered feature areas [process step #2-Sc]; d) after HF-dip (1%, 15 s) [process step #9]. All applied process steps are summarized in Fig. 4.1.6. The features were written with a tungsten tip into ≈ 16 – 18 nm thick PVD-prepared cmc4r resist using 35 V, 20 pA, 1 µm/s for feature I and 35 V, 20 pA, 5 µm/s for feature II, respectively. Scale bars: 250 nm.
Figure 4.1.5: Depiction of the features structure by AFM-section graphs, based on the AFM topographic images of Fig. 4.1.4. The particular sections are measured after distinct process steps: #1 (blue), #2 (green), #2-Sc (red), and #9 (black). All applied process steps are summarized in Fig. 4.1.6. The different parts of the induced feature were identified and labeled by: a) Directly removed / ablated resist (note: depth measurement limited by tip-sample convolution, ref. section 3.3.2); b) not (sufficiently)-crosslinked resist, which is removed during the wet development step; c) crosslinked resist, which is insoluble in the developer solution; d) global resist layer part, which is not removable / soluble by the developer, also called grafted resist; e) SiO$_2$; f) Si-top layer of the SOI test chip. No convolution corrections were applied.

also parts of the center resist are removed during wet development. Deeper insights into the crosslinked vs. directly ablated material correlation as a function of the lithographic parameter set is provided later in frame of section 4.2.2. As pointed out by process step #3-#4, Fig. 4.1.6, an overdevelopment, tried with MIBK and acetone developer solutions, has only a marginal influence on the crosslinked resist parts. In conclusion, overdevelopment is not an issue.

3. Grafted resist layer at the resist-sample interface [Figs. 4.1.4-(c), 4.1.5-(d)]:
The localized AFM-scratching process, which was applied after process step #2 (wet development step), removes the entire resist film independently from its modification state. A global step of $\approx 2\, \text{nm}$ between scratched and non-scratched area is measurable, which is independent of the exposure process. In conclusion, a so called grafted resist layer interfacing the Si-surface is not soluble by the developer. Also a long overdevelopment step (#3) or a development step in acetone (#4) does not remove the grafted layer. As found later, this layer is typical for the PVD resist preparation method. In the case of spin-coating, grafted resist layers were not observed. However, for removal of the grafted layer, e.g. required for an effective pattern transfer, an $O_2$ plasma ashing process (#8) has to be applied.

4. Oxidation of Si bottom layer [Figs. 4.1.4-(c & d), 4.1.5-(e), 4.1.6-(process steps #2-9)]:
The AFM-scratching based local opening of the resist reveals an additional raised structure below the crosslinked resist area, which could be not removed in a mechanical fashion. In both exposure dose cases a height of the buried features of $h_{ox-g} \approx 2.9 - 3.4\, \text{nm}$ is measurable, whereas the width of the buried features is slightly enlarged in case of the upper exposure dose, e.g. $w_{ox-II}(40\, \text{nC/cm}) \approx 153\, \text{nm}$ versus $w_{ox-II}(200\, \text{nC/cm}) \approx 173\, \text{nm}$. A more detailed investigation of the dose dependencies is provided in section 4.2.3. As revealed by the successive process flow, the features were not altered by a wet development step or by $O_2$ plasma ashing (#2-5). Only a
HF-dip, carried out in frame of process step #6, is able to remove the raised features. Thereby, at the former places of the protrusions now trenches with an depth of \( h_{ox-g} = 1.2 \) – \( 1.6 \) nm appear. Concluding therefrom, an oxidation process is supposed at the exposed resist-Si interface. This process consumes \( Si (d_{ox-c}) \) in order to grow \( SiO_2 \) features (\( h_{ox-g} \)). The ratio of grown oxide height and consumed silicon gives the volume expansion factor (VEF):

\[
VEF = \frac{h_{ox-g}}{d_{ox-c}}
\]  

(4.1)

The estimated VEF of \( \approx 2.0 \) – \( 2.7 \) is close to reference data for formation of amorphous (\( a-\)) \( SiO_2 \) ([99]: \( VEF = 2.27 \)). The stacking of the section profiles after particular process steps, e.g. as shown in Fig. 4.1.5, confirms that the width and position of the raised feature parts measured directly after exposure matches exactly with that of the generated \( SiO_2 \) lines. This reveals that the origin of the raised features, which exist in all three line types LT1-LT3, can be attributed to oxidation mechanisms at the bottom layer.

To summarize, the identified tip-sample interactions are:

(i) A Direct removal/ablation mechanism of resist material, which works without the requirement of a development step (= self-developing behavior);

(ii) A chemical modification mechanism of the resist by crosslinking, rendered visible after a wet development step;

(iii) Possible oxidation of the \( Si \) bottom layer

In frame of this section the different feature parts were assigned to a different mechanism. In fact, the superposition of all effects (i-iii) leads in sum to the final feature forms and profiles (LT1-LT3), which are measurable after exposure. As outcome of this section a convenient strategy for evaluation of entire exposure test fields is derived, described in next section.

4.1.5 The Qualitative Progression of the Exposed Line and its Inner Structure as Function of Exposure Dose - The Application of Global Sectioning for Analysis of Entire Exposure Test Field Arrays

The evaluation of the analysis methodology, discussed in previous section, shows that only \( 2 \) – \( 3 \) single process steps after FE-SPL exposure are required in order to generate a full 3D profile comprising the features composition. In particular, AFM imaging directly after exposure delivers the superimposed complete feature (\( i + ii + iii \)). AFM imaging after a wet development step reveals the crosslinked resist, which is superimposed with the buried oxide features induced at the substrate-resist interface (\( ii + iii \)). Finally, AFM imaging after an \( O_2 \) plasma resist stripping process uncovers the formed oxide features (\( iii \)). If desired, AFM imaging after an additional HF-dip delivers further information about the consumed \( Si \) and the total amount of formed \( SiO_2 \) at the Si-resist interface.

Summarized in Fig. 4.1.7, the global sectioning method was applied for analysis of an entire exposure test field array. The individual sections after each process step were superimposed in order to visualize the features’ inner structure as a function of exposure dose, shown in Fig. 4.1.8. Thereby, the geometric properties and amount of (i) directly removed resist, (ii) crosslinked resist and (iii) oxidized \( Si \) can be determined. The progression of the exposed lines inner structure with increasing line exposure dose is understandable by the section series provided in Fig. 4.1.8. In case of ultra-low doses, e.g. Ft #2: \( 10 \) nC/cm, a direct resist removal is not measurable. Only slightly raised features after exposure are visible, which are the result of an oxidation reaction at the Si-resist interface. Thereby, already in the ultra-low dose regime the cmc4r resist is entirely crosslinked, which means that the full thickness of
<table>
<thead>
<tr>
<th>Process step #</th>
<th>Process step description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FE-SPL exposure with 35 V, 20 pA, 1 µm/s (= 200 nC/cm) for feature I and 35 V, 20 pA, 5 µm/s (= 40 nC/cm) for feature II</td>
</tr>
<tr>
<td>2</td>
<td>- Wet development step #1: 10 sec in MIBK solution; - Sc: AFM-based nanoscratching to open resist covered feature areas; contact force was chosen in that manner that all soft matter is removed</td>
</tr>
<tr>
<td>3</td>
<td>Wet development step #2: 15 min in MIBK (over-development)</td>
</tr>
<tr>
<td>4</td>
<td>Wet development step #3: 10 min in Acetone</td>
</tr>
<tr>
<td>5</td>
<td>Etching step #1: ( \text{NH}_4\text{F} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} / 10 : 30 : 100, 1 \text{ min} )</td>
</tr>
<tr>
<td>6</td>
<td>Etching step #2: 1% HF-dip, 15 sec</td>
</tr>
<tr>
<td>7</td>
<td>( \text{O}_2 ) plasma resist strip #1, 150 W, 0.58 mbar ( \text{O}_2 ), 1 min</td>
</tr>
<tr>
<td>8</td>
<td>( \text{O}_2 ) plasma resist strip #2, 300 W, 0.57 mbar ( \text{O}_2 ), 1 min</td>
</tr>
<tr>
<td>9</td>
<td>Etching step #3: 1% HF-dip, 15 sec</td>
</tr>
</tbody>
</table>

Figure 4.1.6: Summary of process steps (#1-9) for feature analysis. Therefrom, alterations of the lines / fences (+ height; - depth) of feature I and II were measured and plotted versus process steps. As shown in Figs. 4.1.4 and 4.1.5, the features were imaged after each process step by AFM. For height / depth measurements the Si top layer, marked with a bold dotted line, was applied as a common global reference plane. The center line altitude of both features were measured in the resist-opened area as well as at the original non-scratched area of the feature (ref. Fig. 4.1.4). Additionally, for feature I the altitude of the fences was measured, depicted by green triangles. The different layers of interactions were marked respectively, e.g. the depth of the directly removed resist \( d_{r-r} \), the height of the crosslinked resist \( h_{r-cl} \), the total height of the formed \( \text{SiO}_2 \) \( h_{ox-t} \), the grown height of the \( \text{SiO}_2 \) \( h_{ox-g} \), and the depth of the consumed Si \( d_{ox-c} \).
Figure 4.1.7: Analysis of entire exposure test field arrays by global sectioning. A line exposure dose ($\Phi_l$) test field, carried out on a Si-test chip spin-coated with $\approx 22 - 23\,nm$ thick cmc4r calixarene MG resist, is shown. AFM imaging was done after distinct process steps, in particular: (a) Directly after exposure; (b) After wet development (WD); (c) After $O_2$ plasma ashing (O2PA). The exposure was carried out with $U_b = 35\,V$, a constant pitch of $220\,nm$, an exposure dose variation of $10 - 880\,nC/cm$ (starting from bottom to topmost corner like pointed out in image (a)) and a tungsten wire with $r_{tip} \approx 6\,nm$. The corresponding 3D sections showing the progression of the exposed line as function of exposure dose is provided in Fig. 4.1.8.
Figure 4.1.8: 3D section series showing the composition of exposed lines as function of exposure dose. The section series corresponds to the AFM image collection of Fig. 4.1.7. 3D sections are compiled for line exposure doses of 10, 100, 220, 350, 550, 880 nC/cm. The sections after each process step (aSPL, aWD, aO2PA) were superimposed revealing the features’ composition. The areas are labeled by: directly removed resist (aSPL-line); crosslinked resist ⇒ colored in green (aWD-line); grown SiO$_2$ ⇒ colored in red (aO2PA-line); pristine resist (unmodified) ⇒ colored in light blue.
the film is linked. As observed, there is a significant difference in exposure thresholds of ablation and crosslinking mechanism. In particular, the direct resist removal reaction is shifted towards higher doses compared to the crosslinking reaction (see ref. section 4.1.4). This leads to an ablation starting in the center of the crosslinked resist feature. This results in a so called self-aligned double-line structure, formed by crosslinked resist, e.g. visible in features #7 - #25. Here, the difference in spatial extension of the lithographic reactions, at a given exposure dose, is directly resolved. For example, in case of feature #25 the crosslinking reaction has a 2.3-times larger lateral extension than the ablation reaction.

In conclusion, with increasing exposure dose the width of the crosslinked as well as the directly removed resist areas are progressing. As expected, with increasing dose the depth of removed resist line is also enhanced (ref. Fig. 4.1.3) whilst at the same time the crosslinked resist height is decreased. Aside from that, with increasing dose the oxidation reaction is also enhanced leading to a broadening and growth of the SiO$_2$ features at the interface Si-resist interface. Thereby, a compensation of the oxide growth by the direct removal of resist is first present at feature #8 (100 nC/cm$^2$). This point marks the transition from line type LT2 to LT1, which occurs in between feature #7 - #9. As revealed, in contrast to PVD resist preparation (ref. Figs. 4.1.4 and 4.1.5), in case of spin-coating, Figs. 4.1.7 and 4.1.8, no grafted resist layer at the Si-resist interface is detectable. Thus, a grafted resist layer is only present in case of PVD preparation. Most likely, this layer is associated with cmc-4 resist fragments, which have a lower evaporation temperature than the entire molecule. Thus, during evaporation the molecular fragments are deposited first, forming a grafted resist layer of various organic material at the Si interface. A detailed quantitative geometric analysis of the features as a function of exposure parameter is carried out in chapter 4.2.3. Therefrom, respective models are derived. In this context, the resist material itself has an influence on the involved lithographic interactions, as discussed in section 4.4.

4.1.6 Greyscale-based Areal Patterning of Calixarene Resist-coated Si- and Pristine Si-Chips

In order to investigate the lithographic reactions across a larger area a greyscale-based areal patterning scheme was developed. In particular, features with extended lateral extensions are required for spectroscopic analysis, applied in frame of the next section 4.1.7. The operation principle of greyscale areal patterning, which is exploited for FE-SPL, is summarized in Fig. 4.1.9. The areal patterning is realized by a dense line patterning routine, which fills the entire field. By choosing a lithographic parameter set, which leads to an overexposure of the single line (refer pitch dependencies discussed in section 4.2.5), the single line widths are overlapping. An uniform areal pattern is formed. For greyscale patterning a modulation of the areal exposure dose is necessary. Instead of a lithographic parameter set modulation scheme, Eq. 2.10, which also alters the basic beam parameters (ref. section 5.3), a multi-pass exposure strategy (4.2.7) was chosen. This implies that the same area is exposed multiple times by the same overlapping dense line pattern. During all exposure passes the same lithographic parameter set is applied. For example, as shown in Fig. 4.1.9, the area dose is linearly increased by an incremental increase of the exposure passes. For highest homogeneity of the exposure alternating horizontal and vertical patterning directions for each pass were applied. A corresponding result of patterning onto an Si chip, spin-coated with $\approx 7 - 8 \, nm$ thick 4m1ac68 resist, is shown in Fig. 4.1.10.

The analysis of the topographic heights/depths of the areal test array, measured with respect to the unexposed surrounding resist, reveals the same general behavior as observed for line exposures (Figs. 4.1.2 and 4.1.3). At lowest dose (1 pass) raised features are present. With an increasing number of passes, which means an incremental increase of the exposure dose, the feature height is lowered. In Fig.
Figure 4.1.9: Greyscale areal patterning implemented for FE-SPL. The schematic shows an areal pattern consisting of an 3x3 array. Each of the single fields has a lateral extension of 5x5μm. The areal patterning is realized by a dense line patterning routine filling the entire field. An overexposure is applied which means that the single line widths overlap forming an uniform areal pattern of the pre-defined spatial extension. In the particular case the areal dose, calculated by Eq. 2.10, was linearly increased by a so called multi-pass exposure process. The number of overlapping exposures, so called passes, are indicated by the numbers marked in the single fields, e.g. 3x (passes) means that the field is patterned 3-times with the same exposure dose. In order to achieve a nearly homogeneous areal exposure the direction of patterning was rotated between each pass by 90° resulting in an alternating horizontal and vertical patterning.

Figure 4.1.10: AFM topographic image of a greyscale-based areal test pattern. The pattern is defined in ≈ 7 – 8 nm thick 4m1ae68 resist, spin-coated on top of a Si surface. For FE-SPL an electrochemically etched tungsten wire tip was applied. The 3x3 array pattern is imaged directly after exposure by AFM. No process steps in between were carried out. A 2D and 3D topographic image is shown in (a) and (b), respectively. The pattern layout is based on the layout of Fig. 4.1.9. The lithographic parameter set of a single pass was $U_b = 40\,V$, $I_{FE} = 8\,\mu A$, $v_{tip} = 4\,\mu m/s$ and $hp = 15\,nm$, which gives an areal dose of $\Phi_A = 6.67\,mC/cm^2$. The linear increase of the areal exposure dose was achieved by a multi-pass scheme. The corresponding number of passes is labeled in (a) by respective numbers, e.g. $3 \Rightarrow 3\,\text{passes}$. Scale bars: 2μm.
4.1.11 the mean area altitude of the exposed areas as a function of the dose / passes is plotted, measured for different resist-sample systems. In case of 4m1ac68 MG resist, show in Fig. 4.1.10, the area mean height/depth level development with dose is given in Fig. 4.1.11-(i) by blue dots. In comparison, the same areal exposure test was conducted for a cmc-4r spin-coated MG resist as well as for a pristine Si chip, which was not coated with a resist layer. For both calixarene MG resist-coated samples the same general behavior is observed. At lowest exposure dose raised areas with respect to the unexposed resist state were generated. With increasing dose the features’ altitude is decreasing linearly. At a certain exposure dose, at which the resist layer seems to be entirely removed to the bottom layer, the area altitude grows again with a linear tendency.

The same greyscale areal exposure dose test as in Fig. 4.1.11 was carried out on an uncoated pristine Si surface, shown in the small inlet AFM images of Fig. 4.1.11-(i). Without resist layer an approximately linear increase of the mean area height with areal exposure dose was measured (slope of $0.0643 \pm 0.0019 \, nm \cdot cm^2/mC$), which indicates a Si oxidation process. As expected, no lowered areas were observed. However, in order to examine if a further deposition process, e.g. of carbonaceous species, is superimposed with the oxidation process, further experiments and analysis were necessary, described in section section 4.3.1. So far, the exposure test on the pristine Si surface has delivered the height growth versus dose function, which is now applied for correction of the experimental area altitude versus dose data of resist-coated samples. As outlined in Fig. 4.1.11-(ii), in this way the directly removed resist function is isolated from the superimposed growth function. In Fig. 4.1.11-(ii) the three different lithographic effects are labeled with: (a) growth (oxidation, superimposed perhaps with a deposition effect), (b) resist crosslinking and (c) direct resist ablation. Three different points of interest of the plot should be noted, marked with <i> - <iii>:

- <i>: At lowest dose the growth leads to raised features. Here, the entire resist is crosslinked and in first approximation no resist is directly ablated.
- <ii>: The height growth and the directly ablated resist depth are equal leading to a zero altitude level with respect to the initial unexposed resist state.
- <iii> The entire resist thickness is removed. A further dose increase leads only to an increased area height.

The growth-corrected experimental data, Fig. 4.1.11-(iii), reveals for both calixarene derivatives a linear dependency of the directly removed resist thickness versus area exposure dose. This confirms the altitude-dose function measured already for single line features, Fig. 4.1.3. The removal rate is nearly identical for both derivatives, in particular $\approx 0.24 \, nm$ per $1 \, mC/cm^2$ area exposure dose increase. This means that with a single exposure pass of $6.67 \, mC/cm^2$ a resist layer thickness of $\approx 1.6 \, nm$ is removed, valid for exposure passes larger than 1. During the first exposure pass the ablation dose threshold is not reached, which means that only resist crosslinking and Si-oxidation are triggered. The shift of the linear slope between both derivatives is minimal, which indicates that no significant differences of the ablation reaction between both resist types is present (detailed comparison summarized in sections 4.2.2 and 6.1.2). The independently measured resist thicknesses, e.g. $6 - 7 \, nm$ for the 4m1ac68 resist film, fit very well with the patterning depths. Thus, the linear removal process proceeds until the end of the resist layer at a constant rate. Further, the growth corrected line altitude remain constant after reaching the total resist removal point (<iii> in Fig 4.1.11-ii), which indicates that the growth effect measured on the pristine Si-sample is comparable to that on the resist-coated samples.

Furthermore, the influence of the resist thickness on the ablation function was investigated, summarized for the 4m1ac68 derivate in Fig. 4.1.11-(iv). The growth-correction delivers the pure ablation function,
Figure 4.1.11: Mean area height/depth as function of exposure dose, plotted for different resist-sample systems tested. In accordance to Fig. 4.1.10, the mean area altitude of each single field was measured with respect to the unexposed resist surface [(+): exposed surface is raised; (-) lowered areas]. The particular graphs show: (i) Experimental data of the area altitude as function of area exposure dose, measured directly after exposure; (ii) Schematics outlining the involved processes. The oxide growth correction of the removed resist thickness versus dose function is described. In graph (iii) the method of (ii) is applied on the experimental results of (i) using the altitude-dose function of the pristine sample; (iv) Altitude versus dose experimental data for differently thick 4m1ac68 resists; (v) Oxide growth corrected plot of (iv). The graphs of (i, iii) and (iv, v) are not directly comparable since different sets of exposure parameters were applied.
shown in 4.1.11-(v). In the case of the ultra-thin resist layer (≈ 6 nm), Fig. 4.1.11-(iv), the tip-induced oxide growth compensates the removal of the entire resist layer at high doses, in particular at ≈ 50 mC/cm². In conclusion, the exposure dose should be controlled very well. Overexposure should be circumvented when a direct removal reaction is targeted. As confirmed by both experiments, Fig. 4.1.11-(i-iii) and -(iv-v), the removal function shows a linear function type. Thus, the removal rate is constant over dose. Interestingly, the rate (= slope of the linear function) seems to be independent of the initial resist layer thickness. In consequence, the number of required passes in order to have a full clearance increases linearly with the resist film thickness (16.5 mC/cm² in the case of a ≈ 6 nm 4m1ac68 film versus 24.6 mC/cm² for ≈ 12 nm resist layer). It has to be noted that the areal exposure experiments summarized in (i-iii) and (iv-v) are not directly comparable since different bias voltages, probes and environmental conditions were applied. In particular, in the experiment (iv-v) a feature growth rate of 2.55 times of that of experiment (i-iii) was measured. Interestingly, the same difference in removal rates comparing (i-iii) and (iv-v) is given. This reveals that both the rates of oxide growth and resist removal are altered by the same effect, in exactly the same manner (ref. section 4.2.2).

4.1.7 Nano-Auger Electron Spectroscopic Measurements of Areal Patterns

For investigation of the chemical composition of FE-SPL exposed features, Nano-Auger electron spectroscopy (AES) methods were utilized. In order to provide sufficiently large measurement areas with an almost uniform lithographically exposed surface, areal patterning processes discussed in section 4.1.6 were applied. For comparison a pristine Si sample (sample without resist), a cmc4r coated, and a 4m1ac68 coated sample were exposed by FE-SPL using the same protocol. AFM images taken directly after exposure are shown in Fig. 4.1.11-(i; iii). For spectroscopic analysis the electron beam, operated at 3 keV having a diameter of ≈ 500 nm, was aligned into the center of each single exposure field. Energy spectra (30−700 eV) were recorded in each field of the 3x3 exposure test array. The Nano-AES measurements were done by a custom-made Omicron system at the Molecular Foundry, Lawrence Berkeley National Laboratory (LBNL), USA. The particular measurements were carried out by my master student Matthias Budden [222], whom I have supervised, supported by Dr. Frank Olgetree and Dr. Deirdre Olynick from LBNL. In the following the most significant results are summarized (more details are given in ref. [222]).

In Fig. 4.1.12 the AES spectra as a function of FE-SPL pass (single exposure pass dose: 6.67 mC/cm²) are summarized, carried out for the three different sample types. In particular, in (i) and (ii) the raw spectra for a pristine Si sample (uncoated) and a 4m1ac68 resist spin-coated Si sample are compared. The correlation of AES peaks with literature data [368, 369, 370, 371, 372, 373, 374, 375] reveals that for both sample types only three basic elements are present:

1. Silicon: Si-LVV, 65 eV − 95 eV with the main peak located at ∼ 91 eV
2. Carbon: C-KLL, 220 eV − 300 eV
3. Oxygen: O-KLL, 507 eV − 510 eV

No trace of tungsten compounds, independently from the exposure dose and sample type, is detected. This confirms that no tip material is deposited on top of the exposed surface. Thus, the field emission process and its feedback loop works stably, without degradation of the tungsten emitter material. For a more detailed investigation of alterations of the Si-, C- and O- peak position and shape as a function of FE-SPL pass (= areal exposure dose), the raw spectra were corrected by a background subtraction and a charge compensation (dielectric resist layer causes charging, which results in an energetic shift of more than 10 eV). Excerpts of the entire spectrum, which correspond to the energy ranges of the
Figure 4.1.12: Alteration of the Nano-Auger spectra (intensity vs. energy) as a function of FE-SPL passes. In (i-ii) the raw AES spectra for the (i) pristine Si sample (ref. Fig. 4.1.11-i; iii) and the (ii) 4m1ac68 coated Si sample (ref. Fig. 4.1.11-i; iii) are shown. For a clear visibility of alterations in the spectra, the measurements of each FE-SPL pass were stacked by an offset of 1250 cts. In (iii) parts of the background-corrected and charge-compensated AES spectra for all three sample types are summarized. Here, the energetic ranges, which fit to the detected AES peaks, in particular the Si-LVV, C-KLL and O-KLL peak, were extracted from the entire spectrum. The individual spectra, which correspond to each FE-SPL pass are labeled respectively by the number of passes from 0 (= initial unexposed state) up to 9 (= 9 exposure passes). For better visibility the individual measurements are stacked by an offset of 3500 cts (= left horizontal scale bar). A respective differentiated spectrum plot $\partial N(E)/\partial E$ as function of energy $E$ is provided in appendix, section A.5.
particular AES peaks, are compared for all three sample types, summarized in Fig. 4.1.12-(iii). A respective derivative plot is provided in appendix section A.5.

The AES measurements carried out on the pristine Si sample confirm that an oxidation reaction of the Si top layer takes place. In particular, the most significant alterations of the AES peaks occur during first and second exposure pass. In particular, the oxygen peak increases, whereas the Si-peak changes in shape. Thereby, the dominating main Si-peak (92 eV) decreases, whereas two side peaks at 79 eV and 66.5 eV appear. This change in spectrum is well known and is attributed to a SiO$_2$ growth, described in refs. [369, 370, 372]. After the second exposure pass the the oxygen and silicon peaks are nearly constant (only minor alterations). An initial carbon and oxygen surface contamination is present. Interestingly, the carbon signal slightly decreases with increasing exposure pass. Only after the initial exposure is a slight increase of the carbon peak present. The general decreasing behavior of the C-peak indicates that, within the tested dose range of the particular experiment, no field-induced deposition of carbonaceous structures (ref. [128]) takes place. This means that the linear growth function measured on the pristine sample, Fig. 4.1.11-(i), is caused mainly by an oxidation process. A superposition with a carbon deposition seem not to take place (a deposition of carbonaceous features seems to occur mainly at higher exposure doses and electric fields, discussed in section 4.3.1).

In contrast to the pristine Si sample spectrum, the AES investigation of the 4m1ac68 sample reveals that with increasing exposure dose (passes) the carbon peak decreases and the oxygen and Si peaks increases. The most significant changes of the peaks occur between forth and fifth exposure pass. After the fifth pass the peaks remain nearly constant. This trend fits very well with the AFM data alterations, Fig. 4.1.11-(i; iii). At approximately the fifth exposure pass the complete resist layer is ablated. As expected, due to the high surface sensitivity of AES, in the unexposed case (0 passes) the resist layer shields the Si layer, which results in a high carbon peak and low Si signal. With the ongoing ablation process the carbon peak decreases and the oxidized Si surface is cleared which results in the observed Si- and O- signal change. After the fifth pass the spectra remains nearly constant, similar to the pristine Si sample. This confirms also the insights gained by the altitude measurements, section 3.3.1, that no re-deposition of resist material fragments occurs.

The cmc4r MG resist coated Si sample shows the same general trend as the 4m1ac68 coated Si sample. However, as a result of the thicker resist layer in case of the cmc4r sample (ref. Fig. 4.1.11-(i & iii)), the alteration rate of the spectrum as a function of exposure pass is lower. In addition, the insert of the Si- and O-peak alterations are shifted towards higher doses. Even after the ninth pass, which is the highest area exposure dose applied, the carbon signal remains. This confirms that resist is still on top covering the oxidized Si. The comparison of the Si peak shapes of the pristine and the 4m1ac68 resist coated sample, at final exposure state (pass #9), shows significant differences (comparison of the center peak shape at \(\approx 92\ eV\) versus the side peaks at 76 – 79 eV and 64 – 67 eV). This could be attributed to different oxide states (in terms of stoichiometry, defects, formed bonds) formed at the Si interface. Also the shift of the Si peak towards lower energies (1 eV – 2.5 eV) in the case of the resist coated sample supports that. Maki and Shigeta [376] have shown that the peak shift is a measure of the oxidized Si amount.

In summary, the oxide formation at the Si-resist interface is confirmed. No evidence for a re-deposition process of resist material or deposition of carbon-based structures is found in the investigated dose range. As indicated by the AES spectra, differences in the formed oxides between the pristine sample and the calixarene MG resist coated sample are likely. Potentially, in the resist covered case the in-situ generation of hydroxide anions (OH$^-$) and hydroxyl radicals (H$^+$O), caused as side effect of the crosslinking and removal process, could facilitate the oxide formation. Thus, in the case of the calixarene resist covered sample the formed oxide seem to be closer to its stoichiometric value.
4.1.8 Exposure Experiments on „Lithographically Inert” Bottom Layers

Since the oxidation reaction is linked with the Si substrate, by using a metal layer the oxidation reaction should be eliminated. Thus, in the following experiments an intermediate Cr (≈ 5 nm) / Au (≈ 15 nm) layer was introduced, placed in between the top MG resist and the Si substrate. The same methods, established in previous sections, were applied in order to extract the feature’s inner composition. Excerpts from an exposure test field, carried out on ≈ 6 – 7 nm thick cmcr4 resist, prepared by PVD on top of the metal stack, are summarized in Fig. 4.1.13. Three different kinds of features are shown:

(a) Low dose exposure at a large pitch (hp = 250 nm);
(b) Medium dose exposure at a large pitch (hp = 250 nm), and;
(c) Medium dose exposure with a decreased pitch (hp = 125 nm).

Case (a) - Low dose exposure at a large pitch: As expected from the previous results, at low exposure doses (Φl = 46 nC/cm) no direct ablation of resist material take place. In contrast, ≈ 0.6 nm raised lines (LT3 features) are measured. A subsequent wet development step reveals that below the raised features, similar to the Si-case, resist material is crosslinked. The experiment reveals that the feature growth is reduced 4 times by introduction of an intermediate Cr/Au layer (with metal layer: hg ≈ 0.6 nm; without: hg ≈ 2.4 nm, Fig. 4.1.3). Without a metal bottom layer, proven by the previous sections, an oxidation reaction is responsible for lifting up the resist, which leads in case of low exposure doses to the observed raised (LT3) features (no ablation is present). However, that could not be the reason for the slightly raised features when a Cr/Au bottom layer is inserted. In order to exclude changes of the Cr/Au layer, induced by the exposure, the similar sectioning method as applied for the Si-samples, section 4.1.2, was exploited. In particular, O2 plasma ashing for resist stripping and local AFM based nanoscratching were used in order to remove all soft material parts. As expected, visible by the bottommost red line in Fig. 4.1.13-(a), the Cr/Au layer was not altered by the FE-SPL exposure process. In turn, this means that the raised features are induced either by swelling of the resist, triggered by the scission and crosslinking process, or by deposition of carbonaceous material on top of the resist (ref. [128]). Since the resist materials consists mainly of carbon, similar to possible carbonaceous depositions, spectroscopic methods are not helpful in clarifying the process. However, evidence was found, described in section 4.3.1, that a local deposition process of carbon-based features occurs. Similar to the previous results, carried out without a metal layer, a ≈ 2 nm thick grafted resist layer was detected, marked in Fig. 4.1.13-(a) by a light green color. As revealed previously, this layer is linked with the PVD preparation process.

Case (b) - Medium dose exposure at a large pitch: By moving towards higher exposure doses, shown in Fig. 4.1.13-(b), the threshold for the direct removal reaction is exceeded. Similar to the Si-bottom layer case, directly after exposure deep line trenches, defined as line type LT1 (ref. Fig. 4.1.2) are measured. However, in contrast to experiments without an intermediate metal layer, ref. Figs. 4.1.2 and 4.1.3, no line fences (small protrusion at both sides of the line) are visible. This is linked with the suppressed oxidation when a Cr/Au bottom layer is introduced. A subsequent wet development step reveals that calixarene resist is crosslinked below the nanoprobe. Identical with previous results, the ablation reaction starts from the top, exactly in the center of the crosslinked resist area. Due to the different spatial extensions of the simultaneously occurring ablation and crosslinking reactions, a self-aligned double line resist structure is formed. A self-alignment effect is occurring since both interactions crosslinking and ablation are induced by the same lithographic source and within the same exposure process. Herein, self-alignment means that the placement of the crosslinked and
Figure 4.1.13: Evaluation of an exposure series carried out in cmc-4r calixarene MG resist (≈6−7 nm), PVD-prepared on top of a lithographically inert bottom layer (Cr/Au bottom layer). The qualitative development of line features and its inner composition is shown. Similar investigation methods as in Fig. 4.1.7-4.1.8 were applied. AFM imaging was carried out directly after FE-SPL exposure (aSPL) and after a wet development step (aWD). In addition, SEM imaging was applied after wet development. For investigation of bottom layer modifications O2 plasma ashing for removal of the resist and local AFM-based scratching 4.1.3 were used, shown in (a). All features were exposed and imaged by the same Ti/Pt-coated cantilever with $r_{tip} ≈ 25 \text{ nm}$. All scale bars: 1 mm. Features (a) and (b) were patterned with a 500 nm pitch, and feature (c) with 250 nm.
the ablated areas to each other is not defined by the alignment capability of the lithographic system, but rather by the physical relation between both initiated lithographic phenomena (investigated in detail in chapter 4.2.3). Thereby, the difference in width between crosslinking ($w_{CL}$) and direct removal ($w_R$) is $w_{CL} \approx w_R + (60 - 80 \text{ nm})$ (exact values depend on the chosen measurement points). The SEM image after wet development shows that the image contrast is identical for the center of the ablated line and the unexposed resist-cleared surrounding. Thus, it could be concluded that the crosslinked resist is entirely ablated in the line center reaching the bottom Cr/Au layer. This points out that the AFM depth measurement which stops at $\approx 1.5 \text{ nm}$ above the Cr/Au layer level, is rather limited by the tip-sample convolution effect (the width of the line is not large enough that the tip can reach the bottom layer, section 3.3.2). Thus, in the case of small lines, linked with the AFM measurement limitation, it could be not answered if a thin residual scum layer is present or if a full clearance to the bottom layer is achieved.

**Case (c) - Medium dose exposure with a decreased pitch:** By reducing the half-pitch (hp) of patterning to 125 nm, as shown in Fig. 4.1.13-(c), the previously (a-b) isolated crosslinked line features (Fig. 4.1.13-b) become a single large uniform areal pattern. Thus, a reduction of the line space results in an overlapping of the crosslinked side areas, whereas the directly ablated lines are still resolved in separate fashion (see AFM zoom image in (c)). In accordance with previous results, it is obvious that the ablation reaction features a higher lithographic resolution capability at the same dose level. However, similar to (b) one cannot doubtlessly measure the depth of the ablated line. As indicated by the SEM image, the in-situ generated trench is scum-free which means that it is opened to the bottom Cr/Au layer.

![AFM depth measurement with a decreased pitch](image)

**Figure 4.1.14:** Excerpt of a test series showing two adjacent features which are exposed with different line doses resulting in different lithographic tones. The particular experiment was carried out using a $\approx 11 \text{ nm}$ thick cmcr resist layer PVD-coated on top of a Cr/Au bottom layer. Similar to Fig. 4.1.13 series, AFM imaging was done after exposure (aSPL) and after a wet development step (aWD). The directly removed and crosslinked resist parts are labeled in the merged section graph. Additional SEM imaging was done after development. A Ti/Pt-coated cantilever tip ($r_{tip} \approx 30 \text{ nm}$) was applied. Scale bars: 1 \text{ µm}. The left feature was patterned with a 500 nm pitch, the right with 250 nm.
A further exposure test, carried out on thicker cmc4r resist (≈ 11 nm), is summarized in Fig. 4.1.14 for two L-corner features patterned at high (left) and low (right) exposure dose. Both patterning tones, positive tone by direct ablation (development-less) and negative tone by crosslinking, are shown next to each other. The high dose exposure (left side) shows, in contrast to the previous examples (4.1.13), broad lines (≈ 225 nm) which are generated by the direct ablation process. Thus, a valid depth measurement to the bottom layer is enabled. Both AFM and SEM reveal that no scum layer on the bottom of the line is present. As a second consequence of the high exposure dose, even at a pitch of 500 nm, the crosslinking reaction extends laterally in such a manner that the entire space between the exposed lines is crosslinked.

In summary, when a lithographically inert bottom layer is applied, the final lithographic outcome can be accordingly described by a superposition of two distinct lithographic interactions, crosslinking and direct ablation of resist material. Thereby, crosslinking represents a material modification, while direct ablation is a material transformation from non-volatile into volatile parts. Whereas the phenomenon of crosslinking of resist is in agreement with the negative tone behavior known from standard Gaussian electron beam lithography (ref. section 2.3.3 and 6.1.1), the direct ablation of resist material is an unexpected phenomenon and contradicts the standard EBL theory.

4.1.9 Phase Contrast Imaging: Measurement of the Crosslinked Resist Areas directly after Exposure

Phase contrast imaging (PCI) is a powerful AFM imaging method using AC-(intermittent-contact)-AFM mode operation. In particular, PCI provides additional information about the compositional and/or energy dissipation variations of the surface with nanoscale spatial resolution [318, 319]. In PCI mode the phase lag (shift) of the cantilever oscillation in reference to the drive signal is measured, while the oscillation amplitude of the cantilever is kept constant tracking simultaneously the topography of the sample. Thereby, the phase shift contains information about alterations of the micro-mechanical material properties like the elastic modulus, the viscoelasticity (damping) as well as the adhesion between probe and sample which is related to the surface energies, capillary forces, and so on (ref. [377]).

The application of PCI directly after the exposure process has revealed remarkable results, summarized by example in Fig. 4.1.15 for a corner test feature. As demonstrated previously, the topographic AFM image directly after exposure, Fig. 4.1.15-(a), indicates only the directly ablated resist areas. By taking the corresponding phase contrast image into account, Fig. 4.1.15-(b), significantly more information is provided. In particular, a relative phase shift of ≈ +0.6° surrounding the directly ablated resist region is measured. A halo around the complete corner feature is visible. The spatial extension of the halo is linked with the line exposure dose - the phase shift region extends laterally with increasing dose. Since the lateral positions of the phase shifts are not overlaid with any topographic alterations of the surface the phase alterations are not a topographic-induced artifact (for example like the line edges). A subsequent wet development step, shown in Fig. 4.1.15-(c), reveals that the shape and spatial extension of the phase shift region corresponds exactly to the crosslinked resist areas. This is confirmed by the section graph, Fig. 4.1.16-(a), which combines the topographic sample information after exposure and development step with the phase contrast signal. The section series of Fig. 4.1.16-(b-d) shows the phase contrast signal for each pattern type introduced previously:

(b) Negative tone lines, defined by crosslinking;
Figure 4.1.15: AFM phase contrast imaging (PCI) of a corner exposure test feature revealing that the phase contrast arises from the crosslinked resist, which surrounds the directly ablated resist areas. The meander-based corner feature \((h_p = 125 \text{ nm})\) was patterned into \(\approx 6 - 7 \text{ nm}\) thick cmc-4r resist using a Pt-coated cantilever at \(U_b = 40 \text{ V}\) and \(\Phi_l = 142 \text{ nC/cm}\). The image series shows (a) the topography directly after exposure, (b) the corresponding phase contrast image, and (c) the topography recorded after a wet development step (10 s, MIBK). Scale bars: 500 nm.

(c) Positive tone lines, defined by direct ablation. The lines are surrounded by crosslinked side lines. Thereby, the single crosslinked lines are still separated (no overlap);

(d) Positive tone lines, whereby the crosslinked side areas overlap.

In all cases the same general relationship between phase image and crosslinked resist area is found. Here, the phase shift measured directly after exposure corresponds exactly to the crosslinked resist area. In particular, a phase shift between crosslinked and pristine resist of \(\Delta_{\text{phase}} \approx +0.6 - 2.0^\circ\) is determined.

Following the references of PCI, e.g. [377], wherein it was concluded that a phase shift increase occurs at the transition from a less stiff to a stiffer material, it can be inferred that the crosslinked material has an increased elastic modulus compared to the unexposed resist. Also differences in the adhesion between crosslinked and pristine resist areas, or other chemical changes which lead to an alteration of the tip-sample dissipation characteristics could contribute to the phase shift. In this context, for deeper insights further tests are required which are beyond the scope of this work.

In conclusion, PCI in AC-AFM can be applied in order to identify and characterize the spatial extension of the crosslinked resist areas, without the requirement of a previous wet development step. The direct applicability of PCI for FE-SPL feature analysis is summarized by Fig. 4.1.17 showing the raw 3D topographic data (a) as well as the topographic image superimposed with the phase information (color-coded) of an entire exposure test array. The previously confirmed relationship between the spatial extension of the directly ablated line vs. the crosslinked surrounding area is clearly observed. Larger ablated lines causes a larger extension of the crosslinked side areas, visible by extension of the phase contrast regions. Additionally, the PCI method can be applied for overlay alignment tasks, which is required for multi-level, multi-pass, and step-and-repeat exposure schemes.

4.1.10 Summary of the Observed Lithographic Interactions and Derived Patterning Tones

The initial investigations of FE-SPL exposed features have revealed that not only a single interaction is induced by the high electric fields and the therefrom related Fowler Nordheim field emission currents...
Figure 4.1.16: Phase contrast imaging (PCI) carried out on different patterning types, exposed at different line doses. AFM sectioning graphs, similar to Fig. 4.1.13, were applied showing the topography directly after exposure (blue line), the topography after a wet development step (green line) as well as the phase contrast signal recorded during AM-AFM imaging directly after exposure (dashed purple line). The different resist areas are labeled by: (i) Directly ablated resist; (ii) Chemically modified / crosslinked resist, and; (iii) Un-modified resist, which is dissolved during the development step. The section graph (a) corresponds to the AFM image series of Fig. 4.1.15. Analogous to that, graphs (b-d) summarize the alterations of the phase contrast image for different exposure doses, in particular: (b) $45.5 \text{nC/cm}$; (c) $182 \text{nC/cm}$; (d) $910 \text{nC/cm}$. A $\approx 10 \text{nm}$ thick cmc4r resist layer was spin-coated on top of a Cr/Au layer. A highly doped Si cantilever was applied using $U_s = 40 \text{V}$ and $I_{FE} = 46 \text{pA}$. 

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Instead, multiple interactions are triggered, and the superimposed interactions lead to the final feature formation. This patterning behavior is very different compared to the standard Gaussian EBL of calixarene, wherein scission and crosslinking processes lead only to a negative tone behavior (ref. section 2.3.3 and 6.1). The identified lithographic reaction types are summarized schematically in Fig. 4.1.18.

Two spatially confined resist-based patterning interactions were identified. Therefrom, the lithographic tone of patterning is derived:

- **(i) Direct removal / ablation of resist material:** In consequence of the lithographic interaction a material conversion from non-volatile into volatile organic compounds is triggered. As a result, the resist material is directly removed / ablated, without the need of a development step. Thus, this patterning tone is called positive-tone, development-less / self-development.

- **(ii) Crosslinking of resist material:** Similar to the standard EBL process on calixarene MG resist (2.3.3; 6.1), a chemical modification of the resist is triggered, which leads to a solubility change of the exposed resist regions. Herein, the exposure process causes a break-up of the arenes, followed by a crosslinking process which renders the exposed resist insoluble in the wet developer. This patterning tone is called negative tone. This mode requires a wet development step after exposure in order to induce a topographic profile.

Aside from the main patterning effects occurring within the resist layer, two side interactions were observed:

- **(iii) Oxidation of the Si bottom layer:** In case of a Si bottom layer a chemical modification takes place, where the Si is locally oxidized. Thereby, a part of the Si bottom layer is consumed for the growth of amorphous SiO$_2$, described by the volume expansion factor ($VEF \approx 2.0 - 2.7$). In consequence of the volume expansion of $Si \Rightarrow a-SiO_2$ raised features are generated. In the case of a resist-covered Si-chip the expansion leads to a spatially localized lifting of the resist layer. Thus, in the resist-covered case the reaction is named a buried local oxidation process since the reaction is taking place below the resist layer at the Si-resist interface.

- **(iv) Deposition of carbonaceous compounds:** Evidence was found (ref. section 4.3.1) that also a material conversion from volatile into non-volatile parts in form of carbonaceous depositions
### Identified Resist Patterning Effects ⇒ Defines the Lithographic Tone:

<table>
<thead>
<tr>
<th>Positive Tone, Self-Development</th>
<th>Negative Tone, with Wet Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Direct Resist Removal / Ablation</td>
<td>(ii) Chemical Modification of the Resist: Crosslinking</td>
</tr>
</tbody>
</table>

![Diagram of resist patterning](image)

### Identified Side Effects of Patterning:

<table>
<thead>
<tr>
<th>(iii) Chemical Modification of the Si Bottom Layer: Oxidation</th>
<th>(iv) Material Deposition of Carbonaceous Compounds</th>
</tr>
</thead>
</table>

![Diagram of side effects](image)

**Figure 4.1.18:** Graphical summary of the identified interaction processes. In (a) the resist patterning interactions which define the lithographic tone of patterning are summarized. In (b) the observed side effects of resist patterning are outlined. The final lithographic feature is defined by a superposition of the single interactions. Color code of the images: light blue (pristine, unmodified resist), green (crosslinked resist), orange (carbonaceous structures), red (oxide), grey (substrate, e.g. Si).
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**Figure 4.1.19:** Formation of the lithographic outcome by superposition of single interactions (ref. Fig. 4.1.18), shown for the case of a calixarene MG resist. The patterning results are outlined schematically as function of bottom layer (rows a - b) and relative exposure dose (columns I - II). The same color code as in Fig. 4.1.18 caption is applied. Deposition effects are neglected.

As revealed, in the FE-SPL exposure process the lithographic interactions do not appear isolated and independently from each other. Typically, multiple interactions are induced simultaneously. In consequence, the superposition of the single effects defines the final lithographic result. As demonstrated by the previous sections, the superposition complicates the identification, investigation as well as application of single patterning effects. Thereby, the individual interactions are characterized by different threshold values, different spatial extensions and parameter dependencies, investigated in section 4.2. In addition, the effects depend on the applied resist, ref. section 4.4, as well as on the bottom layer. This overall combination determines the final features appearance and composition. Using the concept of superposition, the features measured in lithographic experiments can be explained very well. A graphical summary, provided in Fig. 4.1.19, illustrates the observed characteristic superposition cases as function of exposure dose and bottom layer on the example of a calixarene MG resist.

In conclusion, the final lithographic outcome is a function of the threshold and spatial extension of the single lithographic effects, which are superimposed forming the final feature. Thereby, the threshold of the direct removal / ablation reaction is shifted towards higher exposure doses compared to the crosslinking process. In consequence, an exposure at low doses, in particular below the threshold of the ablation reaction, leads only to a crosslinking process (Fig. 4.1.19- column I). Thus, a standard negative tone behavior similar to the standard EBL process is observed. In contrast, moving towards higher exposure doses, when exceeding the threshold for ablation both reactions are superimposed (Fig. 4.1.19-column II). Due to differences in spatial confinement of both tip-resist interactions at a particular dose level (investigated in detail in chapter 4.2) a so called self-aligned double-line feature is formed. In case of a point exposure, demonstrated in section 4.3.1, doughnut-like features result.

When a Si bottom layer is applied, an additional oxidation reaction of the Si is observed (Fig. 4.1.19-row b). The oxidation reaction is superimposed with the respective resist interactions (Fig. 4.1.19-row...
b) leading to the typical geometric appearance of the lithographic features measured after FE-SPL exposure (ref. section 4.1.2). The width of the oxidation seems to be identical with the crosslinking of resist - further details are investigated in next chapter 4.2. As found, the bottom layer oxidation reaction can be suppressed by introduction of an intermediate metal layer (Fig. 4.1.19-row a).

The deposition reaction, which is not included in Fig. 4.1.19, is visible mainly at high exposure doses 4.3.1 (due to the similarity of C-deposits and the resist it is hard to identify deposition effects at low exposure doses on top of the resist surfaces). Thus, we cannot prove if the slightly raised features in the case of a Cr/Au bottom layer (oxidation is suppressed) and low exposure doses (below the ablation threshold) are a result of a resist-based swelling process or of a deposition reaction. However, there is evidence that the slightly raised features in case of a metal intermediate layer are caused by a deposition process, ref. section 4.3.1.

In summary, two promising lithographic paths are accessible by FE-SPL, summarized in Fig. 4.1.20. The features could be either written in negative tone, which requires a subsequent wet development step, or in positive tone, which is directly applicable after the exposure process. In contrast to the negative tone, in positive tone development-less patterning development-related problems like resist swelling or feature collapse by capillary forces are circumvented. In terms of practical applicability both tones show promising characteristics, as demonstrated in Fig. 4.1.20 by large scale patterning examples of line features. Thereby, the FE-SPL exposure process is very stable in both tones delivering consistent larger scale patterns. In particular, a more than 1.6 mm long single meander line was patterned within a single exposure process. The positive tone lines were imaged directly after exposure, whereas the negative tone has required an additional wet development step. In conclusion, mainly the targeted application of the user defines the lithographic tone. By respective modulations of the exposure parameters both tones are accessible which enables the full diversity of patterning using the same resist layer. Also tone switching within a single pattern is enabled, demonstrated in section 7.1.

However, the lithographic exploitation of each tone requires a well-defined control of the induced interactions. In this context, high spatial localization, high reproducibility, stability, and the large process window are essential. In respect thereof, in frame of the next chapter the general influencing factors and lithographic parameter dependencies are investigated in detail.

### 4.2 Investigation of Fundamental Parameter Dependencies

For a deeper understanding of the lithographic processes, required for a well-defined lithographic control, the investigation of the fundamental parameter dependencies is essential. Revealed by the previous sections, different interaction mechanisms exist which define by superposition the final lithographic outcome. Thereby, each single interaction is linked with specific spatial localizations and parameter dependencies. Primary determinants, e.g. the lithographic parameter set, as well as secondary determinants, e.g. environmental conditions, resist, bottom layer, emission source, are investigated and dependencies between these and the lithographic outcome are determined. For feature analysis the developed software tool, described in section 3.3.1, was applied. The hereinafter described knowledge is the prerequisite for a targeted application of FE-SPL for further applications, e.g. the patterning of beyond CMOS devices targeted by the SNM-project [10]. In frame of this chapter only calixarene and resorcinarene MG resist materials were tested, whereas in section 4.4 the question is answered whether the lithographic mechanisms are resist-specific effects or not.
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<table>
<thead>
<tr>
<th>Negative Tone, Imaged after Wet Development</th>
<th>Positive Tone, Imaged directly after Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Negative Tone Image]</td>
<td>![Positive Tone Image]</td>
</tr>
<tr>
<td>![Section Graph]</td>
<td>![Section Graph]</td>
</tr>
</tbody>
</table>

**Figure 4.1.20:** Summary of the lithographic tones by patterning examples. The upper AFM image excerpts, with corresponding section graphs, show a single corner feature array patterned in negative tone (after wet development) and positive tone (without development). In similar fashion, the lower image series (AFM with section graph plus corresponding SEM image) shows a large scale pattern (20x20 µm²) consisting of a single meander line. The total length of the line was 1.64 mm. All features were written into a ≈ 4 – 5 nm thick PVD-prepared cmc4r resist layer. A line pitch of 250 nm was applied. The exposure doses were chosen with respect to the targeted lithographic tones (25 nC/cm for the negative tone and 142 nC/cm for the positive tone).
4.2.1 Fowler-Nordheim Field Emission Measurements

Due to the field enhancement effect at the tip apex only small bias voltages of $10 - 100 \, V$ are required in order to stimulate a Fowler-Nordheim (FN) electron emission process at the tip apex. In this context, the measurement of the emission characteristics gives a proof for operation in FN emission regime. In order to obtain the so called Fowler-Nordheim (FN) plot, discussed in section 2.4.4, the current-voltage ($I - U_b$) characteristics have to be determined and plotted in the form of $\ln \left( \frac{I}{U_b^2} \right)$ vs. $1/U_b$. In the case where the FN plot shows a linear dependency, a cold field emission process dominates. In turn, the calculations discussed in section 2.4.4 could be applied in order to determine the basic emission parameters.

a) Evaluation of basic measurement procedures for determination of the emission characteristics of proximal probe tips: The $I - U_b$ characteristics are typically determined by a bias voltage ($U_b$) sweep while the resulting emission current ($I$) is measured. Thereby, the tip-sample spacing ($d_{ts}$) is fixed. The overall measurement process can be subdivided into three parts:

1. In a first step the tip has to be placed in close proximity to the sample surface. A tip-sample spacing which is characteristic for FN-emission and the associated lithographic operation range is targeted (ref. sections 2.4 - 4.2.2).

2. A bias voltage modulation has to be carried out while the associated current flow between tip and sample is recorded. In order to achieve a fixed tip-sample spacing, the Z-feedback loop which is normally regulating a constant current by adjusting the tip-sample spacing, has to be turned off. On order to keep the initial tip-sample spacing the z-piezoscanner voltage must be maintained constant. In this context, the turn-off time of the Z-feedback loop for the $I - U_b$-measurement should be minimized since thermal drift effects can alter the tip-sample spacing.

3. The $I - U_b$-measurement, step (2), should be repeated several times. In between it is reasonable to correct thermal drift effects. After the measurements the tip is retracted respectively.

Two basic ideas and the associated system configurations, ref. section 3.1.2, were evaluated for placement of the tip within the field emission regime (bias voltage operation of $U_b < 100 \, V$). In particular, both operation principles are based on the implementation of an approach trigger during step (1). Thus, after release of the trigger during approach, the Z-feedback loop is turned off, the tip-sample spacing is fixed and a voltage sweep and current measurement is started.

b) Cantilever system configuration: In the case of the cantilever configuration the initial tip-approach is carried out by an amplitude-distance curve using the AM-AFM mode. Here, the trigger value is defined by a damping setpoint of the oscillation amplitude. A second approach step is done by using a current-based trigger. Unfortunately, due to the parallel cantilever-sample configuration the parasitic electrostatic actuation effect, discussed in section 3.1.7, leads to a significant distortion of the $I - U_b$ measurement. In consequence of the bias voltage sweep a mechanical bending of the cantilever is induced, which results in turn in a modulation of the tip-sample spacing (tip-sample distance decreases with increasing bias voltage). When a critical bias voltage value is exceeded an abrupt snap (pull)-in of the cantilever happens. Despite the application of stiff cantilever ($k_{nom} \approx 40 \, N/m$) exactly this jump-to-contact problem occurs during the performed measurements, summarized in Fig. 4.2.1. In this plot the bias voltage modulation (blue), the measured current (red) as well as the Z-piezo movement...
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Figure 4.2.1: Measurement of the current-voltage characteristics of a cantilever system configuration, performed onto a pristine (without resist) Cr/Au-coated test chip. The bias voltage modulation (blue), the measured current (red) as well as the Z-piezo movement (black) are plotted versus the timescale of the measurement. In (ii) a zoom-in at the place of the cantilever snap-in is shown.

During the first stage the approach of the cantilever towards the sample surface is shown, indicated by the Z-piezoscanner signal. During this step a constant bias voltage is applied (blue line; 45 V) and the current signal (red line) is monitored. After the current trigger (45 pA) is exceeded, the approach is stopped, shown in detail by plot (ii). During stage two the Z-piezo voltage is fixed, the bias voltage is modulated linearly and the resulting current modulation is recorded. As shown in more detail in Fig. 4.2.1-(ii), after a particular bias voltage is exceeded the current rises abruptly reaching the saturation limit of the I-U converter unit. The current remains at the maximum level despite the fact that the bias voltage is reduced to 2 V or the cantilever is slightly retracted by a z-piezo movement (visible at the beginning of stage three). Only a coarse retraction of more than 200 nm, carried out during stage three, leads to a return of the current to the initial state. This jump-like behavior of the current signal indicates a snap-in / jump-to-contact of the cantilever. This is also supported by measurements of the oscillation amplitude as a function of the bias voltage (not shown here). In conclusion, both effects, the modulation of the tip-sample spacing caused by the bias sweep and the pull-in of the cantilever, hamper reasonable I−U_b measurements for a cantilever-system configuration. In this context, Wilder et al. [13, 26, 168, 169, 378] have tried to overcome that problem by controlling both tip-sample spacing and current. In order to enable that, the cantilever force is simultaneously controlled (contact mode) while it is being scanned across the surface. Thus, the resist is exploited as a fixed spacer between tip and sample. However, as revealed later in this work (sections 5.2-5.3), this kind of measurement is not a meaningful current emission characterization method since lithographic alterable resist films leads to significant distortions of the measurement.

c) Tungsten wire system configuration: Since a cantilever based system is not appropriate for emission measurements, a tungsten wire tip system configuration was applied. Due to the construction of the set-up, section 3.1.2, alterations of the tip-sample spacing due to bias voltage modulations are suppressed. Also the pull-in effect is eliminated. In the case of a wire configuration a current-distance curve, with a pre-defined current trigger, was exploited in order to reach the relevant FN field emission distance. Due to the implemented trigger function the tip movement stops automatically when the current setpoint is reached. By that the I−U_b measurement (stage two) is initiated. A corresponding result is summarized in Fig. 4.2.2. As revealed, a clear dependency of the current flow as a function of the bias voltage modulation is given. In particular, with increasing bias voltage the current rises rapidly. The emission measurement is reproducible since up- and down-ramping of the bias voltage
Figure 4.2.2: Probing of the \( I - U_b \) characteristics using a tungsten wire probe system configuration. The emission measurement was performed onto a pristine (without resist) Cr/Au coated test chip. The Z-sensor value indicating the z-piezoscanner movement (black), the bias voltage modulation (blue) and the current flow between tip and sample (red), associated with the bias voltage modulation, are plotted as a function of timescale of the measurement. During the measurement the tip-sample spacing was fixed, revealed by the fixed Z-sensor value.

(linear based triangle function) gives similar results. Therefrom, the relevant \( I - U_b \) characteristics can be extracted and converted into a FN-type plot. However, a drawback of this method is that the initial tip-sample spacing, at which the \( I - U_b \) measurement is performed, is a priori unknown and cannot be determined in direct fashion.

d) Evaluation of Fowler-Nordheim plots: The transfer of the time-dependent measurement data, Fig. 4.2.2, into the Fowler-Nordheim plot reveals a linear dependency between \( ln(I/U^2_b) \) versus \( 1/U_b \) which is in accordance to the FN theory (section 2.4). A corresponding plot, determined by averaging over 4 single bias voltage sweep cycles, is shown in Fig. 4.2.3. In this context, the Fowler-Nordheim emission characteristics was also verified by various other measurements, wherein also different tips and initial approach settings were applied. Thereby, two further plots are summarized in Fig. 4.2.4 corresponding to small-scale (i) as well as large-scale (ii) current alteration cases. In both cases the FN emission process dominates. Thereby, in (ii) measurement the limit of the \( IU \) converter unit is reached leading to a current saturation. The different current ranges shown in Fig. 4.2.4-(i) versus (ii) were induced mainly by different initial tip sample spacings. In particular, in the case of (ii) the tip is approached closer to surface than in (i) by using a lower bias voltage during approach \( (U(\text{approach})_{b-\text{ii}} = 30 \, V \) vs. \( U(\text{approach})_{b-i} = 40 \, V \)). This results in different initial tip-sample spacing giving the different emission onsets, e.g. 15 – 20 V for (ii) versus 35 – 40 V for (i). Since a wire based set-up is used no absolute numbers about the initial tip-sample spacings can be determined. The different numbers in Fig. 4.2.4 correspond to different measurement iterations. As shown in Fig. 4.2.4-(ii), an offset between the initial measurement (#1, black dots) and subsequent measurements is observable. This effect can be attributed to initial tip contamination.

In conclusion, a stable field emission process which is in agreement with the Fowler-Nordheim theory, was demonstrated to work in ambient conditions. This is in accordance with former field emission based
Basic Fowler-Nordheim Theory without Correction Terms (ref. section 2.4):

<table>
<thead>
<tr>
<th>Total apparent emission area ($A$)</th>
<th>$96834 \text{ nm}^2$</th>
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<tr>
<td>Field conversion / enhancement factor ($\beta$)</td>
<td>$6.12 \times 10^7 \text{ m}^{-1}$</td>
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<tr>
<td>From $\beta$ derived tip radius of curvature ($r_{tip}$); assumption: $k = 1.5$</td>
<td>$11 \text{ nm}$</td>
</tr>
<tr>
<td>From $A$ estimated tip radius of curvature ($r_{tip}$)</td>
<td>$124 \text{ nm}$</td>
</tr>
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Extended Fowler-Nordheim Theory using Spindt Approximation (ref. section 2.4.4):

<table>
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<tbody>
<tr>
<td>Field conversion / enhancement factor ($\beta$)</td>
<td>$4.95 \times 10^7 \text{ m}^{-1}$</td>
</tr>
<tr>
<td>From $\beta$ derived tip radius of curvature ($r_{tip}$); assumption: $k = 1.5$</td>
<td>$13.5 \text{ nm}$</td>
</tr>
<tr>
<td>From $A$ estimated tip radius of curvature ($r_{tip}$)</td>
<td>$13 \text{ nm}$</td>
</tr>
</tbody>
</table>

Extended Fowler-Nordheim Theory using Spindt Approximation and Forbes Iteration (ref. section 2.4.4):

<table>
<thead>
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<th>$755 \text{ nm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>From $A$ estimated tip radius of curvature ($r_{tip}$)</td>
<td>$11 \text{ nm}$</td>
</tr>
<tr>
<td>Tip radius of curvature ($r_{tip}$) derived from SEM inspection</td>
<td>$\approx 15 \text{ nm}$</td>
</tr>
<tr>
<td>Estimation of $k$ from $r_{tip}$ (SEM) and $B$ (FN data)</td>
<td>$1.1 - 1.4$</td>
</tr>
</tbody>
</table>

**Figure 4.2.3:** Fowler-Nordheim (FN) plot showing $\ln(I/U^2)$ versus $1/U$. A corresponding FN plot analysis was carried out using the previously introduced FN emission models (ref. section 2.4.4). In accordance to the FN field emission theory the experimental FN plot reveals a linear function type. The experimentally derived slope $S_{exp}$ and intersection $R_{exp}$ of the linear fit were used for the FN theory approximations. A tungsten work function of $\psi = 4.5 \text{ eV}$ was assumed. The experiment was performed on a pristine (without resist) Cr/Au covered Si test chip. An electrochemically etched tungsten wire tip was applied which was characterized by SEM.
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Figure 4.2.4: Fowler-Nordheim plots ($\ln(I/U^2)$ vs. $1/U$) corresponding in (i) to a small-scale ($I \leq 45\ pA$) and in (ii) to a large-scale ($I \leq 4.5\ nA$; up to saturation of the I-U converter unit) current alterations. In both cases a FN emission behavior was measured. The different numbers are corresponding to repeated measurement cycles. The measurements were carried out by different electrochemically etched tungsten wire probes. A pristine Cr/Au covered sample was applied.

exposure experiments, refs. [13, 26, 167, 168, 169, 193, 378]. In turn, the FN emission theory which was elaborated in section 2.4 can now be applied for evaluation of the experimental FN data. The result is shown in Fig. 4.2.3. In particular, the total emitter area $A$, the field enhancement factor $\beta$, and the tip radius of curvature $r_{\text{tip}}$ (Fig. 4.2.4) were calculated by using different model assumptions, summarized in the lower table of Fig. 4.2.3. As predicted by the theory, the basic FN equation without an image potential correction gives a slightly too high total apparent emission area and a therefrom derived emitter radius. The standard FN theory using the Spindt approximation for the image potential effects gives a reasonable value of the emitter area and emitter radius. The estimated radius is in good agreement with the SEM measurement. By using the SEM image data for estimation of the geometric factor $k$ also a reasonable value is derived (ref. section 2.4.3).

e) Fowler-Nordheim Field Emission Measurements on Resist-coated Samples: Fowler-Nordheim field emission measurements, carried out on lithographically non-inert samples, reveal significant differences compared to previous emission measurements which were done on inert Cr/Au samples (c-d). In Fig. 4.2.5 two results corresponding to a small (Fig. 4.2.5-(i): ±11 V) and an enlarged bias voltage modulation (Fig. 4.2.5-(ii): ±22 V), done on calixarene MG resist ($\approx 10\ nm$) coated Si samples, are summarized. Similar to previous experiments, the bias voltage modulation was executed at a fixed vertical (tip-sample spacing) and lateral (spot) position. Due to differences in the initial current set-point settings, e.g. $30\ pA$ for (i) and $80\ pA$ for (ii), the tip approaches closer to the surface in the case of (ii).

As observed in the time-dependent plots, Fig. 4.2.5-(i, ii), the main difference to previous results is that the emission current decreases with progressing exposure time. Thus the current peak of each voltage sweep cycle decreases with increasing number of sweep iterations, summarized in Fig. 4.2.6-(a). This can be attributed to an increase of the tip-sample gap resistivity, shown in Fig. 4.2.6-(b). The most pronounced change occurs during the first five voltage sweep cycles. With increasing number of cycles the differences in the emission current between successive sweeps decreases. This behavior is also manifested by the differences of the current signal which is observable by comparing the up (U)-ramp and the down (D)-ramp of each voltage modulation signal (note: all parameters were kept constant
Figure 4.2.5: Fowler-Nordheim field emission measurements, carried out on lithographically non-inert samples, revealing a lithographic back-coupling effect. A tungsten wire probe and a calixarene resist coated (≈ 10 nm) Si sample were applied as emitter and sample, respectively. Results of two scenarios are shown, a small bias voltage modulation with an enlarged tip-sample spacing (i, iii), and an enlarged bias voltage modulation range with a closer tip-sample spacing (ii, iv). In (i-ii) the time-dependent measurement data, analogues to Fig. 4.2.2, and in (iii-iv) the corresponding Fowler-Nordheim plots are shown (U: linear ramp-up of the bias voltage; D: linear ramp-down of the bias voltage; frequency of the sweep: \( f_{\text{sweep}} = 0.5 \text{ Hz} \)).

during as well as in between each single voltage sweep. In the FN-plot, Fig. 4.2.5-(iii; iv), this is expressed in a hysteresis effect. With increasing number of sweeps the hysteresis effect decreases. Thus, during the initial sweep the differences of the emission current between up-ramp and down-ramp are maximum. With increasing number of sweeps the differences become smaller and smaller. For example, in Fig. 4.2.5-(iii) during the fifteenth sweep the hysteresis is negligible.

Both effects:

1. the reduction of the field emission current with increasing number of sweeps, and
2. the field emission current decrease between up-ramp and down-ramp of each cycle are indications for a so called lithographic back-coupling effect, which is discussed in detail in section 5.3. As revealed by this work, this effect is characteristic when lithographically non-inert samples are applied. In contrast, in the case of pristine Cr/Au coated samples, on which no lithographic interactions have been induced by the exposure process, this effect was not observed (see previous subsections c-d). Thus, the cause can be attributed to the lithographic modifications of the sample surface which are induced by the FN emission current. In particular, the modifications of the sample by the FN emission leads to an alteration of the electric field distribution within the tip-sample gap. In turn, this leads to a change of the field emission process at the tip apex. Thus, a so called back-coupling effect takes place, with the lithographic modification of the sample as feedback path.
Figure 4.2.6: Evaluation of the lithographic back-coupling effect of Fig. 4.2.5 measurement results. In (a) the current peak value of each bias voltage sweep cycle is plotted as a function of the sweep cycle number. The corresponding changes of the tip-sample gap resistivity are calculated, shown in (b).

Applied to the particular sample, the following process sequence results (particular effects are demonstrated later in the work): The initial crosslinking of the resist leads to an increased dielectric constant (ref. section 4.2.5). In turn, the electric field strength within the tip-resist gap is increased resulting in an increase of the emission current. Since only small exposure doses are required for crosslinking, ref. section 4.2.3, this occurs already during the initial bias voltage sweep. With progression of the exposure the dielectric resist layer is removed and a thin oxide layer at the Si interface is formed (ref. chapter 4.1). Thus, with progressing ablation of the resist the tip-resist gap is increased. In consequence, the electric field strength at the tip apex is reduced which leads in turn to a decrease of the emission current. Further details, and evidence for the sequence of effects, are provided in chapter 5 by using analytical as well as simulation tools. In this context, the hysteresis is a measure for the lithographic alteration induced in the resist-sample system during a particular voltage sweep, whereas the alterations between successive sweeps are a measure for the total rate of change. Since the lithographic process has a final state, which is defined by the local removal of the entire resist layer and the self-limited oxide growth (ref. section 4.2), the total rate of lithographically induced changes decreases with proceeding exposure time. Thus, the hysteresis as well as the total change in current signal decreases with proceeding bias voltage sweeps. In the case the hysteresis between up- and down-ramp has vanished, and the current peak remains constant during the sweeps, the final state seems to be reached. No further changes can be induced. In the context of case (ii), Fig. 4.2.5, an enhanced bias voltage sweep range, with a closer tip-sample spacing, results in an enhanced lithographic alteration rate. In consequence, in the case of (ii) a larger hysteresis and a stronger alteration in the current maximum is observable.

In conclusion, the lithographic back-coupling effect contradicts the boundary conditions of the FN emission equation. Thus, field emission measurements which are performed on lithographically non-inert samples are not applicable for characterization of the emission behavior of an emitter. Here, the measurement on an inert sample is required, as shown in subsections (c-d).

4.2.2 Investigation of the Tip-Sample Spacing

The knowledge about the tip-sample separation $d_{ts}$ during the exposure process is of fundamental importance in order to gain a better understanding of the fundamental processes. Since experimentally the change of the tip-sample spacing by lithographic parameter set modifications are unknown, in this
section the tip-sample separation is investigated as function of the bias voltage $U_b$, the current setpoint $I$, and the tip velocity $v_t$. As shown later, this is an important intermediate step in order to reveal the elemental dependencies behind a controlled FE-SPL processing.

**a) Method Development:** In order to determine the alterations of the tip-sample spacing as function of lithographic parameter set modifications, a method has to be derived which provides an additional vertical displacement information during the exposure process. As found, the closed loop displacement sensors of the piezo-scanning stage, so called linear variable differential transformers (LVDT), could be exploited. In addition to the emission current ($I$) also the LVDT-signals of all three movement directions are recorded during FE-SPL operation, shown in Fig. 4.2.7 for a corner feature pattern. Thereby, the X- and Y-LVDT data displays the scanner movement in lateral directions for generation of the basic feature geometry using a vector-based algorithm. In this context, the Z-LVDT sensor data (Fig. 4.2.7, black) gives the vertical movement of the piezostage. The vertical movement ensures a stable emission current by respective modulation of the tip-sample separation.

As shown in Fig. 4.2.7, the Z-sensor data is typically not a straight line which remains on a constant level. In contrast, a significant movement in vertical direction is observable. This is linked with a slope of the sample in X- and Y- direction. So far, mounting of the sample without having any tilt is impractical. Thus, in order to determine tip-sample spacing variations between different lithographic features the Z-sensor data must be corrected by the slope of the tip-sample configuration. This is not a trivial task since the data are superimposed with further nonlinearities coming from the Z-piezostack itself. The nonlinearities have to be determined for the particular scenario and subtracted from the Z sensor signal. Afterward, the slopes in lateral directions (X-Y) could be fitted by a linear function type. Here, a further trick is applied using the AFM imaging functionality of the system for determination of the true XY-tilt (under the assumption of a smooth sample and resist surface). Since during patterning of a single feature the lithographic parameter set is kept constant, and the current feedback loop maintains a constant emission current (condition: regulation parameters, especially the integral part of the PID, have to be optimized!), one can assume that the tip-sample separation is also a constant value.

In conclusion, one could extract from dedicated movements in X- and Y-direction, marked in Fig. 4.2.7 respectively by $\pm X \& \pm Y$, the local slopes of the probe-sample system. By combining all extracted local slopes of a feature a global slope map including all nonlinearities could be generated. The subtraction of that polynomial fit function from the raw Z-sensor data delivers the slope-compensated Z-sensor data, shown in Fig. 4.2.7 as a green graph. When the parameter set during exposure is kept constant, and the lithographic operation is stable, the tip-sample spacing should be constant. In consequence, the slope-corrected Z-Sensor data should be constant, which is confirmed in Fig. 4.2.7. Thus, the derived mean value of the corrected Z-sensor data gives the actual vertical position of the tip. However, due to the relative measurement method the tip-sample spacing is still unknown, but the tracing of tip-sample alterations is possible. Furthermore, the standard deviation of the corrected Z-sensor data is a measure of the stability of the lithographic operation. With respect to Fig. 4.2.7 a standard deviation of the relative tip position of $1.1 \text{ nm}$ is given. Here, one has to take into account that all irregularities of the sample surface and the resist layer are also transferred into the Z-signal (feedback loop is based on a current regulation, discussed in detail in 2.4). Considering a typical surface roughness of the final resist films of $R_a \approx 0.4 - 1 \text{ nm}$ the alteration of the tip position in the case of a fixed parameter set and stable patterning conditions is negligible.

In a next step the slope correction method is applied to entire exposure arrays, in which different features are patterned with different lithographic parameter sets. Thereby, the determined local slopes of the individual features of an array are summarized in order to reveal a global slope map. This
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**Figure 4.2.7:** Displacement data of piezostage, monitored by the LVDT sensors, plotted as function of the total traveled XY-distance. The raw sensor data in Z-(black), X-(red) and Y-(purple) directions are shown. The LVDT data were recorded during patterning of a L-shaped corner feature (AFM image top right corner) \( \approx 10 \text{ nm} \) thick CMC4R resist, \( U_b = 60 \text{ V} \), \( I = 48 \text{ pA} \), \( v_t = 2.5 \mu\text{m/s} \). Based on the XY-slopes of the probe-sample system the raw Z-sensor data were corrected respectively giving the local slope-compensated Z-sensor value, colored in green.

is applied in order to eliminate the global slope of an array. As a result, the relative alterations of the tip-sample separation \( \Delta d_{ts} \) between the individual features are revealed. In Fig. 4.2.8 this methodology is applied on exposure test field arrays, in which the velocity (i, iii) and the bias/current (ii, iv) were modulated, respectively. The global slope corrected plots, Fig. 4.2.8-(iii, iv), give the vertical (Z-) position of the tip as function of the exposed feature. In the case the features of an array are patterned with different lithographic parameter sets, the alterations of the tip position as a function of the lithographic parameters, e.g. \( U_b, I, v_t \), can be revealed. Applied to Fig. 4.2.8 it is obvious that modulations of the velocity cause only marginal changes of the tip-sample spacing, whereas modulations of the bias voltage and current result in significant changes.

By the developed methodology the relative alterations of the tip-sample spacing can be revealed. However, in order to determine the absolute tip-sample spacing the „zero“-level, at which tip is touching the resist surface \( d_{ts} = d_{\text{resist}} \land d_y = 0 \), has to be measured. That is not a trivial task, because:

1. **In the case of a cantilever based system configuration** the determination of the zero level is possible by the AFM imaging mode. Unfortunately, the parasitic electrostatic actuation which is linked with the parallel cantilever-sample configuration (ref. section 3.1.7) leads to falsification of the distance data since an additional bending of the cantilever as a function of bias voltage and distance is overlaid. So far, the measurement of the beam deflection simultaneously with the current signal is not possible (electronic limitation). Due to the significant measurement distortions a cantilever system is not suited for determination of the tip-sample spacing alterations (ref. Fig. 4.2.11).

2. **Instead, a wire-based system configuration** is preferable for accurate measurements. Since only a lithographic operation capability is given, the absolute tip-sample spacing cannot be determined by the AFM-mode. Here, an intended push-in of the tungsten wire probe into the resist surface has
Figure 4.2.8: Determination of the relative changes of the tip-sample spacing ($\Delta d_{ts}$) between different features of an exposure test field by using the global slope correction procedure. Thereby, in (i) the tip velocity $v_t$ was modulated, whereas in (iii) the bias voltage $U_b$ and the current setpoint $I$ were modulated, respectively. In graphs (i) and (iii) the raw Z-sensor data of four different features of a test row are plotted versus the entire (XY) length of the feature (solid lines). Therefrom, the slope-and drift-compensated Z-sensor data are derived, shown by the dotted lines. The slopes between the individual features are eliminated by the global slope correction procedure delivering the relative alterations of the tip-sample separation ($\Delta d_{ts}$) between the individual features. The boundary condition for this is that all features of an exposure test field are exposed without retracting the tip in between. The results are shown for the velocity modulation of (i) in plot (ii) and for the bias/current modulation of (iii) in plot (iv). The final results are summarized in Fig. 4.2.11-(i, ii). A cantilever based system configuration was applied.
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4 to be utilized in order to determine the zero-level \( (d_g = 0) \). To do this, the bias voltage was reduced step-wise until a mechanical scratching interaction occurs between tip and resist. The interpolation of the tip-resist touching point delivers the information required for rescaling of the relative tip-sample spacing plot into absolute values. As a drawback of this method the tip is contaminated and, in some cases, mechanically altered (revealed by Fig. 4.2.9).

**b) Investigation of tip-sample spacing \( (\Delta d_{ts}) \) alterations caused by bias voltage and FN field emission current setpoint modulations:** In conclusion, for all subsequent experiments a tungsten wire based set-up was applied. The experimental results of bias voltage modulation onto tip-sample spacing \( (\Delta d_{ts}) \) alterations are shown in Fig. 4.2.9 As discussed previously, in a first step the relative alterations are determined. In a second step, carried for Fig. 4.2.9-(i) measurement, the absolute tip-sample values were assigned by employing a mechanical interaction of the tungsten wire by scratching the soft resist material. Unfavorably, the tip is contaminated as a result, which distorts the emission properties and in turn also the tip-sample spacing. Thus, as summarized in Fig. 4.2.9-(ii), the next measurements were performed at higher bias voltages of \( U_b \geq 30 \text{ V} \) in order to prevent mechanical tip-sample interactions.

As revealed by graphs (i-ii) of Fig. 4.2.9, with increasing bias voltage the tip-sample spacing also increases. A linear function type between bias voltage and the tip-sample spacing (absolute and relative values) could be ascertained \( (U_b \sim d_{ts} ; \quad U_b \sim \Delta d_{ts} ) \), which is also predicted by the Fowler-Nordheim field emission theory 2.4 for a constant current mode operation (ref. Eq. 2.17). Slopes of the linear function of \( 0.7-1.3 \text{ nm/V} \) were determined, depending on tip and experiment. Figure 4.2.9-(ii) indicates that sharper tips seem to result in steeper slopes. However, due to the many unknown factors like the work function, exact tip shape and errors involved linked with the estimation of the tip radius of curvature by SEM, the height data estimation, tip shape irregularities, the validity of the experiments is limited. However, independently of the tip and particular experiment, a linear behavior between bias and spacing is confirmed. The absolute tip-sample distances are in the range of a few nanometer above the surface at low bias voltages and enlarge to several tens of nanometer at higher \( U_b \). As result of the enlarged spacing the beam diameter broadens. In consequence, the line width increases, observable by the AFM inlet figures in 4.2.9-(i). In addition, with higher bias voltages the probability of multi-tip emission spot sites is increased, obtainable also in Fig. 4.2.9-i and Fig. 4.2.10 at \( U_b \geq 60 \text{ V} \). However, the effect of an altered bias voltage, current setpoint and tip velocity onto the lithographic feature itself is discussed in more detail in sections 4.2.3-4.2.4 for calixarene based resists as well as for other molecular glass resists in section 4.4.

In the same manner the influence of current setpoint modulations onto tip-sample spacing alterations were experimentally investigated, summarized in Fig. 4.2.10. The current setpoint modulation was carried out at different bias voltages. Fig. 4.2.10-(i) shows the exposure test applied, imaged by AFM directly after exposure. Here, the bottommost row works as reference for the relative tip-sample spacing alteration measurement. This means that all measured gap changes are referenced to the parameter set applied for this row. In graphs 4.2.10-(ii) and (iii) the tip-sample gap alterations are plotted as a function of current setpoint. In graph (iv) the bias voltage influence was removed in order to show only the \( \Delta d_{ts} - I_{FN} \) dependency.

In comparison to the bias voltage, the current setpoint has only a weak effect onto the tip-sample spacing in the setpoint range tested \( (5 - 50 \text{ pA}) \). As predicted by the Fowler-Nordheim field emission theory 2.4, in the case of increasing current setpoints the system reacts with a decrease of the tip-sample gap in order to enhance the electric field strength at the tip apex (approximation derived from Eq. 2.17: \( I_{FN} \sim 1/d_{ts}^2 \)). Thereby, a decrease of the tip-sample spacing of approximately \( 4 - 11 \text{ nm} \) is required in
Figure 4.2.9: Alterations of the tip-sample spacing ($\Delta d_{ts}$) as a function of bias voltage ($U_b$) modulations. The experiments were carried out by a tungsten wire tip configuration using a constant current setpoint of $I_{FN} = 32.5\, \mu$A and tip velocity of $v_t = 1.75\, \mu$m/s. In graph (i) the relative alterations of the tip-sample spacing (left axis) are plotted versus the applied bias voltage. By exploiting a scratching interaction at low bias voltage the absolute tip-sample spacing $d_{ts}$ was estimated, indicated by the right axis (measurement uncertainty of „zero” level estimation: $\pm 3\, \text{nm}$). AFM images of the L-shaped corner features ($1.5\times1.5\, \mu$m, pitch $100\, \text{nm}$; scale bar AFM images: $200\, \text{nm}$), which were induced during the bias voltage modulation test, are shown by small inlet figures in graph (i). In graph (ii) two additional measurements, colored in blue and red, are shown, wherein new tungsten wire tips were applied. Here, a scratching operation in order to probe the resist altitude level is prevented by using $U_b \geq 30\, \text{V}$. Thus, only the relative changes of the tip-sample spacing could be determined. [Sample: cmc4r resist with $d_{resist} \approx 11\, \text{nm}$, spin-coated on top of a Si chip]
Figure 4.2.10: Relative alterations of the tip-sample spacing ($\Delta d_{ts}$) as a function of the applied bias voltage ($U_b$) and current setpoint ($I_{FN}$). The relative tip-sample alteration data are extracted from an exposure test field shown in (i). AFM imaging was carried out directly after exposure (scale bar: 1 $\mu m$). The bottommost row (marked with $R =$ reproducibility column), which was written with a constant parameter set ($U_b = 35 V$, $I_{FN} = 35 \mu A$), is applied as global reference, to which all other tip-sample distance variations are referenced. In graph (iv) the bias voltage influence was removed in order to show only the $\Delta d_{ts} - I_{FN}$ dependency. [Experiment: tungsten wire tip system, $r_{tip} \approx 8 \ nm$, constant tip velocity of $v_t = 2 \mu m/s$ for all features, resist cmc4r $d_{resist} \approx 11 \ nm$, spin-coated on top of a Si chip]
order to achieve an increase of the total emission current from 5 to 50 $\mu$A. The experimental results (Fig. 4.2.10-iv) indicate that the tip has to come closer to the sample surface when lower voltages are applied in order to achieve the same current increase than in the case of larger bias voltages. However, due to the relatively large measurement uncertainties further measurements with an improved accuracy are required to confirm this trend. In the particular experiments the PID regulation parameters were optimized for the center area of the parameter test field. During the exposure of an entire array the PID parameters were not changed in order to ensure most comparable patterning conditions. As a result, the measurement deviations are lowest in the middle of the parameter range and highest at the peripheral areas (e.g. 5 $\leftrightarrow$ 50 $\mu$A).

c) Alterations of the tip-sample spacing in the case of a cantilever system: Due to the measurement distortions introduced by the electrostatic bending of the cantilever, only a few measurements were carried out using a cantilever based system configuration. The corresponding results are summarized in Fig. 4.2.11. As expected, a relation between tip velocity $v_t$ and a resulting alteration of the tip-sample spacing $\Delta d_{ts}$ could not be derived, demonstrated in Fig. 4.2.11-(i) and (iii). Here, two independent measurements employing a Pt-coated and a highly-doped Si cantilever are shown. In this context, the $\Delta d_{ts} - v_t$ graph in the case of a wire-based configuration reveals the same behavior (graph not given here).

A bias voltage modulation test, carried out with a cantilever configuration, Fig. 4.2.11-(ii), indicates with increasing bias voltage an enhanced non-linear behavior in the $\Delta d_{ts} - U_b$ plot. This effect could be caused by the electrostatic cantilever bending effect. In particular, the Z-piezoscanning unit compensates the bending of the cantilever by an increased retraction. This results in the perception that the tip-sample spacing increases more than expected from the linear behavior (which is predicted by the FN theory or measured in the case of a wire-based configuration). In order to reveal further insights into the cantilever bending effect further measurement efforts are required (no further relevance for this work).

d) Summary:

1. The spacing between tip and sample during exposure is kept constant by the current feedback loop of the system whilst the lithographic parameter set and the lithographic conditions are not changed. The average of the tilt- and drift-compensated Z-LVDT sensor data gives the actual Z-position of the tip. Thereby, the standard deviation is an evaluation criterion of the lithographic process stability.

2. A linear behavior between bias voltage modulation and tip-sample spacing alteration is observed. This is valid for relative changes of the tip sample spacing as well as for its absolute values. Thereby, an increased bias voltage leads to an enlarged tip-sample spacing, which results in turn in a broadening of the electron beam. The experimental results confirm the predictions of the FN field emission theory 2.4. The applicable bias voltage range is defined by the mechanical interaction / scratching regime occurring at low bias voltages and the extremely broadened / multi-spot emission regime at high bias voltages. As revealed in section 4.2.4, the bias voltage level is in turn a function of the applied resist layer thickness.

3. In order to increase the emission current for exposure, the current feedback loop reacts with a decrease of the tip-sample spacing. As expected from the FN-theory, within the investigated current setpoint range the alteration of the tip-sample spacing is weaker than the bias voltage
Figure 4.2.11: Relative alterations of the tip-sample spacing ($\Delta d_{ts}$) as a function of the lithographic exposure parameters. In particular, the parameter influence of the tip velocity ($v_t$) (i, iii) and the bias voltage ($U_b$) (ii) were investigated for a cantilever-based system (i-ii: Pt-coated cantilever, $\approx 10$ nm CMC4R resist; iii: Si-cantilever, n-doped, $\approx 5$ nm CMC4R resist). Graphs (i-ii) correspond to Fig. 4.2.8 measurements, whereby for graph (iii) the respective AFM topography image is shown aside of the graph (R = row; scale bar: 1 $\mu$m). The numbers on the individual features correspond to the applied tip velocity $v_t$ for patterning. Thereby, row 1 of (iii) is exposed at a constant lithographic parameter set in order to validate the reproducibility of the exposure test. Here, the gap changes of the other features are referenced to the reproducibility row.
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Figure 4.2.12: Development of the line width (i) and line altitude (ii) as a function of the line exposure dose. The geometric data were extracted from an AFM image which was taken directly after exposure. The data correspond to the initial results of the line type change, Figs. 4.1.2 and 4.1.3. As a function of the identified line type (LT1-3, ref. section 3.3.1) different geometric values, which are characteristic for the particular regime, are plotted versus the exposure dose. The respective geometric measurements are illustrated by small graphics in the plots.

dependency. As indicated by the experiments, lower bias voltages require a higher alteration of the tip-sample spacing in order to induce the same current setpoint change.

4. As expected, no dependency between a change of the tip velocity and alterations of the tip-sample spacing could be measured.

5. In the case of a cantilever-based configuration an electrostatic bending of the beam, caused by the coulomb force, has to be taken into account (see also section 3.1.7). This effect distorts the measurement of tip-sample spacing alterations by introduction of additional nonlinearities coming from the voltage-dependent bending effect.

4.2.3 Definition of the Lithographic Feature by the Exposure Dose - Investigation of Current Setpoint and Tip Velocity Dependencies

The line exposure dose defines the amount of electrons applied for exposure of a defined line length. As derived for a vector based FE-SPL routine, ref. section 2.3.1, Eq. 2.8, the line exposure dose is a function of the field emission current on which the system regulates during exposure, and the velocity of the tip. In the following section the final lithographic outcome, and the underlying lithographic interactions, were investigated as a function of both dependencies. The exposure process was carried out at a constant bias voltage. Thereby, the bias voltage was adapted to the particular exposure scenario taking into account the resist thickness and applied tip (process of bias voltage optimization is discussed in detail in section 4.2.4). Later, also complex exposure test arrays in which the bias voltage, the exposure dose, and the line pitch were modulated, were evaluated.
a) Exposure dose dependency breakdown into the individual lithographic interactions, starting from the dose dependency of the superimposed lithographic interaction:

As revealed in chapter 4.1, the superposition of different lithographic interactions is responsible for formation of the final lithographic outcome. In this context, the analysis of an AFM image which is taken directly after exposure, for example shown in Fig. 4.2.12, reveals only the dependencies of the superimposed lithographic effect. As a function of the exposure dose, the superposition effect leads to different line types which are observable directly after exposure (ref. section 3.3.1 and 4.1.2 for line type definitions). Linked with that, different spatial extensions of the individual parts of the feature result, demonstrated by Fig. 4.2.12. In particular, at low exposure doses the lateral extension of the raised features with increasing dose indicates a dose-dependent enhancement of the superimposed crosslinking and oxidation reactions. In contrast, in the case of high exposure doses a broadening of the directly ablated line with increasing exposure dose is observed, which points out a lateral extension of the direct removal interaction. Within the intermediate dose range a transition from line type LT3 to LT1 takes place, which is characterized by a double peak geometry (LT2). As a function of the exposure dose different lithographic interactions seem to dominate (ref. chapter 4.1). Thus, the first conclusion is that not only the geometric values of the feature are defined by the exposure dose but also the lithographic regime (negative tone, positive tone, or both).

In order to gain more insights into the exposure dose dependencies of the individual lithographic interactions, the previously developed methodology for investigation of the internal structure of the lithographic features, section 4.1.3, was used. The geometric data were extracted from AFM topographic measurements which were carried out after each process step. To obtain the individual dependencies, broken down by interaction mechanism, the following processing sequence was applied: (1) Exposure by FE-SPL; (2) Wet development (WD); (3) O₂ plasma ashing (O₂P); (4) HF-dip (HF). Thereby, each AFM-imaging cycle after the process steps (1)-(4) gives further information about the feature. For example, the imaging after the development step reveals the crosslinked resist areas, whereas the imaging after the O₂P and HF process step is required to determine the oxidized Si. As a result, the entire feature stack is characterized. Based on this, the geometric changes which correspond to the individual interactions may be derived. In this context, the line altitudes (height/depth with respect to unexposed surrounding), the line widths as well as related values (aspect ratios, volumes) are calculated for the: (a) Directly ablated resist; (b) Crosslinked resist, and (c) Oxidized bottom silicon.

In the following, the method was applied on entire exposure dose arrays (Fig. 4.1.1) which consist of L-structures, patterned with different exposure parameter sets. The exposure dose dependency of the geometric feature data is summarized in Figs. 4.2.13 and 4.2.14 for two dedicated examples (cmc4r resist, coated on top of a Si test chip). In particular, the vertical (line altitude, feature thicknesses) as well as the lateral (line width) geometric parameters are plotted versus exposure dose. Additionally, the corresponding aspect ratios were calculated. The analysis of the graphs reveals the following insights:

1) Line Altitude - Notation: For determination of the line altitude, reference planes for measurement have to be defined. In the case of AFM imaging directly after exposure the unexposed resist surface was utilized as reference, whereas in the case of imaging after WD, O₂P, and HF processing steps the unexposed and cleared Si surface was applied. In this context, positive altitudes mean an increased feature (height measured) with respect to the reference plane, whereas negative values mean a lowered geometry (depth measured). For clarification, the particular geometric values are specified by inlet graphics in Fig. 4.2.13-(i, iii).

2) Characterization of the Si-oxidation bottom layer effect: The a – SiO₂ formation is characterized by a growth process, which consumes Si. Thus, the entire a – SiO₂ thickness is defined by
Figure 4.2.13: Line altitude (i, iii) and therefrom derived feature thickness (ii, iv) plotted as a function of the line exposure dose. By measurement of the line altitude data after dedicated process steps, indicated by the inlet graphics, the geometric values of the particular interactions (resist ablation, resist crosslinking, Si oxidation) were derived. The introduced procedure is shown for the two particular examples, both prepared on top of a Si-bottom layer. Example 1, graph (i-ii): cmc4r MG resist, ≈ 14 nm PVD coated, $U_b = 35$ V, tungsten tip $r_{tip} \approx 10$ nm; Example 2, graph (iii-iv): cmc4r MG resist, ≈ 25 nm spin-coated, $U_b = 35$ V, tungsten tip $r_{tip} \approx 6$ nm.
the sum of the oxide growth, measured after the O2P process, and the consumed Si, measured after a HF-dip. As revealed in Fig. 4.2.13-(i, ii), the line dose dependency of the oxide growth can be fitted by a logarithmic function type. This is in agreement with already published data and theory of scanning probe induced oxidation lithography, refs. [99, 102, 379] \( \Phi_L \sim t^{-1} \) (tip velocity); \( \Phi_L \sim t \) (dwell time). Thereby, a self-limiting behavior is obtainable, characterized by a rapid drop of the growth rate with increasing exposure dose. The calculation of the volume expansion factor (VEF, Eq. 4.1) reveals a decrease of the VEF with increasing dose \( \Phi_L \), e.g. \( VEF \approx 3 \) (\( \Phi_L < 50 \text{nC/cm} \)) to \( VEF \approx 2.0 - 2.2 \) (\( \Phi_L > 100 \text{nC/cm} \)). Thereby, a VEF of 3 is exactly the value that Avouris et al. [99] have determined for the oxidation reaction of Si by using a biased scanning probe. In contrast, the decreased VEF determined at enlarged exposure doses corresponds to the value for formation of an ideal amorphous SiO\(_2\) layer (\( VEF = 2.27 \), ref. [99]). Due to the increased VEF in the case of scanning probe lithography Avouris et al. [99] concluded that high strains are relieved by the formation of a rather open and defect-rich oxide layer. In this context, the decreasing VEF with increasing dose indicates that with an increasing dose the formed oxides are closer to the stoichiometric \( a - \text{SiO}_2 \), which is associated with fewer defects. This is supported by the AES measurements, section 4.1.7, which point out the formation of different oxides depending on the chip (pristine Si chip versus resist-coated Si chip) and exposure dose. As a possible reason, the resist film influences not only the electric field strength at the Si-resist interface (section 5.2) but also provides additional reactive species. Since the resist material itself contains \( R - \text{OH} \) functional groups, \( \text{OH}^- \) formation is likely supporting the oxidation process at the \( \text{Si} - \text{SiO}_2 \) interface (works in addition to the reactive species supplied by the intrinsic and the top water layer).

Another indication of this is given by the lateral propagation of the oxidation process with exposure dose, Fig. 4.2.14-(i, ii), which is equal to the spread of the crosslinked resist area. This is valid for the entire dose range tested. A fit of the width-dose dependency of the oxidation reaction by a logarithmic function type \( [y = a - b \cdot \ln(x + c)] \) is appropriate. As observed experimentally, the spatial localization of the scission of the resist molecules, which is a preliminary stage of the crosslinking process, has an equal extension as the oxidation reaction occurring underneath the resist at the Si-resist interface. Most likely, in consequence of the resist scission and crosslinking process additional \( \text{OH}^- \) reactive species are provided for an oxidation reaction. Since the oxidation process introduces an additional dielectric layer within the resist-Si interface, the electric field distribution and in turn also the FN emission on the tip is altered with ongoing exposure process. This leads to a self-limitation of the reaction, investigated by respective simulations in chapter 5.

In conclusion, the experimental results indicate that the oxide, which is formed below the resist, is more promising than the \( a - \text{SiO}_2 \) which is induced by a standard water meniscus mediated anodic oxidation SPL. However, since the achievable aspect ratios (AR) of the generated local oxides are very small, in particular in the range of \( AR \approx 0.03 \) (\( \Phi_L \uparrow \)) – 0.07 (\( \Phi_L \downarrow \)), Fig. 4.2.14-(iii, iv), the practical applicability of the oxidation process is limited. The shallow oxide formation is a cause of the self-limiting thickness growth and the significant lateral resolution degradation with increasing exposure dose. As shown in Fig. 4.2.14, across the entire dose range the oxidation reaction has an approx. 60 – 80 nm enlarged lateral extension than the direct resist ablation reaction. In the context of this work, the oxide formation is only a side effect of the FE-SPL exposure process. Due to the minor relevance, no further investigations were carried out. Instead, a reference to the PhD thesis of Y. Krivoshapkina is given [362], in which the oxidation process is analyzed in detail. In the following work the experimentally derived oxide growth functions were mainly applied in order to establish an oxide growth correction of the feature altitude data.

3) Dose-dependency of Resist-mediated Effects - Direct Ablation versus Crosslinking:
Figure 4.2.14: Lateral extension of the lithographic interactions as a function of the line exposure dose. The line width (i-ii) and aspect ratio data (iii-iv) correspond to the feature altitude data of Fig. 4.2.13. In particular, graphs (i, iii) belong to example 1 and graphs (ii, iv) to example 2. In plot (iii-iv) the aspect ratios ($AR$) of the generated features, broken down by the individual parts of the feature, are shown as a function of the exposure dose [note: In (iii) the $AR$ of the entire oxide thickness (sum of grown $SiO_2$ + consumed $Si$) is calculated, whereas in (iv) only the $AR$ of the oxide growth is shown].
After onset of the direct ablation reaction an increase of the patterning depth with increasing exposure dose is observable. Thereby, the SiO$_2$-growth correction of the altitude data, Fig. 4.2.13-(ii, iv), reveals a linear depth-dose dependency. The height of the crosslinked resist, measured within the exposure center after a wet development (WD) step, shows exactly the inverse dose behavior of the ablation function. Thus, the modulus of the slopes of the depth-dose function (direct ablation) and the height-dose function (crosslinked resist in the feature center) are almost identical. This again confirms that the crosslinking and ablation mechanisms are linked. In particular, this points out that during the ablation reaction already crosslinked resist material is removed. In accordance to the qualitative results derived in section 4.1, during the first stage a crosslinking reaction is initiated. When the exposure dose is increased further overcoming a particular dose threshold value, a direct ablation reaction removing the previously crosslinked resist material follows. This transition of regimes is evidently visible in the feature thickness versus dose graphs, Fig. 4.2.13-(ii, iv). At lowest dose the entire resist layer thickness is crosslinked, whereas at highest applied dose the entire resist film is removed. Since the ablation has a linear depth-dose dependency, the process is characterized by a constant ablation rate (=slope of the depth-dose function). In turn, the clearance dose for ablation, which is the dose required to remove the entire resist layer thickness, is also a function of the initial resist layer thickness. For example, a cmc4r resist with a thickness of $d_r \approx 25 \text{ nm}$ requires a clearing dose for ablation of $\Phi_L(\text{clearing}) \approx 900 \text{nC/cm}$, whereas a half as thick resist requires only 50% of the dose ($\Phi_L(\text{clearing}) \approx 450 \text{nC/cm}$). As shown later, this is an important fact in terms of the achievable resolution capabilities. Whereas the clearance dose is resist-thickness dependent, the threshold dose for direct ablation is not a function of the resist layer thickness (see also sub-item (c) of this section), e.g. $\Phi_L(\text{threshold} - d_r \downarrow) \approx 25 \text{nC/cm}$ vs. $\Phi_L(\text{threshold} - d_r \uparrow) \approx 54 \text{nC/cm}$. The marginal difference between the threshold doses between thin ($d_r \downarrow$) and thicker resist layers ($d_r \uparrow$) can be attributed to AFM measurement errors and slight environmental alterations, ref. section 4.2.6. As experimentally revealed, the ablation rate is also independent of the initial resist layer thickness. For example, a deviation in the ablation rate of $\approx 4.5 \cdot 10^{-3} \text{ nm} \cdot \text{nC/cm}^{-1}$ between differently thick resist layer was determined. Thereby, an averaged ablation rate of $\approx 0.031 \text{ nm}$ per $1 \text{nC/cm}$ exposure dose was measured. Here, the minor deviations could also be attributed to slight environmental changes, tip changes or tip-based measurement errors. The examination of the crosslinked resist sidewalls as a function of the exposure dose reveals that these are removed approx. 1.5-times slower compared to the center ablated resist area (Fig. 4.2.13-iv). However, due to the tip-sample convolution in AFM measurement one cannot directly conclude whether the crosslinked sidewalls are removed during the ablation process or by the wet development step. The latter case means that during the exposure process low molecular weight fragments are produced by scission. An insufficient crosslinking is the result. In this terms, the formed fragments are not yet volatile but removable by a development step.

The analysis of the spatial confinement of the individual lithographic interactions as a function of exposure dose, Fig. 4.2.14-(i-ii), reveals the same general trend - with increasing dose the resolution capability drops. As displayed by the qualitative feature investigation, section 4.1, at the same exposure dose the individual interactions show different spatial extensions. Thereby, the direct ablation interaction has the highest lateral confinement, whereas crosslinking and oxidation are significantly enlarged with respect to the ablated region. Furthermore, the width-dose graphs of all three interactions could be described by the same function type, which points out a linkage between the spatial extensions of the individual interactions.

The linkage of the reactions could be depicted well by a simple line dose exposure test, which is summarized in Fig. 4.2.15. Here, during the exposure of a single meander line the line dose was increased linearly in step-wise fashion. Imaging was done directly after exposure by AFM, Fig. 4.2.15-(i),
Figure 4.2.15: Modulation of the exposure dose during patterning of a single L-shaped meander line pattern. In (i) an AFM 3D topography image, measured directly after exposure, shows the directly ablated resist regions. The SEM image (ii) after wet development reveals further the crosslinked resist regions (dark). [Sample: ≈ 10 nm cmc4r resist on top of a Cr/Au layer; Probe: electrochemically etched tungsten wire; Exposure: \( U_b = 40 \) V, linear stepwise line dose increase from 40 nC/cm towards 400 nC/cm] Scale bars: (i) 1 µm; (ii) 500 nm.

as well as after wet development by SEM, Fig. 4.2.15-(ii). Since a Cr/Au bottom layer was applied, the oxidation reaction is suppressed. The example shows very well the coupled lateral extension of the crosslinked resist area (dark) and the directly ablated line (white) with increasing exposure dose. Due to the significantly extended crosslinking reaction, already at lowest dose the area in between the individual lines is slightly crosslinked. A further increase of the exposure dose leads to a crosslinking of the entire area, whereas the lines created by the direct ablation interaction are still well-resolved. As revealed by the width-dose graphs, Fig. 4.2.14-(i & ii), the crosslinking line width \( w_{CL} \) is characterized by a 60 – 80 nm enlarged lateral extension compared to the ablated line width \( w_A \) (determined for the case of widely separated lines). This shift in the lateral confinement is almost constant across the entire dose range which was tested (note: At lowest doses the width of the directly ablated line is difficult to estimate by AFM). By expressing the relationship between the crosslinking and ablation widths by a ratio in the form of \( w_{CL} = f_w \cdot w_A \) shows a decreasing \( f_w \) from ≈ 4 (measured slightly above the ablation threshold) to \( f_w \approx 1.5 \) (determined close to the clearing dose). In this context, the lateral ratio between the crosslinked and ablated region decreases significantly. The general width-dose dependency of both resist-mediated interactions are describable by a logarithmic function type. A corresponding model for explanation of the width-dose dependencies, which is based on a Gaussian current density distribution at the resist interface and dedicated threshold assumptions, is introduced in section 5.1. Based on the model and the logarithmic fit of the width-dose dependency, an exposure threshold for ablation could be determined. The received thresholds, e.g. \( \Phi_L(threshold - d_r \downarrow) \approx 23 \) nC/cm for thin resist layers and \( \Phi_L(threshold - d_r \uparrow) \approx 36 \) nC/cm for thicker ones, are in the same range as the ablation threshold, which is derived from the linear fit model of the thickness-dose dependency.
**Figure 4.2.16:** Exposure test carried out in the ultra-low dose regime of $2 - 130 \text{nC/cm}$. In graphs (i-ii) the line altitude, measured directly after exposure (i) and wet development step (ii) are shown as a function of the exposure dose. The oxide growth function, determined in (i), was applied to correct the line altitude measurement after development (ii). As revealed by the growth corrected data in (ii), the plateau level of about $\approx 6.2 \text{ nm}$ is constant till the onset of ablation starting at $\approx 30 \text{nC/cm}$. In (iii) the corresponding changes of the line width is plotted as a function of dose. [Sample: $\approx 6 \text{nm} \text{ cmc4r resist, PVD-coated on top of a Si chip; Tip: tungsten wire, } r_{tip} \approx 15 \text{ nm; Bias voltage } U_b = 30 \text{ V} ]$
b) Investigation of the superimposed interactions in the ultra-low dose regime:

In order to gain more insights about the threshold of the interactions, exposure tests in the ultra-low dose regime were carried out. Line exposure doses in the range of $\Phi_L = 2 \text{nC/cm}$, which is the minimum applicable exposure dose, towards $\Phi_L = 125 \text{nC/cm}$, which is located close above the onset of ablation, were applied. So far, lower line doses could not be provided due to limitations of the IU-converter circuit and the feedback loop, which restricts the minimum applicable current setpoint to $2 \text{pA}$ and the maximum tip velocity to $10 \mu \text{m/s}$, respectively (ref. section 3.1.3).

An evaluation of the ultra-low dose exposure results, carried out on cmc4r resist, is provided in Fig. 4.2.16. Already within the lowest dose range raised line features are measured directly after exposure (Fig. 4.2.16-i) pointing out a buried Si oxidation process. The subsequent wet development step confirms the crosslinking of the resist (Fig. 4.2.16-ii). By using the oxide growth function (log-fct. type), determined by Fig. 4.2.16-(i), the line altitude after wet development is corrected respectively delivering the crosslinked resist thickness as a function of the exposure dose. The resulting graph, Fig. 4.2.16-(ii), shows that already at the lowest exposure dose the entire thickness of the resist is crosslinked. The crosslinked resist thickness remains on the initial level ($\approx 6.2 \text{nm}$) till the ablation process starts at $\Phi_{L\text{-threshold}} \approx 30 \text{nC/cm}$. The ablation proceeds then by a rate of $\approx 0.045 \text{nm per 1 nC/cm}$. The evaluation of the line width vs. dose data, Fig. 4.2.16-(iii) shows that in the present development status of the system the crosslinking reaction seems not to offer such extreme high resolution capabilities like the direct ablation process. In particular, the line width of the crosslinked line is $\approx 80 - 90 \text{nm}$ at the minimum applicable dose value of $\Phi_L = 2 \text{nC/cm}$. The AFM convolution correction, section 3.3.2, delivers an estimated line width of $\approx 55 - 65 \text{nm}$, which is still significantly larger than line widths achievable by direct ablation. However, one has to take in account that the measurement of the ablation line width in the ultra-low dose regime is rather difficult since tip and characteristic length scales of the lithographically generated features are nearly identical. Thus, the limits of the measurement are reached (section 3.3.2, Fig. 3.3.2).

In summary, the ultra-low dose measurement has revealed that already at the lowest applicable dose, which is limited by the system, the crosslinking process has proceeded through the entire resist film. Since no lower doses can be reached in the present stage, one cannot determine the threshold gel dose, the sensitivity as well as the contrast curve of FE-SPL crosslinking process. In this context, with respect to EBL at higher primary energies, the calixarene MG resist unveils in FE-SPL a remarkable sensitivity, discussed in section 6.1.2. However, due to the system limitation no general answer about the resolution limit of the crosslinking reaction in FE-SPL can be given. It is expected that with a further reduction of the dose an increased resolution can be achieved.

c) Itemization of the exposure dose influence into velocity and setpoint dependencies, carried out for the direct ablation reaction:

The line exposure dose is defined by the field emission current, divided by the velocity of the tip, ref. Eq. 2.8. From technical point of view, e.g. for realization of a lithography software, the assessment of the individual dependencies is important. The split of a line exposure dose test into its individual components is summarized in Fig. 4.2.17. Therefrom derived, 3D plots conflating the dependencies of the ablated resist thickness and the line width are provided in Fig. 4.2.18. In accordance to the exposure dose dependencies revealed previously, both an increasing current setpoint ($I_{FN}$) and a decreasing tip velocity ($v_{tip}$) lead to an increase of the characteristic geometric values of the generated feature (ablation depth and line width). Thereby, the geometric variations induced by modulations
Figure 4.2.17: Itemization of the line exposure dose characteristics of the direct ablation interaction into its tip velocity and current setpoint dependencies. In graphs (i) and (ii) the ablated resist thickness and the corresponding line width are plotted as a function of the line exposure dose. The different symbols point out different emission setpoints. In graphs (iii) and (iv) the ablated resist thickness versus the tip velocity and the current setpoint are displayed, whereas graphs (v) and (vi) provide the corresponding line width versus dose results. Therefrom derived, in Fig. 4.2.18 a summary of the dependencies is shown. [Sample: \( \approx 18 \, \text{nm} \) 4m1ac68 resist, spin-coated on top of a Si-chip; Tip: tungsten, \( r_{\text{tip}} \approx 10 \, \text{nm} \); Constant bias voltage of \( U_b \approx 35 \, \text{V} \) during exposure]
of the setpoint are expressible by a linear function. In contrast, the tip velocity introduces a strong nonlinear behavior, best describable through a reciprocal function. In these terms, the plot of the ablation depth versus \(1/v_{\text{tip}}\), and the plot of the line width versus \(1/\log(v_{\text{tip}})\) gives a linear dependency (graphs not shown here). Due to the strong non-linear behavior, velocity alterations with \(v_{\text{tip}} > 3 \, \mu m/s\) cause only minor variations in the geometric feature values. With decreasing velocity the geometric alteration rate increases significantly. Thus, modulations of the velocity below \(v_{\text{tip}} < 3 \, \mu m/s\) induces significant changes of the feature geometry. In the context of a pattern software module, the different dependencies can be exploited in a strategical manner. Due to the linear dependency the current setpoint should be applied for fine modulations of the features geometry. Compared to velocity modulations, an easy computation scheme is given delivering more accurate predictions with fewer deviations. In addition, in the case of setpoint modulations the process controllability as well as the process latitude are larger. As the feature geometry versus setpoint plots Fig. 4.2.17 show, the slopes can be adjusted accordingly by the tip velocity parameter. A decreased velocity results in an increased slope which means that lower tip speeds give a larger geometric alteration rate. However, the linear dependency between setpoint change and resulting geometric variation remains unchanged. In summary, using the current setpoint for fine geometric alterations of the geometry and the velocity parameter for adjustment of the slopes, on which the current modulation takes place, seems to be a reasonable strategy for a FE-SPL pattern tool. For highest resolution patterning and lowest LER/LWR, the exposure should be carried out at higher tip velocities. In contrast, when large scale patterning is targeted, the operation at low speeds and high setpoints is meaningful. An exposure example, wherein this strategy is exploited in order to identify optimum \(I_{FN} - v_{\text{tip}}\) combinations, is outlined in Fig. 4.2.19. Here, the patterning across a wide geometric latitude is demonstrated by using \(I_{FN} \downarrow - v_{\text{tip}} \uparrow\) pairs for high resolution surface-confined patterning and \(I_{FN} \uparrow - v_{\text{tip}} \downarrow\) pairs for deep low resolution patterning of a \(\approx 24 \, nm\) thick cmc4r resist layer.

d) Investigation of the influence of the resist layer thickness on the direct ablation process and the achievable resist aspect ratios:

The influence of the resist layer thickness on the direct ablation process was investigated for two different calixarene derivatives, in particular a calixarene (4m1ac68) and resorcinarene (cmc4r) MG resist type...
Figure 4.2.19: Strategically optimized exposure parameter sets (optimum $I_{FN} - v_{tip}$ combinations) for patterning across a wide geometric latitude, done for the direct ablation interaction. In (i) and (ii) the directly ablated resist thickness and the line width versus dose characteristics are plotted. The different current setpoints applied are marked by different symbols and colors. In (iii) the ablated resist thickness as a function of the tip velocity for various current setpoints is shown. The 3D plot (iv) summarizes the complex tip velocity (logarithmic scale) - setpoint (linear scale) versus ablated resist thickness dependency. [Sample: $\approx 24\, \text{nm}$ thick cmc4r resist coated on top of a Si chip; Probe: tungsten tip, $r_{tip} \approx 6\, \text{nm}$; Bias voltage $U_b = 35\, \text{V}$]
Figure 4.2.20: Investigation of the influence of the resist thickness on the geometric dimensions of the structure in the direct resist ablation process. In graphs (i-iv) the line dose dependencies and in (v-vi) the feature aspect ratios are provided for the direct ablation, measured in-situ after exposure (line altitude is not oxidation growth corrected; nearly identical oxidation growth in all cases assumed). The graphs are composed of measurements with different resist thicknesses and exposure parameters, coded by different symbols of the measurement points. Resist thicknesses in the range of $6-26$ nm were applied. The experiments were conducted for two different resist derivatives. Graphs (i-iv) are plotted semi-logarithmic. [Sample: Si chip; Probe: tungsten wire]
spin-coated on top of a Si chip. The corresponding results are summarized in Fig. 4.2.20. Herein, the resist thickness was adjusted by variation of the concentration of the spin-coating solution (ref. section 3.2.2). In order to minimize the contribution of other effects, tungsten wire probes with tip radii in the same range of $r_{\text{tip}} = 10 - 20\,\text{nm}$ were applied. Furthermore, the environmental conditions were stabilized for each sample individually. The exposure was done with a constant bias voltage in the range of $U_b = 30 - 35\,\text{V}$. The graphs in Fig. 4.2.20 summarize the geometric values of the directly ablated feature as a function of the exposure dose (i-iv), itemized for different resist layer thicknesses ($d_r = 6 - 26\,\text{nm}$) and derivate. The plot of the line width versus line depth gives the aspect ratio of the lithographically induced feature, shown in graphs 4.2.20-(v-vi).

The graphs (i-iv) reveal that both dependencies, the line altitude versus dose and the line width versus dose curves, are describable by the exactly the same function, regardless of the resist thickness. Thus, within the tested dose range the ablation process does not significantly depend on the resist thickness. The ablation threshold ($\Phi_L(\text{threshold})$) is nearly constant, and the ablation rate shows only marginal variations for the different resist thicknesses (note: line altitude graphs in Fig. 4.2.20-(i-ii) are not oxidation growth corrected). The evaluation of Si-oxidation growth corrected results, Figs. 4.2.13 and 4.2.16, indicate that the ablation rate decreases with increasing resist thickness, e. g. $r_A = 0.045\,\text{nm} \cdot (\text{nC/cm})^{-1} \approx 6.2\,\text{nm}$, $r_A = 0.034\,\text{nm} \cdot (\text{nC/cm})^{-1} \approx 14\,\text{nm}$, $r_A = 0.029\,\text{nm} \cdot (\text{nC/cm})^{-1} \approx 24\,\text{nm}$. Expressed in absolute numbers, the change of the ablation rate between thinnest and thickest resist leads only to an alteration of the ablation depth of $1.6\,\text{nm}$ per $100\,\text{nC/cm}$ exposure dose increase. Taking into account that a resist with $d_r = 6\,\text{nm}$ is cleared already slightly above $100\,\text{nC/cm}$, the alteration of the ablation rate could be neglected in terms of practical application. However, owing to the small thickness differences, influences coming from measurement deviations could not be excluded (standard deviations are labeled in the graphs accordingly).

As revealed, the resist is removed with a constant ablation rate, which is nearly independent from the initial resist layer thickness. In consequence, thicker resist layers require a higher clearing dose. Thereby, the clearing dose is the dose which is required to remove the entire resist thickness reaching the bottom layer. Since a linear dependency between ablation depth and exposure dose was found, the clearing dose increases linearly with increasing resist layer thickness, e. g. $\Phi_{\text{clear}}[d_r \approx 6\,\text{nm}] \approx 230\,\text{nC/cm}$, $\Phi_{\text{clear}}[d_r \approx 12\,\text{nm}] \approx 450\,\text{nC/cm}$, $\Phi_{\text{clear}}[d_r \approx 22\,\text{nm}] \approx 860\,\text{nC/cm}$ (Fig. 4.2.20-i-ii). In terms of practical application, increasing resist layer thicknesses demand higher exposure doses in order to ablate to the substrate surface. In consequence of the surface patterning character of the ablation process, the increased exposure dose leads to an increase of the line width, labeled in Fig. 4.2.20-(i-vi) by vertical interconnections between plots (i-iii) and (ii-iv). Since a full clearance of the resist is required for the subsequent pattern transfer process, the application of thicker resist layers leads to a decrease of the resolution capability. To achieve highest lithographic resolution ultra-thin (sub-10 nm) resist layers are essential.

However, the achievable aspect ratios ($AR$) of the generated nanoscale features, plotted in Fig. 4.2.14-(iii-iv) as a function of the exposure dose, are restricted. For example, the $AR$ of the positive tone (directly removed resist) features range in between $AR = 0.04$, measured at doses close above the ablation threshold, and $AR = 0.15$ at the clearing dose. The limited aspect ratio is associated with two facts. First, a natural limitation represents the resist layer thickness, which is in the case of FE-SPL restricted to ultra-thin layers (ref. section 4.2.4). Secondly, the achievable resolution in FE-SPL drops with increasing ablation depth. This is in agreement with the theoretical considerations explained in sections 2.4 and 5.2. In particular, when thicker resist layers are applied, the tip-sample gap is increased (model explained in section 5.2). Additionally, higher bias voltages are required in order to operate above the threshold for a mechanical tip-sample interaction. Furthermore, thicker resist layers require
a larger clearing dose. All effects lead to an increase of the beam diameter at the resist surface which results in turn in a drop of the lithographic resolution capability. In conclusion, ultra-thin resist layers are essential. However, the limited aspect ratios, combined with the ultra-thin resist layers, represent a significant challenge for the pattern transfer, tackled in section 7.2.

e) Investigation of probe influences on the exposure dose characteristics:

Derived from theoretical consideration, section 2.4, sharp probe tips are essential in order to achieve a high local focusing of the electric field at the tip apex. Thereby, the localized field leads to a spatially confined emission, which in turn is relevant to enable highest resolution lithography. Since in context of a closed loop lithography scheme (section 1.3) ultra-sharp probes are also essential for the AFM imaging at highest resolution, in the following the investigation was focused on tip apices having tip radii of $r_{tip} \lesssim 10\, \text{nm}$. However, the investigation of the probe tip influence in the particular range is challenging and flawed. First, the estimation of the exact tip shape, the tip radius of curvature ($r_{tip}$), and the surface irregularities at the sub-10\,\text{nm} level by SEM is difficult to carry out. Experimental evidence was found, ref. section 4.2.4, that all probes which are applied tend at higher bias voltages to a multi-spot emission. This leads to the conclusion that the tips typically do not have a perfectly round-shaped cone with a single protrusion spot. Secondly, one cannot conclude that the work function at the emission spot is identical for all tips (work function depends also onto the orientation, material alterations, impurities, adsorbates, etc.). Here, also the fabrication method influences the tip properties. Third, to keep all other influential factors constant is challenging - slight fluctuations of the environment, the resist thickness, etc. are likely.

A study in which the influence of probe variations on the exposure dose characteristics is investigated for the ablation process is summarized in Fig. 4.2.21. In particular, tungsten wire probes (W-T) and highly doped Si-cantilever (Si-C), comprised of different tip radii, were tested. In order to operate within an optimum bias voltage range, ref. section 4.2.4, the bias for exposure was adjusted separately for the tungsten wire and cantilever probes. The measurements directly after exposure reveal that the general trends and function types are valid for all applied probe types. The analysis of the line altitude versus exposure dose graphs for the different tungsten wire probes (W-T), Fig. 4.2.21-(i-ii), indicate that decreasing tip radii results in an increased ablation rate (slope of the linear fit is increased). In consequence, the clearing dose is shifted for larger tips towards higher doses, e.g. in the case of $r_{tip} \approx 8 - 10\, \text{nm}$ a clearing dose of $\Phi_L \approx 800\, \text{nC/cm}$ was required for full resist removal, whereas $r_{tip} \approx 6\, \text{nm}$ has required only $\Phi_L \approx 450\, \text{nC/cm}$. Interestingly, the line width versus dose functions of all tungsten wire probes, independent of the tip radius, are nearly identical and describable by a common logarithmic function. Thus, the ultra-sharp tips seem to offer improved feature aspect ratios. However, other effects cannot be excluded. As proposed by Mayer et al. [301], so called supertips, which are small asperities at the tip apex, could be also responsible for the observed effect. However, as mentioned before the determination of these tip asperities by SEM is difficult.

The evaluation of the lithographic results, which were achieved by two different highly n-doped cantilever probes (Si-C), Fig. 4.2.21, reveals large variations (2.7 times) in the line altitude versus exposure dose slope. In contrast, the variation of the line width versus exposure dose function is marginal, which means that a common logarithmic function can be applied. Since the tip radii cannot be determined more precisely than $r_{tip} \approx 2 - 10\, \text{nm}$, it cannot be concluded whether a difference in tip radii or other effects, e.g. a variation of the work function, thin native oxides, etc., are responsible for the large variations in the ablation rate. As already mentioned by Perkins et al. in terms of STM exposure experiments [193], the unknown slight alterations of tip radii, work functions and tip shapes introduce
Figure 4.2.21: Investigation of probe influences on the exposure dose characteristics of the direct ablation (removal) process. In particular, the lithographic results obtained with four different tungsten wire tips (W-T) and two highly doped Si cantilever (Si-C) are compared. Since for cantilever and wire probes different IV-converter boards were applied, the direct comparison between cantilever and tip probes must be considered with care (a current offset of $I_{FN} < 5\, pA$ between cantilever and tip is present). The applied cantilever has nominal force constants of $\approx 42\, N/m$ and is equipped with a highly n-doped tip. In graphs (i-ii) the line altitude versus line dose characteristics are shown in a linear (i) and a semi-logarithmic plot (ii) style. Respective linear fits of the ablation depth-dose are included. In graphs (iii-iv) the line width versus dose characteristics is summarized according to the probes used (color- and symbol-coded). Within graph (iii) the maximum line widths and in (iv) the FWHM line widths are given. [Sample: $d_r \approx 18\, nm$ 4m1ac68 resist, spin-coated on top of a Si chip; Bias voltage: $U_b = 35$; Exposure conditions: identical environmental conditions $r\cdot H. \sim 35\%$]
a random element. In order to pattern the desired geometry, a feedback loop adjusting the lithographic parameter set is required. For this purpose, the application of new tips requires a short exposure test in order to calibrate the pattern generator. The closed loop patterning scheme (1.3), wherein the same cantilever is applied for imaging and lithography, supports this approach. The comparison of the line width versus exposure dose curves for cantilever and tungsten wire probes indicates that the electrochemically etched tungsten wire gives a higher resolution capability. Due to the difference in the emitter material, different bias voltages were required (ref. section 4.2.4). Linked with that, the tip-sample spacing is different leading to a change of the lithographic resolution. However, also other effects like differences in the emitter material or in the tip shape could cause alterations of the line width. Here, more detailed investigations are required which go beyond this work. These aspects could be investigated by following works.

f) Comparison of the ablation characteristics of two different calixarene MG resist derivatives -
Investigation of the line altitude, line width, and derived variables volume, number of molecules, and absolute mass:

The following study shows the differences in ablation behavior of two different calixarene derivatives. In particular, a calixarene (4m1ac68, \( C_{60}H_{60}O_{12} \)) and a resorcinarene (cmc4r, \( C_{32}H_{32}O_{6} \)) based MG resist are compared, summarized in Fig. 4.2.22. The analysis of the line altitude (i), the ablation depth (ii) and the line width of the directly induced feature, plotted versus the line exposure dose reveals only minor deviations between both derivatives. In this context, also the derived variables the ablated volume (iv), the estimated number of directly removed molecules (v), and the absolute ablated mass (vi) are nearly identical for both MG resist types. For both derivatives the same fit function types can be applied. Since both derivatives are very similar with respect to the chemical groups included, this is not surprising. Due to the similarity of both molecules not only the same mixture of fragments are likely to be formed during the degradation process, but also similar reaction paths are effective. The in-depth analysis of the graphs, Fig. 4.2.22, indicates that the smaller cmc4r molecule has a higher ablation threshold, whereas the ablation rates (slope of the depth-dose curve) of both derivatives are nearly identical. Thereby, the exact threshold values depend on the respective definition. The most common method derived previously is to use interpolation of the linear depth-dose function including the oxidation growth correction (Fig. 4.2.22-ii). This gives an ablation threshold of \( \approx 21 \, nC/cm \) for cmc4r versus \( \approx 1 \, nC/cm \) for 4m1ac68. Interestingly, in the course of the standard EBL experiments comparing the derivatives, section 6.1.2, a higher threshold exposure dose for crosslinking is observed for cmc4r. In the case of standard EBL this can be explained by the Charlesby theory \([252]\), which states that for lower molecular weight resists more crosslinks per unit area are required. However, this explanation does not seem to be valid for the direct ablation mechanism in the case of FE-SPL. In the instance of a pure scission process which is responsible for the formation of volatile fragments, the smaller cmc4r molecule should require less dose. But the experiments show the opposite effect, which means that a pure scission model is not appropriate. As elaborated later in the thesis, in consequence of the ambient conditions in FE-SPL, alternative reaction paths are enabled. The comparison of the line width versus dose dependency for both derivatives, Fig. 4.2.22-(iii), indicates a higher confinement at low doses for cmc4r, where at higher doses this is reversed. Thereby, an increased spatial resolution capability for smaller molecules seems reasonable. However, since the difference in the ablation thresholds between cmc4r and 4m1ac68 resists are only minor compared to other effects, e.g. the influence of the exposure

\[ C_{60}H_{60}O_{12} \]

\[ C_{32}H_{32}O_{6} \]
Comparison of the ablation characteristics of a resorcinarene (cmc4r) and calixarene (4m1ac68) based MG resist. Both resist layers with a thickness of \( d_r \approx 18 - 22 \text{ nm} \) were prepared on top of a Si chip using spin-coating. The exposure was done by the same lithographic parameter set at standard environmental conditions (relative humidity \( r.H. \approx 35 \% \), kept constant) using the same tungsten tip \( r_{\text{tip}} \approx 6 \text{ nm} \) at \( U_b = 35 \text{ V} \). In graphs (i-vi) the geometric feature values and derived variables are plotted versus the line exposure dose, in particular: (i) The line altitude, which is measured directly after exposure (aSPL); (ii) The thickness of the directly removed resist, calculated by subtraction of the oxide-based growth; (iii) The line width measured directly after exposure (aSPL); (iv) The ablated resist volume; (v) Calculation of the number of removed molecules; (vi) Calculation of the removed absolute mass. For calculation of the volume, graph (iv), a rectangular shape of the cross-section using the measured line width (iii) and the ablated resist depth (ii) was assumed. To get a volume, discs with a nominal thickness of 1 nm were used (rectangular cuboid assumption). [semi-logarithmic plots: i, iii; double-logarithmic plots: iv-vi]
environment (section 4.2.6), the deviation could come also from other sources. Thereby, also the surface properties of the particular resist has to be taken into account, e.g. cmc4r is hydrophilic and 4m1ac6 hydrophobic. As demonstrated by a block-copolymer resist, section 4.4.3, the surface properties are a significant factor.

On the basis of the geometric feature properties, the directly ablated volume is calculated, Fig. 4.2.22-(iv). Thereof derived, the number of removed molecules and the removed mass are estimated, Fig. 4.2.22-(v-vi). The corresponding double logarithmic plots, Fig. 4.2.22-(iv-vi) display a linear curve indicating a non-linear reaction type. The linear fit can be applied to estimate the threshold for ablation, e.g. $12 \text{nC/cm}$ for cmc4r and $3 \text{nC/cm}$ for 4m1ac6 which is in agreement with previous results. The conversion into an number of electrons required in order to convert a non-volatile molecule into volatile fragments yields $\approx 3250 \text{ e}^-/\text{molecule}$ for cm4r and $\approx 1870 \text{ e}^-/\text{molecule}$ for 4m1ac6. It should be noted, however, that this is only an estimate since as previous reaction crosslinking always occurs. Further, the graphs Fig. 4.2.22-(v-vi) show slightly increased slopes in the case of cmc4r, which means a higher ablation rate is present for cmc4r. In summary, it could be suggested that the initial reactions for cmc4r case require slightly higher amount of deposited energy but result in a higher generation rate of $\text{OH}$ and $\text{H}$ ions and radicals, which further supports the degradation process. However, up to now the involved reaction schemes are unresolved and more than a single reaction is expected.

g) Summary:

1. **Transition of the lithographic regimes:** By the line exposure dose not only the line geometry is adjusted but also the lithographic regime is defined. As a function of the exposure dose crosslinking, ablation, or both, are induced leading to a negative tone, a positive tone, or a superimposed pattern. Thereby, the positive tone is development-less, whereas the negative tone requires a subsequent wet development step.

2. **Reaction thresholds:** Different dose thresholds have been observed for the different reaction types. In particular, crosslinking of the resist occurs already at lowest applicable dose of $2 \text{nC/cm}$. Since a further decrease of the exposure dose is so far restricted by the FE-SPL system capabilities, the threshold for crosslinking and the contrast curve of the resists cannot be determined directly. In comparison to standard EBL the resist sensitivity is significantly enhanced, discussed in section 6.1. Linked with that the absolute resolution limit (minimum achievable feature size) of the crosslinking interaction could not be determined. In comparison to the crosslinking reaction, the threshold for ablation is shifted towards higher exposure doses. In particular, thresholds of $3 - 50 \text{nC/cm}$ depending on the method of determination and the particular sample and measurement are given. Due to the threshold differences between ablation and crosslinking, the self-development is linked with an initial crosslinking process.

3. **Interaction depths:** Already at the lowest applicable exposure doses the resist is crosslinked throughout the entire layer thickness. In contrast, the ablation reaction starts from the surface of the resist and continues in depth. A linear dependency between ablation depth and line exposure dose was measured. Thereby, the slope of the depth-dose curve gives the ablation rate. Typical ablation rates measured are in the range of $0.02 - 0.05 \text{ nm} \cdot (\text{nC/cm})^{-1}$ depending on the sample type, resist, and probe.

4. **Spatial confinement and lithographic resolution:** The lithographic interactions are characterized by different spatial confinements, which results in different lateral expansions. Despite the different lateral spreads, a fixed relationship between the two reaction widths indicates a coupling
of the interactions. Thereby, an increase of the line exposure dose results in an increased line width. Since the interactions are coupled, the particular width increase is similar for all reactions. Thus, an exposure dose increase is linked with a drop in the lithographic resolution. The width-dose dependencies can be described adequately by a logarithmic function type. The origin of the function type can be derived from a Gaussian beam model (Gaussian current density distribution profile) using different exposure dose thresholds associated with the respective interactions. The deduction of the model is explained in detail in section 5.1. In consequence of the exposure dose limitations of the system, the highest lateral confinement and thus lithographic resolution can currently be achieved by using the ablative mechanism. Due to the superposition of ablation and crosslinking reaction, and the difference in spatial confinement, a self-aligned double patterning mechanism is given. In this context, self-aligned double line features were created, which are visible after a wet development of directly ablated resist trenches.

5. **Oxide formation at the Si-resist interface:** The onset and the lateral extension of the oxidation reaction at the Si-resist interface is equal to the crosslinking reaction within the resist. This is valid for the entire dose range that has been tested. Thus, the oxidation and crosslinking reactions seem to be caused by the same initiator. As revealed later in this work, the same chemical reactant which is released by the deposited energy, plays a mediator role. Further, it has to be taken into account that the resist material itself contains \( \text{R} - \text{OH} \) functional groups, which work as a further local source of reactive species supporting the oxidation process (in addition to the environmentally present water). The oxidation process occurring below the resist is a self-limiting reaction which means that the growth rate in the vertical direction significantly drops with increasing exposure dose. This behavior is similar to standard oxidation processes observed without resist material. In consequence, only shallow oxides are formed. The volume expansion factor \((V EF)\) of the formed oxide decreases with increasing line exposure dose. This indicates that the formed oxide is closer to the stoichiometric \( a - \text{SiO}_2 \). Consequently, oxides with fewer defects grow as the dose increases. This is supported by respective AES measurements. In the context of this thesis, oxidation is only a side effect of the resist exposure process. Nevertheless, the formed oxides can be exploited as additional pattern transfer masks or as insulating device layers (ref. chapter 7).

6. **Description of the final feature:** The final lithographic result can be described adequately by a superposition of individual reactions. Therefrom, the geometry and internal structure of the final feature can be deduced. Thereby, the particular exposure dose defines which lithographic interactions are superimposed (exposure dose thresholds are summarized in item 2).

7. **Itemization of the exposure dose influence on the example of the direct ablation reaction:** In the case of a vector based line exposure the line exposure dose is defined by the FN field emission current setpoint, divided by the velocity of the moving probe. The geometric variations which are caused by modulations of the FN field emission current setpoint can be described adequately by a linear dependency. In contrast, the tip velocity dependency is highly non-linear and best describable by a reciprocal function type. In the context of a practical applicability, the pattern software module exploits the different dependencies in a strategic manner. In particular, the current setpoint is used for fine geometric alterations of the geometry, whereas the velocity parameter defines the underlying alteration rate (slope of the linear geometry-setpoint function), on which the current based modulation of the features geometry takes place. Here, a decreased tip velocity results in an increased alteration rate (slope).

8. **Influence of the resist thickness on the ablation process:** Within the investigated resist thickness range \( (d_r = 6-26 \text{ nm}) \) no significant influence of the resist thickness on the exposure dose
dependencies was found. The ablation threshold \( (\Phi_L(\text{threshold})) \) is nearly constant, regardless of the resist thickness, and the ablation rate shows only marginal variations for the different resist thicknesses. Here, a slight decrease of the ablation rate with increasing resist thickness has been indicated. Since the variations are very small, in particular \( 1.6 \, \text{nm} \) per \( 100 \, nC/cm \) exposure dose increase, in a first approximation this dependency can be neglected. In conclusion, as a first approximation the ablation depth is nearly equal in all resist thickness cases. However, due the almost constant ablation rate, thicker resist layers demand higher clearing doses. Since a linear dependency between ablation depth and exposure dose was found, the required exposure (clearing dose) in order to achieve a complete removal till the substrate (or bottom layer) increases linearly with increasing resist layer thickness. In consequence of the surface patterning character of the ablation process an increasing exposure dose leads to an increase of the line width. Since a full clearance of the resist is required for a subsequent pattern transfer step, the application of thicker resist layer leads to a decrease of the resolution capability. Thus, highest lithographic resolution demands ultra-thin resist films of \( 10 \, \text{nm} \) or less. This is a challenging initial state for subsequent pattern transfer processes.

9. **Influence of the probe properties on the ablation process:** Since the probe properties like tip shape, radius of curvature, surface roughness, emitter work function, and so on, are hard to determine, a random element is introduced into the lithographic process. Due to the fact that an ultra-high resolution is demanded for the closed-loop imaging cycle, only tip radii in the range of \( r_{tip} \lesssim 10 \, \text{nm} \) have been investigated. As revealed by the experimental exposure tests, tip radius variations in this range have only a minor effect on the line width, whereas the ablation depth is significantly changed (imaging was done by the same ultra-sharp tip in order to exclude tip-sample convolution effects). In particular, sharper tips have shown higher ablation rates resulting in improved aspect ratios of the generated features. Thereby, the lithographic patterns which were exposed by different cantilever probes have shown significantly larger geometric variations than the same patterns defined by different tungsten wire probes. This can be attributed to the different manufacturing methods of the probes and the variations of the emitter material. For a practical applicability an exposure calibration procedure is suggested, which allows to correct probe-induced variations in the lithographic process. This function is enabled by the closed-loop functionality of the FE-SPL system (ref. section 1.3).

10. **Comparison of the ablation characteristics between a Calixarene and a Resorcinarene based MG resist:** The experimental investigations showed only minor differences in ablation between the two different derivatives. Due to the chemical similarity of both molecules, not only the same fragments are likely to be formed during the ablation process, but also the same reaction paths are expected. In contrast to the EBL process, the initial differences in molecular weight and molecular size of both molecules appear to be of minor relevance. By plotting the ablated mass versus exposure dose in double logarithmic manner a linear trend results indicating a non-linear reaction type.

11. **Mechanisms and further work:** Due to the diversity of the derived lithographic patterns more than a single interaction mechanism is expected. However, at this point of the work there are still too many open questions in order to resolve the involved reaction paths. Thus, the interpretations are rather speculative in nature. By analogy, also in standard EBL the detailed mechanisms of electron beam induced crosslinking could not be unequivocally clarified so far. Here, also multiple mechanisms are induced by the incident radiation. A chemically non-defined final state of the crosslinked resist is generated, discussed in refs. [199, 237]. Thus, more information with respect to the resist influence and the exposure environment are required in order to gain a broader view.
In this context, the influence of the environmental water, section 4.2.6, as well as the lithographic behavior of molecular glass resists having different functional chemical groups, section 4.4, were investigated.

### 4.2.4 The Bias Voltage Parameter

The spacing between the field emitter and the conductive / semi-conductive sample surface plays a significant role for confinement of the lithographic interaction. Since the FN field emission current setpoint feedback is based on the modulation of the tip-sample spacing (ref. section 2.4), the applied bias voltage not only determines the energy of the emitted electrons, but also defines the gap between tip and sample surface. Based on the tip-sample distance versus bias voltage analysis, section 4.2.2, in the following the effects of voltage modulations on the lithographic structure itself are investigated. Unless explicitly stated otherwise, the sample substrate is biased positively (positive bias voltage with reference to the tip voltage), whereas the tip is virtually grounded through the $IU$-converter unit (ref. section 3.1.3).

**a) The optimum bias voltage range investigated for different resist film thickness - From scratching operation towards feature blurring:**

As revealed in section 4.2.2, a linear relationship between applied bias voltage and tip-sample spacing was measured, which confirmed the general operation in the Fowler-Nordheim emission regime. For lithographic operation a resist layer has to be introduced within the tip-sample gap. In the first approximation, the resist layer can be treated as a dielectric layer with defined thickness ($d_r$) and dielectric constant ($\epsilon_r$). As derived by theoretical considerations, section 5.2, the insertion of a dielectric film leads to an increase of the tip-sample spacing. Nevertheless, a minimum bias voltage has to be applied in order to operate at tip-sample spacings which are larger than the dielectric resist film thicknesses. If the tip-sample spacing is smaller than the resist thickness, then mechanical interactions occur. Since mechanical tip-resist interactions like scratching or plowing lead to strong tip wears, to contamination of the tip as well as to cause critical instabilities of the current feedback loop (which leads in turn to tip crashes destroying tip and sample surface), this interaction type should be prevented. In this context, as a function of the thickness and the dielectric properties of the resist, different minimum bias voltages have to be applied in order to prevent mechanical interactions. This relationship is illustrated in Fig. 2.4, which shows AFM images of exposure tests immediately after exposure (aSPL). The corresponding measurement graphs are provided in Fig. 4.2.25-(i-ii). The bias voltage dependency for three different film thicknesses ($d_r$) of 4m1ac68 resist were investigated. For exposure the same lithographic parameter set and tungsten wire probe was applied.

**The mechanical tip-resist interaction regime in the case of insufficient bias voltages:** When the interaction between tip and resist is based on mechanical interactions, this is well visible in the AFM image (Fig. 2.4) immediately after exposure. In particular, a jumping-like behavior of the feedback current occurs, the patterned lines are non-uniform, and a build-up of previously removed material beside the feature (bulges) or within the lines itself is visible. As discussed before, this patterning regime should be prevented during normal FE-SPL operation. As expected from the linear tip-sample spacing versus bias voltage dependency, section 4.2.2, the minimum required bias voltage in order to prevent mechanical interactions is scaling linearly with the resist film thickness. Thicker resist layers need higher initial bias voltages. This relationship is clearly visible in Fig. 2.4, in particular the $\approx 50\,\text{nm}$ thick resist requires a minimum bias of 70 V, whereas for the $\approx 40\,\text{nm}$ resist 60 V and for the $\approx 30\,\text{nm}$
Figure 4.2.23: Investigation of the voltage dependence of the transition from mechanical interaction (scratching) towards the ablation regime, performed for different resist film thicknesses. The AFM topography image series shows excerpts of a bias voltage modulation test (range: 50 V - 70 V), carried out on three different thicknesses ($d_{r-1} \approx 50 \text{ nm}$, $d_{r-2} \approx 40 \text{ nm}$, $d_{r-3} \approx 30 \text{ nm}$) of 4m1ac68 resist films (Substrate: Si, without bottom layer). The same tungsten wire probe ($r_{tip} \approx 13 \text{ nm}$) and lithographic parameter set were used in the exposure series. In a feature row consisting of $1.5 \times 1.5 \mu\text{m}^2$ nested L-features, the line dose and line pitch have not been changed, whereas the bias voltage was incrementally increased in 5 V steps. AFM imaging was done directly after exposure by using a cantilever probe.
4 Basic Experimental Investigations of Field Emission SPL Processes

Figure 4.2.24: Investigation of the voltage dependence on the lithographic resolution in the ablation regime, performed for different resist film thicknesses. The transition from the optimum bias voltage range towards feature blurring as a function of resist layer thickness is visible. Compared to the bias voltage modulation of Fig. 4.2.23, here the voltage was modulated in finer incremental steps (2.5 V) at higher bias voltages of 67.5 – 77.5 V. All nested L-features (1.5 x 1.5 µm²) were exposed by the same tungsten wire probe (r_{tip} ≈ 11 nm) at 75 nC/cm line exposure dose and 40 nm hp.

resist 50 V are sufficient. However, no general value of a minimum bias voltage (U_{b-min}) can be given since the particular spacing depends on diverse factors (ref. FN theory, section 2.4, and respective simulations, chapter 5). For example, the spacing decreases in the case of a blunter tip (larger tip radii result in a decreased field enhancement factor) or an emitter material with an higher work function is applied. Thus, U_{b-min} depends also on the probe properties. In order to ensure a safe operation above the scratching interaction threshold, without an a priori knowledge of the probe radius and work function, an empirical equation for the minimum bias voltage (U_{b-min}) can be given:

\[ U_{b-min}[V] \approx (1.5 - 2) d_r[nm] \]  

(4.2)

The proportionality factor is variable in the range of 1.5 – 2, depending on whether something is known about the tip. In the case of sharper tips the safety factor can be made smaller ensuring a closer spacing. Eq. 4.2 is in general agreement with early STM based exposure experiments done by McCord et al. [164]. The estimated minimum bias voltage, Eq. 4.2, can be applied as starting point for investigations, wherein the lower bias voltage limits can be probed experimentally for different tip radii and tip material classes. The analysis of the mechanical scratching depth as a function of the applied bias voltage, Fig. 4.2.25-(i) green line corresponding to d_r = 50 nm, reveals a linear decline of the depth with increasing bias. This again confirms the linear dependency of bias and separation conducted in section 4.2.2. Having a closer look onto the line width and width fluctuations versus bias dependency, it is obvious that the plowing lines are much wider and irregular than the lines defined in the direct ablation regime. In conclusion, the mechanical interaction regime is not only uninteresting because of the probe wear and tip contamination, but also from the achievable lithographic results.

Feature blurring at enlarged tip-sample separations in the case of high bias voltage oper-
ations: In contrast to EBL, in FE-SPL no additional electrostatic fields for beam focusing are applied. Rather, the beam diverges with increasing emitter to sample spacing. As revealed previously (4.2.2), with increasing bias voltage the tip-sample spacing increases linearly. In turn, this means also that the tip-resist gap increases accordingly, derived by theoretical considerations in section 5.2. FN emission simulations by Mayer et al. [301] as well as my own theoretical investigations, chapter 5, confirmed that with increasing tip-sample spacing the beam diameter increases. Since the total current is kept constant, this leads to a decrease of the local exposure dose. In other words, the same total amount of electrons per unit time are spread over a larger total area. In conclusion, higher bias voltages lead to a degradation of the resolution capability. Since the energy is deposited within the first few nanometers of the resist surface, ref. section 2.2, the beam diameter at the resist-air interface is relevant. In turn, not only the total tip-sample spacing defines the decisive beam diameter, but also the tip-resist gap and its ratio to the tip-sample spacing determines the resolution. A corresponding model is derived in section 5.2.

Figure 4.2.25: Summary of the bias voltage influence on the ablation process result, investigated for differently thick resist films. In particular, in graphs (i, iii) the line altitude and in (ii, iv) the line width, measured both directly after exposure are plotted as a function of the bias voltage. Thereby, graphs (i-ii) correspond to the investigation of the transition from mechanical interaction towards direct ablation, Fig. 4.2.23, and graphs (iii-iv) are related to the transition from optimum bias regime to the blurring of features, Fig. 4.2.24. In graphs (i-ii), the transition region from scratching to ablation is marked by an arrow, which is labeled with $S$. The color-code corresponds to the particular resist layer thickness.

The trend of a degradation of the resolution with increasing bias is also proven experimentally,
summarized in Fig. 4.2.24 and in the corresponding measurement graphs, Fig. 4.2.25-(iii-iv). The same features were patterned at increased bias voltage levels of $67.5 - 77.5\, V$, modulated in $2.5\, V$ steps, on three $4\mu m 68$ resist films of different thicknesses. Thereby, the high voltages ensure an operation far above the mechanical scratching regime. Resist layers in the range of $30 - 50\, nm$ were spin-coated on top of a Si chip. In order to eliminate probe-induced deviations, the same probe was applied for all bias voltage modulation tests. The experimental results clearly show that with increasing bias voltage the surface resolution of the ablation process decreases, visible by an increased blurring of the single lines. This effect is most pronounced for the thinnest resist film ($d_r = 30\, nm$). Here, the individual lines of the $40\, nm$ hp dense line/space pattern are no longer resolved. The observed resolution deterioration behaves as predicted by theory, section 5.2. In the case of the thickest resist layer ($d_r = 50\, nm$) the tip-resist gap is minimum, which results in a much smaller beam diameter at the resist-air interface than in the thinnest resist-highest bias voltage combination case ($U_b = 77.5\, V; d_r = 30\, nm$). However, as revealed in the previous section, thicker resist layers need larger clearing doses in order to achieve a full removal till the substrate layer. In the case of a fixed spacing the tip-resist gap is enlarged leading to a further spread of the beam at the top resist. This back-coupling effect of the patterning process onto the field emission and beam spreading is discussed in context of chapter 5.3.

In conclusion, an optimum bias voltage range exists in accordance with the resist film thickness. The lower bias limit is defined by the mechanical scratching interaction, whereas at enlarged bias voltages a significant beam spreading occurs. Thereby, the particular bias voltage values are not only determined by the probe characteristics but also by the resist properties - thicker resists need a larger bias than thinner ones. When thinner resist layers are targeted, correspondingly reduced bias voltages should be applied. Here, the usage of larger values leads to a degradation of the resolution, which could be mainly attributed to the enlarged tip-resist spacing. To determine the optimum working range a bias voltage modulation test is essential. As a starting bias value, the previously defined rule, Eq. 4.2, is recommended.

b) Thin resist layer application case: Bias voltage modulations at different line exposure dose / pitch combinations, carried out by a tungsten wire probe:

The pattern transfer (section 7.2) after lithographic processing, for example by plasma etching, requires a sufficient patterning depth which is ideally reaching the bottom layer (full clearing). Since with increasing patterning depth the resolution drops ($\Rightarrow$ aspect ratios are limited), thinner resist layers are targeted when highest resolution is desired. In particular, thinner resist layers require a lower bias voltage, which results in turn in a smaller tip-sample spacing. A finer beam is provided giving a higher lithographic resolution. In conclusion, for a lithography with high resolution requirements resist layers with a thickness of $d_r \leq 20\, nm$ are preferred. Further investigations were focused on this kind of resist layers.

A particular example of a complex lithographic parameter screening test field, in which the bias voltage, the exposure line dose and the line pitch were modulated, is shown in Fig. 4.2.26. The usable bias voltage range is defined by the mechanical tip-resist interaction occurring at $U_b \leq 25\, V$ and the onset of a multi-spot field emission, which is visible at $U_b \geq 65\, V$. The bottommost row represents the reference row indicating spontaneous variations of the probe or environment during the test. Here, a significant change within the reference test row is visible between first and second feature (from left). The particular change can be attributed to the tip change caused by the mechanical interactions occurring at $U_b = 25\, V$.

The rise of feature blurring and multi-tip emission effects at enlarged tip-sample spac-
Complex lithographic parameter screening test field showing the influence of a combined bias voltage (25 – 65 V) and line dose/pitch modulation. In (i) the AFM topographic image is provided, whereas the corresponding analysis result is summarized in (ii). The line dose/pitch modulation was carried out column-wise and the bias voltage modulation row-wise, respectively. The bottommost row represents the reference row indicating spontaneous variations of the probe or environment during the test. [Sample: ≈ 18 nm thick cmc4r resist layer, spin-coated on top of a Si chip; Probe: tungsten wire, \( r_{\text{tip}} \approx 10 \text{ nm} \); AFM imaging was done directly after lithography by a cantilever probe]

The increased emitter-to-surface spacing at high bias voltage operation result in an enlarged delocalization of the electric field strength at the tip apex (ref. simulations, section 5.3). This manifests itself in multi-tip emission, feature blurring or in both effects depending on the particular probe shape and surface roughness of the tip emitter apex. Thereby, ragged and rough tip emitter surfaces tend to a multi-tip emission, whereas the field delocalization leads in the case of smooth emitter surfaces to a feature blurring effect, e.g. Fig. 4.2.24. In the case of the previously shown exposure test, Fig. 4.2.26, the tip was certainly damaged during the operation within the scratching regime. As the AFM topographic image indicates, a part of the tip is broken off. In accordance with that, the reference row (R) points out a significant tip alteration between the first and second columns. Thus, a multi-tip emission is most probable. The evaluation of a large number of experiments has shown that at high bias voltage operation multi-tip emission effects are much more likely than stand-alone feature blurring. Advantageously, the multi-tip FN emission from a single probe can also be used in a targeted manner, e.g. for throughput enhancement or ultra-dense feature patterning as shown in related publications [31, 311].

**Determination of the optimum bias voltage range:** In the particular case, the best lithographic resolution, evaluated in terms of resolved line width and line/space gratings, was achieved at \( U_b = 35 \text{ V} \). This was the first value probed above the scratching regime threshold. As the voltage continues to increase, the resolution capability drops. This was valid for all line dose / line pitch combinations independently of the dominating interaction (ablation, crosslinking, oxidation). Linked with the increased line width, the depth of the directly ablated line reduces with increasing bias (row 2 and 3 correspond to 350 nC/cm and 175 nC/cm, respectively). Since the line exposure dose is kept constant within a row, the reduced depth can be attributed to the enlarged beam spreading, which is a consequence of the increased tip-resist gap. Thereby, the increased spreading leads to a decrease of the local exposure dose - the same amount of electrons are spread over an enlarged area. The locally absorbed energy
density is reduced giving a decreased patterning depth. This effect is clearly visible in Fig. 4.2.26-(ii) graph. In contrast to that, the height of the negative tone patterns (crosslinked resist, buried $SiO_2$ growth) were not affected by bias voltage changes (row 4 and 5 correspond to $70\,nc/cm$ and $40\,nC/cm$, respectively).

In order to determine the optimum bias voltage for different line dose / line pitch combinations, an exposure series with a narrowed bias voltage modulation range ($U_b = 30 - 60\,V$) was carried out, summarized in Fig. 4.2.27. The lower bias limit ($U_b = 30\,V$) was chosen in order to avoid mechanical tip-resist interactions (alterations of the tip should be excluded; cf. $U_b = 25\,V$ results in a scratching operation, Fig. 4.2.26). The exposure parameter screening verifies the previously gained knowledge, in particular:

- For both patterning tones the features are best resolved at lower bias voltage operation (line width Fig. 4.2.27-v) close above the scratching bias threshold. At increased bias voltages ($U_b \geq 60\,V$) multi-spot emission sites and broadening effects are dominant.

- In the case of the positive tone (direct ablation regime) with increasing bias voltage the ablation depth is reduced while the line width increases. As the line exposure dose increases, the effects become stronger (rate of line width/line depth changes becomes larger). The ablation process seems to have a local maximum in depth at $U_b = 35\,V$. In contrast, the depth maximum does not correlate with a line width maximum. This trend is still visible after a wet development process (iv).

- In the case of negative tone patterning (crosslinking regime) the height of the crosslinked resist features remain almost constant over the entire bias voltage range. This is verified by both AFM topographic measurements carried out directly after exposure (aSPL) and after wet development step (aWD). In contrast, the achievable resolution is strongly dependent on the bias voltage, e.g. shown by Fig. 4.2.27-(iii). Interestingly, also here a resolution optimum at $U_b = 35\,V$ could be identified at which the $25\,nm$ hp pattern is clearly resolved. The AFM topographic image taken after wet development (aWD) reveals further that a multi-spot emission starts in the particular case already at $U_b = 40\,V$. Thereby, the onset of the second emission spot leads to a blur of the entire feature. As the bias voltage continues to increase, the electric field at the tip is further defocused leading to the appearance of additional emission spots. The activation of additional emission sites can be well identified at the end of each structure. Due to an enlarged dwell time at the end of the L-shaped structure a spot exposure at increased point exposure doses was carried out. This leads to formation of dot features, whereby with increasing bias voltage the amount of dots increases accordingly.

In conclusion, there seems to be an optimum bias voltage at $35\,V$, which (1) gives in the positive tone development-less (ablation) regime the deepest patterning depth and (2) provides in the negative tone (crosslinking) regime the highest lithographic resolution capability. On the basis of STM-based exposure experiments carried out by Zhang et al. [380], a theory was put forward predicting a local minimum of the beam diameter at the sample surface if there is an optimal ratio between tip-sample spacing and tip radius of curvature. Since a bias voltage alteration leads to a change of the tip-sample spacing, the mentioned theory can be an explanation for the appearance of a local maximum (ablation depth) / minimum (crosslinking width). The presence of an optimum ratio can be also assumed in the case of Fig. 4.2.25-(iii:50 nm resist) and Fig. 4.2.29 tests. Since the differences in width/depth of the lines measured at the optimum bias and aside to that are only small, one cannot exclude that the optimum is a cause of measurement or lithographic regulation errors. In fact, the determination of the local bias voltage optimum is inconvenient since it is dependent on the local probe shape and tip radius.
Investigation of the optimum bias voltage range for thin resist layers. An exposure test array similar to Fig. 4.2.26 was applied. In accordance to the thinner resist layer ($\approx 18 \text{ nm}$ thick cmc4r resist spin-coated on top of a Si bottom layer) a decreased bias voltage range of $30 - 60 \text{ V}$ was investigated. The line dose/pitch settings were modulated row-wise, whereas the bias voltage was changed column-wise. AFM imaging was done directly after exposure using a separate cantilever probe. The evaluation of the AFM image data of Fig. (i) is summarized in graphs (ii) and (v). The AFM image comparison of Fig. (iii) shows the exposure row with the lowest dose ($25 \text{ nC/cm}$) / lowest pitch ($25 \text{ nm}$ hp) combination directly after FE-SPL exposure (aSPL) and after a subsequent wet development step (aWD). Graph (iv) displays the line altitude of the crosslinked resist features as a function of the bias voltage for different dose/pitch combinations. [Probe: Electrochemically etched tungsten wire, $r_{\text{tip}} \approx 10 - 15 \text{ nm}$]
of curvature which are typically unknown. For best practice a bias voltage which is close above the scratching threshold should be applied. In this scenario the tip-sample spacing as well as the tip-resist gap are minimized giving the highest possible spatial confinement of the deposited energy. Therefore, in the experiments bias voltages ranging $\approx 5 - 10 \, V$ above the scratching threshold, Eq. 4.2, should be initially used ($\approx 5 - 10 \, V$ recommended as safety factor for feedback regulation).

**c) Thin resist layer application case:** Bias voltage modulations at different line exposure dose / pitch combinations, carried out by a Si-cantilever probe:

In the following the bias voltage dependency of the exposure process when using highly n-doped Si cantilever probes (uncoated tips) was investigated. A bias voltage modulation test, where moreover the line exposure dose as well as the line pitch was changed, is summarized in Fig. 4.2.28. An almost linear dependency between resolution (line width) and bias voltage is observed (Fig. 4.2.28-iv) confirming previous results achieved with a tungsten wire probe. The same line width increase of $\approx +1.95 \, nm$ per $1 \, V$ bias increase is valid for both line exposure doses. Thereby, the absolute line width is always larger in the case of higher exposure dose levels, which is consistent with previous results (section 4.2.3). The results obtained in the row with the lowest pitch (row #4: 25 nm hp) deviate from this. Here, the exposed areas overlap, resulting in an increased ablation depth. Since with increased bias voltages the spatial confinement of the deposited energy is decreased, the line overlap is increased accordingly. This can be verified by plotting the altitude of the line fences (height of the lines left behind between adjacent exposure centers) versus bias, Fig. 4.2.28-(iii), which shows a decreased height with increasing bias. The decrease can be fitted by a linear function type having a slope of $-0.17 \, nm/V$.

In contrast to the bias voltage modulation experiments carried out with tungsten wire probes, wherein an ablation depth increase was observed only in a short range above the scratching limit, in the case of ultra-sharp n-doped cantilever probes the ablation depth increases continuously with increasing bias voltage. A linear relationship having a slope of $-0.15 \, nm/V$ was determined for the particular example shown in Fig. 4.2.28-(ii). A voltage modulation test at a higher bias voltage range, summarized in Fig. 4.2.29, revealed that in the case of highly n-doped cantilever probes the maximum in ablation depth is shifted towards higher values. In the particular case the maximum depth is achieved at $65 - 68 \, V$. In agreement with the previous results the line width increases linearly. A slope of $2.3 \, nm/V$ was extracted. The shift of the ablation depth maximum between highly n-doped Silicon and tungsten probes can be attributed to the difference in the emission characteristics (ref. theory section 2.4). In particular, n-doped Si has a higher work function than tungsten, which results in a decreased tip-sample and tip-resist spacing (ref Mayer et al. [301]). However, due to the measurement limitations the exact tip properties (tip shape, tip radius of curvature, surface roughness, work function at the tip apex, formation of surface oxides, contamination) of both probe types are rather unknown. Since different manufacturing methods and materials are present, significant changes are expected. Thus, no single cause for the slightly different lithographic behavior can be identified. As indicated by the onset of multiple emission sites at $U_b \geq 45 \, V$, Fig. 4.2.28, a rather rugged tip apex structure is present.

In general, the experiments with cantilever probes have shown larger variations of the lithographic results than obtained with electrochemically etched tungsten wire probes. A possible reason could be the larger variations in the cantilever batch fabrication process (difference in doping level, tip height, tip shape, tip radius, spring constant, local work function, oxide formation, etc., ref. [203, 315, 316]). In consequence, after each cantilever exchange the lithographic characteristics have to be evaluated again using a fast exposure test. In the case of tungsten probes this calibration process was not stringently required. Shown by example in Fig. 4.2.21, the electrochemically etched tungsten probes which have
Investigation of the impact of bias voltage modulations ($U_b = 30-45 \, V$) on the exposure process in the case of highly n-doped Si cantilever probes (uncoated, $r_{tip} \approx 5-10 \, nm$). A 3D topographic AFM image of the exposure parameter test array, taken directly after exposure (aSPL), is shown in (i). The nested L-features are patterned with a line exposure dose of $133 \, nC/cm$, rows 1–2, and $100 \, nC/cm$, rows 3–4, respectively. The half line pitch (hp) was reduced stepwise from $100 \, nm$ (row 2), $75 \, nm$ (row 1), $50 \, nm$ (row 3) to $25 \, nm$ (4). Graphs (ii-iv) summarize the line altitude (ii), the fences heights (altitude of the resist between the lines of the L-shaped feature; plot iii), and the line width dependency (iv) as a function of the bias voltage. [Sample: $\approx 8 \, nm$ thick cmc4r resist film, coated on top of a Si chip]
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Figure 4.2.29: Influence of bias voltage alterations on the line altitude (i) and the line width (ii), carried out by a highly n-doped Si cantilever \( (r_{\text{tip}} \approx 5 \ldots 10 \text{ nm}) \) at enlarged bias voltages. The data are based on AFM measurements directly after the exposure process (aSPL). [Sample: \( \approx 20 \text{ nm} \) thick 4m1ac68 resist film, spin-coated on top of a Si-chip]

approximately the same radius of curvature give comparable lithographic results.

d) Application of an intermediate Cr/Au bottom layer:

As found previously, the introduction of an intermediate metal layer blocked the oxidation of the Si substrate. As expected, the Cr/Au layer has no influence on the general bias voltage modulation behavior. However, the material combination metal / resist gives a very good contrast in SEM imaging, which could provide additional insights. In Fig. 4.2.30 particular examples are shown. From top to bottom the bias voltage was increased in 10 V steps. The first two cases show a negative tone pattern (standalone crosslinking) exposed with two different cantilever probes. In the third case the exposure dose was increased leading to an additional removal process in the exposure center. As already known, a coupled spatial extension of the crosslinking and ablation reaction is observed with increasing bias voltage. The coupling between both lithographic effects was confirmed also in the previous section for the line dose dependency (Fig. 4.2.15). Also here at \( U_b = 60 \text{ V} \) the increased bias initiates an emission from multiple spots. Interestingly, the main emission spot still has enough current in order to write large features in the ablative regime. In contrast, the newly appearing emission spot, which is expected to have an enlarged tip-sample spacing, carries less current (splitting of the current to main and side emission). Due to the lower local exposure dose a stand-alone crosslinking reaction is induced (onset of ablation was not reached). This kind of simultaneous multi-spot multi-tone lithography was also indicated by Fig. 4.1.17, where phase contrast imaging was applied for feature analysis.

As experimentally observed, the line width versus bias voltage dependency is also influenced by the probe tip characteristics (radius, shape, surface roughness, work function). This is shown by Fig. 4.2.31-(i), wherein two tungsten wire probes with different tip radii were applied. Directly after exposure the width of the ablated lines areas were measured by SEM. Since the ablation proceeds to the bottom metal layer, an excellent material contrast is given. As revealed by plotting the line width versus bias, the ultra-sharp tip results in a non-linear dependency (slope increases with increasing bias), whereas the blunter tip is characterized rather by a linear relation. Qualitatively, this fits very well with simulation results carried out by Mayer et al. [301] and by Cord and Pease [164, 381], which have predicted such kind of behavior (but they could not measure it). Described in a simplified way, in the case of sharper tips the emission tends to spread expeditiously (in terms of bias voltage increase) over a larger emission
angle than in the case of blunter tips. Thus, sharper tips provide a small beam diameter at low bias voltages (close above the scratching limit), but with increasing bias the angle of emission gets larger leading to a rapid increase of the beam diameter. This explanation, originally derived for crosslinking processes, initiated by STM-based processing, seems to be valid also for the direct ablation reaction.

Further on, the influence of the bias voltage polarity was investigated, shown by an example in Fig. 4.2.31-(ii). Since the novel control electronics were optimized for the application of exclusively positive bias voltages (tip is virtually grounded through the transimpedance converter, the sample is biased positively), the polarity investigation was carried out by using a forerunner FE-SPL system (simple STM set-up, described in ref. [51]). The analysis of the bias polarity test has confirmed that the same dependencies exist for both polarities. In the particular case, a linear increase of the line width with increasing bias is observable. However, the bias threshold values for ablation are significantly different depending on the polarity. In the case of a positive sample voltage (the tip is in all cases virtually grounded), which means that electrons are field-emitted from the tip, an onset of $U_b \approx 7\, V$ could be extrapolated. This matches approximately the onset of the FN field emission regime (ref. section 2.4.1). In contrast, in the case of inverted (negative) sample bias voltages the threshold for ablation is shifted towards $U_b \approx 44\, V$. Further tests supporting this result are provided within my previous work, ref. [51]. In addition, also Kragler has experimentally observed the shift in the threshold when inverting the bias polarity for exposure experiments on Si-CARL resist [167]. He concluded that the threshold difference can be explained by the lower energies of the electrons which are emitted by the flat surface (also attributed by the lower electric field strength within the resist layer). Thus, higher absolute bias voltages are required. This is supported by the fact that below the particular bias threshold also no sufficient crosslinking has taken place (investigations carried out in [51]). In consequence, the difference in the line width comparing positive and negative polarity at the same absolute bias value could be

<table>
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<tr>
<th>Bias</th>
<th>Negative Tone - Single Tip</th>
<th>Negative Tone, Multi-Tip</th>
<th>Positive Tone, Multi-Tip</th>
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<tr>
<td>40 V</td>
<td>SEM</td>
<td>AFM</td>
<td>SEM</td>
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<td>50 V</td>
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<td>60 V</td>
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Figure 4.2.30: Summary of a bias voltage modulation test, which was carried by different cantilever probes on $\approx 10\, nm$ thick cmc-4r resist. A Cr/Au bottom layer was introduced in order to block the local oxidation of the Si substrate. Furthermore, the metal layer enhances the SEM contrast between the resist (dark lines) and bottom layer (bright surrounding). Imaging of the L-shaped features was done after a wet development step by SEM and AFM. In the first two examples a negative tone patterning process was applied, whereas the third example shows a corner feature patterned in positive tone. Here, the wet development step uncovers the extension of the crosslinked area, which surrounds the directly ablated lines. [Scale bars: 2\, \mu m]
Figure 4.2.31: Investigation of the line width in the direct ablation regime as a function of the bias voltage (i) and bias polarity (ii), carried out on thin calixarene resist layers coated on top of Cr/Au intermediate metal layers. In (i) the bias voltage dependency for two differently sharp tungsten wire probes at positive bias polarity (usual set-up) is summarized. The small SEM inlet images (scale bar: 500 nm) displays results of the red star based curve. The intense SEM image contrast is based on the material difference between the metal bottom layer (bright areas) and the resist (dark areas). Since the imaging was done directly after exposure the bright areas correspond to the directly ablated parts (line pitch of 250 nm). In graph (ii) the bias voltage dependency of the line width for both bias polarities is summarized. Since the developed digital based control system was optimized for operation at positive polarities, this particular experiment was carried out by a completely analogue control system. The basics of this system are described in frame of my master thesis work, ref. [51]. The polarity test was carried out at high line exposure doses using a truncated Pt/Ir wire probe (blunt large scale tip apex with ragged surface structure). The background of this experimental study is described in ref. [51].
derived by a simple geometric model, described by Zhang et. al [380]. Experimentally, the differences of the line width depending on the polarity were also observed by McCord and Pease [164] as well as by Zhang et al. [380] in STM-based exposure experiments of diverse organic resist thin films. In the frame of this work focus was placed on the application of positive bias voltages which enables patterning by crosslinking and ablation mechanisms already at lower bias voltages.

e) Summary:

1. Increasing the bias voltage leads to an increase of the tip-sample spacing. Linked with that a spreading / broadening of the electron beam at the resist interface occurs resulting in a decreased resolution capability. The applicable bias voltage range is constrained by the mechanical interaction / scratching regime at low bias voltages and the extremely broadened / multi-spot emission regime at high bias voltages. The operating bias voltage during resist exposure should be in chosen in between the defined boundaries. This applies to both lithographic mechanisms of crosslinking and direct ablation. No specific values can be given because the occurrence of the regimes are also determined by the particular resist properties, mainly the resist film thickness, as well as by the probe characteristics. Thereby, thicker resist layers need higher voltages in order to operate in the optimum operation range. An experimental estimation was derived as described by Eq. 4.2. As found, the general behavior is independent of the applied bottom layer (same trend observed for a Si substrate as well as for a Cr/Au intermediate layer).

2. The spatial localization of the lithographic interaction is highest at a bias voltage close above the threshold for mechanical tip-resist interactions, estimated in first approximation by Eq. 4.2. Thus, a voltage ranging 5 – 15 V above this threshold should be used as starting value for the bias voltage optimization process (provides a safe height also in the case of minor regulation instabilities which are typical for initial emission processes). The fine tuning of the lithographic feature should be achieved by variation of the line exposure dose (and not via the bias parameter). During exposure a constant bias voltage should be used. Enlarged bias voltages are not reasonable when high resolution patterning is intended, but it could be an option if a faster exposure process is demanded.

3. In order to achieve highest resolution capabilities resist layers as thin as possible are preferred (leads to significant challenges in the pattern transfer process). In particular, thinner resist layers require lower bias voltages, which gives smaller tip-sample spacings. In turn, a lower beam spreading is present resulting in a smaller beam diameter at the resist interface. When thicker resist layers are demanded by the application scenario, e.g. for a successful pattern transfer, a degradation of spatial confinement with increasing ablation depth should be taken into account. Here, the lithographically triggered back-coupling effect is relevant, investigated in section 5.3.

4. The probe properties and their variation significantly alter the bias voltage dependency of the lithographic process. Since the measured characteristics depend strongly on the applied tips, no general function type for the bias dependency of the line width or line depth can be given. For example, for tungsten wire probes, both a linear and non-linear width versus bias characteristic were obtained depending on the tip radius (qualitatively, this behavior is in agreement with simulation results). For ease of use, for both probe types a linear function type can be applied in order to get an initial estimation of the line width versus bias voltage behavior. The investigation of the ablation depth versus bias voltage revealed an optimum, at which the ablation depth has a maximum. Since the position of the maximum depends strongly on the probe, no defined values can be specified. However, the optimum bias voltage at which the ablation depth is
maximum and the highest resolution is achieved are not necessarily identical. The investigation of the lithographic reproducibility achieved by different probes of the same type revealed a good consistency for electrochemically etched tungsten wire probes - similar probes give comparable results. In contrast, in the case of cantilever probes the measured deviations are significantly larger. This could be attributed to the larger variations in the batch fabrication process.

5. As observed for the line dose characteristics, both lithographic mechanisms (crosslinking and ablation) extend laterally with the same trend (same width-bias dependency) - the interactions are coupled. Thereby, the ablation depth is influenced by the bias voltage parameter, whereas the height of the crosslinked resist is not altered by bias voltage modulations (the system operates significantly above the exposure dose thresholds of the crosslinking interaction). As observed for the dose dependency of the buried Si oxidation process, also for the bias dependency the lateral extension of the oxide is linked with the crosslinking process of the resist. No alteration of the oxide height due to bias voltage changes were found (results are not shown here since they were not in the focus of this work).

4.2.5 Investigation of Proximity Effects - The Line Pitch Parameter

a) From separated line features towards dense patterning:

In standard EBL it is well known that proximity effects lead to a significant degradation of the resolution, especially in the case of dense patterning (section 2.2.1 and refs. [13, 27, 28, 174, 175, 176, 177]). In order to investigate the occurrence of proximity effects in FE-SPL exposure, the pitch parameter of meander line patterns was modulated. In the tailored experiments the change of the line geometry was determined as a function of the line pitch. In order counter-check for hysteresis effects, the pitch was modulated starting from spatially separated lines, proceeding towards close patterning, and moving backward towards largely separated lines. This kind of pitch modulation test was carried out for both lithographic main mechanisms. Initial experimental results showing the differences between negative tone (crosslinking) and positive tone (direct ablation) are shown by Fig. 4.2.32.

The patterning in negative tone was carried out at highest resolution by using ultra-low exposure doses of $\Phi_L \leq 10 \text{nC/cm}$ and bias voltages close above the scratching regime ($U_b = 30 \text{V}$). The results, labeled with (a)-(d) in Fig. 4.2.32 show no evidence of proximity effects. In all cases the lowest pitch (50 nm) lines are well resolved. AFM imaging directly after exposure (aSPL) as well as after wet development (aWD) proves (zoom-in graphs and corresponding section) that the line width is not significant changed due to modulations of the line pitch / pattern density. Also the height of the structures is constant, regardless of the line pitch. As a consequence of the AFM inspection method, in the case of the lowest pitch (50 nm) the depth measurement is restricted by the tip geometry (ref. section 3.3.2). Thus, the presence of minor interproximity effects cannot be excluded. However, in contrast to EBL no evidence of long range proximity effects exist, which is supported by direct comparison experiments between EBL and FE-SPL, summarized in section 6.1. As demonstrated, in the case of FE-SPL the deposited energy density and the therefrom related lithographic reaction is much more spatially confined than in EBL. This is in general agreement with theory and simulations established by Soh and Quate et al. [13], which have shown that the proximity effects are significantly reduced when going to ultra-low energy exposure. In addition to this work, it is shown here that a 4 times smaller pitch is achievable. In conclusion, for crosslinking no proximity correction is required, which enables an a-priori dense patterning.
Figure 4.2.32: Investigation of the line pitch parameter for negative tone (crosslinking with subsequent wet development step) patterning, features (a)-(d), and for positive tone, development-less (direct ablation) patterning, features (e)-(h). A meander-line type pattern was applied, imaged directly after exposure (aSPL) by AFM. Each meander line was written with a different exposure dose, in particular (a) $4 \text{nC/cm}$; (b) $6 \text{nC/cm}$; (c) $10 \text{nC/cm}$; (d) $8 \text{nC/cm}$; (e) $100 \text{nC/cm}$; (f) $66.7 \text{nC/cm}$; (g) $133.3 \text{nC/cm}$; (h) $400 \text{nC/cm}$. Within each meander the line pitch was modulated from (1) $75 \text{ nm}$ hp, (2) $50 \text{ nm}$ hp, to (3) $25 \text{ nm}$ hp and vice versa in order to evaluate the influence of the line pitch parameter. In the case of the negative tone array (a-d) a zoom-in into meander (c) is provided showing the pattern directly after exposure (aSPL) as well as after a subsequent wet development step (aWD). A corresponding section is given below the 2D topographic AFM images. In the case of the positive tone pattern array the meander patterns of (g) and (h) are compared by AFM zoom-in images as well as by a cross-sectioning graph. The negative (positive) tone patterns were defined in $\approx 5 \text{ nm}$ ($\approx 8 \text{ nm}$) thick cmc4r resist using highly doped Si cantilever probes with $U_b = 30 \text{ V}$. Raw measurement data is shown. No convolution correction was applied.
In contrast, the investigation of the positive tone, development-less (direct ablation) patterning, Fig. 4.2.32 (e)-(h), reveals a strong alteration of the lithographic result as function of the line pitch. With enhanced density the resist in between the initially separated lines becomes removed resulting in a decrease of the height of the interline resist area. Thus, an increase of the final ablation depth is observed, for example in Fig. 4.2.32-g (h) from $2.2 \text{ nm}$ (h: $6.5 \text{ nm}$) at $75 \text{ nm}$ hp, to $2.6 \text{ nm}$ (h: $6.7 \text{ nm}$) at $50 \text{ nm}$ hp, and $3.0 \text{ nm}$ (h: $8.0 \text{ nm}$) at $25 \text{ nm}$ hp. Thereby, the proximity effect scales with the exposure dose. As revealed by section 4.2.4, also an increased bias voltage enhances the proximity effect (increased tip-resist spacing leads to an increased beam spreading). Due to the increased ablation rate within the center of the dense pattern (factor: $\approx 1.25$), the overall resist thickness budget for the subsequent pattern transfer step is reduced.

In order to retrace the origin of the proximity effect in the ablative lithographic regime, the AFM-based sectioning method was applied, ref. section 4.1.3. The corresponding results are summarized in Fig. 4.2.33. The schematic drawings inserted above the individual section graphs outline the composition of the pattern as well as its inner shape. In Fig. 4.2.34 the extracted line altitude and line width data are plotted versus the line pitch parameter. To capture the changes of the lithographic outcome at the transition from separated to dense line features, the line pitch was modulated from $200 \text{ nm}$ down to $50 \text{ nm}$ by $50 \text{ nm}$ incremental steps. The experiments were repeated with 5 different line exposure dose values. Here, as indicated already by previous experiments, in the negative tone pattern (i: $2 \text{nC/cm}$) no proximity effect either in height or in line width is observable. With the onset of ablation (ii) a change of the patterning depth as a function of line separation occurs. With further increasing dose (iii-iv) the proximity effect becomes enlarged, which is clearly visible by the increase of the ablation depth with decreasing pitch, Fig. 4.2.34-(i). Further, with increasing dose the proximity effect becomes visible already at larger line separations. In contrast to that, the line width changes only marginally as a function of the line pitch, Fig. 4.2.34-(ii). Thus, even at lowest pitch the line patterns are still well resolved. Only at the highest dose ($300 \text{nC/cm}$) and the smallest pitch the line pattern becomes completely removed forming an areal pattern (Fig. 4.2.33-iv). Interestingly, by using exposure doses which are close to the threshold for ablation, a decrease of the pitch could lead to complete change of the line type (LT2 $\rightarrow$LT1), e.g. shown in Fig. 4.2.33-(ii).

The analysis of the different lithographic mechanisms as function of pitch, outlined by the drawings in Fig. 4.2.33, reveal that the proximity effect does not start until the crosslinked resist areas of separated ablation lines overlap. Thus, it is reasonable to assume that the increased ablation rate at dense patterning is mediated by the enlarged crosslinked resist areas (schematics of Fig. 4.1.19). As substantiated in section 4.1.5 and 4.2.3, the crosslinking reaction has an approx. $\approx 60 – 80 \text{ nm}$ enlarged lateral extension as the ablation reaction leads in positive tone regime to crosslinked resist sidewalls. While this is irrelevant for large line spacings, it becomes significant when dense patterning in ablative regime is targeted. In particular, at pitches $< 60 – 80 \text{ nm}$ the crosslinked sidewalls are relevant. While the initial line is patterned into an unexposed resist, the following lines of the dense feature are placed into already pre-exposed and crosslinked areas.

b) Exploitation of Fowler-Nordheim constant-current „imaging“ in order to resolve the impact of crosslinked resist on the ablation process:

Derived from previous results, the crosslinking state of the resist seems to have a significant influence on the ablation process. To unveil this link, so called Fowler-Nordheim constant-current (cc) imaging was utilized. This imaging mode (ref. [309, 382]) goes back to the „topografiner” system of Young et al. [281], which was the predecessor of the STM. From a technical point of view this imaging mode is
Figure 4.2.33: Investigation of the line pitch, studied by AFM sectional imaging for different exposure dose parameter (i-iv). The displayed AFM images and graphs show the line pattern directly after exposure. The drawings above the section graphs outline the composition of the exposed features (the color-code is explained in the legend). The underlying results were extracted from AFM images, which were taken after different process steps (ref. section 4.1.3). Four test fields, in which the pitch was decreased in 50 nm steps from 200 nm to 50 nm, are shown. Between the fields (i)-(iv) only the line exposure dose was changed [(i) 2 nC/cm, (ii) 75 nC/cm, (iii) 100 nC/cm, and (iv) 300 nC/cm]. The bias voltage has been kept constant \[U_b = 40 \, V\]. The features were written in \(\approx 8 \, nm\) thick 4m1ac68 resist, which was spin-coated on top of a pristine Si chip. For a better visibility of the single sections an Y-offset (altitude) of \(-3 \, nm\) between following section graphs were applied.
comparable to the FE-SPL process, but instead of moving a pre-defined lithographic path a raster-scan motion is applied in order to generate an interaction image between tip and sample. Thus, while the resist is exposed by low energy electrons, the feedback signals are recorded creating an interaction map of the tip. Since the emission current is kept constant by regulation of the tip-sample spacing, the resulting topographic image represents the changes of the spacing which are required to have a constant electric field strength at the tip apex. Thus, not only surface alterations are visible but also changes of the dielectric resist layer properties ($d_r, \varepsilon_r$). In the case of lithographically inert samples a dielectric mapping of the resist film is achieved. Because the feedback regulation of FE-SPL and Fowler-Nordheim constant-current (FN-cc) imaging are similar, the derived model describing the changes of the tip-sample spacing as a function of dielectric layer alterations, section 5.2, can be applied.

In order to create a well-defined initial resist state, the test samples for FN-cc imaging investigations were exposed by standard Gaussian electron beam lithography at 10 keV and 150 nC/cm line exposure dose. This has resulted in $\approx 150$ nm wide crosslinked lines. A line/space pattern with a pitch of 500 nm was created. A detailed description of the EBL processing is given in section 6.1.1. Since a stand-alone investigation of the crosslinked resist is targeted, an intermediate metal bottom layer was applied to suppress oxidation reactions at the bottom layer (would introduce a further dielectric layer). Directly after EBL exposure the patterns were investigated using different mapping modes, summarized in Fig. 4.2.35. In an initial step (a-i) the pattern was imaged by AM-AFM giving the latent image. The alternating crosslinked and unexposed resist areas are clearly visible. Thereby, the EBL-induced crosslinking process has led to a reduction of the resist thickness of $\Delta d_r \approx -0.79 \pm 0.04$ nm, visible by the darker regions of the latent image (a-i). Thereafter, a topographic image which maps the changes of the dielectric resist layer properties ($d_r, \varepsilon_r$) was carried out by using the FN-cc imaging mode (a-ii). Within this image (a-ii), the differences between the EBL-crosslinked and the unexposed lines are even more pronounced than in the latent image (a-i). As revealed by comparing the latent AFM image and the map in FN-cc mode, in the FN-cc imaging mode the probe does not follow the topographic changes. As illustrated in Fig. 4.2.35-(c), as soon as crosslinked resist areas are reached, the system increases the tip-sample spacing. With respect to unexposed resist areas an increase of the tip-resist gap of $\Delta d_g \approx +2.50 \pm 0.35$ nm was measured. To explain this regulation behavior, the electric field strength above the crosslinked resist areas must be locally enhanced. Under this assumption the system retracts the probe to maintain a constant field emission current. Since the resist thickness is reduced during
Figure 4.2.35: Investigation of the underlying differences in ablation between crosslinked and unexposed resist. Fowler-Nordheim constant current (FN-cc) imaging and AFM imaging were applied as examination methods. In order to have a defined initial resist state, standard Gaussian electron beam lithography (EBL, ref. section 6.1.1) was used to create defined crosslinked resist lines \(10\, keV\) and \(150\, nC/cm\) line exposure dose resulting in \(\approx 150\, nm\) line width, \(500\, nm\) pitch. A \(\approx 17\) to \(18\, nm\) thick \(4m1ac68\) resist, spin-coated on top of a Cr/Au bottom layer, was applied. In the image summary (a) the EBL exposed line/space pattern is mapped sequentially by different modes. Directly after EBL exposure the latent image is recorded by using the AM-AFM imaging mode \(U_b = 40\, V, I_{FN} = 35\, pA, v_{tip} = 5\, \mu m/s\), which gives a line exposure dose of \(80\, nC/cm\). A line spacing of \(h_p = 7\, nm\) was applied. A clear contrast between the EBL crosslinked and the pristine (unmodified) resist areas is visible. Finally, after the dielectric mapping a second AFM topographic imaging process was carried out (a-iii) to determine the changes caused by the FN-cc imaging process. In total, a resist thickness of \(\approx 2.5\, nm\) was removed, determined at the previously unexposed resist regions. Image (b) shows section graphs through images (a-i), (a-ii), and (a-iii). The drawing in image (c) illustrates the underlying effects. For both imaging process (AFM and FN-cc) the same tungsten coated cantilever was used. [Scale bars: 500\, nm]
exposure, the increased tip-resist gap can only be attributed to the change in the dielectric properties of the resist. In consequence of the exposure with electrons, the structure of the resist is changed (the electron beam exposure / EUV radiation causes the break-up of the arenes, followed by a cross-linking process). In turn, also the relative permittivity of the dielectric resist \( (\varepsilon_r) \) is changed during the crosslinking process. The local change of the dielectric constant of the resist can be calculated by using the model of section 5.2, which was developed to describe the changes of the tip-sample spacing and tip-resist gap as a function of the dielectric layer. The following equation is derived:

\[
\varepsilon_{r-d2} = \frac{d_{d2}}{d_{d1}/\varepsilon_{r-d1} - \Delta d} \tag{4.3}
\]

In the particular case an initial dielectric constant of the unexposed resist of \( \varepsilon_{r-d1} = 3.7 \) \([238]\) was assumed. The initial resist film thickness \( (d_{d1} = 17.6\,nm) \) as well as the resist thickness after crosslinking \( (d_{d2} = d_{d1} - \Delta d = 17.6\,nm - 0.79\,nm) \) were measured by AFM. Equation 4.3 returns a dielectric constant of the crosslinked resist of \( \varepsilon_{r-d2} = 6.5 - 8.8 \), which is almost two times the initial value. In conclusion, the standard crosslinking process of calixarene resist leads to a reduction of resist thickness and an increase of the dielectric constant. Thereby, the increase of \( \varepsilon_r \) overcompensates the thickness decrease and the system reacts in sum with an increase of the tip-resist spacing of \( \Delta d_{tr} \approx 3.3\,nm \). As already proven, an increased tip-resist gap leads to a broadening of the beam, which means that the exposure dose is distributed across a larger resist area. The entire chain of action can be described by a back-coupling effect, simulated in the context of section 5.3.

Since during FN-cc imaging (a-ii) the sample is exposed in the same way as during FE-SPL, the imaging process leads to changes of the underlying structures. In particular, an overall resist layer thickness of \( 2.5\,nm \) was removed during the imaging by the ablation process. The AFM topographic image (a-iii) taken directly after the FN-cc imaging process revealed further that EBL-exposed line features show a larger ablation than the unexposed areas. In consequence, the height difference between the EBL-crosslinked lines and the unexposed areas was further enhanced by the factor of 1.8 from \( 0.79 \pm 0.04\,nm \) (measured by AFM at the latent image (a-i)) to \( 1.41 \pm 0.08\,nm \) (measured by AFM after FN-cc imaging (a-iii)). Thus, compared to unmodified (pristine) resist the ablation rate is increased when crosslinked resist is exposed by FE-SPL. In the particular case an increase of \( \approx 1.25 \) times was determined.

In summary, as a mediator of the observed proximity effect in the ablative regime of FE-SPL the crosslinking process could be identified. In contrast to EBL, in which backscattering is responsible for the long-range proximity, in ablative FE-SPL a chemical mediation via crosslinking occurs. Since the crosslinking has a larger extension than the ablation, the overlap of the crosslinking areas occurs far before the overlap of the lines created by the ablation process. Solutions to circumvent the proximity effect are given in the summary subsection (d).

c) Increased Propagation of the FE-SPL induced crosslinking reaction by EBL pre-exposure:

In order to investigate the lateral expansion of the FE-SPL induced crosslinking process, an experiment tailored to clarify the propagation pathways of crosslinking was conceived. In particular, during an initial Gaussian EBL process the resist was exposed slightly above the gel dose leading only to a partial crosslinking. As a result, the sensitivity of the resist is locally enhanced. Already slight changes of the involved processes could be made visible. In a second step a FE-SPL exposure process is superimposed. The results of the described experimental series is summarized in Fig. 4.2.36.

By the EBL pre-exposure process \( (10\,keV) \) a line / space pattern (pitch 500 nm) was defined (similar
Figure 4.2.36: Investigation of the lateral extension of the FE-SPL induced crosslinking process as a function of the pre-exposure state, the bias voltage and the exposure dose. The pre-exposure was done by EBL [10 keV] slightly above the gel dose (ref. section 6.1.1). A line/space pattern was defined [pitch: 500 nm], which results in alternating EBL partially crosslinked and unexposed resist areas. The partially crosslinked lines have a lateral extension of ≈ 400 nm. Directly after the EBL process a FE-SPL based exposure was carried out using different parameter sets. The FE-SPL meander pattern [pitch: 250 nm] was aligned perpendicular to the partially crosslinked EBL lines. Finally, a wet development step was used to remove the not crosslinked resist parts. In the AFM topographic images (i)-(ii) the resulting pattern is shown directly after FE-SPL exposure (i) and after wet development step (ii). The superposition of (i) and (ii), shown in (iii), visualizes the ratio between ablated and crosslinked resist. In the topographic AFM image series (iv-v) the crosslinked resist areas are shown for different FE-SPL exposure parameter sets (note: the exposure dose at the beginning of the meander pattern, at the end, and during the patterning of the short lines connecting the long lines of the meander at twice as high FE-SPL exposure dose was applied). The experimental series was carried out on ≈ 22 nm thick 4m1ac68 calixarene MG resist, which was spin-coated on top of a Cr/Au bottom layer. [Scale bars: 1 µm]
to Fig. 4.2.35). Since the resist should be crosslinked only partially by the EBL process, a line exposure dose close above the gel dose was selected (parameter chosen in accordance to measurements described in section 6.1.1). The EBL pre-exposure resulted in \( \approx 400 \) nm wide partially crosslinked lines. A corresponding latent image (Fig 4.2.36-i) shows slightly visible EBL line features. As revealed by the wet development step, only 8 nm of the entire 22 nm thick 4m1ac6 resist was crosslinked sufficiently in order to withstand the solvent. As a result, an alternating pattern of partially crosslinked and unexposed areas was created by EBL.

Directly after EBL an FE-SPL exposure process was overlaid (no development step in between). Thereby, the FE-SPL meander line pattern was aligned perpendicular to the EBL partially crosslinked lines. This was achieved by using the latent EBL image (detailed information about that are given in section 6.2). As expected, due to the large line spacing no proximity effects in the ablation are observable. This is displayed by the AFM image taken directly after FE-SPL exposure, Fig. 4.2.36-(i). Further, the EBL induced partial crosslinking has no substantial influence on the FE-SPL ablation process. Neither the line width nor the line depth are altered when crossing the partially crosslinked resist areas (note: the exposure dose at the beginning of the meander pattern, at the end, and during the patterning of the short lines connecting the long lines of the meander at twice as high FE-SPL exposure dose was applied; further, increased dwell times at the start and ending point of the meander pattern have led to increased spot exposure doses).

By using a wet development step the crosslinked resist areas have become visible, displayed by the AFM topographic image Fig. 4.2.36-(ii). The superposition of (i) and (ii), shown in (iii), visualizes the ratio between the lateral extension of the ablated and the crosslinked resist. The FE-SPL process has induced a crosslinking through the entire resist film. Both, the remaining \( \approx 14 \) nm within the EBL pre-exposed areas and the \( \approx 22 \) nm resist within the unexposed areas, were crosslinked up to the resist surface independently of the initial crosslinking state. Hence, all resist areas which are crosslinked by FE-SPL have the same final height (\( \rightarrow \) same color in Fig. 4.2.36-ii). In contrast to the ablative regime, the FE-SPL induced crosslinking process unveils significant changes of the line width as a function of the initial crosslinking state. It is obvious that the crosslinking has a larger spread when crossing EBL pre-exposed areas, whereas on areas without pre-exposure the crosslinking process is highly confined. The analysis of the start and end points of the FE-SPL pattern (places of highest exposure dose) demonstrates that the crosslinking can propagate several \( \mu \)m along the EBL pre-exposed line pattern. Here, the lateral extension is significantly defined by the pre-exposure process. This points out that an additional diffusion of reactive species, which are released by the FE-SPL exposure, is responsible for further propagation of the crosslinking process. However, this is not surprising since the deposited energy induces chemical reactions in order to provoke bond scission and crosslinking. In accordance to the theory, section 2.3 and Fig. 2.3.1, the primary chemical processes induced by the electron exposure lead to the release of further active species (e.g. free radicals) and/or to the initiation of ionic mechanisms for secondary chemical reactions. As found by the investigation of the resist material, chapter 4.4, the hydroxyl functional groups (OH-) play a fundamental role for crosslinking (without OH- groups no crosslinking of the resist could be triggered). Most likely, corresponding ions (OH\(^{-}\)) and radicals (hydroxyl radical OH-) constitute the reactive species. Further, also the formation of \( H^{+} \) and \( H^{-} \) is consistent. In this context, it is well known that the hydroxyl radical is chemically very reactive and a powerful oxidizing agent [383]. In fact, the reaction radius of OH: (2.4 Å) is about 5.7 times larger than for \( H^{+} \) (0.42 Å), whereas the diffusion constants behave contrarily \( (D_{OH} = 2 \cdot 10^{-5} \text{ cm}^2\text{s}^{-1} \) versus \( D_{H} = 8 \cdot 10^{-5} \text{ cm}^2\text{s}^{-1} \); data extracted from ref. [383]). The estimation of an average radial diffusion distance (\( \lambda \)), expressed by \( \lambda = \sqrt{6 \cdot \tau \cdot D_{H}} \), gives \( \lambda = 10 \) \( \mu \)m for the hydroxyl radical (ref. [383], typical timescale of \( \tau \sim 10^{-6} \text{ sec} \) applied). Thus, the diffusion distance is in the same range as the...
experimentally observed enhanced propagation of the crosslinking reaction (the lateral spread occurs along the EBL pre-exposed lines).

Further, as demonstrated by Fig. 4.2.36-(iv-v), high exposure doses and large bias voltages lead to an increased expansion of the FE-SPL induced crosslinking along the EBL pre-exposed lines. In contrast, at low bias and dose the modulation effect is almost non-existent (Fig. 4.2.36- v, 20 – 30 nC/cm). In consequence, for the FE-SPL based patterning in negative tone (crosslinking) the diffusion of reactive species is negligible. Here, not enough reactive species are generated in order to have a further propagation of the crosslinking reaction beyond the initial beam area. However, FE-SPL in the direct ablation regime requires higher exposure doses, which means that release of further reactive species, which diffuse through the resist, has to be taken into account. As found, the overlap of the extended crosslinking reaction in the ablative pattern regime is responsible for the onset of a proximity-like effect. As has also been shown in this section, the propagation direction of the FE-SPL induced crosslinking reaction can be controlled by EBL pre-exposure. This could be a possible extension to the mix-and-match lithographic concept, discussed in section 6.2.

d) Summary:

1. In the negative tone mode (crosslinking of the resist, followed by a subsequent wet development step) no proximity effects are observed. The line width and the line height are the same for separated and dense patterns. No dependency from the line pitch was found.

2. In the positive tone mode (direct ablation of resist material) a proximity-like effect exists. As a consequence, the ablation depth increases with decreasing pitch. Further, the spacing between the exposed line vectors (interline area) becomes removed. Despite that, the line width remains nearly constant as long as the interline area is still present. However, the proximity-like effect leads to a reduction of the pattern transfer budget since the overall line height decreases with decreasing pitch. As found, the proximity effect becomes larger with increasing dose and bias voltage.

3. The proximity in the direct ablation regime is mediated by the crosslinking reaction. Since at the same exposure dose the crosslinking has a significantly larger lateral extension than the ablation, the background of subsequent exposure processes is changed when moving towards dense patterning. In fact, the crosslinked resist causes two different main effects:
   (3-1) The tip-resist spacing is increased, which results in an increased beam diameter. The exposure dose is spread across a larger area.
   (3-2) The ablation rate for crosslinked resist areas is higher compared to pristine resist.

4. By the superposition of EBL pre-exposure (in order to induce a partial crosslinking) and FE-SPL post-exposure, the existence of additional diffusion processes leading to a further spread of the crosslinking reaction was found. It is supposed that the initial reactions release further chemically reactive species, which diffuse through the resist. As observed, along the EBL pre-exposed lines the crosslinking reaction extends, whereas perpendicular to the pre-exposure direction the crosslinking seems to be suppressed. Thereby, with increasing exposure dose and bias voltage the crosslinking extends further in the laterally pre-defined direction. As reactive species the radicals and ions related to the hydroxyl functional group (OH−) are supposed.

5. In order to circumvent the proximity-like effect in the positive self-development tone, the following methods can be utilized:
   (5-1) Development and application of a proximity correction, which adapts the lithographic
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Parameter set continuously during the patterning of dense features. Thereby, the decrease of the bias voltage counteracts the increase of the tip-resist gap, whereas a decrease of the exposure dose compensates the enhanced ablation rates crosslinked resist areas.

(5-2) Application of alternative resist materials, which are not crosslinking by electron exposure. By that, the mediator of the proximity effect is eliminated. Advantageously, a proper resist class was found, demonstrated in chapter 4.4. In particular, the molecular glass resist mixture UBT+C60 shows superior resolution capabilities of sub-10 nm dense patterning without the appearance of proximity effects.

4.2.6 Impact of Changes in Ambient Conditions

a) General: Already during the initial period of STM-based exposure experiments it was recognized that water, both in its liquid and gaseous form, plays a significant role when operating in ambient conditions. It is well known that in ambient conditions a thin water layer is formed at the resist-air interface. Thereby, the water film thickness depends not only on the hydrophilic/hydrophobic properties of the resist but also on the temperature and relative humidity of the environment. Further, depending on the hygroscopic properties of the resist, also water is embedded within the resist film itself.

In general, water works as an additional source for reactive species. Since the MFP as well as the IMFP of the low energy electrons are below the typical water layer thicknesses at ambient conditions, the initiation of reactions already in the water film are most likely (ref. section 2). Here, the generation of highly reactive hydroxyl radicals and ions could be seen as chemical enhancement / amplification of the lithographic reaction. In this context, in earlier works it was reported, e.g. by Zhang et al. [170], that the relative humidity affect the lithographic resolution capability. It was found that degradation processes are enhanced with increasing humidity, which result in a loss of resolution. Already O’Donnell [206] recapitulated for polymeric resists that during irradiation with water involvement degradation processes are favored, which is valid for various lithographic methods. This is attributed to participation of water products in the lithographic reactions. In the case of low energy electron exposure, Kragler [167] has reported that for crosslinking of polymeric resists on days with increased relative humidity the surface degradation of the resist film was enhanced. Hence, all previous works point out an amplification of the degradation with increased water content.

However, no specific investigations were carried out in order to confirm, validate or specify this behavior. Since FE-SPL is carried out in ambient conditions, the investigation of the influence of the exposure environment is of significant importance. In order to extract the impact of environmental changes, a special system modification and related method was conceived. Here, especially the influence of the ambient water was the main focus. In general, the exposure environment is defined by the local partial gas pressures and the temperature surrounding the probe-sample vicinity. Typically, the environment of the processing chamber is controlled, which means that the temperature and relative humidity of the entire chamber volume is regulated at a constant value. As a result of this approach, there is only limited flexibility in order to change the ambient conditions (huge timescale required due to the large chamber volume; parameter range is restricted). To bypass this problem a fast environmental modification system was invented (ref. [325]). The background is explained in detail in section 3.1.5. As a result, the probe-surrounding local environment could be switched between different environmental conditions within the timescale of a few seconds. Since the total chamber environment remains almost unchanged, the operation out of the equilibrium guarantees a fast return to the initial conditions. However, the disadvantage of this method is that the local environmental conditions, which are present at the probe place, cannot by determined (the spatial confinement of the modulation volume is too
In the following experimental part the micro-needle based fast environmental modification system was
mainly applied for modulation of the gaseous water content in the tip-surrounding environment. In
particular, an inert gas (N$_2$) was moisturized by a gas washing bottle, which was filled with water. By
switching from dry N$_2$ to moisturized gas (N$_2$ + H$_2$O) and vice versa, the impact of the gaseous water
in the exposure environment on the lithographic outcome was determined. Thus, only the composition
of the gaseous environment was modulated, but no other lithographic parameter. In the following two
distinct experiments are summarized, a dynamic modulation of the exposure environment within a
single meander pattern (sub-section b), and an environmental modulation which was performed in
between single exposure dose arrays (sub-section c).

b) Dynamic modulation of the exposure environment within a single meander line pattern: Since
the delay time for switching is very low (a few seconds), the change of the local exposure environment
within an individual pattern is feasible. In particular, a meander line with a total length of 2 mm was
exposed using a constant lithographic parameter set. Thereby, every $\approx 1-2$ min the gaseous mixture
was switched in alternating manner from dry N$_2$ to N$_2$ + H$_2$O and vice versa (N$_2 \Rightarrow N_2 + H_2O \Rightarrow N_2 \Rightarrow ...$).

As a result, the exposure environment within a single meander pattern has been changed several times
(typically 9 – 10 cycles). The corresponding results are shown in Figs. 4.2.37 and 4.2.38. In the case
of Fig. 4.2.37 the exposure was carried out on spin-coated 4m1ac68 MG resist using a relatively high
exposure dose ($\Phi_L = 150 nC/cm$), whereas in Fig. 4.2.38 a three times lower exposure dose was used
to expose a PVD prepared cmc4r MG resist. In both experiments the same environmental modification
process was applied. The corresponding changes of the line geometry, extracted by the feature analysis
program, are summarized in Fig. 4.2.39. Based on AFM topographic imaging after different process
steps (ref. 4.1.3), the ablation depth, the remaining resist height, and the oxidation growth height were
calculated, summarized in Fig. 4.2.39-(iii).

The experiments, summarized in Figs. 4.2.37, 4.2.38, 4.2.39, reveal that the gaseous water in the exposure
environment has a significant influence on the lithographic outcome. In particular, a water-enriched
environment amplifies the direct ablation process, whereas in a dry N$_2$ environment the direct ablation
reaction is suppressed. In conclusion, by setting the exposure environment the dominating reaction
can be chosen (positive tone versus negative tone). For example, by setting a dry N$_2$ environment
the complete resist layer is crosslinked, whereas the ablation reaction is almost suppressed. This was
achieved even at higher exposure doses, carried out on 4m1ac68 resist (Fig. 4.2.37, and corresponding
corresponding graphs Fig. 4.2.39-iii, iv). The transition to a moisturized environment leads immediately to a
measurable enhancement of the direct ablation process, in which the crosslinked resist is converted into
volatile degradation products. In consequence, the modulation of the environmental condition could
also initiate a switch of the lithographic regime itself. As found, with increasing exposure dose the
impact of environmental changes is enhanced. The supply of gaseous water leads to an increase of the
line width of all involved lithographic interactions (crosslinking, ablation, buried Si oxidation), which
results in a general loss of the resolution capability. Thus, the experimental results are in agreement
with previous findings [ref. sub-section (a)]. To take up an analogy, increasing the water content has
the same effect as an increase of the exposure dose. Hence, the impact of modulations of the exposure
environment can be described by respective alterations of ablation threshold dose, which is confirmed
in sub-section (c).

Further, the dynamic environmental modulation experiments reveal a hysteresis effect. With increasing
number of cycles (N$_2 \leftrightarrow N_2 + H_2O$) the impact of identical modulations is reduced. In addition, with
Figure 4.2.37: Investigation of the impact of dynamic changes of the gaseous water content within an individual pattern on the lithographic outcome. During patterning of large-scale meander \(12 \times 25 \mu m^2,\) \(250 \text{ nm}\) pitch, total length of \(2.05 \text{ mm}\) by FE-SPL \([U_b = 35 \text{ V},\]
\(\Phi_L = 150 \text{ nC/cm}]\) the probe-surrounding environment was changed in alternating manner between dry \(N_2\) and moisturized \(N_2 (N_2 + H_2O)\) processing gases. The corresponding sections of a meander which were exposed at a constant environment, are labeled accordingly. AFM imaging was carried out directly after exposure (aSPL) as well as after a subsequent wet development step (aWD). For the section plots an averaging over 300 single lines was applied. In the lower part of the image a zoom-in is provided showing the last \(7 \mu m\) of the meander pattern. [Sample: \(\approx 12 \text{ nm}\) thick 4mlac68 resist, spin-coated on top of a pristine Si chip; Probe: electrochemically etched tungsten wire \((r_{\text{tip}} \approx 16 \text{ nm})\).] Scale bar: \(2 \mu m\). A corresponding evaluation of the line changes is given in Fig. 4.2.39-(i-ii).
Figure 4.2.38: Dynamic changes of the gaseous water content within an individual pattern in cmc4r resist (ref. Fig. 4.2.38: 4m1ac68 resist). In contrast to Fig. 4.2.38, the meander was exposed at a lower line exposure dose \( \Phi_L = 50 \, nC/cm \), at \( U_b = 35 \, V \). The same modulation as in Fig. 4.2.38 was applied. AFM topographic imaging was carried out directly after exposure (aSPL), after wet development (aWD), and after an \( O_2 \)-plasma ashing process (aO2PA). A derived sectioning summary (averaged over 600 single line sections) gives detailed information about the change of the composition of the lithographic feature. In the lower part of the image a zoom-in is provided showing in detail the change of the line type caused by the modulation of the exposure environment (dry \( N_2 \rightarrow \) LT3; moisturized \( N_2 \rightarrow \) LT2). [Sample: \( \approx 15 \, nm \) thick cmc4r resist, PVD-coated on top of a pristine Si chip; Probe: electrochemically etched tungsten wire (\( r_{tip} \approx 16 \, nm \))] Scale bar: 2 \( \mu m \). A corresponding evaluation of the line changes is given in Fig. 4.2.39-(iii-iv).
Figure 4.2.39: Evaluation of the line changes which are caused by dynamic variations of the gaseous water content in the exposure environment. Graphs (i-ii) correspond to the measurement of Fig. 4.2.37, whereas graphs (iii-iv) are related to Fig. 4.2.38. In graphs (i-ii, iv) the geometric line data are plotted versus the exposure ambient. Based on AFM topographic imaging after different process steps (ref. 4.1.3), the ablation depth, the remaining resist height, and the oxidation growth height were calculated, summarized in graph (iii).
increasing cycles the transition between the line changes at the switching point occur more abruptly. For example (Fig. 4.2.37), while at the initial switchover between \( N_2 \Rightarrow N_2 + H_2O \) the change occurs gently, with subsequent cycles a more abrupt line transition is formed. The hysteresis effect can be attributed to the added influence of the water film on top of the resist, and depending on the hygroscopic properties of the resist on the absorbed water within the resist. As expected (ref. [379]), the analysis of the Si oxidation process below the resist confirms that a water enriched environment causes a significant enhancement of the oxide growth (Figs. 4.2.38 and 4.2.39-iii, iv).

The same dependency on the environment condition was found for both MG resist types [calixarene (4m1ac68) and resorcinarene (cmc4r)]. The results indicate some minor deviations, e.g. in the case of 4m1ac68 a slightly higher impact onto the same environmental modulation can be measured. Further, the transition between dry and moisturized \( N_2 \) occurs more abruptly in the case of cmc4r. This effect may be attributed to the hydrophobic properties of 4m1ac68 resist films, whereas cmc4r resists are hydrophilic.

c) Modulation of the exposure environment between different exposure arrays in order to trace the shift of the ablation threshold: As unveiled, environmental changes of the gaseous water content could be described qualitatively by a shift of the ablation threshold. In order determine quantitative numbers of the shift, a static environmental modulation experiment was designed, summarized in Fig. 4.2.40. In particular, the same exposure dose test was repeated after different stages of the environmental modification. To prevent dynamic effects, the environmental modification system was switched off during exposure. Imaging by AFM directly after exposure (i, iii, v) and after wet development (ii, iv, vi) were carried out in order to extract the line altitude versus line exposure plots. In the graphs the raw measurement data as well as the oxide growth corrected line altitude data are plotted.

The evaluation of the sequential exposure dose tests, which are carried out after the different stages of environmental modifications, yields the following results (Fig. 4.2.40):

1. Initial exposure dose test at standard environmental chamber conditions (\( T \approx 22^\circC, rh \approx 35\% \)): Up to the maximum dose (80 nC/cm) only a crosslinking process takes place. The onset of the direct ablation reaction was not reached. Thus, the oxidation-corrected height data of the crosslinked features give a constant value, independently of the exposure dose. Thus, the initial ablation threshold ranges above a line exposure dose of 80 nC/cm. Compared to the previous experiments, a significant shift towards higher values is observed. This is a consequence of the initial conditioning of the sample (storage in a dry nitrogen atmosphere).

2. Rerun of the exposure dose test after a 5 min treatment with a moisturized nitrogen process gas flow (\( N_2 + H_2O \)): The direction ablation reaction is already initiated at low exposure doses. In particular, the threshold for ablation is shifted to \( \approx 12 nC/cm \). Compared to (1), when reaching a line dose of 80 nC/cm an ablation depth (oxidation-corrected) of \( \approx 3.2 nm \) is present.

3. Rerun of the exposure dose test after recovery of the initial environmental conditions (\( T \approx 22^\circC, rh \approx 35\% \)): The threshold value for ablation has not returned to its original value of (1). Compared to (2), the threshold dose is shifted towards slightly higher doses (\( \approx 30 nC/cm \)). Despite that, the slopes of the ablation depth versus exposure dose curves of (2) and (3) are equal, which means that the ablation rates have not changed.

d) Conclusions - Impact of the ambient conditions on the lithographic process:

- The onset / threshold for ablation depends on the water content of the exposure environment. This includes the influence of the relative humidity, as well as the water adsorbed at the resist-air
(0) Conditioning of a defined initial state by storage in dry $N_2$ ($\approx 20\ min$)

(1) Initial exposure at standard environmental conditions ($T \approx 22^\circ C$, $rh \approx 35\%$):

(2) Exposure after $5\ min$ of local moisturized process gas ($N_2 + H_2O$) treatment:

(3) Exposure similar to (1), after a recovery time of $\approx 10\ min$:

Figure 4.2.40: Tracing of the ablation threshold shift, caused by changes of the gaseous water content within the exposure environment. For this purpose an identical exposure dose test [$U_b = 30\ V$] was repeated after distinct environmental modification steps [the same probe was used to exclude tip-induced effects], summarized by (1)-(3). Before the initial FE-SPL exposure (1) the sample was stored $\approx 20\ min$ in a dry nitrogen atmosphere to have a defined initial state (0). In order to determine the ablation threshold in an exact way, the line altitude was measured directly after exposure (i, iii, v) and after a wet development step (ii, iv, vi). [Sample: 5 – 6 $nm$ thick cmc4r resist layer, PVD-coated on top of a Si chip]
interface (water layer) and the water absorbed within the resist film itself (depends on hygroscopic properties of the resist). In consequence, the threshold for ablation can be modulated by the probe-surrounding environment.

- As proposed, the environmental modulation of the water content is describable in quantitative manner by a shift of the ablation threshold. Thereby, only the threshold value is altered but not the removal rate itself.

- Thereby, an increase of the gaseous water content induces a shift of the threshold towards lower exposure doses. Thus, a treatment with moisturized process gases promotes the direct ablation, whereas a treatment with dry inert gases suppresses the ablation yielding a sole crosslinking process.

- Since the absorbed and adsorbed water within and on top of the resist influences the lithographic process, too, a hysteresis effect between gaseous treatment and lithographic reaction exists. This means that the ablation threshold is not restored immediately after a turn back to the initial conditions. Instead, some intermediate state is present. In consequence, also the „background and history” of the lithographic sample matter.

- In summary, due to the strong dependence on the exposure environment, so far it is hard to give a fixed threshold value for ablation. Instead, within the threshold definition the environmental conditions should be taken into account (threshold definition at a well-defined environmental condition).

Since the lithographic process is strongly influenced by the humidity level, it is crucial to maintain a stable exposure environment. In addition, also the treatment history of the sample has to be controlled in order to achieve reproducible results. The analysis of further experiments has also proven that there are no indications for a meniscus build-up between tip and sample. An exposure test, which was carried out within a water droplet (not shown here) revealed that a bias voltage of only a few millivolts is sufficient to trigger an immense faradaic current, which by far exceeds the range of the IV-converter unit. Further, the lithographic reaction has been spread across the entire water droplet area - no spatially confined reactions were possible.

As described initially, \( H_2O \) molecules work as a chemical enhancement of the direct ablation reaction. Thus, the findings support that the direct resist removal (ablation) mechanism is based on an oxidative degradation of the resist. During that, volatile products are formed. This is also supported by the resist material investigation, ref. section 4.4. In summary, the probe-surrounding environment has turned out to be another parameter that can be tuned to achieve the desired lithographic interaction. By using a moisturized environment the direct ablation effect is enhanced giving a positive self-development tone pattern. In contrast, dry environments suppress the resist removal yielding a sole crosslinking process (standard negative tone resist patterning). The transfer of the results to FE-SPL exposure in UHV (ultra-high vacuum) would suggest that - as with dry nitrogen - only the negative tone is accessible (suppression of the ablation reaction). Due to the complexity of this task, exposure experiments in UHV could not be conducted within the scope of this thesis.

### 4.2.7 Multi-Pass Line Exposure

Multi-pass exposure strategies are well-known in electron beam lithography (EBL) in order to face heating, charging and proximity problems \([28, 384]\). Multi-pass means that the same line or area is patterned multiple \((n−)\) times. Instead of patterning a feature with a high exposure dose within a single
Figure 4.2.41: Investigation of a multi-pass patterning strategy for enhancement of the ablation depth. The multi-pass patterning strategy was evaluated on two differently thick 4m1ac68 resist films (spin-coated on top of a Si chip), in particular (i) $\approx 30\,nm$ and (ii) $\approx 42\,nm$. The AFM topographic images, which were taken directly after exposure, and the corresponding section graphs display the development of the line profile as a function of the patterning pass. The number of passes were incrementally increased from 1 (single pass exposure) to 5. Thereby, a single pass has a line exposure dose of $\Phi_{L,\,\text{single\,pass}} = 220\,nC/cm$. All exposure passes were conducted by the same probe [tungsten wire, $r_{\text{tip}} \approx 15\,nm$] and with an identical lithographic parameter set [$U_b = 60\,V$]. Graphs (iii) and (iv) summarizes the geometric line alterations as a function of exposure pass (in a second x-axis the accumulated total exposure dose is given).
exposure pass, multiple exposure passes with a lower exposure dose are applied. The total exposure
dose is then defined by summing up the doses of all individual passes. This strategy was already applied
for areal patterning, described in section 4.1.6.

In order to evaluate the applicability of multi-pass strategies for FE-SPL line patterning within the direct
ablation regime, respective experiments were carried out, summarized in Fig. 4.2.41. Here, identical
exposure conditions and parameter sets for each pass were applied. No parameter adjustments in
between the passes were done. As could be seen by the 3D AFM topography images and corresponding
section graphs, Fig. 4.2.41-(i-ii), the ablation depth is significantly increased with increasing number
of exposure passes. The plot of the ablation depth versus dose / pass shows that between the first
and second pass a substantial increase of the ablation rate occurs (≈ 0.081 nm/(nC/cm)). This is an
increase of almost 2 − 2.5 times compared to a single-pass process.

However, the line profile also changes. While the line profile after a single pass is steep, and a nearly
rectangular-shaped edge between ablated and surrounding resist is present, with increasing number of
passes the edges becomes more rounded. Linked with that, also the line width increases respectively.
By plotting the line width versus the number of passes, Fig. 4.2.41-(iv), shows that the line width (at
the FWHM) increases almost linearly with the number of exposure passes. For example, in the case of
the \( d_r \approx 30 \text{ nm} \) thick 4m1ac68 resist an increase of the FWHM width of ≈ 26 nm/pass is determined.

To express the enhanced rounding of the edge with increased passes, the line width at the opening of
the line was measured. An increase of ≈ 97 nm (≈ 86 nm) per pass for \( d_r \approx 30 \text{ nm} \) (\( d_r \approx 42 \text{ nm} \)) were
determined (graphs not shown). The width-dose behavior of the multi-pass patterning strategy differs
considerably from that of single pass processes, wherein the exposure dose is adjusted via setpoint and
current velocity modifications (ref. section 4.2.3). In the case of a single pass exposure process the
width-dose relation is described by a logarithmic function type (the rate of width changes decreases
with increasing dose). Instead, for multi-pass patterning a linear width-dose behavior is present. Most
likely, the flattening of the curve is shifted towards higher passes / exposure doses - further tests are
required to confirm that. In contrast to the ablation process, the width of the buried Si oxidation
process extends only marginally with increasing exposure passes. Linked with that, also the width of
the crosslinked resist areas remain nearly constant.

The observed changes between single and multi-pass patterning can be attributed to the lithographic
back-coupling effect, which is also responsible for the proximity in positive tone patterning (ref. section
4.2.5). In summary, three main findings are relevant:

1. Initial crosslinking of the resist by FE-SPL exposure, followed by ablation;
2. Enhanced ablation rate of already crosslinked resist;
3. Lithographic back-coupling effect, which circumscribes the change of field emission at the probe
   apex with progressing exposure process.

How the changes of the resist are coupled back into the source is described in detail in section 5.3 by
an analytical model as well as by simulations. Briefly summarized, during the initial exposure pass the
dielectric constant of the resist is increased, whereas the resist thickness is simultaneously decreased.
In consequence, the exposure conditions for the subsequent pass are changed. Since all passes have the
same lithographic parameter set, the changed conditions lead to a significant increase of the tip-resist
spacing (in contrast, the overall tip-sample spacing is decreased). As a result, the spread of the beam is
increased giving a broader distribution of deposited energy.

To counteract the back-coupling effect in multi-pass patterning, the lithographic parameter set has to
be adapted in between each pass. Most importantly, after each pass the bias voltage should be reduced
in order to decrease the tip-sample spacing. As a result, also the tip-resist gap is reduced. However, an
evaluation of this strategy is pending and may be part of a follow-up work.
4.3 Spot Exposure and Patterning of Dot Features

In order to define quantum islands (0D objects) with a well defined size, aligned with nanometer-precision within a gap structure, a pixel-based patterning concept is necessary. Therefore, a so called spot exposure process is required. In contrast to vector based patterning, the pixel based routine is a discontinuous exposure process (ref. section 3.1.4). This means that the lithographic exposure process is only activated at previously defined lateral positions. According to FN field emission theory, section 2.4, this could be achieved either by modulation of the tip-sample spacing, or by modulation of the bias voltage. In the following work the focus was placed on the first method. The emission was initiated at a fixed XY scanner position by modulation of the tip-sample spacing. The implemented routines for patterning are explained in more detail in section 3.1.4.

Hereafter, the main results of spot exposure experiments are summarized. Thereby, initial routines and work were carried out by myself. With ongoing progress, further improvements were implemented by my student supervised, M. Budden, described in an associated master thesis work, ref. [222].

4.3.1 The Diversity of Lithographic 0D Structures - An Analogy to Line Features

In general, for investigation and analysis of dot (0D) features, the same methodology and software as for the 1D-line features can be applied. Therefrom, the same measurement limitations arise. In analogy to the 1D line features, also the same basic lithographic interactions, and their superposition take place. Thus, the patterning regimes are identical. A graphical abstract summarizing the different 0D features, ordered by ascending point (spot) exposure dose, is shown in Fig. 4.3.1.

(a) Patterning of dots in negative tone (crosslinking) and positive tone (ablation) regime:

In analogy to the line features, at low point exposure doses a crosslinking process of the resist is initiated. The negative tone regime leads after a subsequent wet development step (aWD) to the appearance of single dot structures. This case is schematically drawn in Fig. 4.3.1-(a). A corresponding negative tone dot exposure test array is shown in Fig. 4.3.2. 27 × 27 individual dots with a spacing of 250 nm were defined in a ≈ 5 nm thick cmc4r MG resist film. AFM topographic imaging was done after wet development. Within the array the point exposure dose was varied. With increasing exposure dose the dot diameter increases accordingly, summarized by Fig. 4.3.4-(a) graph. In agreement with the line dose-line width dependency, the dependence of the point exposure dose on the dot diameter is describable by a logarithmic function type. This kind of function can be derived from a Gaussian beam model with fixed threshold values for the lithographic interactions, explained in detail in section 5.1. As expected, the smallest dots are obtained at lowest dose.

Also here, similar to the vector-based line exposure process, the minimum applicable point exposure doses are limited by the system. Thereby, in order to measure the exact point exposure dose the emission current was recorded during exposure. The integration over dwell time yields the total point exposure dose. A custom-built routine was implemented, described in [222]. Unfortunately, the current signal could be recorded only with a sampling rate of 2 kHz, which give a resolution of 0.5 ms. In consequence, the minimum applicable dwell time is limited to that value.

However, even at lowest applicable doses the dot features are clearly resolved (Fig. 4.3.2). With the actual setup the smallest detectable dots were achieved at a point exposure dose of 1.89 fC (at 30 V
bias voltage). This corresponds to an amount of less than $1.2 \times 10^4$ electrons per single dot. A diameter (FWHM) of the corresponding dot, Fig. 4.3.2-(AFM zoom-in image and section graph), of $\approx 25 \, \text{nm}$ was measured by AFM. When considering the measurement error induced by the tip-sample convolution ($r_{\text{tip}} \approx 10 \, \text{nm}$), a real dot diameter of smaller than 10 nm can be estimated, schematically drawn within the section graph, Fig. 4.3.2, by red dotted lines. The estimate of how many electrons per single molecule are responsible for the reaction results in a value of approx. 7 electrons per single calixarene molecule for crosslinking (assumptions: $1.2 \times 10^4$ electrons per single dot; radius and height of the dot of approx. 5 nm; size of the molecular units of the resist: 0.75 nm). Derived from the fit of the diameter versus dose plot, Fig. 4.3.4-(i), a spot dose threshold for crosslinking of $\approx 1.7 \, \text{fC}$ can be extrapolated. However, exposure experiments with such low doses are currently not possible due to the hardware limitations. Similar to the vector-based line patterning, also in spot exposure no contrast curve of crosslinking process can be measured (this could be a task of an upcoming work).

In standard EBL (50 kV) minimum dot diameter of $\approx 12 \, \text{nm}$ was demonstrated in calixarene resist by Fujita et al. [182]. A corresponding point exposure dose of $1 \times 10^5$ electrons/dot for calixarene derivatives was determined. This dose is 10 times larger than that required for FE-SPL crosslinking. In comparison, the threshold spot dose for crosslinking in FE-SPL is even lower than the EBL threshold dose for the high sensitivity positive tone PMMA polymeric resist ($5 \times 10^4$ electrons/dot, minimum dot sizes of $\approx 20 \, \text{nm}$, ref. [182]). In consequence, this means that the FE-SPL based low energy electron exposure is more efficient than the EBL based high energy electron exposure processes. Thereby, the
Figure 4.3.2: Patterning of single dots in negative tone (crosslinking) within a \( \approx 5 \text{ nm} \) thick cmc-dr MG resist. The AFM topographic image series, which was taken after a wet development step, shows a large dot array consisting of \( 27 \times 27 \) individual dots [lateral spacing: \( 250 \text{ nm} \)]. Within the array the point exposure dose was modulated, whereas the bias voltage was kept constant \( [U_b = 30 \text{ V}] \). The smallest dots achieved within the array have a diameter (FWHM) of \( \approx 25 \text{ nm} \). The estimation of the real diameter by correcting the tip-sample convolution (Eq. 3.15) yields a value of \( \approx 7 \text{ nm} \) (marked in the section graph by red dotted line). To create this dot a point exposure dose of \( \Phi_D \approx 1.89 \text{ fC} \) was applied.

spot exposure dose in the fC-range for low energy electron exposure is in agreement with a theoretical study of Fujita et al. [235]. Here, in accordance to Bethe’s law (ref. section 2.2) a decrease of the electron energy results in an enhanced sensitivity - under the assumption that the energies fit to the appropriate energy bands, which are responsible for the lithographic interactions.

In accordance with the vector-based line patterning results, at a particular point exposure dose the onset of the direct ablation reaction is reached resulting in a positive tone development-less dot patterning. This is schematically drawn in Fig. 4.3.1-(b). A corresponding experimental result of a dot array is shown in Fig. 4.3.3. Imaging by AFM was done directly after exposure. By modulation of the dwell time a wide range of diameters could be addressed. Hole diameters from \( 30 \text{ nm} \) up to \( 350 \text{ nm} \) were induced in \( \approx 38 - 40 \text{ nm} \) thick 4m1ac68 MG resist. Thereby, increased dwell times result in larger point exposure doses (the emission current was measured and integrated over time in order to determine the exact exposure dose values) yielding larger hole diameters.

The analysis of the hole diameter versus point exposure dose, summarized in plot 4.3.4-(ii), shows that the same general logarithmic function type can be applied as for the crosslinking process (plot 4.3.4-i). Thus, the same correlation between crosslinking and ablation, which was already observed for the vector-based line patterning process, is valid also for the spot exposure. Thereby, the threshold point exposure dose for ablation is approx. 2 – 3 orders of magnitude larger than for the crosslinking process. Threshold doses in the range of \( 100 \text{ fC} \) up to several \( \text{pC} \) were measured. As shown for the line patterns, due to the influence of the exposure environment, especially of the water content / humidity (ref. section 4.2.6), no fixed threshold values can be given. In the given example, Fig. 4.3.4-(ii), an ablation threshold of \( 1.2 \text{ pC} \) can be extrapolated. This is equivalent to \( \approx 7.5 \cdot 10^6 \) electrons/dot. In order to achieve a complete removal of a single calixarene molecule (and conversion into a volatile
end product), in average $\approx 350 - 1000$ electrons per individual molecule are required (estimated from the first hole feature which appears closely above the threshold value at $\Phi_D = 2\, pC$; a characteristic dimension of a single molecule of 0.75 nm was assumed). This value is 50 – 150 times larger than that for the crosslinking reaction. However, since the AFM measurement errors become larger with decreasing feature size, ref. section 3.3.2 (it is not clear if the measured depth of the holes is limited by the tip or if this is the real depth $\Rightarrow$ only at larger diameter a reliable depth value can be determined), the electrons/molecule information represents only a rough estimation.

(b) Superposition of crosslinking and ablation - The formation of doughnut structures:

Similar to the lines patterned in development-less positive tone mode, a wet development of the hole pattern reveals the crosslinked resist areas surrounding the holes. Whereas for the 1D case a double crosslinked line is generated (ref. section 4.1.5), in 0D a doughnut-like rotational symmetric structure is formed. This is schematically drawn in Fig. 4.3.1-(b; after wet development: aWD). A corresponding experimental proof is given in Fig. 4.3.5. The inner and outer diameter of the doughnuts correspond to the different lateral extensions of the ablation and crosslinking reaction, respectively. The correlation between inner and outer diameter as a function of point exposure dose is summarized for a complete spot exposure test array in Fig. 4.3.6. Both diameter versus dose dependencies are described by a logarithmic function type. In accordance to the results found for the line patterning (section 4.2.3), a constant shift of $\Delta w = w_{CL} - w_R \approx 75\, nm$ between inner and outer diameter is present (Fig. 4.3.6-ii). However, for low exposure doses close above the ablation threshold deviations from this are noticeable. In particular, the difference between inner and outer diameter decreases (Fig. 4.3.6-i). The low spot doses lead to the formation of very small doughnuts structures as shown in Fig. 4.3.5. Typical inner diameters of 10 nm, which are surrounded by a ring of crosslinked material with diameters of 30 nm are present. The smallest inner diameters achieved are 8 nm. Since the tip radii are in the same range as the formed structures, the AFM measurements are linked with increased limitations and errors. Hence, AFM delivers no reliable information about the clearance of the smallest doughnut features. Based
Figure 4.3.4: Plot of the dot diameter for negative tone (i) and positive tone (ii) lithography as a function of the point exposure dose. The dot diameters were extracted from AFM topographic images (diameter not convolution-corrected). The diameter of the crosslinked dots (negative tone) were determined after wet development (aWD). In the case of positive tone lithography the diameter of the holes was measured directly after exposure (aSPL). [Sample: $\approx 6-7\,\text{nm}$ cmc4r resist, coated on top of a Si chip]

Figure 4.3.5: Individual doughnut structures formed by superimposed crosslinking and ablation in the spot exposure mode. SEM (i) and AFM topographic imaging (ii) were done after a wet development step. The doughnuts created in the $\approx 6\,\text{nm}$ thick cmc4r resist have typical inner and outer diameters of $\approx 10\,\text{nm}$ and $\approx 30\,\text{nm}$, respectively. The smallest inner diameters achieved are $8\,\text{nm}$. The AFM image and section graph display raw data (no convolution correction was applied).
Figure 4.3.6: Plot of the inner and outer diameters of the doughnut features as a function of point exposure dose. The diameters were measured after a wet development step by AFM. Thereby, the outer diameter of the doughnut corresponds to the crosslinking width, whereas the inner diameter is the width of the ablation process. A linear (i) as well as a semi-logarithmic (ii) plot are shown. In accordance to the line features (section 4.2.3), a logarithmic function type is utilized. [Sample: \( \approx 7 - 9 \text{ nm} \) thick 4m1ac68 MG resist, spin-coated on top of a Si chip]

on the SEM measurement, a clearance to the bottom layer can be assumed, which is favorable for a subsequent pattern transfer process.

(c) Additional deposition of carbonaceous structures:

At large exposure doses an additional deposition effect within the cleared exposure center was observed. This scenario is outlined in Fig. 4.3.1-(c). A corresponding spot exposure example, which was patterned by bias pulse at a fixed tip-sample spacing, is shown in Fig. 4.3.7. Within the ablation center a relatively tall dot appeared. Comparable deposition effects were observed also in the case of vector-based line patterning at high line exposure doses, described in detail in my previous work [51]. The investigation of the composition reveals that the additional material is neither a formed oxide nor crosslinked resist. So the conclusion is reasonable that these are carbonaceous deposits. Most probably, the gaseous source therefore is provided directly by the degradation process. In related studies which have investigated SPL-induced deposition effects, e.g. by Garcia et al. [128], a field-induced splitting process is supposed. The allocation to this effect is evident since the deposition rate increases linearly with increasing bias voltage (deposition rate increase of \( 0.29 \text{ nm/V} \)), summarized in Fig. 4.3.8. In contrast, the oxide growth at the bottom Si layer remains almost constant. Further, with increasing bias voltage also the impact of modulations of the exposure dose on the structure height is increased for the deposition effect (Fig. 4.3.8). As found, the dot height increases almost linearly with the spot exposure dose (ref. [222]).

In summary, the final lithographic outcome (Fig. 4.3.7) is describable by a superposition of single effects, in particular of a crosslinking of resist (green), a direct ablation of resist, an oxidation of the Si substrate (red), and deposition of carbonaceous material (dark blue). Since in the typical operation regimes of (a-b) the exposure doses and bias voltages are significantly lower, the deposition effect in practical positive and negative tone patterning has only minor relevance. Thus, this effect is not further investigated in this work.
Figure 4.3.7: AFM image and section showing an additional deposition process within the ablation center (ref. Fig. 4.3.1-c). AFM topographic and phase contrast imaging were carried out directly after exposure (scale bars: 1 µm). Within the section graph the composition of the induced feature is mapped. The feature was induced by a bias voltage pulse (+80 V) at a fixed tip-sample spacing. [Sample: ≈ 10 nm cmc4r resist film, spin-coated on top of a pristine Si chip]

Figure 4.3.8: Comparison of growth height versus bias voltage dependency of the Si-oxidation and the C-deposition process. Therefore, the heights of the central elevation of the features are measured by AFM after wet development and after O2 plasma ashing. In the determination of the feature height an averaging of heights, which were achieved at different exposure doses, was carried out. As a result, the error bars in the plot reflect the impact of exposure dose modulations on the variation of the feature height (at different bias voltages). More details of this investigation are provided in ref. [222].
4.3.2 Proof-of-Concept of Different Spot Exposure Strategies - From a Static (DC) towards a Dynamic (AC) Distance Modulation

The previously shown dot arrays were patterned by a static (DC) distance modulation scheme, in which the movement of the Z-piezoscanner was utilized for modulation of the tip-sample spacing (ref. section 3.1.4). Thus, the probe is approached to the sample surface until a pre-defined field emission current is reached. After a specified dwell time the probe is retracted. The disadvantage of the method is that the mechanical properties of the system restrict the lithographic parameter space. In particular, the approach and retract velocity, as well as the minimum current setpoint and dwell time are limited by the mass inertia of the system. In consequence, the point exposure dose depends also on the vertical tip velocities and on the reaction time of the current setpoint trigger. If the approach velocity is too low, the setpoint is reached only slowly. However, too high velocities lead to a current overshoot. In both cases an overexposure takes place. In consequence, the approach velocity must be tuned to the current setpoint.

In conclusion, the DC mode is neither an ideal solution for spot exposure at low doses, nor it is suited for a pixel-based patterning routine (movement of the entire probe head limits the approach/retract velocities). Alternatively, the tip-sample spacing can be modulated in a more dynamic manner by using the resonant cantilever oscillation (ref. section 3.1.4). Within this so called „AC” method the emission process is only activated at the bottom reversal point of the tip, which is the smallest tip-sample distance during the cantilever oscillation process. Instead of defining a real dwell time, the number of oscillation cycles determines the total point exposure dose. Thus, by summing up the incremental exposure events the targeted point exposure dose is reached.

Figure 4.3.9: Demonstration of the pixel-based patterning in positive tone (direct ablation) by an oscillating cantilever feedback. The pattern is imaged directly after exposure by AFM. A soft cantilever was forced to oscillate off-resonance during a vector-based line patterning process. This has resulted in a dynamic modulation of the tip-sample spacing. The movement path of the tip for the first line of the L-shaped feature is drawn by a thin black line. The spacing of the dots along the line were modulated by the integral gain of the current feedback loop. This slows down the feedback (⇒ increase of the spacing) or accelerates it (⇒ decrease of the spacing). [Sample: ≈ 8 – 10 nm thick cmc4r resist; Probe: tungsten coated cantilever; Bias voltage: $U_b = 30$ V]
The proof-of-concept of this method is given in Fig. 4.3.9. Here, the mechanical instability of the cantilever system in an electric field was utilized in a well-aimed way (bistable system, ref. theory section 3.1.7). For this purpose a soft cantilever with a low spring constant of \( k \approx 3 \text{ N/m} \) was used. The cantilever was forced to oscillate by a mismatch between spring constant, current feedback loop integral gain (set too high in order to provoke an overshoot) and current setpoint. In contrast to previous experiments the tip-sample distance modulation was not achieved by a defined z-piezoscanner movement, but by means of an off-resonance cantilever oscillation. As a result, instead of line patterning a single pixel exposure along the tip path is achieved. In the example approx. 15 nm holes were formed by each individual exposure process. Thereby, a single pixel exposure event corresponds to a point exposure dose of \( \approx 600 \text{ fC/event} \). For an entire degradation of a single molecule into volatile compounds a value of \( \approx 500 \text{ electrons / molecule} \) can be estimated. This is in agreement with previous results.

Since the bandwidth of the actual current feedback loop is limited, a minimum exposure time of \( \sim 5 \text{ ms} \) can be set. Further improvements of the system, and the implementation of advanced feedback regulation algorithms are required to enable a later application. However, this is beyond the scope of this work.

4.4 Tailored Resist Materials Beyond Calixarene

The focus of this chapter is placed on the investigation of the influence of the resist material on lithographic process. The objectives are to:

1. Understand the impact of functional groups;
2. Develop advanced resist materials tailored to the specific lithographic mechanisms;
3. Utilize differences in ablation in order to achieve a selective removal of resist components.

The results of this chapter represent a shared work, which was carried out in teamwork with Y. Krivoshapkina (the same department). The work was distributed as follows: Whereas I was focused on the concept, the investigation of the general lithographic phenomena, and on the analysis of the lithographic outcome, Y. Krivoshapkina examined the chemical background of the resist. The counterparts are described in frame of her PhD thesis, ref. [362]. The novel molecular glass resists, which were investigated in this chapter, have been synthesized by Dr. Christian Neuber and team from University of Bayreuth (UBT) in frame of the SNM project [10]. Further, the PVD preparation of the resist films was conducted at the University of Bayreuth. Some of the results were published by joint works, refs. [225, 226]. The block-copolymer (BCP) thin films, which were examined in the latter part, were provided by Dr. Deirdre Olynick and team (Molecular Foundry, Lawrence Berkeley National Laboratory, USA).

4.4.1 Investigation of Single Component Molecular Glass Resists - The Effect of Different Functional Groups

a) Target and Methodology:

The molecular glass (MG) resist can be tailored to match the certain requirements of the targeted lithographic mechanism. For this purpose different functional groups or further resist components can be introduced. In a first step the impact of various chemical groups on the lithographic outcome have to be studied in order to get a clearer idea about the chains of action. In particular, it should be determined whether the lithographic effect is resist-specific or non-specific. In a second step it should be investigated how the resist material can be tuned providing a better lithographic and pattern transfer
capability. Here, different molecular glass resist materials were selected for FE-SPL exposure tests. The resists were synthesized by UBT and coated on top of Si chips by a physical vapor deposition (PVD) process (section 3.2.2). A list of the evaluated MG resist materials is given in the Appendix, section A.2. In an initial step the surface morphology of the prepared resist films was investigated. All resists, which do not fulfill the following criteria have been rejected:

(i) Formation of amorphous thin films without any crystalline parts;
(ii) Homogeneous surface morphology without segregation and a low defect density;
(iii) Capability of PVD preparation of thin films with at least a thickness range of $5 - 20\, \text{nm}$;
(iv) Low surface roughness, which is less than $0.7\, \text{nm}$, and ideally better than $0.5\, \text{nm}$;
(v) Long term stability - no aging and recrystallization;
(vi) No evidence of delamination and dewetting from substrate during different processing steps.

A complete list summarizing the AFM surface morphology measurements is provided in the Appendix, section A.4. For initial lithographic investigations an MG resist with a fluorine functional group (UBT7) and two MG resists without any functionalization (UBT8, UBT9) were chosen. The molecules for UBT7 and UBT8 resists have a propeller shaped spiro core. In contrast to UBT8, the benzene groups of UBT7 were perfluorinated. In the case of UBT9 amide linkages (able to form hydrogen bonds) were introduced between the spiro core and the benzene substituents to have strong intermolecular interactions. The particular molecular design was carried out by UBT in order to achieve stable aromatic units (ref. [225, 226]). Within the lithographic benchmark the resorcinarene based cmc4r MG resist was applied. This MG resist type contains hydroxyl ($\text{OH}^-$) functional groups.

Next, the influence of the molecular glass resist material on the FE-SPL patterning process was examined. The same methodology and analysis methods as established for the calixarene MG resists were applied. To enable a direct comparison of the results, identical exposure tests with the same probe were conducted. AFM imaging after each process step was performed to determine the amount directly removed and of crosslinked resist. To verify the reproducibility of the process, after each material test the same exposure was repeated on the cmc4r resist sample.

b) Lithographic Comparison of Fluorine-, Hydroxyl-, and Non-Functionalized MG-Resist Types:

The results of the exposure dose tests for the three different types of MG resists are summarized in Figs. 4.4.1 (UBT7: fluorine-functionalized spiro MG resist), 4.4.2 (UBT8: none-functionalized spiro MG resist) and 4.4.3 (UBT9: amide-linkage added spiro MG resist). In Fig. 4.4.1 the composition of induced features for the 3 MG resists are compared by section graphs. For every resist type two L-shaped corner features are shown, which were exposed at different line exposure doses (FT20: $\Phi_L = 50\, \text{nC/cm, 25\, nm hp}$; FT17: $\Phi_L = 400\, \text{nC/cm, 100\, nm hp}$). The line geometry versus exposure dose characteristics for each resist is given in Fig. 4.4.2. A direct comparison of the MG resist types is provided in Fig. 4.3.9.

As revealed by the exposure comparison, the different MG resist types have different exposure characteristics. This confirms the initial concept that also in FE-SPL the lithographic response can be tailored by functional groups. The comparison of the exposure characteristics of UBT7 and UBT8, which solely differ in the fluorine end-groups, point out that only the F-termination is responsible for a transition of the lithographic tone. In the case of UBT7 a sole resist crosslinking reaction is present. Within the investigated dose range no ablation reaction could be induced (note: threshold for ablation may be located above the tested dose range). Thus, an F-termination led to a suppression of the
Figure 4.4.1: Series of section graphs through line patterns defined in different MG resist types. As a result, the composition of the generated lithographic feature as a function of resist type is shown. The same methods as developed for the calixarene MG resist were applied (ref. Figs. 4.1.8 and 4.1.13). By AFM imaging after each process step [after exposure (aSPL); after wet development (aWD); after resist removal by O2 plasma ashing (aO2PA); after oxide removal by a HF-dip (aHF)] the section graphs have been created. The different areas of interaction are identified as follows: pristine resist removed during WD (light blue); crosslinked resist (green); oxide (red).
Figure 4.4.2: Comparison of the exposure characteristics of the different MG resist types. In the graphs the thickness of the ablated and the crosslinked resist is plotted as a function of the line exposure dose. The ablation depth is measured directly after exposure (positive tone, development-less mode; colored blue), whereas the crosslinking height is determined after wet development (negative tone mode; colored green). All measurements were done by AFM. The oxidation effect was subtracted from the measurements (ref. Figs. 4.4.1 and 4.4.3). All tests were carried out by the same probe at a fixed bias voltage \((U_b = 35 \text{ V})\). The thickness of the resist films is in the range of \(\approx 9 – 15 \text{nm}\).
ablation. Most likely, due to the induced fluorine radicals (fluorine has the highest electronegativity and is highly reactive) a strong resist network is formed during crosslinking, which is comparable to that induced by electric field SPL on fluorocarbon resists (ref. Rolandi et al. [131]). Also Ito et al. [205] pointed out that fluorine-groups strongly enhance the crosslinking tendency in standard optical microlithography. In consequence, the formed fluorinated network blocks the direct ablation reaction. Hence, an F-functionalization led to a sole negative tone resist behavior (subsequent wet development step required). These findings are supported by another fluorinated MG resist, where the same general behavior was measured (UBT12, not shown here, ref. Appendix A.2). The width versus dose characteristics for the UBT7 resist is comparable to that of the cmc4r MG resist (Fig. 4.4.3-iii). Thus, the negative tone resolution capability of UBT7 is comparable to that of the cmc4r resist. In contrast to the calixarene (cmc4r) resist, no ablation reaction is superimposed giving the possibility of sole negative tone patterning at enhanced dose ranges.

Figure 4.4.3: Direct comparison of the exposure dose characteristics for the different MG resist functionalization. (i) Directly removed resist thickness plotted as a function of the line dose (positive tone, development-less patterning). A common linear fit for the ablation characteristic is applied. (ii) Line width of the directly ablated line plotted versus line dose. (iii) Line width of the crosslinked features plotted as a function of the line dose. (iv) Plot of the total oxide thickness, which is grown at the Si-resist interface, as function of exposure.

The non-functionalized spiro MG resist (UBT8) yields a sole positive tone, development-less FE-SPL exposure characteristics. Since the functional groups for crosslinking are missing, no sufficient crosslinking network can be formed. In contrast, even resists with only aromatic compounds, like UBT8, enable a direct patterning by ablation. The same was found for the amide-linkage added spiro MG
resist UBT9. In conclusion, the direct ablation mechanism is not demanding any functional groups. The comparison of the direct ablation characteristics of the different resist types, summarized in Figs. 4.4.2 and 4.4.3-(i, ii) reveal that only minor differences are present. Hence, for the ablation depth versus dose a common linear fit can be applied. This means that the ablation rate ($\approx 0.0253 \text{ nm/(nC/cm)}$) is independent of the resist functionalization (only exception: F-terminated resist $\Rightarrow$ here, no ablation occurs).

As discussed in section 4.4.2, stand-alone UBT8 resist is not stable to yield uniform lines. Thus, the line width versus dose shows no clear trend. The comparison of the other width-dose behavior in ablation shows that the widths for the UBT8+C60 and the UBT9 resists are almost identical. Benchmarked against calixarene, the line widths at higher exposure doses are slightly smaller. With respect to the buried oxidation process, summarized in Fig. 4.4.3-(iv), in all cases a self-limiting growth is observed. The non-functionalized aromatic resist types exhibit the lowest bottom layer oxidation. The oxidation in the calixarene MG resist case is slightly higher. This could be attributed to the resist-specific $OH^−$-groups, which act after release as additional reactive species. The $F^−$-terminated resist UBT7 yields the largest growth at the bottom Si layer. Since the feature heights after exposure and after plasma ashing are identical, an enhanced oxidation process takes place (ref. Fig. 4.4.1). Thereby, no hints for an overlaid expansion of the resist due to the crosslinking process were found. Further investigations are necessary to find out the reason the enhanced oxidation (could be part of a follow-up investigation).

c) Summary:

Thus, neither the introduction of strong dipole moments, provided by the amide groups (UBT9), nor the absence of $OH^−$-functional groups (UBT8) have a strong influence on the ablation process. Since the strong dipole moment of the amides introduces absolutely no changes in ablation, a pure electrostatic extraction of the resist molecules, as proposed by [156] and [38], are unlikely. In this context, it is demonstrated that also pure aromatic resist types - without dipole moments - could be patterned in positive, development-less tone. Instead, chemical reaction paths are plausible. Here, an oxidative degradation of the molecules forming volatile end products is most likely. Only an $F^−$-termination introduces an effective blockade against the direct resist removal interaction. Thereby, the fluorinated network inhibits the oxidative degradation into volatile fragments (within the tested dose and bias voltage range). In terms of the crosslinking process, the functionalization of the resist has a strong impact: Without $OH^−$ and $F^−$-groups no sufficient crosslinking can be achieved. The $F^−$-termination results in a strong crosslinked network, which is not able to be directly removed by the FE-SPL interaction. Among them, the $OH^−$-functional groups yield a crosslinking process, but still allow an effective ablation.

In contrast to the calixarene based MG resist, the investigated novel MG types are only suited for a single patterning tone. Thus, depending on their molecular functionalization a lithographic mechanism is favored. Only the hydroxyl groups of the calixarene / resorcinarene MG resist enable a patterning in both tones as well as a switching and superposition of the lithographic mechanisms. Further, the experiments have shown that the hydroxyl groups in calixarene MG resist are responsible for the crosslinking process. In contrast, the ablation mechanism does not inevitably require $OH^−$-groups. Even in non-functionalized resist systems an ablation reaction is possible - with the condition that the environment provides the reactive species (ref. section 4.2.6).

Since in the non-functionalized resist systems, e.g. UBT8 and UBT9, the crosslinking process is absent, also the proximity effect in ablation (ref. section 4.2.5) is suppressed. This could be seen already within
Figure 4.4.4: Comparison of the resolution capabilities in positive tone (ablation) for a single component MG resist, in particular UBT8 (a), and two-component MG resist achieved by co-evaporation of UBT8 and C60 (ratio 1 : 1) (b). Both corner features were patterned at identical lithographic parameter sets [$U_b = 35 V; \Phi_L = 31 nC/cm$] and by the same probe. In both cases a resist layer of $\approx 12 - 14 \text{nm}$ were PVD-coated on top of a Si chip. AFM imaging was done directly after FE-SPL exposure. Scale bars of the AFM topographic images: 200\text{nm}.

the single section graph in Fig. 4.4.1. Compared to the calixarene MG resist case, Fig. 4.2.32, the dense patterning causes no changes of the line geometry, neither in depth nor in width. However, the surface mobility of the small UBT8/9 molecules results in a rather soft and smearing resist layer, which significantly limits the resolution and line quality (high LWR). The solution of this problem is deduced in the next section.

### 4.4.2 Two-component Molecular Glass Resists - Promising Mixtures with Fullerenes for Highest Resolution Capabilities

Due to the inhibition of the crosslinking process, the foundation of the proximity effect in the positive tone is suppressed. In consequence, highest resolution capabilities are expected. So far, in the single component MG resist types (UBT8 and UBT9) it was not possible to achieve a high resolution, e.g. of sub-20 nm, with a sufficient quality. Despite the high thermal stability and the extreme high glass transition temperatures (for UBT8 and UBT9: 173 °C), the intermolecular network of the ultra-thin resist films is rather weak. This leads to a distinct surface mobility of the single molecules (the properties of thin films are rather different than that for bulk materials; in the case of thin films the properties depend strongly on the interfaces). This causes a blurring and refilling of the ablated line features. This effect is displayed in Fig. 4.4.4-(a), in which a 25 nm hp dense line/space pattern is defined by ablation in 10 – 14 nm thick UBT8 resist. As a result, the line edge roughness is increased and several lines are bridged. In fact, the pattern is not resolved. This also explains the distorted line width versus dose characteristics for the UBT8 resist, which is shown in Fig. 4.4.3-(ii).

To exploit the full potential of the novel MG resists, the surface diffusion capability of the resist molecules has to be significantly constrained. The next focus was placed on the application of material mixtures in order to strengthen the intermolecular resist network. Since amorphous resist films are targeted, any crystalline order has to be prevented. For resist film preparation with distinct mixture
Figure 4.4.5: AFM sections through a line pattern defined in UBT8+C60 (1:1) resist by ablation. In accordance with previous results, Fig. 4.4.1, the composition of the features is displayed: Pristine resist removed during WD (light blue); Resist left behind after WD (light green); Grown oxide (red). AFM imaging was carried out after distinct process steps [after FE-SPL exposure (aSPL), after wet development (aWD), after resist strip by O2 plasma ashing (aO2PA), after removal of the oxide by a HF-dip (aHF)]. [Bias voltage $U_b = 35$ V; Sample: UBT8+C60 resist of $\approx 12 - 14$ nm thickness prepared by PVD co-evaporation on top of a pristine Si chip]

ratios a PVD-based co-evaporation process, ref. section 3.2.2, was applied. As a potential partner of the co-evaporation process the Buckminsterfullerene $C_{60}$ was chosen. The introduction of the $C_{60}$ molecule was mainly due to the increase of plasma durability. As a side effect, an enlarged process window for the pattern transfer is yielded. As discussed in a joint study (collaboration of TUIL with UBT, Imec and Oxford Instruments in framework of the SNM project) an outstanding etching durability of $C_{60}$ was demonstrated, published in [225, 226]. Thus, the fully aromatic spiro UBT8 resist was co-evaporated with the Buckminsterfullerene $C_{60}$ in a 1:1 ratio, which should give a dense packaging. As expected, by the integration of the $C_{60}$ the etching durability is doubled (etching rate decreased about the factor 2). Compared to standard resists an improvement of 3 times is achieved by MG material mixtures. No resist alteration, e.g. cracking, at low temperatures is observed, which makes them ideal candidates for plasma etching at cryogenic temperatures, ref. section 7.2. In terms of surface morphology the UBT8+C60 resist forms very smooth, amorphous, and long term stable films. A surface roughness of $< 0.3$ nm RMS is provided, which is similar to that of calixarene MG resists. Knowing that sole $C_{60}$ films tend to aggregate and to crystallize (ref. Appendix, section A.4), it is remarkable that in the case of co-evaporation these processes are completely suppressed.

The FE-SPL exposure experiments on the UBT8+C60, summarized in Fig. 4.4.3, show that the same patterning behavior as for the single component resist UBT8 is present. In this context, also the buried oxidation process seems to be unchanged compared to the single component variant. Thus, the incorporation of fullerene does not influence ablative patterning characteristics. As it seems, the patterns are stabilized by the $C_{60}$ molecule, outlined by the AFM topographic image comparison of Fig. 4.4.4. Here, a 25 nm hp dense line/space pattern is exposed once in a single component UBT8 resist (a) as well as in a two component co-evaporated UBT8+C60 resist (b). The same probe and identical lithographic parameter sets for exposure are used. For the MG resist mixture with $C_{60}$ the achieved lithographic resolution is enhanced and the line quality (LWR, LER) is obviously improved. Further, due to the absence of a crosslinking mechanism the proximity effect is suppressed. This is revealed also by the section graphs, Fig. 4.4.5. Despite the dense patterning, the neighboring lines
have no influence on each other. Following that path, 10 nm hp dense line/space patterns have been demonstrated by Y. Krivoshapkina in UBT8+C60 MG resist. These results should be reported in an upcoming joint publication.

After wet development a grafted resist layer with a thickness of \( \approx 2 \) nm was left behind, colored in the section graphs by light green (Fig. 4.4.5). By an \( O_2 \) plasma ashing process the grafted layer is removed. Since this layer is not observed for the single component UBT8 resist, it is assumed that the grafted layer is formed mainly by the \( C_{60} \) molecules. To reveal the remaining issues of mixed MG resist films, further investigations are underway by Y. Krivoshapkina [362].

### 4.4.3 Beyond MG Resists: The Patterning of Block-Copolymer Materials

The combination of bottom up and top down lithographic strategies is seen as a promising approach to overcome the throughput-resolution trade-off (ref. section 6.2.1). At present, the directed self-assembly of block-copolymer (BCP) thin films is a promising attempt toward that. Block-copolymers consist of two or more different monomer units, which are connected serially by covalent bonds. By microphase separation highly regular structures with nanometer periodicity can be formed by self-assembly across large areas. This capability has received widespread attention, reviewed for example by [385, 386, 387].

![Figure 4.4.6: Summary of the concept for a localized selective patterning of block-copolymer (BCP) materials.](image)

However, additional lithographic methods are required to transfer the BCP structure into the target design. The general concept is summarized in Fig. 4.4.6, whereas a proof-of-concept is shown in Fig. 4.4.7. The concept envisages that the differences in ablation can be exploited in such a way that one material / block is removed with a high selectivity with respect to the other material / block. That this can be basically achieved was already demonstrated by the comparison of the ablation between crosslinked and pristine (unexposed) calixarene resist (ref. section 4.2.5).
Figure 4.4.7: Proof-of-concept of material (block) - selective ablation, demonstrated by FE-SPL exposure of a polystyrene-b-polyvinyl pyridine (PS-b-PVP) block-copolymer (BCP) film. The PS-b-PVP film was spin-coated on top of a Si chip. Subsequently, for phase separation annealing was carried out. As a result, alternating lines of PS and PVP are formed (pitch $\approx 20 \text{nm}$). In a next step, FE-SPL exposure was done at $U_b = 60 \text{V}$ and $\Phi_L = 300 \text{nC/cm}$ patterning a L-shaped corner meander feature. For feature inspection directly after exposure, AFM topographic imaging was applied. The BCP-samples were provided by Dr. Deirdre Olynick and team (Molecular Foundry, LBNL, Berkeley).
exploited in order to ablate one material (block) with high selectivity with respect to another material (block). This enables the editing of block-copolymer materials with an additional level of selectivity. Depending on the exposure dose, either one block or both blocks can be removed. Further, a high spatial confinement and AFM-based alignment is provided. Since no solvents are required for development of the BCP films, pattern collapse and development-related problems are circumvented. In this way, high resolution patterns can be achieved. A joint patent of this method was filed, ref. [389].
5 Lithographic Model and Simulations

In order to understand the experimental observations, respective lithographic models and simulations were developed. In the first section a Gaussian beam exposure model is described. Based on this, the correlation between crosslinking and ablation can be reproduced. Within the second part the influence of the dielectric resist layer on the electric field distribution and the therefrom derived field emission at the tip apex was investigated. For the simple case of a homogeneous unstructured resist layer a respective relation was deduced. In the third part of this chapter the lithographic back-coupling effect was investigated. In previous works, e.g. by Mayer et al. [301], the electric field distribution and the therefrom derived parameters (FN-emitted current density) were treated as a constant (global) parameter. However, in consequence of the close proximity of emitter and lithographic feature, the electric field strength at the tip apex changes with progressing exposure. To understand the chain of action and impact of this effect, specific simulations were carried out. Here, in an iterative manner the lithographically induced changes of the dielectric resist layer properties were introduced, and the caused changes of the local electric field strength and the current density distribution were mapped.

5.1 Application of a Gaussian Beam Exposure Model

As found, the final lithographic outcome can be accordingly described by a superposition of two distinct lithographic interactions: crosslinking and direct ablation of resist material. Thereby, crosslinking represents a material modification, while direct ablation is a material transformation from non-volatile into volatile compounds. Whereas the phenomenon of crosslinking is well-known from standard Gaussian electron beam lithography (refs. [182, 233, 272]), the direct ablation effect is unexpected and contradicts the standard EBL processing schemes (cf. section 6.1).

For both feature types - dots (0D) and lines (1D) - the same superposition of crosslinking and ablation was found (Fig. 5.1.2). In both cases the directly ablated region is surrounded by a crosslinked resist area. As is apparent after wet development, the spot exposure mode gives doughnut structures, whereas the vector-based line exposure results in the formation of double lines. In both cases the relation between ablated and crosslinked areas is the same. Since crosslinking and ablation are induced by the same exposure process, a self-alignment of both reactions to each other is present. Thereby, self-alignment means that the alignment between crosslinked and the ablated areas is not defined by the alignment capability of the lithographic system, but rather pre-defined by the physical relation of the processes. Hence, it is not surprising that the same general width-dose behavior was found experimentally for the crosslinking and ablation process.

To describe the lateral expansion versus dose characteristics, a Gaussian beam model is proposed. This model was initially suggested by Wilder et al. [26] in order to describe the crosslinking process in low energy electron exposure. Simulations [26, 301, 305] as well as experimental results supports the assumption that the electron exposure dose distribution on the sample surface can be adequately described by a Gaussian function type. Since there are no proximity effects in FE-SPL crosslinking, no double-Gaussian function as in standard EBL is required (ref. sections 6.1, 4.2.5, 6.1).
5 Lithographic Model and Simulations

Figure 5.1.1: Gaussian beam exposure model with separated exposure dose thresholds for crosslinking and ablation. For visualization of the model, a 17-times difference in the threshold values for crosslinking and ablation was chosen. In (a) an electric field simulation of the tip-sample gap is shown \[d_g = 15 \, nm; \, U_b = 40 \, V; \, d_r = 20 \, nm; \, \varepsilon_r = 3.7; \, r_{tip} = 15 \, nm\]. By a black line the Gaussian distribution of electrons on the sample surface is shown. In (b) different Gaussian electron exposure dose distributions at the sample surface are plotted as a function of the lateral position. The zero lateral position represents the center of the incident low energy electron beam. Two independent threshold values for crosslinking and ablation were introduced, marked by by green and blue bold horizontal lines, respectively. The red-colored curve in (b) highlights the first Gaussian which exceeds the threshold of both lithographic reactions. For this particular case the extension and position of the lithographic interactions are labeled by schematic (c). Graph (d) shows the width-dose function derived from the model (b).
Figure 5.1.2: In graphs (a-b) the experimental width-dose data for spot (a) and line (b) exposure are shown, respectively. The blue dots and the green stars correspond to the lateral extensions of the directly ablated resist (measured directly after exposure) and the crosslinked resist (measured after a wet development step). The experimental results are fitted by a logarithmic function type, which is derived from the Gaussian exposure model, Fig. 5.1.1. The corresponding fits are labeled in (a) and (b) by continuum lines. Thereby, the blue line corresponds to the direct ablation effect and the green line marks the crosslinking reaction.

The concept behind the Gaussian beam exposure model is summarized in Fig. 5.1.1. The application of the model on experimental width-dose data is demonstrated in Fig. 5.1.2. As known, the applied electric potential difference between probe tip and sample causes a strong electric field (Fig. 5.1.1-a) within the vicinity. In consequence, a spatially confined Fowler-Nordheim field emission process at the tip apex is triggered (ref. section 2.4). As derived previously, the resulting electron exposure dose distribution (and derived values such as the absorbed energy density) at the resist interface can be described by a Gaussian function type. With constant exposure parameters, the increase of the dose with exposure time can be defined as the sum of Gauss distributions. This is outlined in Fig. 5.1.1-(b; note: semi-logarithmic plot). Thus, each curve in Fig. 5.1.1-(b) shows a Gaussian electron exposure dose distribution at the sample surface plotted as a function of the lateral position. Thereby, the zero position in lateral direction represents the center of the incident electron beam. The total electron exposure dose is defined as the area under each curve. In this context, the transition of the Gaussians from bottom to top represents a linear increase of the total exposure dose.

By definition, a lithographic reaction is triggered at all spots where the dose threshold for the particular reaction type is exceeded. According to the experimentally observed findings, two individual electron exposure dose threshold values for crosslinking and ablation are introduced, marked in Fig. 5.1.1-(b) by green and blue bold horizontal lines, respectively. As has already been proven, the direct ablation is characterized by a significantly higher threshold value than the crosslinking of the resist. However, for a better graphical visualization of the model, a 17 times threshold difference was chosen. The red-colored exposure dose distribution in Fig. 5.1.1-(b) highlights the first curve (in the graphics) which exceeds the thresholds for both lithographic reactions. In accordance to the threshold definition, the lateral confinement of the corresponding reaction is determined by the intersection of the dose distribution function with the fixed threshold value. For the red-highlighted graph in (b) the expansions and positions of the lithographic interactions are exemplified by schematic (c). A further increase of the dose leads to an outward shift of the intersections of dose distribution and threshold towards. Thus, the widths of the superimposed crosslinking and ablation reactions are increased.
If the model is calculated with small increments of the dose, a logarithmic function type for the 
width-dose dependency of both reactions is derived, shown in Fig. 5.1.1-(d). Further, also the lateral 
shift between ablation and crosslinking is reproduced adequately. In terms of the self-alignment, the 
correlation between crosslinked area and ablation is defined by the difference in the dose thresholds. 
However, the model does not take into account the diffusion effects of reactive species. As summarized 
in Fig. 5.1.2, the experimental width-dose data for spot (a) and line (b) exposure can be fitted very 
well by the derived logarithmic function type (this function was already applied in chapter 4 to fit the 
experimental data).

In conclusion, in order to characterize the system behavior, which is operated in constant current mode, 
the FN field emission theory can be applied (ref. section 2.4). In this context, the operation in FN-regime 
is experimentally proven, e.g. by FN emission measurements as well as by the bias voltage versus 
distance dependency, which follows the theoretical prediction. As revealed by theoretical investigation 
of the FN field emission for FE-SPL, section 2.4, a constant field emission current regulation means 
nothing else than maintaining of a constant electric field strength at the tip apex. In principle, the 
entire system’s regulation behavior can be therefrom derived. On this basis, the variation of the beam 
spot size at the resist interface can be simulated. This was already investigated in previous studies, e.g. 
by Mayer et al. [301] and Wilder, Soh and Quate et al. [13, 26, 168, 169, 378]. As discussed in the 
particular experimental sub-sections of this work, the obtained experimental results [e.g. bias voltage 
versus feature dependencies (4.2.4), tip-sample spacing dependencies (4.2.2)] are in agreement with 
those theoretical assumptions.

Since new insights cannot be expected from the reproduction of these simulations, hereinafter the 
focus was placed on some novel issues and weaknesses of the previous simulations. In particular, in the 
preceding works the influence of the dielectric resist layer and its properties were considered. Further, 
a time-independent Gaussian-shaped beam was assumed. Within the simulation part it is shown that 
these boundary conditions are invalid because of the lithographic back-coupling effect. Thus, the 
previous simulations are only valid in the case that no lithographic reactions are induced.

5.2 Modification of the Electrical Field Distribution by Dielectric 
Resist Films

![Figure 5.2.1: Insertion of a dielectric resist film within the tip-sample junction. Schematic (a) shows 
the system without resist layer, schematic (b) with resist.](image)

In a first approximation, the system can be seen as an ordinary tip-sample configuration, outlined in 
Fig. 5.2.1-(a). Based on the bias voltage, the electric field strength within the tip-sample gap is then 
calculated by using Eq. 2.24. Thereby, in the case of a parallel plate model $\beta = 1/d_{ts}$ ($\equiv$ Eq. 2.14) is
used, whereas for a hemispherical tip model Eq. 2.25 is required. However, these models do not take into account the presence of a resist as shown in Fig. 5.2.1-(b). In general, the resist can be described as a dielectric layer with a defined thickness \(d_d\) and relative permittivity \(\epsilon_{r-d}\). The evaluation of the impact of the dielectric layer on the system is of crucial importance in order to predict the lithographic result.

The tip-sample system to be examined consists of a vacuum gap (\(d_g\): spacing between tip and dielectric layer, vacuum assumed in between) and a dielectric resist layer. In simplified form, a two-capacitor-in-series model can be applied (Fig. 5.2.1-b). As derived from Gauss law, when no charges exist at the interface between dielectric and vacuum, the normal components of the electric displacement fields \(D_n\) at the interface are equal. In consequence of the dielectric boundary condition \(D_n-d_d = D_n-g\) the electric field strength in the vacuum gap can be described by a simple linear relationship:

\[
E_g = \epsilon_{r-d}E_d
\]  

(5.1)

Since the relative permittivity of the resist is typically \(\epsilon_{r-d} > 1\), the electric field strength within the intermediate vacuum gap (\(E_g\)) is enhanced by the factor of \(\epsilon_{r-d}\) with respect to the electric field strength within the dielectric film (\(E_d\)). Thus, the introduction of the dielectric layer leads to shift of the electric field strength within the vacuum gap. This effect is also obviously noticeable in the electric field simulations, Fig. 5.2.4. Further, the insertion of the resist changes the voltage drop across the vacuum gap. Without resist the applied bias voltage is equal the voltage drop across the gap \(U_b = U_g\); Note: other resistances originating from the system are neglected), whereas in the scenario with resist a serial connection has to be considered giving:

\[
U_b = U_g + U_d
\]  

(5.2)

In the setup, however, only the bias voltage \((U_b)\) is set and the distribution is determined depending on the properties of the resist layer and the lithographic configuration. Since the properties of the resist changes as a result of the exposure process, the ratio changes as well. At the end of this section, the consequences of this effect are discussed.

Further, when introducing a resist (Fig. 5.2.1) also the tip-sample capacity changes from \(C_{t-tip-pp} = \epsilon_0 A_{pp}/d_{ts}\) (parallel plate model) to:

\[
C_{t-tip-pp} = \frac{\epsilon_0 A_{pp}}{d_{ts} - d_d(1 - 1/\epsilon_{r-d})}
\]  

(5.3)

To get a better understanding of what happens when the resist film properties are changed, a simple thought experiment was created, visualized in Fig. 5.2.2. Here, the changes of the system (tip-sample distance, tip-resist gap, emission current) are investigated as function of resist alteration for both operation modes - constant height (ch) and constant current (cc) regulation. While in cc-mode the system attempts to maintain a constant current by respective modulations of the tip-sample spacing (\(\Delta d_g\)), in ch-mode the tip-sample spacing is held constant. In order to determine the exact chain of effects, the following boundary conditions have been assumed:

- Simplification of the system by a serial connection of two plate capacitors (neglection of other geometrical effects);
- During the experiment the bias voltage is not changed, which means \(U_{b1} = U_{b2} \Leftrightarrow U_{g1} + U_{d1} = U_{g2} + U_{d2}\) (annotation 1 corresponds to case 1 in Fig 5.2.2 and annotation 2 to case 2);
- The normal components of the electric displacement fields \(D_n\) at the interfaces are constant, which
means that Eq. 5.1 is valid for both cases;

- In the **ch-mode** the total tip-sample distance is kept constant, which gives $d_{ts1} = d_{ts2} \succ d_{g1} + d_{d1} = d_{g2} + d_{d2}$;

- In the **cc-mode** a constant current is maintained by adjustment of the vacuum gap $\Delta d = d_{g2} - d_{g1}$.

This means that the electric field strength within the vacuum gap is equal in both cases $E_{g1} = E_{g2}$ (ref. Eq. 2.17).

### a) Constant height (ch) mode:

In order to describe the alteration in the electric field strength due to changes in the dielectric layer (case 2) with reference to an initial field strength (case 1), the following equation has been derived ($E_g$: electric field strength within the vacuum gap):

$$E_{g2} = E_{g1}c_E \cdot c_E = \frac{d_{g1} + d_{d1}}{d_{g1} + d_{d1} - d_{d2}/\epsilon_{r-d2}}$$

(5.4)

Thereby, the proportionality factor $c_E$ contains all changes of the resist layer properties. In same way, the alteration of the voltage drop across the gap can be derived by:

$$U_{g2} = U_{g1}c_U \cdot c_U = \frac{1}{d_{g1}} \cdot \frac{(d_{g1} + d_{d1}/\epsilon_{r-d1})(d_{d1} + d_{d1} - d_{d2})}{d_{g1} + d_{d1} - d_{d2}/\epsilon_{r-d2}}$$

(5.5)

### b) Constant current (cc) mode:

In the cc-mode the alteration of the vacuum gap, caused by changes of the dielectric layer properties, can be described by:

$$\Delta d_g = d_{g2} - d_{g1} = \frac{d_{d1}}{\epsilon_{r-d1}} - \frac{d_{d2}}{\epsilon_{r-d2}}$$

(5.6)

In case that only the layer thickness ($\Delta d = d_{d2} - d_{d1}; \epsilon_{r-d} = \epsilon_{r-d1} = \epsilon_{r-d2}$) is changed, the equation can be simplified yielding:

$$\Delta d_g = \frac{d_{d1} - d_{d2}}{\epsilon_{r-d}} = -\frac{\Delta d_d}{\epsilon_{r-d}}$$

(5.7)

As shown in Fig. 5.2.2, when the probe crosses a step at which the resist layer thickness is abruptly decreased (resist type and thus the relative permittivity is not changed), the gap increases accordingly in order to maintain a constant FN field emission current. In both operation modes (ch/cc) mechanical interactions between tip and resist should be prevented ($d_{ts} > d_d \succ d_g > 0$). In consequence, the applicable resist thicknesses are limited (see Fig. 5.2.3).
In order to outline the analytical relationships, the system response to changes of the resist properties was calculated for different scenarios, summarized in Fig. 5.2.3. Thereby, a decrease of the film thickness (a-b), an increase of the film thickness (c-d), and a change of the relative permittivity (e-f) was considered for each operation mode (ch/cc). Since the initial parameters of the electric field strength and the voltage drop across the vacuum gap are unknown, only relative changes were calculated, expressed by $c_E$ and $c_U$. As a result, the impact of changes of the dielectric layer properties ($d_2$, $e_{r-d}$) on the electric field, the voltage drop and the total tip-sample capacitance were derived. On this basis, the reaction of the current feedback loop in cc-operation mode was calculated.

As supposed, the insertion of a dielectric resist layer and its increase leads to an increase of the electric field strength at the tip surface (Fig. 5.2.3-c). In consequence, in the cc-mode the system decreases the vacuum gap $d_g$ accordingly, whereby the overall tip-sample distance $d_{ts}$ increases (Fig. 5.2.3-d). Due to the increased tip-sample spacing $d_{ts}$, as discussed in section 4.2.4, the beam diameter at the sample surface increases leading in turn to wider features. In the case when a resist thickness is decreased, the effects are vice versa, summarized by the calculations in Fig. 5.2.3. In conclusion, highest lithographic resolution inevitably requires ultra-thin resist layers. As revealed by graphs (e) and (f) in Fig. 5.2.3, slight variations of the relative permittivity result in a significant variation of the electric field strength. In cc-mode this leads to a relatively large vertical displacement of the probe (Fig. 5.2.3-f). However, the strength of this effect decreases with increasing relative permittivity of the resist (limit: $e_{r-d_2} \rightarrow \infty$), $d_{g1} = d_{g2} = d_g$) $c_E \rightarrow d_{g1}/(d_{g1} - d_{g2})$, $\Delta d_g \rightarrow d_{g2}$). The analysis of the total tip-sample capacitance ($C_{t-pp}$) shows that it increases with increasing dielectric layer thickness and relative permittivity. Thereby, in ch-mode a change of the dielectric resist layer leads to a change of the capacitance while the distance regulation in cc-mode gives a constant $C_{t-pp}$.

Since many simplifications have been made to compile the analytical solution, a corresponding electric field simulation was carried out to validate the analytical equations, summarized in Fig. 5.2.4. In particular, the effect of introducing a dielectric resist layer within the tip-sample junction was investigated. This scenario is similar to that in Fig. 5.2.3-(c, d), where an increasing resist layer was investigated. Thus, a direct comparison of the results obtained by simulation and analytical equations is given. The simulation shows that the maximum value of the electric field (Fig. 5.2.4-i) is raised by a factor of $c_E = 2.2$ when a resist layer is introduced (case a→b; tip-sample spacing is not changed). In comparison, the analytical solution is very close to that value ($c_E = 2.7$, by Eq. 5.4).

As determined from simulation and analytical solution, the voltage drop across the vacuum gap is changed (Fig. 5.2.4-iv) by a factor of $c_U = 0.7$ vs. $c_U = 0.6$ (Eq. 5.5). In order to return to the initial emission current, case (a), the raised electric field has to be compensated by retraction of the tip. The analytical solution, Eq. 5.6, delivers a value of $\Delta d_g = +32 \text{ nm}$. This value is now fed forward to the numerical simulation for the increase of the vacuum gap (transition case b→c). As a result, in (c) the enhanced electric field strength is compensated accordingly. In fact, the electric field strength and the corresponding current density at the tip apex, Fig. 5.2.4-(i) are identical for cases (a) and (c).

In summary, the derived analytical solution for the cc-mode (Eq. 5.6 and 5.7) describes the system behavior adequately. In the case of the ch-mode, slight differences between analytical calculation (Eq. 5.4 and 5.5) and numerical electric field simulation are given. This could be attributed to the parallel plate model, which was applied for the analytical solution. If the boundary condition $r_{tip} \rightarrow \infty$ (parallel plate) is used in the simulation, the derived values for $c_E$ and $c_U$ are identical to that of the analytical solution. However, in order to get a first approximation the analytical solution is sufficient. For the cc-mode operation this kind of error is eliminated since the electric field strength is kept constant by changes of the vacuum gap.
Figure 5.2.3: Calculation of system responses to changes in resist properties, broken down by the operation mode. In graphs (a) and (c) the relative changes of the electric field strength ($c_E$), the voltage drop across the vacuum gap ($c_U$) and total capacity ($C_{t-\text{tip-pp}}$) are determined for the ch-mode in the case where the resist layer decreases (a) or increases (c), respectively (calculation in 0.5 nm steps). Thereof derived, the relative change of the vacuum gap $d_g$ and the tip-sample distance $d_{ts}$ in the cc-operation mode are calculated, shown in graphs (b) and (d). The calculations are done for two different relative permittivities. In graphs (e) and (f) the influence of relative permittivity changes in ch- (e) and cc- (f) operation mode are determined for two different initial gaps and spacings ($d_g = 30 nm$ with $d_g = 10 nm$ and $d_d = 10 nm$ with $d_g = 30 nm$).

$d_g = 2$
$d_g = 5$
$d_g = 7$
$d_d = 2$
$d_d = 5$
$d_d = 7$
Figure 5.2.4: Simulation of the electric field within the tip-sample junction and its variation due to insertion of a dielectric resist layer. In particular, the tip-sample system is shown: (a) At the initial state without dielectric layer ($r_{tip} = 15\, nm; d_{ts} = 50\, nm, U_b = 40\, V$); (b) After insertion of a dielectric layer ($d_d = 40\, nm, \epsilon_r - d = 5$) without changing the spacings (ch); (c) After retraction of the tip by $\Delta d_g = +32\, nm$ in order to have the same emission current as at the initial state (a). The required retraction distance of the tip in order to have equal emission currents (a–c) was calculated via Eq. 5.6. In the derived graphs (i–iii) the modulus of the electric field strength along to the tip surface (i), perpendicular to the sample through the tip center (ii), and along the surface of the dielectric (resist) layer (iii). In (iv) the electric potential is plotted as a function of the vertical position, which is measured in the center starting from the sample surface. Additionally to the electric field strength in graph (i), the current density along the tip surface is calculated using the FN-equation (MG-treatment with Spindt approximation, Eq. 2.22, with $2.23$ and $\psi = 4.5\, eV$).
5.3 Investigation of the Lithographic Back-coupling Effect by Electric Field Simulation

In the previous section the effects of global changes of the resist properties were examined. As found, these can be described with sufficient accuracy by an analytical solution. However, lithography means the introduction of highly spatial confined changes of the resist layer. Thus, a constant (global) resist parameter change is not appropriate. Further, during the exposure the dielectric resist layer properties are permanently changed. Thereby, the rate of change depends on the particular exposure parameter. In consequence, the properties of the resist (thickness \(d\); relative permittivity \(\epsilon_r - d\)) are dynamic (time-variant) and spatially variable values.

The chain of action leading to the back-coupling effect is schematically summarized in Fig. 5.3.1. In particular, the applied bias voltage results in a strong electric field within the tip-sample gap, which further causes a FN field emission process at the tip apex. As found, as a result of the FE-SPL exposure crosslinking and ablation reactions are induced within the resist layer. While the crosslinking leads mainly to localized increase of the relative permittivity \(\epsilon_r - d\) of the resist, the ablation results in a decrease of the local resist thickness \(d\). Due to the close proximity of emission source (probe tip) and resist, the change of the dielectric resist properties \(d, \epsilon_r - d\) results in a change of the electric field in the tip-sample junction. As a result, the change of the electric field causes a change of the FN field emission current. In the case of the cc-mode, this is compensated by a modification of the tip-sample spacing, which in turn causes a change of the beam diameter at the sample surface. Thus, a complex chain of action is present. In conclusion, the electric field and in turn the FN field emission cannot be presumed as a constant parameter. Instead, both depend on the progress of the lithographic interaction. In turn, also the beam shape and the particular exposure dose distribution are altered during the lithographic process.

As elaborated by the following scenarios, the impact of spatially confined changes of the dielectric layer properties on the local electric field and current density distribution at the tip apex are investigated. Thereby, lithographic type-specific changes of the resist properties were assumed as starting point. In contrast to the global changes of the dielectric layer, the spatially highly confined changes of the resist could only be described by numeric simulations (2D-simulation; Comsol Multiphysics; as many
parameters as possible were transferred from experiments). Starting from the local electrical field distribution at the tip apex, the local current density was calculated using the FN-equation including the MG-treatment with Spindt approximation (Eq. 2.22 with 2.23 & $\psi = 4.5 \text{ eV}$).

(1) Impact of a bare crosslinking process:

Figure 5.3.2: Simulation model (i) and electric field simulation results (ii-iii) of a laterally extending crosslinking reaction. The width parameter of the modified dielectric area $w_{CL}$, colored in dark green, is increased stepwise simulating a symmetrically propagating crosslinking reaction. The electric field simulation results of (ii) and (iii) compare the initial state (without crosslinked area; ii) with a spatially confined crosslinked state (20 nm wide crosslinked area within the exposure center; iii). [Parameter: $\varepsilon_{r-d-calix-unmodified} = 3.7$, $\varepsilon_{r-d-calix-crosslinked} = 6.6$, $d_d = 20 \text{ nm}$, $d_{ts} = 35 \text{ nm}$, $r_{tip} = 15 \text{ nm}$, $U_b = 40 \text{ V}$, $\psi = 4.5 \text{ eV}$]

As experimentally determined (section 4.2.5), a crosslinking reaction leads to an increase of the relative permittivity. Assuming an initial relative permittivity of the unmodified calixarene MG resist of $\varepsilon_{r-d-calix-unmodified} = 3.7$ (ref. Appendix A.1), the crosslinking process almost doubles this value ($\varepsilon_{r-d-calix-crosslinked} \approx 6.6$, ref. section 4.2.5; The exact $\varepsilon_{r-d}$ value can vary depending on the degree of crosslinking and the initiated process; However, this is a sufficient approximation in order to describe the underlying effects). Thus, the symmetrically extending crosslinking reaction is simulated by a gradually
Figure 5.3.3: Simulation results showing the impact of an extending crosslinking reaction \([w_{CL} = 0 - 100\, \text{nm}; h_{CL} = 20\, \text{nm (const.)}]\) on the: (i) Electric field distribution along the tip surface; (ii) Electric field within the exposure center, plotted as a function of tip-sample distance; (iii, iv) Current density along the tip surface [graph (iv) is the logarithmic representation of (iii)]. The crosslinking process was simulated by an extending area of increased relative permittivity \(\epsilon_{r_{\text{d}}-\text{calix-unmodified}} = 3.7\) to \(\epsilon_{r_{\text{d}}-\text{calix-crosslinked}} = 6.6\); height of the resist was not changed. [Parameter: \(d_d = 20\, \text{nm}, d_{ts} = 35\, \text{nm}, r_{\text{tip}} = 15\, \text{nm}, U_b = 40\, \text{V}, \psi = 4.5\, eV; \text{CL} = \text{crosslinking}\)]
enlarged area ($w_{CL}$) with a larger $\epsilon_{r-d}$ value. The reaction starts from the exposure center (spot of the maximum dose; in ideal case exactly below the center of the tip apex) and spreads symmetrically in all directions as shown schematically in Fig. 5.3.2-(i).

In consequence of the extending high-$\epsilon_{r-d}$ area, the electric field strength along the surface of the tip apex increases gradually (Fig. 5.3.2-(ii) versus (iii), summarized in Fig. 5.3.3-(i-ii)). As described by the FN-equation, this leads to a significant enhancement of the current density ($J_{FN} \sim E^2$; MG-treatment with Spindt approximation used for calculation of the local current density), shown in Fig. 5.3.3-(iii-iv). Thus, the back-coupling effect (Fig. 5.3.1) via the crosslinking reaction results in a self-amplification causing an enhancement and further spreading of the FN emission at the tip apex. As a result, the crosslinking reaction further extends which results again in a beam spread. In case no ablation occurs, a maximum enlargement will be reached. Since the ablation threshold value is typically exceeded beforehand, ablation starts first. Since in the real case the $\epsilon_{r-d}$ value will be increased gradually (in simulation a jump from $\epsilon_{r-d-calix-unmodified} = 3.7$ to $\epsilon_{r-d-calix-crosslinked} \approx 6.6$ was assumed), a further beam modulation could be expected. This could be a cause of further beam blur.

(2) Impact of a bare ablation process:

The experimental results, chapter 4, have revealed that within the center of the crosslinked area a direct removal / ablation process starts and propagates spatially with increasing exposure dose. In order to evaluate the back-coupling impact of the ablation on the FN field emission in depth (Fig. 5.3.4-i) and width (Fig. 5.3.4-ii) independently, both propagation directions were initially considered separately. The corresponding simulation results are summarized in Fig. 5.3.5. As expected, in both directions the progressive ablation reaction reduces the electric field strength at the tip apex, Fig. 5.3.5-(i, ii). In consequence, the current density decreases significantly ($J_{FN} \sim E^2$), displayed by Fig. 5.3.5-(iii, iv). Especially the propagation in width (Fig. 5.3.5-iv) shows a dramatic impact on the current density.
Figure 5.3.5: Simulation results showing the impact of a spatially extending ablation reaction. The propagation in depth (graphs i, iii, v; $w_R = 7 \text{ nm}$, $d_R = 0 \rightarrow 20 \text{ nm}$) and width (graphs ii, iv, vi; $w_R = 0 \rightarrow 100 \text{ nm}$, $d_R = 20 \text{ nm}$) were simulated separately. Graphs (i, ii) show the electric field distribution along the tip surface. Derived therefrom the current density distribution along the tip surface was calculated, shown in graphs (iii, iv). Graphs (v, vi) display the electric field strength along the resist-air interface. [Parameter: $\epsilon_r - d - \text{calix-unmodified} = 3.7$, $\epsilon_r - d - \text{calix-crosslinked} = 6.6$, $d_d = 20 \text{ nm}$, $d_e = 35 \text{ nm}$, $r_{tip} = 15 \text{ nm}$, $U_0 = 40 \text{ V}$, $\psi = 4.5 \text{ eV}$; CL=crosslinking; R=removal/ablation]
In conclusion, the back-coupling effect (Fig. 5.3.1) leads in the case of a direct removal of resist to a self-limiting behavior. Further, a strong alteration of the beam shape itself can be expected due to the spreading of the reaction in a lateral direction. The simulations show that between the initial state (no ablation, \( w_R = 0 \text{ nm} \)) and the 100 nm \( (w_R) \) wide trench the beam considerably broadens. This effect of a beam shape alteration with progressing exposure is discussed in more detail within the next subsection (c) by a superimposed crosslinking plus removal reaction.

In addition, also the electric field distribution along the resist-air interface changes, which is plotted in Fig. 5.3.5-(v, vi). While the crosslinking changes the electric field at the resist interface only slightly, after onset of ablation the field strength drops significantly. Thereby, the field strength maximum moves outwards (ref. series subsection (c), Fig. 5.3.7) with progressing ablation reaction (local field enhancement effects at the remaining crosslinked edges of the lithographic feature). Because the corners of the lithographic feature are rounded in the real case, a flattening of the local peaks could be expected. The alteration of the electric field distribution along the resist-air interface could lead to a further alteration of the beam shape (ref. Fig. 5.3.7). Here, it is expected that the electron trajectories within the tip-resist gap are influenced (simulations including the electron trajectories is provided in the PhD work of Steve Lenk, ref. [305]) resulting in a change of the exposure dose distribution. It can be assumed that the crosslinked edge receives a higher dose compared to the initial case without back-coupling effect. This may imply that the removal reaction results with increasing exposure time in a wavefront-like migration of the electric field strength and resulting current distribution to the outside area of the tip.

(3) Superposition of crosslinking and ablation:

<table>
<thead>
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</tr>
</thead>
<tbody>
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</tr>
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<tr>
<td>#2</td>
<td>( w_{CL} = 20 ); ( h_{CL} = 20 )</td>
</tr>
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<td>#3</td>
<td>( w_{CL} = 40 ); ( h_{CL} = 20 )</td>
</tr>
<tr>
<td>#4</td>
<td>( w_{CL} = 60 ); ( h_{CL} = 20 )</td>
</tr>
<tr>
<td>#5</td>
<td>( w_{CL} = 100 ); ( h_{CL} = 20 )</td>
</tr>
<tr>
<td>#6</td>
<td>( w_{CL} = 160 ); ( h_{CL} = 20 )</td>
</tr>
<tr>
<td>#7</td>
<td>( w_{CL} = 320 ); ( h_{CL} = 20 )</td>
</tr>
</tbody>
</table>

As revealed by the experiments, in the case of calixarene MG resist the initiation of an ablation always involves also a crosslinking reaction. Due to the lower threshold dose the resist crosslinks first. When the...
Figure 5.3.7: Series of electric field simulation results showing the impact of a superimposed extension of a crosslinking (indicated by green dashed lines) and ablation reaction. The individual images illustrate the different states of a progressing lithographic reaction, defined in the model Fig. 5.3.6: (#0) Pristine resist; (#1) Confined crosslinked area within the exposure center ($w_{CL} = 5 \text{ nm}$, $d_{CL} = 20 \text{ nm}$); (#2): Extending crosslinking reaction ($w_{CL} = 20 \text{ nm}$) with superimposed removal reaction in an early state ($w_{R} = d_{R} = 5 \text{ nm}$); (#3)-(#7) propagation of the superimposed lithographic reactions (#3: $w_{CL} = 40 \text{ nm}$, $w_{R} = d_{R} = 10 \text{ nm}$; #4: $w_{CL} = 60 \text{ nm}$, $w_{R} = d_{R} = 15 \text{ nm}$; #5: $w_{CL} = 100 \text{ nm}$, $w_{R} = d_{R} = 20 \text{ nm}$; #6: $w_{CL} = 160 \text{ nm}$, $w_{R} = 40 \text{ nm}$, $d_{R} = 20 \text{ nm}$; #7: $w_{CL} = 320 \text{ nm}$, $w_{R} = 80 \text{ nm}$, $d_{R} = 20 \text{ nm}$) [Parameter: $\epsilon_{r-d-unmodified} = 3.7$, $\epsilon_{r-d-crosslinked} = 6.6$, $d_{d} = 20 \text{ nm}$,$d_{r} = 27.5 \text{ nm}$, $r_{tip} = 15 \text{ nm}$, $U_{b} = 40 \text{ V}$, $\psi = 4.5 \text{ eV}$]. The given electric field strength color bar is valid for all images (#0-#7).
Figure 5.3.8: Graphs derived from simulation result type Fig. 5.3.7 depicting the progress of the superimposed crosslinking and ablation reaction. As described in the model Fig. 5.3.6 the back-coupling effect is reproduced by a stepwise simulation of the superimposed lithographic reaction. The different reaction states are defined in Fig. 5.3.6-(#0-#7). The simulation was carried out for two different initial tip-sample spacings of $d_{ts} = 35$ nm (i, iii, v) and $d_{ts} = 27.5$ nm (ii, iv, vi). The following graphs are shown: (i, ii) Electric field distribution along the tip surface; (iii, iv) Current density distribution along the tip surface, derived from graphs (i, ii); (v, vi) Electric field along the resist-air interface [Parameter: $\epsilon_{r-d-unmodified} = 3.7$, $\epsilon_{r-d-crosslinked} = 6.6$, $d_d = 20$ nm, $r_{tip} = 15$ nm, $U_b = 40$ V, $\psi = 4.5$ eV].
Figure 5.3.9: Influence of the tip radius of curvature on the lithographic back-coupling in ablation, investigated by simulations. The electric field simulations were carried out at different tip radii \( r_{tip} = 15; 7.5; 30; 60 \text{ nm} \) focusing on the lithographic state #5, Fig. 5.3.6 \( (w_{CL} = 100 \text{ nm}; h_{CL} = 20 \text{ nm}; w_R = 20 \text{ nm}; d_R = 20 \text{ nm}) \) at fixed tip-sample spacing \( d_{ts} = 27.5 \text{ nm} \) [further parameter: \( \epsilon_{r-d-unmodified} = 3.7, \epsilon_{r-d-crosslinked} = 6.6, d_d = 20 \text{ nm}, U_b = 40 \text{ V}, \psi = 4.5 \text{ eV} \)]. The graphs provide: (i) The electric field distribution along the tip surface; (ii) The derived current density distribution; and (iii) The electric field strength along the resist-air interface.
exposure dose threshold for direct ablation is exceeded too, a direct removal of crosslinked resist starts as a second process within the center of exposure. With increasing exposure dose both reactions extend spatially. A simulation model which covers this scenario is outlined in Fig. 5.3.6. Here, the effects discussed separately before are now considered in superposition. As found experimentally (section 4.2.3), and explained by the exposure model (section 5.1), both reactions are coupled respectively. Thus, this model comes close to the real lithographic process. An electric field distribution image series, which illustrates the different states of the progressing lithographic reaction (defined in model Fig. 5.3.6) is given in Fig. 5.3.7. Further, in Fig. 5.3.8 the simulation results for two different initial tip-sample spacings, $d_{ts} = 35\,nm$ (i, iii, v) versus $d_{ts} = 27.5\,nm$ (ii, iv, vi), are compared.

Derived from: (1) in which a self-amplification effect was determined in the case of crosslinking, and; (2), in which a self-limiting type was determined for ablation, the behavior in the case of a superimposed reaction can now be assessed. First, in a first phase the crosslinking reaction ($\#0 \rightarrow \#1$) amplifies the electric field at the tip surface resulting in an enhanced current density. Also between step $\#1 \rightarrow \#2$ the laterally extending crosslinking reaction leads to an amplification of the emission process. In the initial phase of the ablation reaction only a minor impact of the back-coupling effect is present. In consequence, the lateral expansion of the crosslinking reaction dominates the back-coupling effect in the beginning ($\#0 \rightarrow \#2$). Thus, the electric field and the derived current density are mainly enhanced. With further spatial expansion of the reactions ($\#2 \rightarrow \#7$) the self-limiting behavior caused by the ablation dominates. In particular, a significant drop of the electric field strength is present while the current density distribution broadens (in the case of larger tip-sample spacings, graph iii) or the current density peak moves outwards (in the case of lower tip-sample spacings, graph iv). In this context, also the beam shape is significantly modulated in between the initial state ($\#0$) and the final state ($\#7$) of the lithographic reaction. When the ablative process has reached approximately the same dimensions as the typical tip radius of curvature and tip-resist spacings, which is valid for the lithographic states $\#4 \rightarrow \#6$, the largest beam shape deformation is present. As revealed by the simulation, Fig. 5.3.8, this effect becomes larger with decreasing tip-resist spacing. For example, in the case of a tip-resist gap of $7.5\,nm$ (Fig. 5.3.8(ii, iv)) the current density peak [initial state ($\#0$)] splits into two side peaks, which shift outwards as the reaction progresses [in between state ($\#3$)$\rightarrow$($\#6$)]. This is linked with a broadening of the overall current density distribution. As revealed by Fig. 5.3.9, this effect is enlarged in the case of larger tip radii of curvature. In particular, with increasing tip radii the broadening is enhanced. In consequence, at $r_{tip} = 30 - 60\,nm$ almost a ring instead of a Gaussian shaped beam is formed (two orders of magnitude difference in current density between beam center and current peak outside of the center is indicated by the simulation). Considering that larger tip radii lead to smaller tip-sample spacings at the same bias voltage (effect not considered in simulation) in order to have the same FN field emission current, a further modulation of the beam shape could be expected.

In the realistic event, a gradient in the crosslinking and ablation reaction would lead to a further blur of the beam. As revealed by the simulation results, the back-coupling effect leads to a significant change in the electric field and current density distribution at the tip apex. The following processes occur as part of the superimposed reaction:

1. In the initial state a main emission is present, describable by a Gaussian beam distribution;
2. With progressing crosslinking an enhancement of the electric field and current density occurs;
3. With progressing ablation the electric field and current density distribution decreases, broadens and flattens, which could be coupled with a shift of the maximum towards to outer sites of the tip;
Once the ablation process reaches its maximum extension, the initial emission Gaussian shape becomes restored, but with significantly decreased amplitude.

Unfortunately, due to the back-coupling effect an analytical description is not possible. Further, the effect depends on various other factors like the tip-sample spacing ($d_{ts}$), the resist thickness ($d_d$), the tip radius of curvature ($r_{tip}$), the properties of the unmodified and the crosslinked resist ($\epsilon_r-d$), the applied bias voltage ($U_b$), and so on.

(4) Consideration of a moving probe in the case of vector-based line patterning:

Within the sub-sections (1-3) a stationary probe at a fixed tip-sample spacing (ch-mode) was investigated corresponding to the spot exposure mode (section 3.1.4). Considering a vector-based patterning routine, in which the probe moves constantly, no radially symmetric system is given. In contrast, in tip movement direction an asymmetric configuration is present, drawn schematically in Fig. 5.3.10 (the plane perpendicular to the tip movement direction could be treated as a symmetrical configuration). In particular, the area which was already passed by tip is ablated, whereas the area ahead of the tip is crosslinked.

Thus, in the case of the line patterning the ablation and crosslinking front moves with the tip. In the first approximation, it can be assumed that the ablation front is located within the tip center, whereas the crosslinking front is ahead of the ablation (Fig. 5.3.10). Since the exact places of the front in tip movement direction are unknown, the simulation was carried out at different scenarios, defined in Fig. 5.3.11 by #0-#7. As supposed, the asymmetric geometrical configuration results in an asymmetric electric field distribution, which causes in turn an asymmetric current density distribution, shown in Figs. 5.3.10-(iii) and 5.3.11. The transition from the initially symmetric case (#0-a) to the asymmetric case (#0-b) has two major consequences:

(1) The maximum of the electric field and current density shifts outwards in tip movement direction. Thus, the center of the beam is shifted away from the geometrical center of the tip apex (at which tip-sample spacing is a minimum). An increased exposure dose is deposited in tip movement direction. In consequence, the beam shape could not be fitted by a Gaussian beam, which is centered with the geometrical tip apex.

(2) The electric field as well the current density are significantly decreased compared to the initial symmetric scenario (#0-a). Thus, also the total (integral) emission current is decreased. While operating in cc-mode, the system decreases the tip-sample spacing in order to restore the initial current setpoint [is the consequence of the transition between case (#0-a) to (#0-b), Fig 5.3.10]. As a result, also the tip-resist gap is decreased. In turn, this causes a further deformation of the FN field emission in direction of the tip movement.

Further conclusions can be drawn from the evaluation of the other simulation results, Figs. 5.3.10 and 5.3.11:

(3) The crosslinking reaction in direction of the tip movement (#0-b→#4) enhances the electric field (Fig. 5.3.10-(iii), (#0-b)→(#2)). In turn, the current density is raised and the beam deformation in direction of the movement is slightly enhanced (Fig. 5.3.11-(i, ii)).

(4) A shift of the ablation front in direction of the movement (ablation front ahead of the tip center plane: #5→#7) leads to a decrease of the electric field strength / current density. In addition, the deformation in direction of the tip movement is enlarged.
5 Lithographic Model and Simulations

![Diagram](image)

<table>
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<th>Case</th>
<th>Parameter [nm]</th>
</tr>
</thead>
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<td>#0-a</td>
<td>initial symmetric case with resist layer, CL &amp; R = 0</td>
</tr>
<tr>
<td>#0-b</td>
<td>initial case, resist removed from one side as drawn in (ii), CL &amp; R = 0</td>
</tr>
<tr>
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</tr>
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</tr>
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<td>as drawn in (ii): $w_{CL} = 50$ ; $h_{CL} = 20$ ; $w_R = 20$ ; $d_R = 20$</td>
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</table>

**Figure 5.3.10:** Simulation describing a moving tip with progressing ablation front. As found experimentally, crosslinking is ahead of the ablation front. The model corresponds to the typical vector-based line exposure process. The model outlined in (i-ii) shows that there is an asymmetric configuration in the direction of the tip movement. Both lithographic reactions propagate in tip movement direction (removal: $d_R$, $w_R$ ; crosslinking: $w_{CL}$). The electric field simulations in (iii) compare a symmetric configuration case (#0-a), an asymmetric scenario, in which the resist is removed at one side - without having a crosslinking reaction (#0-b), and an asymmetric scenario, in which the resist is additionally crosslinked 10 nm ahead of the ablation front (#2). [Parameter: $\epsilon_{r-d-unmodified} = 3.7$, $\epsilon_{r-d-crosslinked} = 6.6$, $d_d = 20$ nm, $r_{tip} = 15$ nm, $U_b = 40$ V, $\psi = 4.5$ eV; in (iii): $a_{ls} = 27.5$ nm]
Figure 5.3.11: Summary of the simulation results corresponding to an asymmetric tip-sample configuration, which is relevant for a vector-based line patterning process. The crosslinking and ablation reaction propagate with the tip in tip movement direction. As described in the model Fig. 5.3.10, different scenarios (#0-#7) were simulated having different extensions of the crosslinking (i-ii) and ablation (iii-iv) reactions with respect to the center of the tip. Graphs (i, iii) plot the electric field along the tip surface. Derived therefrom, in (ii, iv) the current density distribution is calculated. [Parameter: $d_{tx} = 35 \text{ nm}$, $\epsilon_{r-d-unmodified} = 3.7$, $\epsilon_{r-d-crosslinked} = 6.6$, $d_d = 20 \text{ nm}$, $r_{tip} = 15 \text{ nm}$, $U_b = 40 \text{ V}$, $\psi = 4.5 \text{ eV}$]
The deformation of the beam (off-centered emission) increases with decreasing tip-sample spacing as well as with increasing tip radius of curvature (Fig. 5.3.12). In addition, an increase of the tip radius of curvature leads to a reduction of the electric field strength and current density (in the case of a fixed tip-sample spacing). Thus, in order to have the same total current, blunter tips require in comparison to sharp tips a lower tip-sample spacing. This results in a further increase of the beam deformation.

However, in the experimental case the tip movement in cc-mode is relatively slow (µm/s). It can be assumed that the system regulates a corresponding tip-sample spacing at which the pre-defined lithographic current setpoint is achieved. This resulting tip-sample spacing ranges in between the symmetric and asymmetric scenario. The beam shape could be deformed having a ring shape with an opening in the opposite direction of tip movement. This means that the electric field as well as the emission is shifted towards the tip movement direction. As described previously, the strength of this effect depend on varies parameters. Since the electric field and current density distribution at the tip are a function of the crosslinking and removal front position, also the tip velocity \( v_t \) matter.

As found, the back-coupling effect has a significant influence on the current density distribution. This effect was also found in various experimental scenarios, described in chapter 4. The assumption of a Gaussian shaped beam is therefore only appropriate in a first approximation. The lithographically induced back-coupling effect is unique for the FE-SPL processing. In contrast, in standard electron beam lithography (EBL) the incident electron beam is independent of the lithographic progress (e.g. the crosslinking reaction). Thus, in FE-SPL the possibility of an asymmetric beam shape as well as a modulation of the beam shape as a function of the lithographic progress has to be taken into account. In other words, the back-coupling effect leads to a direct influence of the lithographic modification and structuring process onto the electric field distribution at the tip surface. Linked by the Fowler-Nordheim emission process, also the current density is changed respectively \( J_{FN} \sim E^2 \).

**Estimation of the influence of a water layer / water meniscus on the electric field distribution:**

Since the FE-SPL exposure process takes place in ambient conditions, with a typical relative humidity level between \( rh = 20 – 40\% \), the formation of a thin water layer (0.5 nm up to a few nm) at the resist-air interface is most likely [390, 391]. As shown, the interfacial water film has a significant influence on the electric field and current density distribution. Thereby, the calixarene- and resorcinarene-based MG resist contain (phenolic) \( OH \)-groups, which gives a hydrophilic character. This enhances the formation of a thin water layer at the resist-air interface by adsorption of ambient moisture. In a first assumption of an electrostatic model (as previously discussed), the water layer can be treated as additional inert dielectric layer, which is placed on top of the dielectric resist (conductivity, dissociation of the water as well as reactions of and within the water layer are neglected). In analogy to Eq. 5.6, the alteration of the tip-sample gap \( \Delta d_g \) for multi-(n)-dielectric layer systems could be described by:

\[
\Delta d_g = d_{g2} - d_{g1} = \left\{ \frac{d_{11-1}}{\epsilon_{d1-1}} + \frac{d_{1-n}}{\epsilon_{d1-n}} + \ldots \right\} - \left\{ \frac{d_{21-1}}{\epsilon_{d2-1}} + \frac{d_{2-n}}{\epsilon_{d2-n}} + \ldots \right\}
\]

\[(5.8)\]

(due to the tip-enhancement effect 2.4.3 the numeric simulation results differ slightly from the analytic solution). Due to the high relative permittivity of water \( \epsilon_r - d-H_{2}O = 78.3 \) ([392], A.1), an already thin water layer causes a strong increase of the electric field strength within the tip-sample gap, shown by an electric field simulation series Fig. 5.3.13 and 5.3.14. Additionally, the impact of the water layer for different lithographic scenarios as discussed before is summarized by Fig. 5.3.15. As a direct
Figure 5.3.12: Investigation of the tip radius of curvature influence in the case of an asymmetric tip-sample configuration. Therefore, the example of scenario #3, Fig. 5.3.10 was simulated by using different tip radii. Graph (i) shows the electric field distribution along the tip surface. The derived current density is plotted in (ii). [Parameter: $d_{ts} = 27.5$ nm, $w_{CL} = 20$, $h_{CL} = 20$, $w_R = 0$, $d_R = 0$, $\epsilon_{r-d-unmodified} = 3.7$, $\epsilon_{r-d-crosslinked} = 6.6$, $d_d = 20$ nm, $r_{tip} = 15$ nm, $U_b = 40$ V, $\psi = 4.5$ eV]

Figure 5.3.13: Electric field simulation showing the influence of an additional water layer (treated as additional dielectric layer with $\epsilon_{r-d-H2O} = 78.3$), placed on top of the dielectric resist film ($\epsilon_{r-d-unmodified} = 3.7$, $d_d = 20$ nm). The electric field distribution is calculated for different water layer thicknesses of $d_{H2O} = 0$ nm (i), $d_{H2O} = 0.5$ nm (ii), and $d_{H2O} = 2$ nm (iii). [Parameter: $d_{ts} = 35$ nm, $r_{tip} = 15$ nm, $U_b = 40$ V, $\psi = 4.5$ eV]
Figure 5.3.14: Evaluation of simulation results giving the influence of a water layer, which is present at the resist-air interface. The graphs display the electric field distribution along the tip surface (i), the resulting current density (ii), and the electric field measured along the center cross-section (iii) and alongside of the resist surface (iv). [Parameter: \( \epsilon_{r-d-H2O} = 78.3; d_{H2O} = 0 - 4 \text{nm} \) \( r_{tip} = 15 \text{nm} \), \( U_b = 40 \text{V} \), \( \psi = 4.5 \text{eV} \), \( \epsilon_{r-d-unmodified} = 3.7, d_d = 20 \text{nm}, d_{ts} = 35 \text{nm} \)]
Figure 5.3.15: Comparison of the impact of a water layer \( \epsilon_{r-d-H_2O} = 78.3 \), \( d_{H2O} = 2 \text{ nm} \) having a partial (p) or a complete (o) coverage of the resist film. The simulation results display the electric field (i, iii) and the resulting current density (ii, iv) distributions for two different scenarios: (i-ii) Superimposed crosslinking and removal reaction corresponding to Fig. 5.3.6; (iii-iv) Moving tip with progressing ablation front, in relation to Fig. 5.3.10. [Parameter: \( d_{ts} = 35 \text{ nm} \), \( \epsilon_{r-d-unmodified} = 3.7 \), \( \epsilon_{r-d-crosslinked} = 6.6 \), \( d_d = 20 \text{ nm} \), \( r_{tip} = 15 \text{ nm} \), \( U_b = 40 \text{ V} \), \( \psi = 4.5 \text{ eV} \)]
consequence of the electric field strength increase at the tip surface, also the current density is enhanced respectively (Fig. 5.3.14-ii). As supposed, with increasing water layer thickness this effect increases. Due to the enhanced total emission current, the feedback system further retracts the tip leading to an enlarged tip-sample distance \(d_{ts} = d_g + d_{d1-1} + d_{d1-n} \); \(d_g\) defined by Eq. 5.8. Effectively, an enhanced beam broadening results. The same general behavior is valid for the various other lithographic case scenarios simulated, summarized in Fig. 5.3.15. Thereby, two different cases of water layer coverage were considered in simulations, a partial coverage (water layer covers only the pristine and non-ablated areas) and a total coverage (water layer covers the entire surface homogeneously). In both scenarios the same general behavior is obtainable. However, as supposed the total coverage has the strongest impact on changes of the electric field strength. Thus, in order to achieve highest lithographic resolution a low relative humidity level is targeted, which minimizes the interfacial water layer. In addition, the presence of a water layer leads to a shielding of the resist layer from the electric field. A flattening of the field distribution below the nanoprobe occurs, demonstrated in Fig. 5.3.14-(iv). However, since the electric field simulations consider neither chemical reactions nor related dynamic effects, the simulation results give only a first approximation (deeper insights are provided in the work of S. Lenk, ref. [305]).

As indicated by anodic oxidation SPL, the formation of a water meniscus bridging the tip and the resist surface is likely to happen in the case of ambient conditions, close tip-sample spacings and high electric fields. In particular, the close proximity of the tip apex and the resist surface facilitate a spontaneous capillary condensation. If the spacing is small enough, the formation of a water meniscus is likely, ref. [390, 393]. Thereby, the concave meniscus, which is in equilibrium with the surrounding vapor, could have an extension of only 4 – 8 nm in diameter [394]. Since the water bridge formation could also be induced and enhanced electrostatically, the electric field in between the tip-sample gap plays an important role, ref. [394, 395]. When a critical electric field strength of approx. 0.7 – 1.9 V/nm is exceeded, the formation of an electric field induced liquid water bridge is likely [394, 395]. The exact threshold value is mainly a function of the gap distance, the tip radius of curvature and the relative humidity.

Thus, the impact of a water meniscus formation should be discussed, based on electric field simulations. The boundary conditions for simulation are identical with previous assumptions, which means that the water is treated as an inert, dielectric layer in a static simulation (no reactions occur). However, despite of the limited significance of the boundary conditions, a basic idea is gained how the electric field distribution is changed due to the introduction of a high \(\varepsilon_{r-d}\)-channel between tip and resist (for more meaningful results an electrodynamic simulation is required and the conductivity of the water layer as well as chemical reactions have to be taken into account; ref. [305]). The corresponding simulation results are summarized in Figs. 5.3.16 and 5.3.17 for different lithographic scenarios, defined by (#0-#7).

As supposed, the introduction of a meniscus (high \(\varepsilon_{r-d}\) bridge in simulations) leads to a significant change of the electric field distribution (Figs. 5.3.16 and 5.3.17, cases #0-#1 simulations without meniscus, cases #2-#7 with meniscus). In particular, the electric field strength at the tip apex (interface tip-meniscus) is significantly reduced compared to the results, which do not consider a meniscus. Contrary to this, the field strength within the dielectric resist layer is enlarged. Thus, there is a shift of the maximum field strength from the tip-resist gap (in the case without meniscus) into the resist layer. This leads to a reversal of the known and experimentally verified system behavior. As known, a decrease of the tip-resist gap \((d_{ts} \downarrow\) at \(d_{d} = \text{const.}\)) leads to an increased electric field strength. In contrast, in the case of a bridging high \(\varepsilon_{r-d}\) meniscus the decrease of the gap results in a decreased field strength at the tip apex, whereas the field strength within the resist layer is increased (cases #5-#7). Both main results - (1) that the field strengths are too low to explain a Fowler-Nordheim
Figure 5.3.16: Simulation series showing the influence of a water meniscus ($\epsilon_r - d - H_2O = 78.3$) on the electric field distribution. The different scenarios, defined by #2, #4, and #7 are defined in Fig. 5.3.17. [Parameter: $d_{H2O} = 2\,nm$, $r_{tip} = 15\,nm$, $U_b = 40\,V$, $\psi = 4.5\,eV$, $\epsilon_r - d - unmodified = 3.7$, $d_d = 20\,nm$]

Figure 5.3.17: Simulation results showing the influence of a water meniscus ($\epsilon_r - d - H_2O = 78.3$) on the electric field distribution for different scenarios, defined by the table. The graphs summarize the electric field distribution along the tip surface (i), along the resist surface (ii), and in the center cross-section (iii) [Parameter: $r_{tip} = 15\,nm$, $U_b = 40\,V$, $\psi = 4.5\,eV$, $\epsilon_r - d - unmodified = 3.7$, $d_d = 20\,nm$].
field emission process; and (2) that the inverted gap distance versus electric field dependency results in a reversed distance-regulation feedback loop - indicates that in the experimental case the formation of a water bridge is not likely. As described in section 4.2.6, this is also supported by experimental measurements.

In summary, a water layer on top of the dielectric resist film alters the electric field but does not change the general behavior of the system. In contrast, the presence of a water meniscus bridging tip and resist leads to a radical change of the system behavior. In this context, several issues (simulation as well as experimental) were discussed already, which exclude the formation of a water meniscus during normal FE-SPL exposure processes. Only in exceptional system situations a formation of a water meniscus could be concluded. For example, in the case of some lithographic errors a step-like current increase exceeding the IV-converter range occurs. In consequence, the current feedback loop becomes unstable resulting in a crash of the probe. Due to that behavior a water meniscus formation, with subsequent electrochemical reactions (faradaic current $\gg$ FN field emission current) can be assumed. Since these effects are not controllable, and the spatial confinement of the reactions are constrained, this regime should be prevented during a FE-SPL exposure process.
6 Comparison and Combination of EBL and FE-SPL

In order to benchmark FE-SPL with respect to the well-established EBL, in the following chapter a comparative study is given. Beyond literature data, directed EBL exposure experiments were also carried out using the same calixarene MG resist coated samples as for the FE-SPL experiments. Thus, a direct comparison is enabled. The different lithographic mechanisms are worked out, and the capabilities are rated with respect to specific lithographic applications. The outcome of the study reveals that the techniques are rather more complementary than competing. Thus, in a second part of this chapter a novel complementary mix-and-match lithographic approach combining EBL and FE-SPL is introduced. Thereby, the problem of any serial lithographic technology is that the throughput decreases drastically with increasing resolution capability. In frame of this section FE-SPL has been ranked with respect to other mask-less nano-patterning methods. So far, the challenge affecting all lithographic methods is to find ways to increase resolution and throughput simultaneously. In this context, for FE-SPL different throughput enhancement strategies were figured out and assessed with respect to EBL. One of the most promising paths turned out to be the complementary mix-and-match approach, which is favored by the closed loop functionality of the FE-SPL system (ref. section 1.3). For proof-of-concept a standard electron beam lithographic work flow was combined with the novel closed loop FE-SPL processing. Various lithographic combinations were demonstrated revealing a significant improvement compared to stand-alone EBL and FE-SPL. The development methods were patented, ref. [35], and published, ref. [31, 312], respectively.

6.1 Comparison of EBL and FE-SPL Exposure on Calixarene Molecular Glass Resist

6.1.1 Exposure of Calixarene Thin Films by Standard Electron Beam Lithography

To determine the exposure characteristics of calixarene MG resist in standard electron beam lithography (Gaussian beam system, thermal Schottkey emitter, primary beam of 10 keV), respective line exposure dose tests were carried out. For best comparability of the exposure results, exactly the same samples were applied for FE-SPL and EBL. The focus was placed on two different sample types: (1) 4m1ac6 resist spin-coated on top of a Cr (5 nm)/Au (15 nm) bottom layer; And (2)cmc4r resist spin-coated on top of a pristine Si chip. After exposure, identical wet development step conditions were applied as for FE-SPL (time: 10 sec, solution: Xylene for 4m1ac6, MIBK for cmc4r). In order to suppress the influence of proximity effects, the EBL line exposure dose test consisted of widely separated lines (pitch: 500 nm). An EBL beam current of 0.21 nA and a fixed step size of 6.4 nm were applied. The line dose \( \Phi_L \) was stepwise increased by increasing the dwell time parameter (ref. Eq. 2.7). By AFM imaging directly after exposure, the latent image formation in EBL for calixarene MG resist was investigated.
Comparison and Combination of EBL and FE-SPL

Figure 6.1.1: EBL line exposure test, imaged by AFM after wet development. The AFM topographic images and corresponding section graphs show the line alteration as a function of the line exposure dose. The line exposure (pitch: 500 nm) was carried out at 10 keV. The line exposure dose was increased step-wise (dose listed from right to left side; steps row 1–4: 5 nC/cm; steps row 5–7: 125 nC/cm), in particular from 1–50 nC/cm (row 1), 50–100 nC/cm (row 2), 100–150 nC/cm (row 3), 150–200 nC/cm (row 4), 0.2–1.45 μC/cm (row 5), 1.45–2.7 μC/cm (row 6), 8.95–10.2 μC/cm (row 7). [Sample processing: 4m1ac6 MG resist, spin-coated on top of a Cr (5 nm)/Au (15 nm) bottom layer (1% wt solution in monochlorobenzene); Measured resist thickness of 22.9 nm by AFM and 21.1 nm by ellipsometry; Pre-bake step at 175°C for 5 min; wet development: 10 s dip in Xylene]

As is well-known, in EBL the calixarene MG resists gives a negative tone behavior (ref. section 2.3.3). The process of crosslinking as a function of exposure dose is visualized by AFM imaging and sectioning after wet development, shown in Fig. 6.1.1 for 4m1ac6 resist features. The height of the crosslinked resist as a function of exposure dose is plotted in semi-logarithmic style in Fig. 6.1.3. Four characteristic regimes can be identified (sections marked respectively in Fig. 6.1.3-i):

(1) Sub-threshold regime: At line exposure doses below the threshold (gel) dose \( \Phi_L < \Phi_{L-0} \), no sufficient crosslinking process occurs. In consequence, the entire resist film thickness is removed during wet development (WD).

(2) Regime of the contrast curve: Between the threshold gel dose and the saturation dose \( \Phi_{L-0} < \Phi_L < \Phi_{L-1} \) the remaining resist height after wet development step increases significantly. At the saturation dose \( \Phi_{L-1} \), which is also called resist sensitivity, the complete thickness of the resist layer is crosslinked. The contrast of the resist is defined by:

\[
y = \left[ \frac{1}{\log \left( \frac{\Phi_{L-1}}{\Phi_{L-0}} \right)} \right] \tag{6.1}
\]

The fits for determination of the contrast curve are marked in Fig. 6.1.3-(ii) by dashed lines. The values for \( \Phi_{L-0} \), \( \Phi_{L-1} \) and \( y \) are summarized in tabular form in 6.1 for both resist types and initial resist thicknesses. As supposed, the resist layer thickness has no influence on the threshold dose, sensitivity and contrast of the resist. The derived contrast of \( y \approx 2 \) for 4m1c6 is in agreement with
published reference data [182, 238, 396]. No reference data for line exposure dose experiments were found (conversion from area to line dose was not possible because not all relevant data are given in the related publications, e.g. the step size). The comparison of the 4m1ac6 calixarene and the cmc4r resorcinarene MG resist reveals a ∼4 times lower sensitivity for the latter derivative. In consequence of the huge difference in molecular weight [4m1ac6 has a ≈1.7 times higher molecular weight than the resorcinarene derivative cmc4r, ref. Appendix A.2], this was expected (ref. theory section 2.3). In other words, the cmc4r resist requires more crosslinks per unit area in order to generate an insoluble state. Further, the contrast in the case of cmc4r is nearly doubled compared to 4m1ac6.

(3) Plateau regime: Above the saturation dose the resist is fully crosslinked. With increasing line exposure dose only the width ($w$) of the negative tone lines is increased while the height remains constant. For EBL the most practical line exposure dose is at the beginning of the plateau regime.

(4) Resist decay regime: Due to the proximity effects, a further increase of the exposure dose leads to an overlap of the single lines forming a large crosslinked resist area. This transition from separated lines to a uniform crosslinked field is visible in row 5, Fig. 6.1.1. Interestingly, a positive tone line appears at the initially negative tone line position. As revealed by the AFM measurement, the resist height is reduced again. Most surprisingly, the normalized plot of the resist height versus line exposure dose, Fig. 6.1.3-(ii), demonstrates that the resist thickness decrease is independent of the applied resist, resist thickness and substrate (Si and Cr/Au tested). The trend can be fitted well by an exponential decay function. Thereby, the fit tends to a minimum crosslinked resist thickness of $d_{r\rightarrow\text{crosslinked}}(\Phi_L \to \infty) = 0.73 \cdot d_{r-0}$.

In order to get more insight into the exposure process, the latent image formation was investigated as a function of the exposure dose. Therefore, AFM imaging was carried out directly after the EBL exposure process, which is shown in Fig. 6.1.2 for the 4m1ac6 derivative. To obtain the full information content, the same features were investigated also after wet development (WD). The results for the 12 nm thick 4m1ac6 resist film investigation is summarized in Fig. 6.1.3-(iii-iv). The AFM analysis of the latent image confirms that a spatially localized decrease of the resist thickness is responsible for the appearance of the positive tone lines, which are visible after wet development. In other words, the decrease of the resist thickness is caused directly by the incident high energy electron irradiation, and not by the subsequent development process. The question now is whether the processes of EBL latent image formation and FE-SPL ablation are comparable or not.

As indicated by the red checks in Fig. 6.1.3-(iii), the decrease of the resist during exposure is enhanced with increasing line exposure dose. Thereby, the depth-dose dependency can be described by the same exponential decay function as applied for the resist reduction versus dose function measured after wet development (section 4, Fig. 6.1.3-i, ii). It is worth mentioning that even at the lowest dose, at which no sufficient crosslinking process has taken place, a latent image is measurable ($\Phi_L = 5 \text{nC/cm} \to d_{r-\text{latent}}/d_{r-0} \approx 0.9\%$). For dose values at the plateau regime (marked with 3 in 6.1.3-i, ii) the latent image is characterized by a resist decrease of already $d_{r-\text{latent}}/d_{r-0} \approx 5\%$.

Table 6.1: Summary of the calculated threshold (gel) dose ($\Phi_{L-0}$), the saturation dose ($\Phi_{L-1}$), and the resist contrast, broken down by the resist type and initial layer thickness (ref. Fig. 6.1.3-ii).

<table>
<thead>
<tr>
<th>Resist, Thickness &amp; Correction Terms</th>
<th>$\Phi_{L-0}$ [nC/cm]</th>
<th>$\Phi_{L-1}$ [nC/cm]</th>
<th>$y$ [%/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4m1ac6 - 24 nm-without latent image correction</td>
<td>13.3</td>
<td>37.9</td>
<td>2.2</td>
</tr>
<tr>
<td>4m1ac6 - 12 nm-without latent image correction</td>
<td>13.3</td>
<td>45.4</td>
<td>1.9</td>
</tr>
<tr>
<td>4m1ac6 - 12 nm-with latent image correction</td>
<td>13.8</td>
<td>43.9</td>
<td>2.0</td>
</tr>
<tr>
<td>cmc4r - 12 nm-without latent image correction</td>
<td>91.7</td>
<td>164.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

6 Comparison and Combination of EBL and FE-SPL
Comparison and Combination of EBL and FE-SPL

Figure 6.1.2: Investigation of the latent image formation in standard EBL, conducted on ≈ 12 nm thick 4m1ac6 resist. The decrease in resist thickness is measured directly after exposure by AFM (2D images and section graphs). A line array (pitch: 500 nm) was defined by EBL exposure at 10 keV. The line exposure dose was increased step-wise (dose listed from right to left side; steps row 1 – 2: 5 nC/cm; steps row 3 – 5: 125 nC/cm), in particular from 1 – 50 nC/cm (row 1), 150 – 200 nC/cm (row 2), 0.2 – 1.45 µC/cm (row 3), 1.45 – 2.7 µC/cm (row 4), 2.7 – 3.7 µC/cm (row 5). [Sample processing: 4m1ac6 MG resist, spin-coated on top of a Cr (5 nm)/Au (15 nm) bottom layer (0.5% wt solution in monochlorobenzene); Measured resist thickness of 12.4 nm by AFM and 11.9 nm by ellipsometry; Pre-bake step at 175°C for 5 min]

The latent image depth tends to $d_{r\rightarrow\text{latent}}(\Phi_L \rightarrow \infty) = 0.185 \cdot d_{r\rightarrow0}$ (Fig. 6.1.3-(iii)), which is in accordance with the behavior measured after wet development. To get the correct values for the resist performance parameter, table 6.1, a correction by the latent image resist reduction is required, shown by Fig. 6.1.3-(iii) example. In this context, the correction by the latent image term proves that at the plateau regime ($\Phi_L \approx 100 nC/cm$) the initial resist thickness is present (measured independently by ellipsometry), which means that $d_{r\rightarrow0} = d_{r\rightarrow\text{crosslinked}} + d_{r\rightarrow\text{latent}}$. Further, the latent image correction reveals that also a part of the resist in the resist decay regime (4) is rendered again soluble and washed away during the wet development step. Since both $d_{r\rightarrow\text{latent}}$ and $d_{r\rightarrow\text{crosslinked}}$ tend to fixed limits, also a boundary value for the dissolved resist part in the decay regime can be determined, which is $d_{r\rightarrow\text{dissolved}} = 0.085 \cdot d_{r\rightarrow0}$.

The analysis of the line width versus line dose, shown in Fig. 6.1.3-(iv), demonstrates that the crosslinking processes increase stronger in width than the corresponding latent image line. Supported by the investigation (Figs. 6.1.3-(iv), 6.1.1, 6.1.2), the latent image and the positive tone pattern observed after WD are the same phenomena. In conclusion, the latent image observed directly after exposure is not a direct measure of the width of the crosslinked structure. This is clearly visible in Fig. 6.1.2, in which the sections after exposure (latent image) and after wet development (WD) are
superimposed.

The same general width-dose behavior can be measured for different resist thicknesses, as well as for the resorcinarene based resist (cmc4r), summarized in Fig. 6.1.3. Due to the lower sensitivity of cmc4r, the entire graph is shifted towards a higher exposure dose range. More insight gives the normalized 1/dose versus lateral distance (x-position along the resist-air interface; The zero value corresponds to the center of the incident beam) plot, shown in Fig. 6.1.3-(v). Thereby, the 1/dose plot gives an indication of the absorbed energy density distribution within the resist layer. The underlying method to calculate the plot, based on the line width versus dose data of Fig. 6.1.3- (iv, vi), is described in refs. [13, 26, 397]. As is well known for EBL, the energy density profile can be described adequately by the sum of two Gaussian distributions [397, 398] - one for description of the incident primary beam (forward scattering) and one for the backscattering. This could be confirmed also for the EBL induced crosslinking process in Fig. 6.1.3-(v, green stars and blue dots). In contrast, the analysis of the corresponding latent image data of Fig. 6.1.3-(v, red checks) outlines a much higher localization for the latent image formation process. Further, no tails of the distribution are observable, as is characteristic for the EBL crosslinking process (a fit by a single Gaussian function is appropriate). Consequently, it can be assumed that the latent image is triggered by the incident primary beam, but not by the backscattered electrons (which are responsible for the large broadening of the crosslinking reaction in μm-range). As previously concluded, the latent image in the case of calixarene MG resist is not a direct measure of the crosslinked resist area - the width-dose functions of the latent image and the crosslinked image are fundamentally different.

If the formation of the latent image is attributed to a shrinkage process, caused by the crosslinking, then two different rates of shrinkage are present. In the incident primary beam area a high shrinkage is present, whereas in the surrounding crosslinked area absolutely no shrinkage is measurable. However, this is a rather unlikely explanation - a gradient of the shrinkage should be determinable (but it isn’t). A possible alternative explanation would be that the incident primary beam leads to a removal / ablation process. So far, it is not clear why the removal process seems to stop at ≈ 18.5% of the total resist layer thickness (after WD the resist layer thickness tends to a minimum of ≈ 73% of the initial value). Further, this effect seems to be independent of the calixarene resist type, the resist thickness and substrate type. This supports the assumption that the incident primary beam is responsible for the removal (backscattering is quite different for Si and Au bottom layers, Fig. 6.1.3).

To my knowledge, this kind of behavior has not been published so far. Since the EBL-related latent image formation in calixarene MG resist was not in main focus of this work, a subsequent work could bring more clarity. The EBL-related measurement data obtained so far are used for the comparison to FE-SPL in the following section. Beyond that, the characterization of the latent image formation is significant for the latter mix-and-match complementary lithography, wherein the latent marks are used for overlay alignment.

### 6.1.2 Comparison of EBL and FE-SPL on the Molecular Glass Resist Calixarene

As already derived from theoretical investigations, standard electron beam lithography (EBL) and field emission scanning probe lithography (FE-SPL) are rather different. While the lithographic source - electrons - is identical, the underlying principles of operation differ, summarized by table 6.2. Supported by the experiments (chapter 4), not only the electron energy seems to matter, but also the exposure conditions, in which the lithographic operation takes place. Thus, different lithographic paths are enabled by EBL and FE-SPL. In the following summary the experimentally derived differences between FE-SPL (ambient conditions) and EBL (UHV conditions) are elaborated.
Figure 6.1.3: Summary of the EBL exposure characteristics of calixarene based MG resists. In particular, the graphs show: (i) The height of the resist after wet development (WD), plotted as a function of the line exposure dose; (ii) The normalized plot of (i); (iii) The latent image formation during EBL exposure (the purple colored measurement points and corresponding connection line shows the latent image corrected height of the resist after WD); (iv) The line widths as a function of the exposure dose; (v) The derived normalized absorbed energy density distribution as a function of the lateral position (applied method described in ref. [26]); (vi) The line width as function of the line exposure dose, subdivided according to resist layer thicknesses. The data were extracted from AFM topographic images by the feature analysis program (averaging over 400 single AFM section plots).
### Table 6.2: Comparison of EBL and FE-SPL from a theoretical point of view. The summary is based on investigations of section 2.2.

<table>
<thead>
<tr>
<th>Subject</th>
<th>Standard EBL</th>
<th>FE-SPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Energy</td>
<td>1 keV - 300 keV</td>
<td>10 eV - 100 eV</td>
</tr>
<tr>
<td>Emission</td>
<td>Field emission gun; Emitter is placed far away from the sample surface</td>
<td>A field enhancement at the tip apex, which is in close proximity to the sample surface, stimulates a localized Fowler-Nordheim field emission process</td>
</tr>
<tr>
<td>Beam formation</td>
<td>Yes, provided by a complex electron optical system</td>
<td>No, the beam localization is provided by the close proximity and the highly localized electric field itself</td>
</tr>
<tr>
<td>Exposure conditions</td>
<td>Ultra-high vacuum (UHV) ⇒ is essential because of the large distance between electron emission and sample surface</td>
<td>Ambient conditions ⇒ since the tip-surface distance is significantly smaller than the mean free path of the related electrons in ambient conditions, no vacuum conditions are required</td>
</tr>
<tr>
<td>Inelastic mean free path (IMFP) of the electrons</td>
<td>The IMFP of the incident primary electrons are significantly larger than the typical resist layer thicknesses</td>
<td>The IMFP is typically smaller than the applied resist thicknesses; The typical depth of interaction has a range of less than a nanometer up to 3 nm</td>
</tr>
<tr>
<td>Exposure process and electron-sample interaction</td>
<td>A continuous slowing down approximation is valid; Lithographic interactions are typically triggered by induced secondary electrons</td>
<td>The low energy electrons, which are emitted from the nano-tip, gain again energy in the field after having energy losses</td>
</tr>
</tbody>
</table>

#### a) Lithographic interactions:

In FE-SPL the induced lithographic interaction is defined mainly by the electron exposure dose. At low electron exposure doses a crosslinking process of the calixarene MG resist gives a standard negative tone characteristic. If a certain threshold value is exceeded, a direct ablation reaction is superimposed, which leads to a significant change of the lithographic output. Thereby, crosslinking is a material modification, while direct ablation is a material transformation from non-volatile into volatile molecules. Whereas the phenomena of crosslinking is in agreement with the negative tone behavior of standard EBL, the direct ablation of resist is unexpected and contradicts the standard EBL processing scheme.

As experimentally substantiated, in EBL even at highest line doses no typical ablation reaction (linear depth-dose curve) could be induced (ref. section 6.1.1).

In terms of ablation in FE-SPL, it has been found that the relative humidity has an influence on the ablation threshold. Here, an increasing OH-group content (humidity) results in an enhancement of the ablation reaction, which could be described by a shift of the ablation threshold dose towards lower values. Thereby, only the threshold value is shifted, the ablation rate remains constant. In general, it has been reported for many polymeric resists that degradation processes are favored during irradiation when water is involved (ref. section 2.3.1). In accordance to the work of Kondo et al. [153], in ambient conditions chemical reaction pathways are supported by lower activation energies. In the case of UHV, these reaction mechanisms are not available. In summary, the results imply that an oxidative degradation mechanism is responsible for the conversion of non-volatile into volatile compounds. Thus, the combination of ultra-low energy electrons and the ambient conditions enables novel mechanisms which are not accessible via standard EBL in UHV.
b) Threshold values in spot exposure mode:

At lowest possible exposure doses a sole crosslinking process is induced. Thereby, the lowest applicable exposure dose is defined by the technical capability of the FE-SPL tool. In particular, in spot exposure a minimum dose of 1.9 \( fC \) is capable, whereas in line exposure 2 \( nC/cm \) is the limiting value. However, the threshold for crosslinking are below this dose value. Thus, the gel and saturation dose, as well as the contrast curve of calixarene molecular glass resist could not be determined for FE-SPL exposure (neither in spot nor in line patterning mode). Nonetheless, by using an extrapolation of the width-dose function in spot exposure (ref. section 4.3.1), a threshold for crosslinking of 1.7 \( fC \) could be approximated. The smallest dots defined by the actual setup at 30 \( V \) have been achieved at approx 1.9 \( fC \). This gives an amount of less than 1.2 \( x10^4 \) electrons per single dot, which corresponds to approx. 10 electrons per single calixarene molecule. In contrast, in the case of EBL at 50 \( kV \) Fujita et al. [182] have found a minimum point exposure dose of 1\( x10^5 \) electrons/dot for calixarene derivatives. Thus, the dose in FE-SPL is 10-times smaller than in EBL. Further, the FE-SPL spot dose is even lower than the EBL dose for the high sensitivity PMMA polymeric resist (positive tone, 5\( x10^4 \) electrons/dot for minimum dot sizes of \( \approx 20 \) nm [182]).

With increasing exposure dose the onset of ablation is exceeded, which leads to a superposition of crosslinking and ablation interactions. In standard environmental conditions a threshold dose of 1.2pC for ablation was measured, which corresponds to approx. 7.5\( x10^6 \) electrons/dot. The smallest dots in development-less positive tone have been defined close above the threshold at a spot dose of 2pC (ref. section 4.3.1). In average, an amount of 350 – 1000 electrons per single molecule are required in order to achieve a complete degradation of a single molecule into volatile end products. This value is 50 – 150 times greater than that for the crosslinking reaction. In contrast, in standard EBL even at highest doses no direct removal is triggered.

c) Threshold values in vector-based line exposure mode:

For vector-based line patterning an even higher difference in the exposure thresholds between EBL and FE-SPL is observed. A direct comparison of the EBL and FE-SPL exposure characteristics, investigated for the two different calixarene MG resist types (4m1ac6(8) and cmc4r), is summarized in Fig. 6.1.4. Outlined by graph 6.1.4-(i), the crosslinking thresholds are significantly different for EBL and FE-SPL. As derived in previous section, for 10 \( keV \) EBL a gel dose of \( \approx 92 (14) \) \( nC/cm \) was measured for the cmc4r (4m1ac68) derivative. A corresponding saturation dose (=sensitivity of the resist) of \( \approx 164 (44) \) \( nC/cm \) and a contrast of \( \approx 3.9 \) were determined, marked in Fig. 6.1.4-(i) for EBL by a red (blue) line. The EBL data are in agreement with published references [182, 238]. In contrast, in the case of a FE-SPL exposure already at the technically lowest (hardware limited) exposure dose of 2\( nC/cm \) a complete crosslinking process through the entire resist film thickness has taken place. This is valid for both calixarene resist derivatives, plotted in Fig. 6.1.4-(i) by dark green colored dots (below exposure doses of 10\( nC/cm \) the crosslinked resist height was measured). Since the onset of crosslinking is below the measurement limit of the FE-SPL system, the threshold/saturation dose and the resist contrast cannot be determined. Nevertheless, it is known that the saturation dose is below 2\( nC/cm \), which is a significant improvement in sensitivity compared to a standard EBL exposure. In particular, the sensitivity for the 4m1ac6(8) derivative is improved by a factor of 20, whereas for the smaller resorcinarene (cmc4r) molecule an improvement by a factor of 80 is obtained (minimum values, estimated by the reference of 2\( nC/cm \); In accordance to Charlesby’s law [252], the smaller molecule in standard EBL requires higher exposure doses).
Figure 6.1.4: Comparison of the exposure characteristics in EBL and FE-SPL, shown for two different calixarene MG resist types (4m1ac6(8) and cmc4r). EBL was carried out at 10 keV in UHV conditions, whereas FE-SPL was performed at 40 eV in ambient conditions. Graph (i) shows the normalized resist thickness as a function of the line exposure dose. In the case of EBL the remaining resist height after wet development (WD) is plotted (left vertical axis). For FE-SPL two different values, depending on the dose level, are plotted. At low exposure doses, in particular ≤ 10 nC/cm, the remaining resist height after wet development (WD) is plotted (left vertical axis), whereas for > 10 nC/cm the ablation depth is given, measured directly after exposure (right vertical axis). In graph (ii) the line width versus line dose characteristic is shown (CL: crosslinking of resist; R: removal/ablation of resist), whereas (iii) points out the normalized absorbed energy density distribution (method applied from [13, 26]). For a better visibility of graph (iii) a semi-logarithmic plot is provided in (iv).
If higher exposure doses exceeding a threshold value of $20 - 40 \, nC/cm$ (at standard environmental conditions) are applied in FE-SPL, a direct ablation occurs in the center of the crosslinked line feature. Here, the exact threshold dose values for ablation depends on various parameters, e.g. the applied resist derivative and the influence of environmental water, which makes a direct comparison difficult (ref. chapter 4). In Fig. 6.1.4-(i) at exposure doses larger than $10 \, nC/cm$ the normalized ablation depth, measured directly after exposure, is plotted as a function of the line dose. As demonstrated, the threshold dose for ablation in FE-SPL is located in the area of the gel exposure dose of standard EBL. In contrast to FE-SPL, an increase in dose does not lead to an ablation at EBL. Here, only a resist shrinkage is observed, which seems to tend to a fixed minimum value (ref. section 6.1.1). The comparison of exposure characteristics [FE-SPL (ablation) and EBL (crosslinking), Fig. 6.1.4-(i)] of the two different resist derivatives reveals that the differences in crosslinking behavior present in EBL disappear in the FE-SPL ablative regime. In particular, the 4m1ac6(8) molecule has a 1.8 times higher molecular weight than the smaller cmc4r molecule. In EBL crosslinking, this difference manifests in a different sensitivity. That is not valid in the ablative FE-SPL regime. Here, the exposure characteristics are almost identical for both derivatives (Fig. 6.1.4). Thus, the Charlesby theory [252] is not valid for the direct ablation process in FE-SPL. This supports the fact that in FE-SPL exposure, which is carried out in ambient conditions, a chemical reaction pathway is present (as already previously concluded).

d) Lateral confinement and proximity effects:

In order to evaluate the lithographic resolution capability, the lateral confinement between standard EBL and FE-SPL exposure are compared, summarized in Fig. 6.1.4-(ii-iv). In particular, Fig. 6.1.4-(ii) provides the line width versus line exposure dose data for standard EBL (crosslinking: CL) and FE-SPL (ablation: R, crosslinking: CL). In accordance to the Gaussian exposure model (ref. section 5.1), starting from the width-dose data the lateral distribution (x-position) of the absorbed energy density in the resist is derived, plotted in Figs. 6.1.4-(iii-iv). In accordance to ref. [13, 26], the 1/dose plot is a measure for the absorbed energy density in the resist. Each curve was normalized independently, based on the corresponding lithographic interaction threshold value. Since for crosslinking in FE-SPL no threshold value could be determined, the corresponding curves for FE-SPL are not included.

It is obvious that in the direct ablation regime of FE-SPL a generally higher lithographic resolution is obtained. In accordance to the work of Wilder et al. [13, 26], the EBL crosslinking process can be modeled by a double Gaussian beam distribution. Thereby, the long tails of the distribution (better visible in the semi-logarithmic plot, Fig. 6.1.4-(iv) correspond to the backscattered electrons. This backscattering, which is responsible for the long-range proximity effects, is characteristic for standard EBL. If this component is deducted, a single Gaussian fit with a FWHM of 97 nm is derived (Fig. 6.1.4-(iii), marked by a blue dotted line). This value corresponds to the forward scattering in the resist (ref. [13, 26]). In the case of direct ablation in FE-SPL, a single Gaussian function type, which is in accordance to previous model description, can be applied. A FWHM width of 25 nm is estimated, which is about 4 times lower than that for the crosslinking reaction in EBL. This proves that FE-SPL gives significantly higher resolution capabilities than ordinary crosslinking in EBL. As demonstrated in section 5.1, both reaction types in FE-SPL (ablation and crosslinking) can be described by a single Gaussian function type distribution. Although it is not possible to prepare the absorbed energy density distribution plot for crosslinking in FE-SPL, it can be concluded that the FWHM width is larger than for ablation. However, no long-range tails of the distribution are present, which supports the fact that proximity effects are effectively suppressed (ref. section 4.2.5). In consequence, in reaction types in FE-SPL enables a higher resolution capability than standard EBL.
d) Summary and conclusion:

As demonstrated, the irradiation by low energy electrons in ambient conditions enables novel reaction paths, which are not accessible via standard EBL in UHV. This is manifested by two lithographic relevant observations:

1. The increase of the sensitivity of calixarene MG resist: So far, previous studies of FE-SPL exposure have shown a lower sensitivity when high sensitivity EBL resist systems are used. This was reported by Perkins et al. [193] for chemically amplified resist (CAR) systems as well as by Wilder et al. [13, 26] for polymeric resists like SAL601 and PMMA. Since the obtained exposure characteristics contradict the initial theory of low energy electron exposure, this has led to the assumption that in FE-SPL fundamentally different mechanisms are involved ([13, 26, 193]). Unlike previous studies, calixarene is a very insensitive resist type. As experimentally obtained, in comparison to EBL the sensitivity in FE-SPL is enhanced by a minimum factor of 10 and 80 for line and spot exposure, respectively (for the smallest calixarene derivative: cmc4r). Thus, the trend is reversed, which means that FE-SPL is a more effective exposure method. In this context, a further improvement of resist sensitivity is expected if the hardware of the system can be further improved (current detection and regulation is currently the limiting factor).

In terms of EBL exposure of calixarene, the involved mechanisms could not be unequivocally clarified so far. Experiments carried out by Ruderisch [237] and Sailer [199, 236] pointed out that the aromatic systems are partially broken. Further, the oxidation state of the carbon atoms, at which originally the phenolic hydroxyl group were bonded, are raised. Spectroscopic investigations showed no defined final state after crosslinking. Instead, an increase of the chemical inhomogeneity was measured. In consequence, it is expected that multiple mechanisms are triggered by the incident radiation. Sailer [199] suggested that a partial oxidation of the molecular structure is most likely. Also Prins et al. [276] concluded a break up of the arenes as the main mechanism, followed by a linking to other arenes or functional groups. Derived from laser-based dry development experiments, which were combined with EBL, Olynick et al. [253, 254] suggested the formation of aromatic OH, followed by aromatic OH$_2^+$. In this context, the laser-induced ablation process is promoted by an interplay between phenolic units and extended conjugation in the aromatics [253].

The insights gained in ambient low energy FE-SPL support the indication that the hydroxyl (−OH) functional groups of the calixarene molecule play a significant role in the crosslinking process. Here, MG resists without functional groups do not show a sufficient crosslinking process (ref. section 4.4). In consequence, the experiments support a model in which the crosslinking process is rather a resist-specific mechanism. Since compared to EBL lower doses are required, it could be supposed that the hydroxyl groups works as an effective crosslinking mediator, which is released in a more effective way by low energy electron exposure.

In this context, the heuristic exposure model of Fujita et al. [182], in which a more efficient process by low energy electron exposure is suggested, could be confirmed. Here, the exposure process was explained by specific energy transfers to narrow energy bands of the resist molecules. Thereby, the target bond excitation efficiency is a function of the energy loss of the involved electrons. Only energy losses which are in the range of several eV are able to excite the target bond reaction. Thus, in standard EBL the induced secondary electrons are responsible for the lithographic process. In accordance with this, the calculated Vriens exposure reaction cross-sections are located in this energetic range (8 – 12 eV for relevant binding strengths ranging between 3.60 eV (C-C) and 4.77 eV (O-H), ref. section 2.2). Since the low energetic electrons in FE-SPL are close to those energetic bands, the increased exposure efficiency
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of FE-SPL could be explained. So far, in EBL and in FE-SPL the exact mechanisms of crosslinking are still unresolved. In practical applications the exposure by low energy electrons (\(< 100 \text{eV}\)) enable a higher sensitivity while preserving and enhancing the ultra-high resolution capabilities of molecular glass resists. Thus the main drawback of this resist class has been overcome. Further, the exposure by low energy electrons effectively suppresses backscattering. Thus, practically no proximity effects are present.

\(<2>\) The direct ablation of resist: A second fundamental difference to standard EBL represents the direct ablation of resist material, wherein volatile end products are formed. As experimentally derived, an oxidative degradation process is supposed. The ablation process needs a significantly higher exposure dose (10 and 150 times) than crosslinking. The high local threshold doses required imply that only a small portion of the total beam diameter contributes to the direct ablation. In consequence, a higher spatial confinement is achieved giving sub-10 nm isolated lines and 10 nm hp dense line/space patterns.

In general, the direct ablation leads to a positive tone, development-less or self-development lithography mode. The ablation mechanism seems to be a residual free process since no re-deposited material was found either on the tip surface or aside of the pattern on the resist surface. This had been verified by large scale patterns (ref. [40]). In the ablative regime, explained by a two-threshold Gaussian dose distribution model (ref. section 5.1), a superposition of lithographic reactions occurs. Due to the explained self-alignment process, the system-defined alignment capability is relaxed when using the superimposed patterns in a targeted manner. For example, in the case of spot exposure doughnut features are created, in which the ablative spot is perfectly centered within the crosslinked spot.

In the case of calixarene MG resist the direct ablation of resist always implies a previous crosslinking process. This is given by the fact that the crosslinking mechanism is characterized by a lower threshold dose than the ablative mechanism. In this context, the lithographic experiments with alternative MG resists (ref. section 4.4) show that an initial crosslinking process is not a stringent requirement for the ablative reaction. Even MG resists which consist of mainly aromatic units, without any functional chemical groups, have shown a direct ablation (but no crosslinking). Interestingly, the threshold dose for ablation is almost independent of the functional resist groups (with the exception of \(F\)-termination).

Thus, the hydroxyl functional groups in calixarene resist are responsible for an effective crosslinking process, but they are not relevant for ablation. The conclusion is that the ablative mechanism is a more a general than a resist-specific effect. In particular, the same ablative regime is demonstrable in polymeric resist materials, e.g. PMMA, PS, PHS, shown by the work of Y. Krivoshapkina [209, 362] (work was supervised in frame of this thesis; resolution capability is limited in this resist type). In this context, it is proposed that the effects described by Lyuksyutov et al. [156], called electrostatic nanolithography, can be assigned to the same mechanisms as the herein observed ablation (oxidative degradation processes). This again confirms that the direct ablation in ambient conditions is rather a resist-unspecific mechanism. From theoretical point of view, in FE-SPL thermal effects can be excluded. This is substantiated by calculations of Perkins et al., [193], which have investigated the low current operation range (\(\leq 100 \text{pA}\)) for polymeric resist materials. The significant influence of the exposure environment affirms that chemical reaction pathways are triggered. Here, an enhancement of the ablation reaction by an increased environmental water content was observable. Thus, environmental (gaseous) water promotes an ablation reaction by the release of additional oxidative species. Vice versa, the ablation reaction can be shifted towards higher threshold doses by dry environments. This yields a pure crosslinking reaction, which is favorable for standard negative tone lithography. The experiments indicate that no water meniscus is present during lithography, supported by the fact that:
(1) A characteristic FN field emission behavior is measured; (2) A linear dependency between tip-sample spacing and applied bias voltage is present, and; (3) Multi-emission effects are given at higher bias voltages, to mention only a few arguments. The comparison reveals that the operation in tailoriable ambient conditions in FE-SPL enables novel reaction pathways which are not accessible via standard EBL in UHV.

6.2 Towards a Mix-and-Match Lithography

6.2.1 The Throughput Dilemma of Serial Lithographic Methods and Throughput Enhancement Strategies

The main limiter of scanning probe technology turns out to be the low throughput capability in consequence of the serial imaging and patterning process. Similar to other serial lithographic methods, e.g. EBL, FE-SPL also obeys Tennant’s law \[27, 399, 400\]. This empirically derived relation describes the dramatic drop of the throughput with increasing resolution. In particular, D. M. Tennant has found a power-law relationship between areal throughput \(A_t\) and the lithographic resolution \(R\):

\[ A_t = k_T R^5 \]  \hspace{1cm} (6.2)

with Tennant’s constant \((k_T = 4.3 \, \text{nm}^{-3} \, \text{s}^{-1})\). A comparison between different SPL methods in terms of patterning speed, throughput and resolution, provided in a pursuant publication \[31\], confirms this trend also for FE-SPL. An excerpt of this investigation is summarized in Fig. 6.2.1. As a benchmark reference standard Gaussian EBL was chosen, which is the most-advanced state-of-the-art mask-less patterning tool. Based on the proposed layout, the patterning time of 100 identical features was estimated for a single probe and a parallel probe setup (256 cantilever operating in parallel). A great diversity in the patterning speed is present ranging from \(\text{nm/s}\) (patterning time increases up to a few centuries) up to a few \(\text{cm/s}\) (patterning time drops to a few minutes). The comparison of the resolution versus throughput relation reveals that Tennant’s law is still valid. Patterning at ultra-high resolution level incurs immense costs in time. In consequence, the single nanometer resolution capability means a dramatic loss of throughput. Thus, the challenge affecting all serial lithographic technologies comprises to meet the resolution and throughput demand of upcoming nodes. In order to face this trade-off, different strategies and/or their combinations are conceivable:

**Strategy <1> Enhanced tip velocity / optimized resist sensitivity:** In frame of this strategy, the patterning speed (= tip velocity) is increased by introduction of high speed scanners \[403, 404, 405\]. In this context, an optimized resist sensitivity is demanded which fits to the available exposure doses (ref. \[131, 171\]). However, the comparison of different SPL methods, Fig. 6.2.1, demonstrates that an enhancement of the throughput by high speed SPL implies a loss in lithographic resolution capability.

**Strategy <2> Upscaling:** The upscaling of the physical process is achievable either by utilization of cantilever/probe arrays \[87, 203, 316, 406, 407\] or by introduction of conductive stamps, which mimic parallel probes \[402, 408\]. The parallel probe approach is realizable by cantilever array technology, which is based on a thermally driven self-sensing probe concept, ref. section 3.1.7 and \[39, 203, 316\]. Here, the actuator and the sensor are integrated in the cantilever itself. Thereby, each cantilever stand-alone is capable to perform simultaneously a closed-loop lithography scheme. As outlined by Fig. 6.2.1, a huge amount of simultaneously operating probes (minimum 256, preferably 1000) are necessary.
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Figure 6.2.1: Comparison of different high resolution mask-less lithographic methods in terms of patterning resolution and throughput capabilities. The focus of the investigation was placed on SPL, whereas EBL was applied as benchmark reference. As an example for the evaluation of the throughput, a layout was proposed (inlet figure), which should be patterned 100 times. Per definition only the yellow-marked surface area is patterned (in overall \( \approx 2 \text{ mm}^2 \)). A single layer and single pass patterning process was assumed.

References: #1->[129, 133]; #2-3->[148, 149]; #4->[401]; #5->[156, 157]; #6->[402]; #7->[171]; #8->[76]; #9->[131]; #10->[75, 76]; #11->[403].

in order to ease the throughput situation. Since each probe has to be individually addressable, this upscaling strategy is accompanied by a rapid increase of engineering efforts and tooling costs, especially in the context of control electronics (high speed data handling and management system).

Recently, Mirkin et al. [87, 407] have suggested two cantilever-free, tip-based up-scaling approaches. Here, the application of passive arrays simplifies the probe addressability and offers significant advantages in terms of scalability and costs. The decrease in system complexity is connected with the loss of the “read-back” capability of each individual probe. However, the imaging mode is essential for a closed-loop scanning probe lithography scheme. Thus, neither a pre-inspection, nor a pattern overlay alignment and post-inspection are possible. Thus, passive arrays have significant drawbacks for practical applications. In this context, the “read-back” functionality of a closed-loop scheme is essential especially for arrays, wherein individual differences of the probe shapes can be compensated by a software correction of the patterning parameter. The basis therefore is the imaging of the lithographic result directly after exposure. In conclusion, passive arrays are suited for applications wherein a direct feedback is not essentially required and pixel variations and placement errors are acceptable. However, for highest resolution lithography, critical dimension patterning, and in applications where high overlay and stitching accuracy is required, active cantilever probe arrays are essential.

Strategy <3> FE-SPL with variable beam diameter: In consequence of Tennant’s law, the resolution should be adapted to the individual application scenario. The highest resolution should only be used where absolutely necessary. Based on this approach, a variable beam diameter FE-SPL scheme is derived, published in ref. [37]. As experimentally observed, in FE-SPL the beam diameter is a function of the applied lithographic parameter set (4.2). A beam modulation from a few nanometers up to a
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Figure 6.2.2: Estimation of the improvement in throughput and patterning time by applying a variable beam diameter approach. In graph (i) a calculation of the area throughput as a function of the beam diameter for a typical FE-SPL vector-based patterning scheme is shown (tip velocity $v_t = 20 \mu m/s$; overlapping of patterning lines: 5% of the line width). The calculation was done for a single cantilever setup as well as for cantilever arrays consisting of 16 and 256 active cantilever. In graph (ii) the writing time is plotted as a function of the beam diameter for a $10^2$, $100^2$, $1000^2 \mu m^2$ square patterning field. In (iii) the calculation result of the patterning time for a realistic $100 \times 100 \mu m^2$ patterning field having a feature size distribution as shown in Fig. 6.2.1 is given. Here, the writing times for a fixed beam size of $5 nm$ versus a variable beam FE-SPL with adjustable beam diameter are compared ($v_t = 20 \mu m/s$; 5% line overlap), based on ref. [37].

![Graphs showing area throughput and writing time as functions of beam diameter.](image)

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Estimation of the improvement in throughput and patterning time by applying a variable beam diameter approach. In this context, large beam sizes are utilized for writing of low resolution features, whereas at higher resolution smaller beam sizes are applied. Thus, by selecting an appropriate beam diameter to match the feature size, the throughput can be optimized without degrading the resolution of the pattern. The concept is stated in Fig. 6.2.2 by showing respective throughput calculation results for a typical vector-based FE-SPL patterning routine. In accordance to Tennant, the FE-SPL patterning scheme is governed by the same general power law (Fig. 6.2.2-i), which means that with decreasing beam diameter the throughput capability drops dramatically. In the case of a $100 \times 100 \mu m^2$ patterning field (Fig. 6.2.2-ii) the writing time can be reduced from initially $\approx 38 h$ at a $4 nm$ beam diameter to $\approx 23 min$ by using a $400 nm$ beam (vector-based line patterning at a constant velocity; current setpoint is adjusted accordingly in order to meet the required exposure dose). As shown by a more practical example of a $100 \times 100 \mu m^2$ writing field, defined in Fig. 6.2.2-(iii), a $\approx 23$-fold reduction of the writing time is achievable by a variable beam diameter FE-SPL approach. However, as indicated by Fig. 6.2.2-(i) even a FE-SPL scheme combining the variable beam diameter
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approach and a parallelization by 256 active cantilever is not able to reach a mask production level (1 complete mask patterned in 8 hr, which requires an area throughput of $A_t \approx 10^9 \mu m^2/hr$). Instead, a minimum upscaling by 1000 cantilever operating in parallel is needed in order to reach the projected throughput capability.

**Strategy <4> Mix-and-match lithography:** Mix-and-match circumscribes the combination of different lithographic methods in a so-called hybrid approach [28, 409]. In general, the dilemma is present that high throughput lithographic methods cannot fulfill the high resolution requirements, whereas the ultra-high resolution SPL methods cannot achieve the demanded throughput. Thus, the combination of a high throughput and a high resolution method in a mix-and-match approach seems to be a promising strategy. For instance, the pattern in Fig. 6.2.1 can be divided into large scale features, which are definable by conventional optical lithography (contact pad areas), and into high resolution critical dimension (CD) features, which have to be defined by a high resolution method (nanowire-gap structure in between both contact pad areas). Thus, high resolution patterning is only applied when it is absolutely necessary. In the context of this work, the mix-and-match strategy was examined in more detail using FE-SPL as highest resolution lithographic method. The results are discussed in more detail in the next section.

**6.2.2 Complementary Mix-and-Match Lithography combining EBL and FE-SPL**

Mix-and-match approaches are based on a data splitting strategy. In particular, all large-scale and non-critical dimension (CD: critical dimension) parts of the pattern are defined by conventional lithography, e.g. by optical lithography (EUVL), NIL, or EBL. In a subsequent lithographic step all CD high resolution parts are patterned by the closed-loop FE-SPL method. In order to achieve a nanometer precise overlay alignment and stitching, the AFM-functionality of the FE-SPL system is utilized (ref. section 1.3). Further, a direct feature inspection and quality control are given. Two different mix-and-match strategies, which differ in the number of process steps and resist layers, are conceivable. In the dual resist method, each resist layer is individually transferred into the underlying hard-mask layer. Thus, the final pattern is the sum of both cycles, whereby each cycle consists of an exposure process, followed by a wet development and a pattern transfer step [409].

The more sophisticated way is the single resist strategy, wherein only a single resist layer is exposed by successive lithographic exposure processes without having an intermediate development and pattern transfer step. In the following work this approach is followed. Here, the same resist layer is modified by both subsequent lithographic processes. The challenge is that the resist system has to be compatible with both methods in terms of sensitivity, resolution, and line edge roughness (LER). Advantageously, the calixarene MG resist type is suited for FE-SPL, EBL, and EUVL. For a proof-of-concept FE-SPL is combined with EBL. Thereby, EBL serves as substitute for the high throughput optical lithography process (EUVL is not available in our facility, but the mechanisms in the resist induced by EUVL and EBL are comparable). Since the FE-SPL method includes an in-situ imaging and overlay alignment capability, it is reasonable to carry out EBL for large-scale feature exposure as first lithographic step. As described in the ITRS [4], via and cuts in extreme dense line/space patterns are one of the most critical and challenging processes. In order to address this kind of patterns, different complementary lithographic approaches are developed combining negative tone EBL with positive tone / negative tone FE-SPL. As a result, novel methods were patented [35] as well as partly published in refs. [31, 312].
Figure 6.2.3: Complementary mix-and-match lithographic concept combining negative tone EBL (crosslinking reaction) and positive tone, self-development FE-SPL (direct ablation reaction).

Figure 6.2.4: Summary of the processing scheme for negative tone EBL and positive tone FE-SPL mix-and-match combination. In the left column the process steps are schematically drawn, whereas in the right column corresponding AFM topographic images are given. The following process steps were applied: (a) EBL exposure; (b) Imaging of the latent image caused by the EBL exposure process; (c) Wet development step; (d) Imaging after wet development revealing the crosslinked resist features; (e) Definition and alignment of the FE-SPL pattern, followed by the FE-SPL exposure process; (f) Final imaging of the mix-and-match pattern. [EBL exposure parameter: 10 keV, 0.21 nA beam current, 150 nC/cm line dose, 500 nm line pitch; FE-SPL exposure parameter: 40 V sample bias voltage, 80 nC/cm line dose, 40 pA current set-point]
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Figure 6.2.5: FE-SPL patterning by direct ablation of previously crosslinked and developed resist features in a mix-and-match lithographic scheme. The SEM image (i) shows the residual-less ablation of an entire area of a EBL-crosslinked 24 nm thick resist layer [40 V, 60 nC/cm, 4 nm line pitch]. The SEM image (ii), which is taken at an angle of 52°, displays a EBL pattern [150 nC/cm, 500 nm pitch], which is crossed by FE-SPL lines (30 V, 300 nC/cm). Both layouts were patterned in 24 nm resist according to Fig. 6.2.4 process scheme. In the AFM topographic image and section series of (iii) the modulation of the FE-SPL lines, which crosses a EBL pattern, is demonstrated [FE-SPL line dose: (a) 300 nC/cm; (b) 40 nC/cm; EBL line dose (a-b): 150 nC/cm].
a) Mix-and-match combining negative tone EBL and positive tone FE-SPL:

The general concept of combining negative tone EBL and positive tone FE-SPL in a complementary way is schematically drawn in Fig. 6.2.3. In particular, EBL has been applied as the first lithographic step in order to define all large-scale line features. Subsequently, all non-crosslinked resist parts were removed by a wet development step. FE-SPL is applied as the second lithographic step in order to interrupt the EBL crosslinked resist lines. Thereby, the imaging capability of the FE-SPL system (1.3) is applied to align the pattern respectively. The precision of the patterning placement/overlay alignment in the closed loop lithography is mainly determined by two factors. By measurement errors which occur in the preceding imaging step, and by placement errors of the probe itself. Here, especially slow drift effects which take place between the beginning of the imaging and the start of the exposure process cause significant deviations. This issue can be minimized by reduction of the time delay between both processes. In particular, a drift correction carried out shortly before exposure is recommended.

The entire process scheme, with a corresponding AFM image series, is summarized in Fig. 6.2.4 (ref. [31]). In particular, after spin-coating of calixarene resist, an initial pattern consisting of separated lines is defined by conventional EBL exposure (a). If necessary, the latent image can be imaged (b) and used for preliminary pattern inspection. Subsequently, a wet development step [10 sec in Xylene developer] (c) removes all non-crosslinked resist parts. AFM-imaging afterward reveals the final EBL pattern (d). A line width of 450 nm (gap between individual lines: 50 nm) is measured. By FE-SPL exposure operating in the ablative regime (e) the EBL resist pattern is modified. For demonstration, the EBL crosslinked resist lines were separated by the FE-SPL exposure process giving a checkerboard structure (90 deg angle between EBL and SPL lines). In a final AFM imaging process (f) the mix-and-match pattern is visible. Thereby, a line width in the FE-SPL ablation process of 40 nm (pitch: 250 nm) is measured.

In summary, even an already developed EBL pattern can be modified by FE-SPL. As already found, the EBL crosslinked resist requires a lower dose for ablation than pristine resist. Due to the increased dielectric constant of the crosslinked resist (4.2.5), the FE-SPL exposure at decreased bias voltages is reasonable in order to obtain highest resolution capabilities. In particular, bias voltages of well below the experimentally found minimum bias voltage condition, Eq. 4.2, can be used (e.g. $U_b = 30 \, V$ for $\approx 24 \, nm$ thick 4m1ac6 resist films, Fig. 6.2.5, ii-iii). In addition, in Fig. 6.2.5-(i) the residual-free removal of a larger area of EBL-crosslinked, $\approx 24 \, nm$ thick 4m1ac6 resist is demonstrated. Throughout the experiments no traces of displaced or redeposited material was measured. There is no evidence for mechanical, plowing-like interactions. As found by the FE-SPL stand-alone experiments, the line width depends significantly on the line exposure dose. Transferred to the mix-and-match method, the width of the cut can be adjusted by FE-SPL dose parameter, shown by Fig. 6.2.5-(iii). A 7.5 times lower line dose (b) has resulted in a 3 times smaller cut (a).

b) Mix-and-match combining negative tone EBL and negative tone FE-SPL:

Instead of a direct ablation, the FE-SPL exposure can also induce a crosslinking reaction similar to EBL processing. In this context, negative tone EBL and FE-SPL can be overlaid defining a merged final pattern. The basic underlying concept is schematically summarized in Fig. 6.2.6. Here, the initially separated EBL resist lines are connected at pre-defined areas by a superimposed FE-SPL exposure process. A corresponding example is summarized in Fig. 6.2.7 by an AFM / SEM image series. Since two consecutive crosslinking steps within the same resist layer are targeted, the wet development process has to be the final process step. In this context, for alignment of the FE-SPL pattern the latent
image of the EBL exposure is applied. In the particular case the FE-SPL lines are aligned exactly perpendicular to the EBL lines, with one FE-SPL line terminating exactly all EBL lines (marked in Fig. 6.2.7-e by a red rectangle). After both exposure process steps a common latent image is measured, shown in Fig. 6.2.7-(e). The subsequent wet development step (Fig. 6.2.7-d) reveals superimposed pattern in the resist (Fig. 6.2.7-e).

As targeted, the lines defined by FE-SPL connect the EBL lines exactly in an angle of $90^\circ$. By evaluation of the terminating FE-SPL line, an alignment accuracy of sub-5 nm was achieved. As expected from the stand-alone FE-SPL experiments (ref. section 4.2.5), no proximity effects between EBL and FE-SPL lines are measurable. Further, the FE-SPL exposure shows a significantly higher spatial localization than the standard EBL process. In consequence, FE-SPL enables an effective high resolution patterning, whereas the associate lithographic partner (EBL as a substitute of EUVL) provides the enhanced throughput capability.

However, as already demonstrated in section 4.2.5, in FE-SPL the tip-sample spacing is modulated by changes of the dielectric resist properties (crosslinking state). In order to compensate that effect, the bias voltage has to be adapted respectively (application of lower bias voltages when moving across the crosslinked resist state). As a result, very dense patterns are enabled, shown in Fig. 6.2.8. Here, a large-scale EBL line pattern was overlaid by a fine FE-SPL line pattern (25 nm hp lines/space pattern), exposed with a bias voltage of $U_b = 25$ V (this value is well below the estimated critical bias voltage value for unmodified resist, Eq. 4.2). A dense asymmetric grid structure is formed having well-resolved lines. No proximity, neither in between the FE-SPL crosslinked lines nor between the FE-SPL and EBL lines, is measurable. In this context, this kind of complementary negative tone EBL and FE-SPL strategy provides a large process window in terms of resolution, alignment and throughput.

c) Mix-and-match combining negative tone EBL and tone-switching FE-SPL:

As drawn schematically in Fig. 6.2.9, the combination of both previously introduced lithographic strategies (a)-(b) offers completely novel opportunities for rapid nanoscale prototyping of large-scale resist patterns. Thereby, the fixed large scale (non-CD) features are defined by conventional lithographic methods, which are ideally mask-based (EUVL). In a subsequent variable modification step, which is enabled by FE-SPL, the fixed pattern can be individually edited defining the final CD-structures. Thereby, individual connections between EBL-crosslinked lines can be defined (via crosslinking in negative tone FE-SPL) or previous fixed connections can be separated (via ablation in positive tone FE-SPL). For both processes the same tool base is used.
Figure 6.2.7: Process steps and corresponding experimental images of a combined negative tone EBL and FE-SPL mix-and-match patterning. The image series show: (a) Initial EBL exposure leading to a crosslinking of the resist. The corresponding AFM topographic and phase images reveal the latent image measured directly after exposure; (b) Second exposure process by FE-SPL. Thereby, the latent image is used as reference for overlay alignment. The exposure path is highlighted by yellow lines; (c) Combined latent image, measured by AFM. The FE-SPL exposed lines are observable, aligned perpendicular to the EBL lines; (d) Subsequently, a standard wet development step was carried out; (e) Resulting pattern imaged by AFM (left) and SEM (right) after wet development. [EBL exposure parameter: 10 keV, 0.21 nA current, 100 nC/cm line dose, 500 nm line pitch; FE-SPL exposure parameter: 25 V sample bias voltage, 25 nC/cm line dose; Probe: tungsten coated cantilever; Resist: ≈ 12 nm thick 4m1ac6 MG resist]
Comparison and Combination of EBL and FE-SPL

Figure 6.2.8: High resolution grid structure fabricated by a combined negative tone EBL plus FE-SPL exposure process. The large scale EBL lines, patterned at a half-pitch (hp) of 250 nm are superimposed by a 90° rotated dense FE-SPL line pattern (10-times lower pitch than EBL pattern). The grid structure is imaged after a common wet development step by SEM (i) and AFM (ii). [EBL exposure parameters: Identical to that of Fig. 6.2.7; FE-SPL exposure parameters: \( U_b = 25 \text{ V}, 20 \text{nC/cm line exposure dose} \)]

By using a finely tuned exposure dose in FE-SPL, the difference in ablation dose thresholds between the different resist crosslinking states can be exploited. As demonstrated in Fig. 6.2.10, the main FE-SPL patterning tone is switched only by variation of the crosslinking state of the resist. In particular, only half of the area was exposed by EBL, while the other half was left unexposed. In a subsequent FE-SPL exposure step (without a development step in between) a line pattern exactly perpendicular to the interface between EBL crosslinked / not crosslinked resist was defined. During FE-SPL exposure the lithographic parameter was kept constant. At the transition between the EBL crosslinked areas the patterning tone of FE-SPL automatically changes. While within the unexposed region the resist is crosslinked, in the EBL crosslinked area the resist is directly ablated. Since no other parameters were changed, the switching of the FE-SPL tone is exclusively caused by the threshold dose difference, explained in section 4.2.5. In particular, an EBL crosslinked area needs significantly less dose for ablation than an unexposed resist area.

d) Summary:

In next generation lithographic methods both resolution and overlay alignment at sub-10 nm (resolution) / sub-1 nm (alignment) becomes an extremely challenging issue (ref. [28, 410, 411]). A symbiosis of conventional methods (e.g. EUVL, EBL) with FE-SPL gives a significant capability improvement of both lithographic approaches. In particular, in the case of FE-SPL the throughput is significantly increased bypassing the serial process limitations, whereas the process window of conventional lithographic methods is enhanced by FE-SPL. Here, pre- and post-modification capabilities of already patterned and developed resist patterns are given. Further, an individual editing of patterns, without the requirement of mask modifications, is enabled. Due to the closed-loop FE-SPL patterning scheme, the well-established AFM techniques are applicable for in-situ overlay alignment, stitching and feature inspection. For an initial proof-of-concept, the benefits of EBL and FE-SPL are combined in a novel way. Thereby, EBL can be replaced by various other conventional methods like optical (EUVL) or nanoimprint (NIL) lithography.

In frame of this work, a resist system was found that is suitable for both exposure processes (EBL/EUVL...
Comparison and Combination of EBL and FE-SPL

Figure 6.2.9: Complementary mix-and-match lithographic concept combining negative tone EBL and tone-switching FE-SPL. In accordance to Figs. 6.2.3 and 6.2.6, by choosing appropriate FE-SPL exposure parameters either a primary crosslinking (indicated by a black-colored tip path, achieved by usage of low exposure doses below the ablation threshold) or a primary ablative reaction (indicated by a red-colored tip path, achieved by usage of high exposure doses above the ablation threshold) can be induced.

and FE-SPL). Thus, a single resist layer strategy has been demonstrated, followed by common pattern transfer step. The general concept of a complementary mix-and-match lithography works well for both lithographic tones of FE-SPL. Based on the developed process chain, fixed (mask-based) layouts can be customized directly within the resist layer. This gives a vast number of novel opportunities in research, prototyping and low volume manufacturing of highly-individual layouts. The underlying method has been patented, ref. [35].
Figure 6.2.10: Lithographic result of a complementary mix-and-match lithography combining negative tone EBL with both lithographic tones of FE-SPL. The tone-switching in FE-SPL was induced only by the threshold dose difference in ablation of EBL-crosslinked and unexposed (pristine) resist areas (no lithographic parameters were changed during the line pattern; FE-SPL: \( U_b = 40 \text{ V}, \Phi_L = 60 \text{nC/cm} \)). In a first process step a part of the resist area was crosslinked by EBL while the other resist area was left unexposed. Directly after EBL, without a development step in between, a second exposure process by FE-SPL crossing the transition between exposed and unexposed areas was carried out. After FE-SPL exposure a wet development step revealed the final pattern. A subsequent AFM and SEM analysis show the transition of the FE-SPL pattern tone at the interface between EBL exposed/unexposed resist regions.
7 FE-SPL Towards Applications

The ability of rapid manufacturing of features in the sub-10-nm scale, in a reproducible manner, has been identified as the most significant bottleneck in order to enable future nanoelectronic, NEMS, photonics, and bio-nanotechnology-based devices. Here, a suitable combination and joint optimization of lithographic and structural transfer processes is essential. The outcomes, which were achieved in teamwork within the TU Ilmenau group and by collaborations within the SNM-project, are described below (respective teams and SNM-partners are mentioned in the sub-sections). A broad application range of FE-SPL was targeted. In the frame of the SNM-project [10] a variety of different sample processing work flows were elaborated, tailored to FE-SPL exposure method. A more detailed description of the processes, which addresses the specific application scenarios, is given in the published articles, ref. [2, 5, 31, 35, 36, 37, 40, 51, 225, 226, 304, 310, 311, 312, 314, 315, 325, 367, 389]. Thereby, the achievements are based mainly on the previous investigations, described in the frame of chapter 3, 4, 5, 6. The first part of this chapter summarizes the lithographic capability of FE-SPL. Building on this, the second part focuses on the pattern transfer by plasma etching and lift-off strategies. Since ultra-thin resist layers of typically 5 – 15 nm are demanded for highest resolution, the pattern transfer becomes an extremely challenging task. In this context, promising strategies, e.g. the etching at cryogenic temperatures, are elaborated.

7.1 Summary of the Lithographic Capability of FE-SPL

a) Patterning tones and basic lithographic feature types:

Two very promising lithographic pathways are enabled by FE-SPL exposure on calixarene MG resist materials. In particular, as a function of the exposure parameters and conditions a mask-less patterning in negative tone (via crosslinking of resist) as well as in positive tone (direct ablation of resist) is accessible. Thereby, only in the case of the negative tone a wet development step after FE-SPL exposure is required. In contrast, the direct ablation is a self-developing effect, which means that the resulting pattern in the resist is directly applicable after exposure. This is summarized in Fig. 7.1.1 for L-shaped nested line features, which are patterned in vector-based mode in an ultra-thin resist layer. In frame of this work the well-defined generation of 2-1/2D (greyscale patterns), 2D (areal patterns), 1D (line patterns), and 0D (dot patterns) features is demonstrated. By combining the available feature types, the entire nanofabrication spectrum can be covered.

In addition, by superposition of the lithographic interaction types, which occur in a self-aligned fashion, completely novel fabrication strategies are opened. In this context, a self-aligned double patterning mechanism was found. As a result, in the case of vector-based line exposure self-aligned double crosslinked lines are formed, whereas in spot exposure doughnut features are revealed after wet development. In terms of the practical applicability both lithographic tones, as well as their superposition, show promising patterning characteristics. Consequently, rather the application scenario determines the tone/interaction to be used. Since both tones are accessible by modulation of the
Positive Tone,
Development-less (Self-development),
imaged directly after exposure

<table>
<thead>
<tr>
<th>Molecular Resist</th>
<th>Semiconductor Substrate</th>
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Negative Tone,
with Wet Development,
imaged after wet development

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<th>Molecular Resist</th>
<th>Semiconductor Substrate</th>
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**Figure 7.1.1:** Summary of the lithographic tones in FE-SPL. The lithographic outcome (L-shaped nested line patterns, 125 nm hp) are imaged by AFM (positive tone imaged directly after exposure; negative tone imaged after a wet development step). The exposure was carried out in a $\approx 7$ nm thick calixarene molecular glass resist layer.

exposure parameters, an easy tone switching is possible, demonstrated later in this section. This enables the access of the full diversity for patterning at the nanoscale. Since also a direct ablation of already crosslinked resist is possible, the modification of already crosslinked or even developed resist patterns is possible (demonstrated in the mix-and-match lithographic section 6.2).

b) **FE-SPL closed loop lithography for a sequential multi-step and multi-layer patterning:**

Since a complete AFM functionality is integrated in the FE-SPL system, the in-situ imaging capability enables a closed loop lithographic scheme (ref. section 1.3). In practice, read (AFM imaging) and patterning (by FE-SPL) cycles are applied in sequence, which allows: (1) An inspection before patterning; (2) An AFM-based registration, stitching, and overlay alignment; (3) An exposure by FE-SPL at variable exposure parameters; and (4) A direct inspection after each patterning cycle. As a result of this combination, the table-top FE-SPL platform is capable of nanometer precise pattern generation, pattern overlay alignment as well as metrological measurement.

According to that an easy scheme for a multi-layer lithography is enabled, where subsequent lithography layers are precisely overlaid with respect to the previous layer. An example is given in Fig. 7.1.2. The image series Fig. 7.1.2-(a-f) show the stacked patterning of two L-shaped corner features in positive tone. In Fig. 7.1.2-(g-h) the corresponding results for the negative tone are given. The following sequence for multi-step and multi-layer lithographic processing is typically applied:
Figure 7.1.2: Sequential read/write based multi-layer lithography, demonstrated by a stacked patterning of corner features using either the positive tone (a-f) or the negative tone (g-h). The image series show: (a) Optical image; (b-e) AFM 2D topographic images; (f) AFM 3D topographic image; (g) SEM image; (h) AFM 2D topographic image. Scale bars: (a) 32 µm; (b-e) 400 nm; (f) 500 nm; (g) 5 µm; (h) 500 nm. Results published partially in [311].
7 FE-SPL Towards Applications

(a) Optical imaging and pre-alignment of the cantilever with respect to the alignment marks of the chip pattern;

(b) Imaging of the region of interest (ROI) by the AFM-AC mode;

(c) Definition of the first lithographic layout (blue lines) and alignment of the pattern with respect to the initial pattern (or reference marks present in the first layer). In the case of a multi-step FE-SPL processing either the latent image (negative tone) or the ablated structures (positive tone) were used as alignment reference (ref. mix-and-match section 6.2). After verification of the alignment and correction of the drift the FE-SPL exposure process is carried out defining the target pattern;

(d) An in-situ imaging of the exposed region by the AFM-AC mode serves as target inspection;

(e) In a next lithographic step the subsequent lithographic layout is defined, aligned with respect to the previous pattern, and exposed by FE-SPL.

(g) Finally, the read-back of the pattern by AFM-AC mode imaging is used as final inspection;

(h) When errors in the pattern are detected, an additional repair step of the resist pattern is possible.

This approach is best suited for practical lithography since it combines high resolution AFM imaging for pattern placement and inspection with high resolution non-contact low energy electron exposure for pattern definition. In this context, the overlay alignment without the requirement of external tools or marks is possible. In order to minimize thermal drift effects the following methods are utilized:

(i) The sample is stored within the process chamber before processing in order to achieve a thermal equalization; (ii) The time between imaging and lithographic exposure is minimized by introduction of a fast switching principle; (iii) Correction of the pattern placement immediately before exposure by a reduced imaging step (only a few lines were imaged).

A further example, in which the patterning tone was changed in between the multi-step pattern, is summarized in AFM image series Fig. 7.1.3. Here, both the SNM project logo and the TU Ilmenau logo were defined in a step-wise fashion (letter by letter in successive closed loop sequences). The SNM logo was defined in negative lithographic tone, whereas the TU Ilmenau logo was patterned in positive tone. AFM-based Imaging, alignment and inspection were carried out directly after exposure of each individual letter. In overall, the entire pattern was created by four sequential read/write cycles. Thereby, the previously taken AFM image was applied for overlay alignment of the next patterning cycle. For exposure of the SNM-logo the same lithographic parameters were applied, whereas for the TU Ilmenau logo an increased exposure dose was utilized.

Furthermore, due to the closed loop functionality not only a multi-step scheme is enabled, but also a multi-layer lithography. In a multi-layer process the pattern is placed into a new resist film instead of being exposed the same resist layer. Thus, the previous pattern was already transferred into the underlying substrate or functional layer. Due to the integrated current feedback regulation in FE-SPL the patterning across an existing surface topography is feasible. In consequence, the probe follows in a first approximation (under the assumption of a homogeneous resist layer) the surface topography (range limited by Z-scanner). Appropriate feedback loop parameters have to be chosen in order to achieve a fast tracking of topographic changes (if the regulation is not appropriate, a modulation of the beam diameter as a function of the surface topography is obtainable). The patterning across an existing surface topography within a multi-layer lithography is demonstrated in Fig. 7.1.4. The FE-SPL exposure process in positive tone (direct ablation) is applied in order to define a line crossing a FinFET / nanowire structure (Fig. 7.1.4-a). The challenge involved is to achieve a sufficient overlay alignment.
Figure 7.1.3: Sequential read/write cycle based FE-SPL. The AFM topographic image series show the generation of a pattern in a stepwise fashion with intermediate imaging, alignment and inspection sequences. In (a-g) the SNM letter is defined in negative tone, whereas in (h) the TU Ilmenau logo is patterned within the same field in positive tone. The final lithographic outcome is shown in (i). The imaging in AFM mode (a-i) was with the same cantilever as applied for lithography. The pattern was not developed, either in between or at the end of the processing sequence. The imaging contrast corresponds only to topographic changes. Scale bars: 500 nm. The particular pattern was realized by K. Nieradka and C. Aydogan, published in a common work in ref. [37]. The image summary was carried out by the author.

with the previous lithographic layer, which is buried under the resist. Without alignment marks that is not possible in conventional lithographic schemes. However, even after the spin-coating of relatively thick resist layers [initial structure height: ≈ 12 nm; resist layer thickness: ≈ 20 nm] the initial surface topography is still measurable (Fig. 7.1.4-b). Since the buried topography can be reliably detected by the AFM mode, an overlay alignment by the previously developed process scheme is possible. The outcome of the multi-layer lithographic process is shown in Fig. 7.1.4-c. After FE-SPL exposure further process steps can be carried out, e.g. a lift-off or selective ALD. Furthermore, the closed loop functionality enables an efficient step-and-repeat scanning probe lithography scheme for patterning of large areas, demonstrated in ref. [37]. As outlined in the previous chapter, only by the closed loop functionality a practical mix-and-match lithography is possible (ref. 6.2; [31]). In conclusion, the unique combination of read/write cycles in a closed loop scheme allow rapid prototyping of nanoscale features with much faster turnaround times compared to conventional lithographic methods.
Figure 7.1.4: Patterning across existing surface topography in positive tone FE-SPL (direct ablation). In the particular example a gate line with a width of $\approx 30\, \text{nm}$ was patterned crossing the FinFET / nanowire structure. The AFM topographic image series shows: (a) The initial device; (b) The device after spin-coating of a $\approx 20\, \text{nm}$ thick calixarene MG resist layer; (c) The device after positive tone FE-SPL exposure (resist layer was removed reaching the bottom layer). For pattern placement of the crossing line even the resist-covered topographic changes (b) are sufficient. The particular example was carried out in teamwork with Y. Krivoshapkina (spin-coating, imaging; author: FIB-preparation; Teamwork: lithographic optimization). The results were published in ref. [37].

c) Lithographic resolution:

As revealed during the work, the lithographic resolution capability is highest in the case of: (1) Ablative positive tone (easier accessibility and controllability due to the higher threshold doses; the negative tone is also promising but requires a further improvement of system performance); (2) Ultra-thin resist layers; (3) Smaller tip-sample spacings requiring low bias voltages which are close above the scratching limit; (4) Low exposure doses (elaborated by an previous exposure dose test), combined with the application of sharp and well-defined probe tips; (5) Respective tuning of the local exposure environment (low water content, but sufficiently high in order to trigger a direct removal; r.h. $\approx 30 - 35\%$); (6) Tailored molecular glass resist systems (application of ideal MG resists which show no crosslinking reaction in order to suppress the crosslinking-mediated proximity effect in positive tone, ref. section 4.4). In Figs. 7.1.5 and 7.1.6 examples of ultra-high resolution pattern at sub-$10\, \text{nm}$ scale, defined by FE-SPL positive tone, are given. In particular, Fig. 7.1.5 shows a pattern defined by two individual lines, which each have a line width of below $5\, \text{nm}$ (line half-pitch of $7.5\, \text{nm}$). Here, the imaging was carried out by SEM. A corresponding averaged intensity profile indicates the exact line width and pitch values. Fig. 7.1.6 provides a resolution test pattern, imaged directly after exposure by AFM. Since the tip radius of curvature is in the same range as the lithographic resolution, the AFM image is highly convoluted. This
Figure 7.1.5: SEM image (a) and corresponding arithmetically averaged intensity profile (b) of a sub-5 nm line feature (7.5 nm hp), defined by positive tone FE-SPL. The lines are written into 10 nm thick calixarene resist (spin-coated on top of a Cr/Au covered chip) with a sample bias voltage of $U_b = 40$ V and a line dose of $30 \, nC/cm$. The results were published in ref. [31].

Figure 7.1.6: AFM topographic image (a) and corresponding section graph (b) of a lithographic resolution test pattern. The lines are defined in positive-tone (ablation) in a 5 nm thin calixarene molecular glass film. The smallest line feature, marked by a white rectangle, has a pitch of 13 nm and a line width at FWHM of $\approx 7$ nm. The result was achieved in teamwork with Y. Krivoshapkina (particular result achieved by Y. Krivoshapkina; the required parameter tuning were carried out in team with the author), published in a common work in ref. [37].
Figure 7.1.7: Patterning of a nanowire device by multi-step FE-SPL in positive tone. AFM-imaging based feature inspection was carried out directly after exposure. A 30 nm thick calixarene MG resist layer, spin-coated on top of a SOI chip, was applied. The results were achieved by M. Budden, which was supervised by the author.

is obviously visible in the corresponding section graph. The estimation of the convolution-corrected line width at FWHM (full width half maximum) reveals a value of 7 nm. In the terms of spot exposure, 8 nm features in diameter have been defined in positive tone (ref. section 4.3.1 and Fig. 4.3.5). Further, the exposure by multi-spot emission sites, which are a result of corrugated tips (multiple tips at the foremost probe shape), show also sub-10 nm patterning capabilities, described in refs. [31, 311]. However, as discussed in section 3.3.2 the metrology by AFM in the sub-10 nm regime is a critical aspect. In addition to the errors in the width measurement, the depth of high resolution patterns cannot be unequivocally determined by AFM measurements. Also by SEM cross-sectioning the patterning depth is hard to estimate. Further research is required in order to enable suitable process control solutions at the sub-10 nm level.

d) Patterning of device layouts:

Layouts for devices can be defined in a straight-forward fashion by combining the previously developed patterning routines. An example of a nanowire based device, patterned by direct ablation in positive tone, is shown in Fig. 7.1.7. A three step exposure process was applied. Within the first step the highest resolution CD-part of the feature was defined by the smallest possible beam diameter. By a multi-pass exposure the required ablation depth is achieved while the widening of the critical line width is kept at a minimum (ref. multi-pass patterning 4.2.7). A 30 nm wide line with a length of 750 nm was achieved having a full clearing to the substrate. The V-shaped connections to the nanowire were exposed in a second step. Therefore, the AFM-based overlay alignment capability was utilized. The larger contact pads were defined in a third step by using a broader beam diameter in order to decrease the overall patterning time (ref. variable beam diameter FE-SPL, section 6.2.1). The general
strategy described here enables a fast and reliable prototyping of nanometer-scale device layouts. The developed methods have been applied in the following projects for device fabrication, e.g. in frame of the SNM-project [10].

7.2 Beyond Lithography: Pattern Transfer of FE-SPL defined Structures

The integration of the lithographic method into conventional manufacturing process flows is a stringent requirement to enable the applicability of the novel solution. In these terms, a pattern in a resist layer is only useful if the structure can be transferred into an underlying functional layer. Thus, the evaluation of the transfer capability either by etching or deposition techniques is of significant relevance for any practical application. Here, the challenge of the pattern transfer is given by the requirement of ultra-thin resist layers (5 – 50 nm) for FE-SPL. Moreover, if highest resolution at sub-10 nm level is targeted, resist layer thicknesses of ≤ 10 nm are essential in order to minimize the lithographic interaction volume (ref. chapter 4: An increased tip-sample spacing causes an increased beam spreading, which results in a broadening of the lithographic interaction).

In this context, the development and optimization of lithographic and pattern transfer techniques in a closed loop fashion is required in order to enable functional applications. Advantageously, with decreasing lateral feature sizes also the requirement in pattern transfer depth/height decreases typically. In the case of nanoelectronic devices, a so called FD-SOI wafer, described in section 3.2.1, can be applied. Here, an etching depth of only 14 nm is required to reach the BOx layer. Also in the case of lift-off the thickness for deposition can be reduced to the 10 nm scale (still produces closed and homogeneous films in PVD processing when using low deposition rates).

To provide an overview of the general applicability of the FE-SPL method, first studies for pattern transfer are carried out. In particular, plasma etching as well as lift-off were evaluated. Since the pattern transfer was not in the main focus of this particular work, only some initial approaches are summarized here. Beyond that, further development steps towards atomic layer methods are recommended. Atomic Layer Etching (ALE) as well as selective Atomic Layer Deposition (selective ALD) offer promising novel routes to achieve a 3D control of the pattern transfer process.

a) Pattern transfer by plasma etching:

Dry plasma etching is the most common method to transfer a resist pattern into the underlying functional layer or substrate [412]. In particular, the cleared resist areas are etched by dry plasma as etchant. Similar to the lithographic process, with decreasing feature sizes the pattern transfer becomes challenging. While in conventional plasma etching scenarios the resist residual (scum) layer is in the 5 – 15 nm range, in high resolution FE-SPL the total resist thickness is typically ≤ 10 nm. In consequence of the ultra-thin resist layers, a high etching selectivity is required. Further, relatively short etching times are necessary in order to have a sufficient etching control. Due to the thin resist layers, large etching depths are not considered. Advantageously, with the down-scaling of the relevant lateral features size also the requirement on the etching depth is reduced. In particular, in the context of this work etching depths of only a few 10 nm are targeted in order to enable the fabrication of beyond-CMOS devices.

The first plasma etching experiments of calixarene MG resist systems, carried out by Fujita and Ohnishi et al. [182, 233], have revealed a selectivity in CF4-plasma of 1 : 1 (resist:Si). Compared to the PMMA
reference, the etch rate of the resist was 4 times lower (≈ 10 nm/s for calixarene resist). However, considering resist thicknesses of only 10 nm in the case of FE-SPL a resist etching rate of ≈ 10 nm/s is far too high. Already after 1 sec etching time the complete resist layer will be gone. Thereby, the stabilization of the plasma conditions requires more time than the etching itself, which means that the process cannot be properly controlled. Further, an etching selectivity of 1 : 1 is not sufficient, limiting the etching depth to 5 – 15 nm depending on the initial resist thickness.

In consequence, for any practical usage an improved plasma etching processes has to be demonstrated. In this context, anisotropic etching processes are demanded to enable vertical sidewall profiles. Further, etching processes with low etching rates have to be found in order to have a sufficient process control (requirement for high reproducibility). In order to achieve a larger etching depth, a higher selectivity is required. In close collaboration with external partners (Oxford Instruments; Imec) and in teamwork within Prof. Rangelow’s research group (Dr. Burkhard Volland; Dr. Valentyn Ishchuk, Cemal Aydogan, Marin Hoffmann) three different approaches were pursued: (1) Etching by a HBr containing plasma in a triode plasma source; (2) Etching by a SF6/CH2F2 chemistry in a 300 mm TCP reactor; (3) Etching by a SF6/O2 chemistry at cryogenic temperatures.

a-1) Etching by a HBr containing plasma (60 MHz triode plasma source):

Figure 7.2.1: Pattern transfer of a FE-SPL defined resist structure into the Si substrate by a HBr based plasma etching process. The L-shaped dense line pattern was written in positive tone (direct ablation) into a ≈ 14 nm thick calixarene resist film. The image series (i-iii) show the corner feature after the plasma etching process [2 min, 300 W table power, 500 W source power, 186 V DC bias]. The resist was stripped by a O2 plasma ashing. The SEM image in (i) was taken at a sample tilt of 52°. The images (ii; 2D image) and (iii; 3D image) show the topography of a single corner feature, measured by AFM. The section series in (iii) demonstrate the change of the line width before and after plasma etching. An etching depth in Si of approx. 60 nm is revealed. Scale bars (i-ii) 1 μm; (iii) 500 nm. The etching process was carried out in the frame of the SNM-project by Dr. Andy Goodyear and Dr. Mike Cooke, Oxford Instruments Nanotechnology Tools. The result were published in a common work, ref. [225].
In collaboration with Oxford Instruments Nanotechnology Tools (OINT, Dr. Andy Goodyear and Dr. Mike Cooke, which carried out the respective etching), the plasma etching by an HBr containing plasma [50 sccm at 20 mTorr] at room temperature (20 °C) was evaluated. Thereby, the HBr chemistry is very selective and enables, in general, anisotropic etching profiles (ref. [412]). A PlasmaPro 1000 chamber with a 60 MHz triode plasma source and a RF power of 13.56 MHz was applied. The calixarene resist was spin-coated on top of a pristine Si chip, followed by a prebake step (20 min at 120 °C). Etching rates of 6.2 nm/min and 21.2 nm/min were measured for the resist and the Si, respectively (results published in ref. [225]). Considering the typical resist thickness in FE-SPL, etching times of approx. 1 – 2 min result, which give a good controllability of the process. Further, an improved selectivity of 3 : 1 is achieved.

In Fig. 7.2.1 the result of a pattern transfer by the HBr based plasma etching process is summarized. Here, an L-shaped dense line pattern, defined by FE-SPL positive tone (direct ablation) in a ≈ 14 nm thick calixarene MG resist, was etched demonstrating an etching depth of approx. 60 nm (etching time of 2 min). Thereby, the width of the line structure was maintained - no degradation of the resolution was observed [the application of broad lines (≈ 90 nm) was chosen in order to measure the etching depth by AFM). The analysis of the surface roughness of the Si bottom layer before and after plasma etching reveals an increase of about 4 times. This indicates that the entire resist layer was consumed during the etching. This fits also to the previously determined etching rates. In the particular case a selectivity of better than 4 : 1 was measured (in comparison, the selectivity of PMMA:Si is 1 : 1, ref. [13]). Since during the applied etching process the entire resist layer was consumed, the derived selectivity and corresponding etching depth seem to be the current limit of the particular etching recipe.

a-2) Plasma etching using a $SF_6/CH_2F_2$ chemistry in a 300 mm TCP reactor:

In collaboration with Imec (Dr. Jean-Francois de Marneffe, Dr. Ziad el Otell, which carried out the respective etching) plasma etching processes using a $SF_6/CH_2F_2$ chemistry in a 300 mm TCP reactor at room temperature were evaluated. In the case of $SF_6/CH_2F_2$ the atomic fluorine, which is produced by $SF_6$ dissociation, is responsible for the etching of silicon via formation of $SiF_X$ volatile products. Thereby, the dissociation of $CH_2F_2$ is expected to generate passivating species, which protect the sidewalls of the pattern (ref. [412, 413]). The particular $SF_6/CH_2F_2$ etching recipe was initially developed by Imec and is hence not published here.

The transfer of FE-SPL patterns, which were defined in ultra-thin ≈ 5 nm thick calixarene MG resist layers, was targeted. The resist was prepared by PVD on top of pristine FD-SOI chips. The initial situation for plasma etching is schematically drawn in Fig. 7.2.2-(1). Indicated by the etching table in Fig. 7.2.2-(2), Si etching rates of ≈ 60 nm/min were measured. Compared to the resist thickness, this rate is quite high leading to ultra-short etching times. The analysis of the Si surface roughness as function of etching time (Fig. 7.2.2-2 table) reveals a strong increase after 12 s etching time. This indicates that already after this time the complete resist mask is consumed (the optimum etching time is located in the range of $T = 8 – 12 \text{ sec}$). Further, the selectivity between Si and resist was quite low, approx. 1 : 1. As shown in Fig. 7.2.2-(3), this results in limited etching depths, which are in the same range as the initial resist thickness. A maximum etching depth of ≈ 6 nm in the Si top layer was measured. Using this recipe, thicker resist layers are necessary to achieve deeper etchings.
Figure 7.2.2: Transfer of ≈ 5 nm thick calixarene MG resist patterns by plasma etching using SF₆/CH₂F₂ chemistry in a 300 mm TCP reactor (room temperature conditions). The drawing in (1) visualizes the patterning stack. In table (2) the etching depth and surface roughness after different etching times are listed (an increase of the surface roughness indicates that the complete resist layer is consumed). The AFM image and section series in (3) compare the corner features directly after patterning (i; iii) and after pattern transfer plus subsequent resist strip (ii, iv). The section graphs are averaged across 30 lines. The resist patterns were defined by positive tone (direct ablation) FE-SPL. SF₆/CH₂F₂ plasma etching was carried out by Imec (Dr. Jean Francois de Marneffe, Dr. Ziad el Otell) in the frame of the SNM-project.
3) **Plasma etching at cryogenic temperatures using $SF_6/O_2$ chemistry:**

As indicated from previous results, and supported by literature (ref. [182, 233]), common plasma etching recipes seem to be not appropriate for the pattern transfer of ultra-thin resist layers. Decreased etching rates and increased selectivity are required. A more exceptional approach is given by plasma etching at cryogenic temperatures, which is also investigated by the research group of Prof. Rangelow. Here, the decrease of the etching temperature increases the sticking probability of the reactants. This promotes the formation of an ultra-thin $SiO_xF_y$ passivation layer across the entire feature surface. By a low energy ($< 30\, eV$) ion bombardment, provided by a fluorine ion flux, the local removal of the passivation layer is enabled [414]. In particular, the layer remains at the sidewalls creating a so called sidewall passivation layer. In accordance to ref. [414, 415, 416], the cryogenic $SF_6/O_2$ plasma etching technique offers multiple benefits: (1) The low temperature reduces the etching rate of the resist mask. In particular, a 30% decrease is reported comparing $-120^\circ \text{C}$ and $+20^\circ \text{C}$ etching temperature [416]; (2) The combination of low temperature and low bias power deliver a high selectivity of $5:1$ up to $10:1$ Si:resist [414, 416]; (3) Since the removal of the passivation layer requires an ion bombardment, an excellent anisotropic etching is achieved; (4) Since no gas chopping is required, smooth sidewalls are provided.

**Figure 7.2.3:** Image series of L-shaped dense line features transferred by plasma etching at cryogenic temperatures ($\sim -120^\circ \text{C}$; etching time: 120 sec) using a $SF_6/O_2$ recipe. The patterns were defined in $\approx 12\, nm$ thick calixarene MG resist layer by positive tone FE-SPL. The image series show the corner test array after plasma etching and resist strip. Image (i): 2D AFM topographic image; (ii): Section profile averaged across 5 single lines. The initial resist layer thickness is indicated by a dashed line; (iii): AFM 3D topographic image; (iv): SEM image at $52^\circ$ of a single structure. Image scale bars: (i) 2 $\mu$m; (ii) 1 $\mu$m; (iii-iv) 500 nm. The particular result was achieved in team of C. Aydogan (FE-SPL exposure, plasma etching), B. Volland and M. Hoffmann (plasma etching) and Y. Krivoshapkina (resist) and the author (reference imaging, SEM, supervision).

By teamwork within Prof. Rangelow’s research group, in particular Dr. Burkhard Volland, Dr. Valentyn Ischuk, Yana Krivoshapkina, Cemal Aydogan and Martin Hoffmann, plasma etching at cryogenic temperatures ($SF_6/O_2$) was investigated as a novel etching technique for FE-SPL defined features. A Cobra Oxford Instruments system was applied (DC-bias of $< 100\, V$). The sample was cooled down to $-120^\circ \text{C}$. An initial pattern transfer result is summarized in Fig. 7.2.3. L-shaped dense line patterns, which were defined in $\approx 12\, nm$ thick calixarene MG resist (positive tone FE-SPL), have been etched.
achieving a final depth in the underlying Si substrate of approx. 60 nm. The recipe gives a selectivity of approx. 5:1 Si:resist, while the Si etching rate is kept low at 0.5 nm/sec. In conclusion, the cryogenic plasma etching process delivers a promising approach for pattern transfer of ultra-thin FE-SPL resist patterns.

a-4) Fabrication of a SET device demonstrator, based on FE-SPL exposure and subsequent cryogenic plasma etching:

In order to fabricate a beyond-CMOS device demonstrator, in a next step FE-SPL exposure has to be combined with cryogenic plasma etching. In the frame of the SNM-project, a Single Electron Transistor (SET, ref. [5]) layout is targeted. The device design and the corresponding process flow was developed in team of TU Ilmenau with Imperial College London (Dr. Zahid Durran, Dr. Mervyn Jones, Dr. Chen Wang). The results achieved up to the submission of the thesis work are summarized in Fig. 7.2.4 (more details and measurements are described in upcoming publications 2016-2017). In particular, a layout containing 4 individual SET device features are defined in a first step by positive tone FE-SPL. Ultra-thin (5 - 10 nm) calixarene MG resist layers were applied, spin-coated on top of a pre-structured FD-SOI chip (chip layout: Fig. 7.2.4-a, section 3.2.1). To transfer the pattern into the top layer Si, the previously developed cryogenic plasma etching recipe was exploited (Fig. 7.2.4-b). In consequence of the device concept, an etching stopping at the BOx layer is required. Since FD-SOI wafer with ultra-thin top layer Si was applied, an etching depth of 14 nm was sufficient in order to achieve an electrical isolation of the functional areas (gate, source, drain regions). This requirement can be achieved already with a resist layer thickness of $\approx 5$ nm. In Fig. 7.2.4-c the final SET device is imaged by AFM after stripping of the resist. An etching depth of $\approx 16$ nm was achieved, which confirms the reaching of the BOx layer. Within the center of each SET device a small nanowire between source and drain remains (the gate is separated from source and drain). By a subsequent thermal oxidation process the quantum island and the surrounding tunneling barriers for the SET operation are defined (carried out by Imperial College London). The formation of the island/tunnel barrier system is induced by a pattern-dependent oxidation (PADOX) processes in the nanowire region (ref. [417]). The electrical characterization of the device features, done at Imperial College London, had revealed Coulomb blockade effects already at room temperature operation. A joint publication is targeted in the upcoming period. Here, the entire process is described and SET device measurements are shown (content is beyond the scope of this thesis work).

b) Pattern transfer by lift-off

Lift-off strategies are a common transfer technique in microfabrication (ref. [13, 164]). A reversed resist profile of the pattern is transferred into the evaporated metal layer. The customization of the method to the FE-SPL positive tone (direct ablation) is outlined in Fig. 7.2.5-(i). Since the lithographic process is development-less, the positive tone is directly applicable after exposure. In consequence of the metal deposition, an inversion of the patterning tone takes place. The exposed areas define the remaining metal layer. Here, a dissolving step removes the metal, which is deposited on top of the remaining resist areas. To get a working lift-off process, a sufficient difference between resist thickness and the deposited metal layer thickness is required. As derived from the experimental investigations, a minimum ratio of 3:1 is required. Further, an undercutting resist edge profile supports the release of the final metal structure (enables attack of the solvent and defines ridge of the metal structure). Since with increasing resist layer thickness the lithographic resolution capability decreases, the thinnest possible metal layers are targeted. In this context, metal layers with low surface roughness are targeted. As revealed in
Figure 7.2.4: Fabrication of a Single Electron Transistor (SET) device demonstrator by combining FE-SPL exposure and cryogenic plasma etching. The SET layout contains four single devices, which were defined by positive tone FE-SPL in $5 - 10 \text{nm}$ thick calixarene MG resist layers. For pattern transfer into the underlying FD-SOI pre-patterned chip (ref. section 3.2) cryogenic plasma etching was applied (etching was stopped at the BOx layer). Image (a) shows the device chip layout according to section 3.2 containing 4x3 contact areas. In (b) a scheme of the cross-section of the chip and the derived specification of the etching depth is outlined. In (c) the final SET fabrication result is summarized, imaged after pattern transfer and resist strip by AFM (3D images are given). The results were achieved in frame of the SNM-project in teamwork with Imperial College London (Dr. Zahid Durrani, Dr. Mervyn Jones, Dr. Chen Wang). Further, within the TU Ilmenau group the team of Claudia Lenk, Cemal Aydogan, Wojciech Michal Majstrzyk, Dr. Burkhard Volland, Yana Krivoshapkina and Diana Nechepurenko, coodinated by the author, were mainly involved in order to develop the details of the process flow for the final SET device demonstrator chip.
section 3.2.2, a low deposition rate (0.02 nm/s) is beneficial. The initial metal deposition experiments, ref. section 3.2.2, demonstrated that metal layer thickness of approx. 5 – 7 nm, deposited by electron beam evaporation, delivers closed and homogeneous metal films. Unfortunately, thinner films have only a partial coverage of the surface, characterized by metal clusters. In conclusion, further down-scaling of the metal layer thickness by conventional methods is limited. Since a minimum ratio between resist and metal layer thickness of 3 : 1 is required, resist thicknesses of larger than 21 nm are required. Further, FE-SPL positive tone gives no undercutting profile, and most likely a thin residual resist film is left behind on the bottom of the pattern. In this context, a further increase of the required resist layer thickness to 30 – 40 nm is necessary. In order to guarantee a full clearance of the patterns (interface Si-resist has to be residual-free in order to improve the adhesion of the evaporated metal layer), a so-called descumming process before metallization was applied. For this purpose, a short oxygen plasma treatment was utilized. To maintain the resist/metal layer ratio, the descum process should be kept as short as possible. In respect thereof, the FE-SPL exposure parameters were optimized to achieve a full clearance of the resist patterns (lithographic resolution is limited, ref. chapter 4). The lift-off was carried out in heated acetone (40°C), supported by an ultrasonic treatment.

A corresponding lift-off result is summarized in Fig. 7.2.5-(iii) showing a nanowire based device (two contact areas are connected by a nanowire bridge). The device layout was defined by positive tone FE-SPL. The AFM topographic images in Fig. 7.2.5-(ii) display the exposed resist after the descum process. Thereby, the black colored parts of the image correspond to resist-cleared areas. In these regions the metal layer should remain after lift-off. The SEM images in Fig. 7.2.5-(iii) show the final device, which is defined in the metal layer, after lift-off. A nanowire width of ≈ 29 nm was achieved. For device isolation from the bottom Si substrate, the oxide formation process (ref. chapter 4) during FE-SPL was exploited. As confirmed by the SEM images, the nanowire is placed exactly above the SPL-induced oxide.

In the initial layout an additional side gate was targeted. Despite multiple optimization runs, the close proximity of the gap to the nanowire has led to a failure of the lift-off process (bridging of the gap or no detachment of the metal film is achievable). In this context, lift-off seems to be not an optimum technique for pattern transfer of dense nanoscale features. To improve the lift-off process, a multilayer approach could help in order to amplify the ratio of resist to metal layer thickness. In addition, alternative deposition techniques may be more promising in terms of resolution. Selective atomic layer deposition (ALD) may be such a technique, which should be evaluated in upcoming works.
Figure 7.2.5: Pattern transfer of an FE-SPL defined nanowire device by lift-off. In (i) the developed process flow is schematically summarized. The AFM topographic images in (ii) show the device after FE-SPL exposure and descumming process (positive tone FE-SPL). The SEM images in (iii) demonstrate the final device after Cr ($\approx 3\,\text{nm}$) / Au ($\approx 4\,\text{nm}$) lift-off. A minimum nanowire width of $\approx 29\,\text{nm}$ was achieved. Due to FE-SPL oxidation process, the Cr/Au nanowire is directly deposited on top of the formed $\text{Si}_x\text{O}_y$ layer. For a successful lift-off a resist layer thickness of $\approx 35\,\text{nm}$ was necessary. The results were achieved by M. Budden, which was supervised by the author during his master thesis work.
Summary and Conclusion: FE-SPL based Nanofabrication beyond the 10 nm Frontier

The ability of nanofabrication at the sub-10 nm scale, the so called single digit nano regime, has been identified as one of the most important steps in order to enable future nanoelectronic, NEMS, photonic, and bio-nanotechnology-based devices. In this work, a novel lithographic concept based on low energy electron exposure (typically < 100 eV) of molecular glass (MG) resist thin films was investigated. As a result, a new method called field emission scanning probe lithography (FE-SPL) has emerged. In this context, the following key results have been achieved in frame of this work:

(I) Field Emission From a Scanning Proximal Probe Tip: A stable field emission process at the tip apex of a scanning proximal probe was utilized for resist exposure with low energy electrons. In accordance to theory, a Fowler-Nordheim based emission behavior was confirmed by the experiments. The emission current is regulated properly by modulation of the tip-sample spacing. A linear behavior between bias voltage and tip-sample spacing was observed, which is in agreement with the FN field emission theory. Here, with increased bias voltage the tip-sample spacing increases. This results in an enhancement of the spreading of the beam. As experimentally found, the mechanical stability of the probe (tip and cantilever) is a crucial factor for the entire system regulation stability. This was derived also from theoretical considerations. Respective design rules and selection criteria for cantilever dimensions and tip shapes are defined.

(II) Development of a Closed Loop FE-SPL System and Integration of Active Cantilever: During the thesis work a prototype of a Field-Emission Scanning Probe Lithography (FE-SPL) technology platform was developed. By employing active cantilevers, which integrate thermomechanical actuation and piezoresistive deflection read-out, a compact and easy to use table-top system was enabled. For a spatially confined exposure of molecular resist materials the low energy electrons emitted from the tip apex (I) were utilized. Imaging is provided by the integrated conventional amplitude modulation AFM capability. In order to regulate the ultra-low emission currents, novel hardware for the lithographic loop was developed. The overall system performance has been demonstrated by regulating exposure doses as low as 1.9 fC in spot and 2 nC/cm in line exposure mode. Further, concepts for line, spot and area exposure were elaborated and implemented within an FE-SPL pattern generator software. Respective control schemes were developed. In order to investigate the impact of the exposure environment, a fast environmental modification system was developed and integrated.

(III) Development of Resist and Sample Preparation Schemes: Since the lithographic resolution in FE-SPL is directly linked with the resist thickness, ultra-thin amorphous molecular resist films in the range of 5 – 50 nm are targeted. These kinds of films were prepared either by spin-coating or by physical vapor deposition (PVD). Respective preparation protocols were evaluated. As a result, resist films with a surface roughness (RMS) of 0.25 – 0.35 nm have been achieved. In the case of highly pre-structured layers / substrates, a PVD preparation scheme is favored because a more uniform resist coverage can be achieved. Since in the case of these ultra-thin resist layers no planarization effect occurs, an overlay alignment by measurement of the resist relief by the integrated AFM mode (II) is
enabled (buried features under the resist layer are still visible).

(IV) Investigation of the Lithographic Interactions and Conclusion of its Superposition:
For the first time a comprehensive view including all involved lithographic phenomena, processes and interactions was gained. Thereby, as a function of exposure parameters and secondary exposure conditions (environment, resist, etc.), multiple individual lithographic interactions are induced. By the concept of superposition the final lithographic pattern can be described as a sum of the individual lithographic reactions. In particular, two competing mechanisms occurring in the resist were identified:

(a) Crosslinking: This effect describes a chemical modification of the resist, which leads to a solubility change of the exposed resist regions. Here, the electron exposure process causes a break-up of the molecules, followed by a crosslinking. In consequence, the exposed areas are insoluble in the wet developer, whereas the unexposed areas are dissolved. This patterning type is called negative tone. After exposure a wet development step is required in order to use the negative tone pattern.

(b) Ablation: This effect is a material conversion of non-volatile into volatile organic compounds. As a result, the resist material is directly removed without the requirement of a development step. This patterning type is called positive-tone with a development-less / self-development character. As the underlying mechanism, a non-specific oxidative degradation process under the influence of the exposure environment is supposed.

In addition to the interactions in the resist, two secondary interactions in the substrate and on top are observed:

(c) Oxidation of Si: In the case of a Si bottom layer, a chemical modification in form of an oxidation takes place. A part of the Si bottom layer is consumed for the growth of a spatially confined amorphous SiO$_2$ layer. In consequence of the volume expansion, a local raising of the resist layer exactly above the region of the buried oxidation is observed. In order to suppress the oxidation reaction, a metal bottom layer or a hardmask stack is required.

(d) Deposition of carbonaceous compounds: Evidence of additional deposition effect was found. It is assumed that a material conversion from volatile into non-volatile parts in form of carbonaceous compounds takes place. Similar to the oxidation effect, also this kind of secondary interaction leads to a growth of the exposed feature. Since the deposition occurs only at highest exposure doses in combination with high bias voltages, this effect is negligible for typical FE-SPL exposure parameter sets.

(V) Elaboration of a Methodology for Feature Analysis: In order to investigate the individual lithographic phenomena (IV), a novel methodology which is based on a combination of selective/non-selective and spatially confined/delocalized removal processes with intermediate analysis steps was developed. As a result, the composition of the nanometer-sized lithographic features was determined. In consequence, the dependencies of the individual interactions were determined. For the AFM analysis of the lithographically defined features an automated analysis routine was programed. In these terms, limitations of the AFM measurement method, which are introduced by the tip-sample convolution, were taken into account. As found, AFM phase contrast imaging reveals fine details of differences in the crosslinking state of resist materials (IV-a). This mode is very promising, since there is no development step required in order to reveal the spatial confinement of the crosslinking reaction. In particular, a phase shift between crosslinked and pristine resist of $+0.6...+2.0^\circ$ was determined. Here, a positive phase shift corresponds to an increased elastic modulus of the crosslinked resist.

(VI) Determination of the Individual Dependencies of the Lithographic Interactions: In the frame of this work the lithographic phenomena were investigated as a function of the exposure parameters and the secondary exposure conditions. In particular, the individual dependencies from (a) the bias voltage, (b) the field emission setpoint and tip velocity, which defines the exposure dose, and
(c) the local exposure environment were determined:

(a) Bias Voltage: As a function of the resist layer properties an optimum bias voltage range was found. When too low voltages are applied, mechanical tip-resist interactions in the form of scratching/plowing occur. In contrast, in the case of too high bias voltages the resolution drops and the emission tends to multiple spots. The observed behavior is explained by the linkage between bias voltage and tip-sample spacing (I).

(b) Exposure Dose: The different lithographic reactions (IV) are characterized by different exposure dose thresholds. Crosslinking of the resist (IV-a) occurs already at lowest exposure doses. Since the threshold for crosslinking is below the system-limited minimum exposure dose value, the sensitivity, gel dose and the resist contrast cannot be determined experimentally for the negative FE-SPL tone. In consequence, a further improvement of the resolution in the negative tone is possible by reducing the exposure dose limit of the system. The direct ablation of resist (IV-b) is characterized by significantly higher exposure doses. In particular, doses of $10^{-150}$ times larger than for crosslinking (IV-a) are required. Thus, compared to the crosslinking interaction only a small part of the total beam diameter contributes to the direct ablation. As a result, at the same dose level a higher spatial confinement is achieved in the ablative mode (IV-b). With increasing exposure dose the line width increases, characterized by a logarithmic function type. This is valid for both interaction types (IV-a and IV-b).

(c) Tuning of the Interaction by the Exposure Environment: The onset / threshold for resist ablation (IV-b) depends on the amount of $\text{OH}^-$-groups provided by the exposure environment (surrounding tip-sample system environment). Thereby, an increasing local relative humidity level causes a shift of the ablation threshold towards lower exposure doses. Thus, a treatment of the exposure region with moisturized process gases promotes a direct ablation. In contrast, a dry process gas suppresses the ablation process resulting in a sole crosslinking interaction.

(VII) Dependency of the Lithographic Interaction from the Molecular Resist Material: In analogy to conventional lithographic processes, also in FE-SPL the lithographic interactions depend on the applied molecular resist and the involved functional groups. As experimentally revealed, a fluorinated ($F$-terminated) resist gives a sole crosslinking process (IV-a) resulting in a pure negative tone behavior. Thereby, the formed fluorinated network inhibits a further oxidative degradation within the evaluated exposure dose range. In consequence, no ablative reactions (IV-b) were observed. In contrast, molecular resists that do not have functional groups still show a direct ablation. However, without $\text{OH}^-$ and $F^-$-groups no sufficient crosslinking reaction was observed. In conclusion, the hydroxyl ($\text{OH}^-$) groups of the calixarene molecule enable an effective crosslinking process at low doses, but still facilitate a direct ablation reaction at increased dose levels. In this context, only in the case of calixarene MG resists a superposition of crosslinking (IV-a) and direct ablation (IV-b) was observed. Only by that unique combination of crosslinking and ablation is enabled leading to the formation of self-aligned double line (in the case of vector based line exposure) and doughnut (in the case of spot exposure) features. Further, only in calixarene resist a tone-switching from negative to positive tone with increasing dose can be utilized. In conclusion, the hydroxyl groups in calixarene are responsible for an effective crosslinking process, whereby these groups are not necessarily required for direct ablation. Here, the ablative processing of resists is still enabled when having only pure aromatic systems without any functionalization. In conclusion, the combination of different kinds of resist materials, which are associated with different ablation thresholds, leads to a material-selective, spatially confined process scheme. This concept is demonstrated on the example of a block-copolymer thin film patterning strategy.
In order to improve the stability of non-functionalized molecular resists, a mixture of MG resists with $C_{60}$ fullerenes prepared via PVD co-evaporation has shown great promise. As a side effect of this, an increased etching durability is achieved (lithographic resolution is not affected by the incorporation of $C_{60}$ fullerenes).

(VIII) Exposure Model: The experimentally derived feature width versus exposure dose dependency can be adequately described by an exposure model having a Gaussian electron exposure dose distribution with two separated dose threshold values. Thereby, the individual threshold values correspond to the onset of the crosslinking (IV-a) and the ablative (IV-b) reaction within the resist layer. By that model not only the lateral confinement as a function of exposure dose can be explained, but also the self-alignment in the case of superimposed reactions (IV-a and IV-b). Self-alignment in this context means that the relationship between the crosslinking and ablative reaction is given by the underlying physical relationship (ref. exposure model) instead of the system alignment capability.

(IX) Lithographic Interactions beyond a Standard Electron Beam Lithography (EBL) Exposure: As was shown for the first time in the course of the work, the exposure by low energy electrons in ambient conditions enables novel reaction paths which are not accessible via standard high energy EBL (which has to be carried out in ultra-high vacuum conditions). This is supported by the following experimental results:

(a) A significant improvement of the sensitivity in standard negative tone (IV-a) was measured. In particular, the FE-SPL crosslinking reaction is at least 10 times (spot exposure) / 80 times (line exposure) more effective than the corresponding EBL-induced crosslinking interaction. However, due to the hardware based limitation with respect to the lowest achievable exposure dose, the threshold dose for crosslinking in FE-SPL has not been reached. There is still room for further improvements with respect to the lithographic resolution and the resist sensitivity.

(b) A second fundamental difference compared to standard EBL is the observed degradation of organic resist molecules resulting in a formation of volatile end products. This so called ablative reaction (IV-b) leads to a direct feature formation in positive tone without the requirement of a wet development step. As revealed by the experiments, the exposure environment in FE-SPL plays a decisive role and is - besides the electron energy - the most significant difference between standard EBL and FE-SPL. In this context, in standard EBL the exposure environment is restricted to ultra-high vacuum conditions. Here, the lithographic route of direct ablation is not accessible.

(c) Due to the low energy of the applied electrons, proximity effects in the crosslinking process (IV-a) are effectively suppressed. This enables a dense patterning at highest resolution. No proximity corrections have to be applied.

In conclusion, as a function of exposure parameters a mask-less patterning in negative tone (by crosslinking) as well as positive tone (by direct ablation) is possible. Further, the self-aligned superposition of multiple lithographic interactions is not accessible by standard EBL. By employing ablative and crosslinking in superimposed fashion, novel routes for nanofabrication are enabled. This range of functionality is unique in nanolithography and has not been published or demonstrated before.

(X) Identification and Investigation of the Lithographically induced Back-Coupling Effect: In consequence of the close proximity of emitter and resist-coated sample, a so called lithographically induced back-coupling effect was found. In general, this effect contradicts the classic boundary conditions, which were applied for simulations the electric field distribution and the therefrom derived values (e.g. the current density). In consequence, the electric field distribution at the tip apex - and the related variables - cannot be treated as constant lithographically independent parameters. In particular, lithographic back-coupling means that the electric field and the related field emission at the tip apex changes as a function of the lithographic progress. As revealed, in consequence of the crosslinking
process the dielectric constant of the resist increases locally. In consequence, in constant height mode the emission is enhanced. When the FE-SPL system operates in the constant current mode, the probe is retracted respectively in order to decrease the electric field strength. In contrast, a local removal of the dielectric resist leads to the opposite effect. Whereas in the case of a global change of the resist layer this chain of action can be described by derived equations, the spatially confined changes of the resist require a description by iterative simulation. The lithographic back-coupling effect is of significant importance for the positive tone, especially when a dense patterning or a multi-pass scheme is targeted. Here, a chemically mediated proximity effect was found, which is a direct consequence of the lithographic back-coupling effect, which is further amplified by a decreased threshold dose value of ablation for already crosslinked resist areas. In order to achieve a sub-10 nm resolution capability, strategies to circumvent this effect were elaborated and demonstrated (e.g. the application of resist, which shows no crosslinking reaction).

(XI) Practical Usage and Resolution Capability of FE-SPL: In the evaluation of the practical applicability, both resist-based lithographic interactions (IV-a ; IV-b) as well as their self-aligned superposition (IV-a + IV-b) show promising characteristics. Here, joint efforts have enabled an FE-SPL based nanolithography in the single digit nano-regime. In particular, patterning of single lines with a width of < 5 nm, dots with diameter as low as 8 nm, and dense line patterns with a half-pitch of 7 nm have been demonstrated. Especially the superposition of crosslinking and ablation enables novel routes of nanolithography at the single-digit nano level, which is further supported by a self-aligned positioning. Line, spot, areal and greyscale FE-SPL have been demonstrated. In terms of the development-less positive tone mode, development-related problems like resist swelling and pattern collapse are circumvented. In addition, the closed loop lithographic scheme provides a unique set of integrated functionalities such as an in-situ inspection, alignment and analysis capability. This spectrum cannot be addressed by conventional lithographic methods. In this context, sequential patterning schemes, a simple patterning across already existing topography with in-situ alignment, and a novel complementary mix-and-match as well as step-and-repeat lithographic approaches have been demonstrated.

(XII) Novel Complementary Mix-and-Match Lithographic Schemes integrating FE-SPL as High Resolution Method: The limitation in throughput constitutes the natural drawback of serial lithographic methods. Related to Tennant’s law, the throughput scales to the resolution by the fifth power. Thus, an improvement of the resolution by the factor 2 results in a 2^5-times decrease of the throughput capability. Thus, for practical applications throughput enhancement strategies are required. In this context, novel complementary mix-and-match lithographic concepts were elaborated, demonstrated and patented. The concept uses FE-SPL as the highest resolution lithography in order to define all critical dimension (CD) features. As a counterpart to this, conventional lithographic methods are applied (e.g. EUVL, replaced in this work by conventional EBL) to enhance the throughput capability. The modification of large-scale EBL-exposed patterns before as well as after a development step was demonstrated by using positive tone, negative tone as well as dual-tone FE-SPL modes. Thus, either EBL unexposed resist areas are crosslinked by FE-SPL exposure, or EBL crosslinked areas are directly removed by FE-SPL exposure. Thereby, the incorporated AFM-based imaging capability is exploited in order to enable an in-situ high resolution pattern placement and overlay alignment. Thereby, either the latent image of the preceding exposure process or the topographic image of the developed pattern were applied. On the basis of this concept, the individualization of fixed mask-based layouts is enabled by a subsequent fine patterning process given by FE-SPL.

(XIII) The Challenge of the Pattern Transfer:
The challenge in pattern transfer is linked with the requirement of ultra-thin resist layers (in the range
of 5 – 50 nm) in order to achieve highest resolution in FE-SPL. Conventional pattern transfer techniques like plasma etching and lift-off have been adapted as far as possible. Since a practical lift-off process (as experimentally evaluated) requires a minimum resist layer thickness of 35 nm, the corresponding lithographic resolution capability in FE-SPL is rather limited. So far, a minimum nanowire width of 29 nm was demonstrated. More promising are plasma etching strategies. However, the high etching rates and low selectivity of common techniques like a \( \text{HBr} \) containing plasma or a \( \text{SF}_6/\text{CH}_2\text{F}_2 \) based recipe, which were carried out at room temperature etching conditions, have revealed only a limited practical applicability. Here, cryogenic plasma etching (sample cooled down to \(-120^\circ \text{C}\)) using a \( \text{SF}_6/\text{O}_2 \) chemistry has outlined a promising alternative route. Etching rates of 0.5 nm/sec and an enhanced selectivity of 5 : 1 have been demonstrated. The complete transfer of FE-SPL defined patterns from an ultra-thin resist film into the top layer of a FD-SOI chip have been shown, which enabled a practical applicability for a beyond-CMOS device prototyping.

(XIV) Fabrication of a Single Electron Transistor (SET) as a Beyond-CMOS Device Demonstrator: The previously obtained results (I-XIII) had been combined in order to define novel routes for nanofabrication. As a result, the prototyping of a beyond-CMOS device demonstrator was carried out. In team with Imperial College London a Single Electron Transistor (SET) layout was defined successfully. Here, FE-SPL was applied in a mix-and-match approach, wherein optical lithography was used as first lithography in order to define all large scale (> 1 \( \mu \)m) features. For pattern transfer a cryogenic plasma etching step was carried out. The electrical characterization of the devices had revealed reproducible Coulomb diamonds at room temperature operation confirming quantum island sizes of less than 2 nm.

In summary, a promising novel nanofabrication route is demonstrated, which is based on the unique exposure technique of field emission scanning probe lithography. The semiconductor history teaches us that novel fabrication technologies are a driver of future innovations. As an outcome of the Single Nanometer Manufacturing project, novel device-driven applications are expected. So far, a novel route toward the fabrication of devices with single-digit nanoscale dimensions and placement accuracy is opened. The gained knowledge could be used in upcoming projects for fundamental studies of novel device concepts, which were so far not accessible by conventional lithographic approaches. Further, in combination with atomic layer based methods for pattern transfer, in particular Atomic Layer Etching (ALE) and selective Atomic Layer Deposition (selective ALD), alternatives for a more efficient transfer are given.
9 Thesen Zur Dissertationsschrift


3. Molekulare Resistfilme lassen sich als amorphe Dünnfilme von 5 − 50 nm Dicke mit niedriger Rauhigkeit unter Anwendung des Aufschleuderns oder alternativ via eines thermischen Aufdampfprozesses präparieren.

4. Die erzeugte lithographische Struktur stellt, als Funktion der Belichtungsbedingungen und -Parameter, typischerweise eine Überlagerung (Superposition) mehrerer lithographischer Einzelsections dar. Die identifizierten lithographischen Einzelsections sind einteilbar in Reaktionen im Resistmaterial selbst (a-b) und in Nebenreaktionen außerhalb des Resistmaterials. Im Resist konnte als lithographisch nutzbare Reaktion eine chemische Modifizierung in Form einer Resistvernetzung (a), als auch eine direkte Entfernung von Resist (b), hier Ablation genannt, identifiziert werden. Der Mechanismus der direkten Resistentfernung (b) wird einem nicht spezifischen, oxidativen Abbau- oder flüchtige Produkte zugeschrieben. Zur Untersuchung der Einzelsections wurde eine neue Methodik entwickelt, welche auf der sequentiellen Anwendung von selektiven und nicht-selektiven Entfernungsverfahren mit intermediärem Einsatz von Nano-Analyseverfahren basiert.

5. Die lithographischen Einzelsections (#4) ergeben in Überlagerung die lithographische Gesamtstruktur. Dabei ist sowohl der Negative Resist-“Tone”, basierend auf (#4-a) nach einem Entwicklungsschritt, als auch der Positive Resist-„Tone“, basierend auf (#4-b), welcher keinen Entwicklungsschritt erfordert, technologisch nutzbar. Darüber hinaus zeigt die Überlagerung beider Reaktionen (#4-a + #4-b) neuartige selbst-gesteuerte Strukturformen. Charakteristisch ist, dass die direkte Entfernung (#4-b) eine signifikant höhere Belichtungsdosis als die Vernetzung (#4-a) erfordert. Daraus ergibt sich bei gleicher Belichtungsdosis eine höhere Lokalisierung und damit Auflösungsfähigkeit der direkten Entfernung (#4-b) im Vergleich zur Vernetzung (#4-a).

6. Die lithographischen Einzelsections (#4) sind primär abhängig von der Belichtungsdosis, der Biasspannung als auch der Belichtungsumgebung. Eine gezielte Strukturierung im Resist ist über die Kontrolle dieser Parameter möglich. Ebenfalls ist eine Abhängigkeit der lithographischen Reaktionen (#4) vom Resistmaterial feststellbar. Unterschiedliche Reaktionen und ein damit verbundener Resist-“Tone” als Funktion der funktionellen Resistgruppen ist nachweisbar. Dabei wirkt eine Fluor-Funktionalisierung vernetzend (#4-a), während im unmodifizierten Fall der Resistmoleküle ausschließlich ein alleiniger
direkter Abtrag (#4-b) vorhanden ist. Im Vergleich dazu befähigen die im Calixaren-Resist vorhandenen Hydroxylgruppen im untersuchten Dosisbereich beide Reaktionstypen (#4-a + #4-b), was ein Schalten zwischen den „Tones“ als auch die Ausnutzung der selbst-ausgerichteten Überlagerung ermöglicht (#5).

7. In erster Näherung ist die Beschreibung der experimentellen Beobachtungen (#4-6) über ein Gauß'sches Belichtungs-Strahlenmodell mit zwei unterschiedlichen Dosis-Schwellewerten, assoziiert mit den Einzelreaktionen (#4-a & #4-b), möglich. Dadurch ist ebenfalls die Entstehung der Doppellinien- und der Donut-Strukturen im Falle einer Überlagerung von (#4-a) & (#4-b) erklärt.

8. Im Vergleich zum Standardverfahren der Elektronenstrahl lithographie (EBL) konnte durch die Anwendung niederenergetischer Elektronen im Rahmen der FE-SPL Methode
   (i) im selben molekularen Resistystem (Calixaren) im vernetzendem Regime (#4-a) eine höhere Sensitivität und damit eine geringere notwendige Dosis zur Vernetzung nachgewiesen werden.
   (ii) das Vorhandensein einer neuartigen lithographisch nutzbaren Reaktion in Form einer direkten Entfernung von Resistmaterial (#4-b) nachgewiesen werden.


10. Im Regime der direkten Entfernung (#4-b; positiver „Tone“, ohne Entwicklung) konnte ein „chemisch“ vermittelter Proximity Effekt festgestellt werden. Erklärbar ist dieser Effekt via der vorangegangenen Vernetzung des Resistmaterials (#4-a) und dem lithographischen Rückkopplungseffekt (#11). Der Effekt ist kompensierbar über: (i) die Anpassung der lithographischen Parameter, oder alternativ über (ii) die Verwendung eines Resistmaterials, welches keine vorangehende Vernetzungsreaktion zeigt (#6).

11. Aufgrund der Nähe der lithographisch zu bearbeitenden Oberfläche und der Spitze, an welcher der Feldemissionsprozess stattfindet, ist ein lithographischer Rückkopplungseffekt nachweisbar. Dieser Effekt der Rückkopplung von der Lithographie auf die Emission kann im einfachen Fall (i) einer homogenen Veränderung über die gesamte Resistfläche via einer herleitbaren Beziehung beschrieben werden, wohingegen für die Beschreibung im Realfall (ii) einer lateral begrenzten Strukturierung die Beschreibung nur über iterative Simulationen möglich ist. Der Rückkopplungseffekt ist immer dann experimentell sichtbar, wenn die vernetzenden Resistbereiche überlappen, z. Bsp. im Falle einer dichten Strukturierung im positiven Resist-“Tone“ (#10).


13. Eine neuartige komplementäre Mix&Match Lithographie unter Anwendung der FE-SPL Methode als Feinstrukturierungsmethode ermöglicht eine signifikante Erhöhung des Durchsatzes. Im Rahmen des Mix&Match Ansatzes konnte die Anwendung beider lithographischen Reaktionspfade demonstriert werden. Dadurch entsteht ein Synergieeffekt, in welcher die lokale Nachvernetzung von Resist (via #4-a), die nachträgliche lokale Entfernung von Resist (via #4-b), als auch deren Kombination möglich ist, was die Individualisierung eines ansonsten festgelegten (Masken-basierten) Layouts ermöglicht. Dies ist besonders attraktiv zur Untersuchung neuartiger wissenschaftlicher und technischer Fragestellungen.


15. Die neuartige Technologie, (#1) - (#14), ist anwendbar für die nanoskalige Fabrikation von „beyond CMOS“ Bauelementen, demonstriert anhand eines Einzelelektronentransistor-Layouts (SET).
10 Acknowledgment

“The greatest achievements come when people work together.” — Joseph Rain

“You can do anything as long as you have the passion, the drive, the focus, and the support.” - Sabrina Bryan

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• Francesc Perez-Murano, Matteo Lorenzoni and Laura Evangelio (CSIC Barcelona) for discussions regarding scanning probe methods and BCP films

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• TAB in the frame of the projects TNA I-2/2009 and Si-MEMS-2009FE9099

Thank you, to all of you!
11 Affidavit

Ich versichere, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet.


Die Arbeit wurde bisher weder im In- noch im Ausland in gleicher oder ähnlicher Form einer Prüfungsbehörde vorgelegt.

Ich bin darauf hingewiesen worden, dass die Unrichtigkeit der vorstehenden Erklärung als Täuschungsversuch bewertet wird und gemäß § 7 Abs. 10 der Promotionsordnung den Abbruch des Promotionsverfahrens zur Folge hat.

Ilmenau, den 05. Juli 2016

(Marcus Kästner)
# Appendix

## A.1 Material Parameters from Literature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value applied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_r$</td>
<td>SiO$_2$</td>
<td>3.9</td>
<td>[418]</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>c-methylcalix[4]resorcinarene (CMC4R)</td>
<td>3.7</td>
<td>[238]</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>calix[4]arene</td>
<td>4.1</td>
<td>[238]</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>hexaacetate-p-methylcalix[6]arene</td>
<td>7.1</td>
<td>[238]</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>water (H$_2$O) $\equiv$ 298.14 $K$, 0.1 MPa</td>
<td>78.3</td>
<td>[392]</td>
</tr>
</tbody>
</table>

Tabular summary of applied material parameter values.
### A.2 List of Applied Molecular Glass Resist Materials

<table>
<thead>
<tr>
<th>Resist Short Name</th>
<th>Chemical Formula</th>
<th>Structural Formula</th>
<th>Molecular Weight</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC4R</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{32}H_{32}O_6$</td>
<td>544.59</td>
<td>SC &amp; PVD</td>
</tr>
<tr>
<td>4m1ac68</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{60}H_{60}O_{12}$</td>
<td>973.11</td>
<td>SC</td>
</tr>
<tr>
<td>UBT3</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{38}H_{22}F_6N_2$</td>
<td>620.6</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT4</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{42}H_{36}N_2$</td>
<td>568.8</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT5</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{42}H_{30}F_6N_2$</td>
<td>676.7</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT7</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{49}H_{12}F_{20}$</td>
<td>980.61</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT8</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{49}H_{32}$</td>
<td>620.80</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT9</td>
<td><img src="#" alt="Chemical Structure" /></td>
<td>$C_{53}H_{36}N_4O_4$</td>
<td>792.90</td>
<td>PVD</td>
</tr>
</tbody>
</table>

Summary of molecular glass resist materials - table #1 (SC: spin coating; PVD: thermal based physical vapor deposition).
<table>
<thead>
<tr>
<th>Resist Short Name</th>
<th>Chemical Formula</th>
<th>Structural Formula</th>
<th>Molecular Weight</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBT12</td>
<td><img src="image" alt="UBT12" /></td>
<td>$C_{51}H_{30}F_{18}$</td>
<td>984.8</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT14</td>
<td><img src="image" alt="UBT14" /></td>
<td>$C_{42}H_{30}$</td>
<td>534.17</td>
<td>PVD</td>
</tr>
<tr>
<td>Fullerene C60</td>
<td><img src="image" alt="Fullerene" /></td>
<td>$C_{60}$</td>
<td>720.64</td>
<td>PVD</td>
</tr>
<tr>
<td>UBT8/C60 [1:1]</td>
<td><img src="image" alt="UBT8/C60" /></td>
<td>$C_{49}H_{32} / C_{60}$</td>
<td>620.80 / 720.64</td>
<td>PVD, co-evaporated, ratio 1:1</td>
</tr>
<tr>
<td>Calix[4]arene</td>
<td><img src="image" alt="Calix[4]arene" /></td>
<td>$C_{28}H_{24}O_{4}$</td>
<td>424.49</td>
<td>PVD</td>
</tr>
<tr>
<td>4-tert-Butyl calix[4]arene</td>
<td><img src="image" alt="4-tert-Butyl calix[4]arene" /></td>
<td>$C_{44}H_{56}O_{4}$</td>
<td>648.91</td>
<td>PVD</td>
</tr>
<tr>
<td>4-tert-Butyl thiacalix[4] arene</td>
<td><img src="image" alt="4-tert-Butyl thiacalix[4] arene" /></td>
<td>$C_{46}H_{48}O_{4}S_{4}$</td>
<td>721.06</td>
<td>PVD</td>
</tr>
</tbody>
</table>

Summary of molecular glass resist materials - table #2 (SC: spin coating; PVD: thermal based physical vapor deposition).
## A.3 Conditions Applied for Wet Development

<table>
<thead>
<tr>
<th>Resist</th>
<th>Wet Development Step (Solvent / Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC4R</td>
<td>Methyl isobutyl ketone (MIBK), 10 s</td>
</tr>
<tr>
<td>UBT3</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>UBT4</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>UBT5</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>UBT7</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>UBT8</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>UBT9</td>
<td>Dimethyl sulfoxide (DMSO), 10 s</td>
</tr>
<tr>
<td>UBT12</td>
<td>Tetrahydrofuran (THF), 10 s</td>
</tr>
<tr>
<td>UBT14</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>Fullerene C60</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>UBT8/C60 [1:1]</td>
<td>Acetone, 10 s</td>
</tr>
<tr>
<td>MoO3</td>
<td>Deionized water (DI water), 10 s</td>
</tr>
</tbody>
</table>

Summary of the wet development process conditions.
### A.4 Surface Morphology and Surface Roughness Measurement carried out on PVD-prepared MG Resist Thin Films

<table>
<thead>
<tr>
<th>Resist Short Name</th>
<th>AFM - 10x10 µm</th>
<th>AFM - 1x1 µm</th>
<th>Rq [nm]</th>
<th>Ra [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine Si, cleaned + HF-dip</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>0.20 ... 0.23</td>
<td>0.15 ... 0.20</td>
</tr>
<tr>
<td>CMC4R</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>UBT3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>11.6</td>
<td>9.6</td>
</tr>
<tr>
<td>UBT4</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>7.6</td>
<td>6.4</td>
</tr>
<tr>
<td>UBT5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>4.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

AFM measurement of PVD-prepared molecular glass resist thin films - table #1. Scale bar 10x10 (1x1) µm AFM topography image: 1 µm (100 nm).
<table>
<thead>
<tr>
<th>Resist Short Name</th>
<th>AFM - 10x10 µm</th>
<th>AFM - 1x1 µm</th>
<th>Rq [nm]</th>
<th>Ra [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBT7</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>0.4</td>
<td>0.3</td>
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<tr>
<td>UBT8</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>0.4</td>
<td>0.3</td>
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<tr>
<td>UBT9</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>UBT12</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>0.8</td>
<td>0.5</td>
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<td>UBT14</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>22.0</td>
<td>18.2</td>
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</table>

AFM measurement of PVD-prepared molecular glass resist thin films - table #2. Scale bar 10x10 (1x1) µm AFM topography image: 1 µm (100 nm).
<table>
<thead>
<tr>
<th>Resist Short Name</th>
<th>AFM - 10x10 ( \mu m )</th>
<th>AFM - 1x1 ( \mu m )</th>
<th>Rq [nm]</th>
<th>Ra [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fullerene C60</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>11.6</td>
<td>7.7</td>
</tr>
<tr>
<td>UBT8/C60 [1:1]</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Calix[4]arene</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>31.6</td>
<td>19.0</td>
</tr>
<tr>
<td>4-tert-Butyl calix[4]arene</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>3.7</td>
<td>2.7</td>
</tr>
<tr>
<td>4-tert-Butyl thiacalix[4] arene</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>8.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>

AFM measurement of PVD-prepared molecular glass resist thin films - table #3. Scale bar 10x10 (1x1) \( \mu m \) AFM topography image: 1 \( \mu m \) (100 nm).
A.5 Nano-Auger Electron Spectroscopy - Differential Spectra

Derivative ($dN(E)/dE$) of the Nano-Auger electron spectroscopy spectra shown in Fig. 4.1.12-(iii). The derivative summarizes the alterations of the Si, C and O peak energetic areas as function of SPL pass (= area exposure dose) for the three different sample types investigated: pristine Si sample (without resist) as well as the 4m1ac68 and cmc4r spin-coated Si sample.
A.6 Publications, Patents and Conferences

Peer-reviewed Journals:


Conference Proceedings:


**Book Chapters:**


**Conference Presentations (only as Speaker / Presenter):**

   Talk, SNM Special SessionConference Proceedings: “Scanning probe lithography with electrons”

2. **NanoFIS 2016** (2nd International Conference Functional Integrated nano Systems), 27. - 29. June, University of Graz, Austria:
   Talk, Session Smart Manufacturing Processes I: “Active cantilever: a multi-talented sensor and nano-tool”
3. **CPFN 2016** (3rd International Conference and 5th International MacroNano-Colloquium on the Challenges and Perspectives of Functional Nanostructures), 20. - 22. June, Technische Universität Ilmenau, Germany:
   Invited Talk, young scientist session: „**Fowler-Nordheim Scanning Probe Single-Digit Lithography**“

   Plenary Talk: “**Scanning probe lithography using low energy electrons**”

   Talk, Session Stencil and Tip Based Patterning, Wed-A7-c4: „**Field emission scanning probe lithography and etching at cryogenic temperatures – A closed loop technology towards beyond CMOS device manufacturing**”

6. **SPIE Advanced Lithography 2015**, 22. - 26. February, San Jose, California, USA:
   Invited Talk, 9423-13, Session 4: Scanning Probe Lithography: “**Single-digit nanomanufacturing by electric-field scanning probe lithography on molecular resist**”

7. **Mikro-Nano-Integration 5. GMM Workshop 2014**, 08. - 09. October, Technische Universität Ilmenau, Germany:
   Talk & Poster: “**Micro enables Nano - Active cantilever microsystems for single digit nanofabrication**”

8. **MNE 2014** (The 40th International Conference on Micro- and Nano-Engineering), 22. - 26. September, Lausanne, Switzerland:
   Talk, Session Emerging Nano-Patterning Methods I, A5L-A-1: „**Tone-switching scanning probe lithography for sub-10 nm patterning**”

   Talk: “**Positive and negative tone mode closed loop scanning probe lithography on calixarene molecular glass resist**”

    Poster: “**High frequency and low stiffness cantilever for high speed AFM**”

    Poster and slide presentation of the EU-FP7 IP Project: “**Single Nanometer Manufacturing for beyond CMOS devices**”, acronym: **SNM**

    Talk, Session 6B, Tip-based Processing: “**Mix&Match electron beam and scanning probe lithography for sub-5 nm patterning**”

    Talk, 8680-45, Session 11: Nanoprobe Array Direct-Write Technologies: “**Mix and match electron-beam and scanning probe lithography for high-throughput sub-10 nm lithography**”

14. **SPIE Advanced Lithography 2012**, 12 - 16 February, San Jose, California, USA:
    Talk, 8323-51, Session 11 Frontier Lithographic Techniques and Applications: “**Progress in scanning proximal probe nanolithography on calixarene**”
Talk, Session BEAMS 2, O-LITH-39: “Scanning probe nanolithography on ultra-thin calixarene-based molecular resist”

Poster, Session P7.1, Maskless Lithography: “Scanning proximal probe lithography (SPPL) with sub - 10 nm resolution on calix[4]resorcinarene”

**Patent Applications:**


Bibliography


BIBLIOGRAPHY


## Frequently Used Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope / Atomic Force Microscopy</td>
</tr>
<tr>
<td>aHF</td>
<td>after HF-dip (process step)</td>
</tr>
<tr>
<td>aO2P</td>
<td>after O2 plasma ashing treatment (process step)</td>
</tr>
<tr>
<td>aSPL</td>
<td>after FE-SPL exposure</td>
</tr>
<tr>
<td>aWD</td>
<td>after wet development (process step)</td>
</tr>
<tr>
<td>BEE</td>
<td>ballistic electron emission</td>
</tr>
<tr>
<td>CAR</td>
<td>chemically amplified resist</td>
</tr>
<tr>
<td>cc</td>
<td>constant-current (operation mode)</td>
</tr>
<tr>
<td>ch</td>
<td>constant-height (operation mode)</td>
</tr>
<tr>
<td>cmc4r</td>
<td>C-methyl-calix[4]arene (resorcinarene derivate)</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>EBID</td>
<td>electron beam induced deposition</td>
</tr>
<tr>
<td>EBL</td>
<td>electron beam lithography</td>
</tr>
<tr>
<td>EF</td>
<td>electric field</td>
</tr>
<tr>
<td>EUV(L)</td>
<td>extreme ultraviolet (lithography)</td>
</tr>
<tr>
<td>FD-SOI</td>
<td>fully depleted silicon on insulator (wafer/chip)</td>
</tr>
<tr>
<td>FE</td>
<td>field emission</td>
</tr>
<tr>
<td>FE-SPL</td>
<td>field emission scanning probe lithography</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam based processing (Dual-Beam System applied)</td>
</tr>
<tr>
<td>FN</td>
<td>Fowler-Nordheim (field emission)</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>GND</td>
<td>electric ground / grounded</td>
</tr>
<tr>
<td>HM</td>
<td>hard mask (stack)</td>
</tr>
<tr>
<td>hp</td>
<td>half pitch (of a dense line/space patterning)</td>
</tr>
<tr>
<td>IMFP</td>
<td>inelastic mean free path (of electrons)</td>
</tr>
<tr>
<td>LAO</td>
<td>local anodic oxidation</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir-Blodgett (thin film preparation method)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>LER</td>
<td>line edge roughness</td>
</tr>
<tr>
<td>LPF</td>
<td>(programmable) low pass filter</td>
</tr>
<tr>
<td>LVDT</td>
<td>linear variable displacement transducer</td>
</tr>
<tr>
<td>LWR</td>
<td>line width roughness</td>
</tr>
<tr>
<td>MFP</td>
<td>mean free path (of electrons)</td>
</tr>
<tr>
<td>MG</td>
<td>Murphy and Good (treatment of FN cold field emission)</td>
</tr>
<tr>
<td>MIM</td>
<td>metal-insulator-metal</td>
</tr>
<tr>
<td>MR</td>
<td>molecular (glass) resist</td>
</tr>
<tr>
<td>MVM</td>
<td>metal-vacuum-metal</td>
</tr>
<tr>
<td>NGL</td>
<td>next generation lithography</td>
</tr>
<tr>
<td>PID</td>
<td>proportional-integral-differential regulator</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>QCM</td>
<td>quartz crystal microbalance (measurement)</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive ion etching</td>
</tr>
<tr>
<td>ROI</td>
<td>region of interest</td>
</tr>
<tr>
<td>RLD</td>
<td>Richardson-Laue-Dushman equation for thermionic emission</td>
</tr>
<tr>
<td>RMS</td>
<td>root mean square (surface roughness)</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayers</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope / Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SNM</td>
<td>single nanometer manufacturing (methods / project)</td>
</tr>
<tr>
<td>SPL</td>
<td>Scanning Probe Lithography</td>
</tr>
<tr>
<td>SPM</td>
<td>scanning probe microscope (microscopy)</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscope / Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>TF</td>
<td>transfer function</td>
</tr>
<tr>
<td>UBT</td>
<td>University of Bayreuth (one project partner in SNM project)</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
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4m1ac68 4-methyl-1-acetoxy-calix[6/8]arene (calixarene derivate)
## Frequently Used Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>SI-Unit</th>
<th>Description</th>
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<tbody>
<tr>
<td>$J$</td>
<td>A/m²</td>
<td>current density</td>
</tr>
<tr>
<td>$e$</td>
<td>C</td>
<td>charge of the electron</td>
</tr>
<tr>
<td>$h$</td>
<td>C·V·s</td>
<td>Planck’s constant</td>
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<tr>
<td>$\Delta S_i$</td>
<td>m</td>
<td>width of the potential barrier at Fermi level with image potential</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>m</td>
<td>width of the potential barrier at Fermi level without image potential</td>
</tr>
<tr>
<td>$S_1, S_2$</td>
<td>m</td>
<td>limits of barrier at Fermi level; $\Delta S_i = S_2 - S_1$</td>
</tr>
<tr>
<td>$\bar\phi$</td>
<td>eV</td>
<td>mean (potential energy) barrier height (above Fermi level)</td>
</tr>
<tr>
<td>$\phi_e(X)$</td>
<td>eV</td>
<td>potential energy of an electron as function of distance (X)</td>
</tr>
<tr>
<td>$\phi_o$</td>
<td>eV</td>
<td>height of rectangular potential energy barrier</td>
</tr>
<tr>
<td>$U_b$</td>
<td>V</td>
<td>bias voltage (voltage difference applied between tip and sample)</td>
</tr>
<tr>
<td>$m_e$</td>
<td>kg</td>
<td>mass of electron</td>
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<tr>
<td>$\eta$</td>
<td>eV</td>
<td>Fermi level</td>
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<tr>
<td>$\psi$</td>
<td>eV</td>
<td>work function of the emitter</td>
</tr>
<tr>
<td>$d_{ts}$</td>
<td>m</td>
<td>distance between tip and sample surface</td>
</tr>
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<td>$d_{resist}$</td>
<td>m</td>
<td>resist thickness</td>
</tr>
<tr>
<td>$d_g$</td>
<td>m</td>
<td>distance between tip and resist surface (&quot;vacuum“ gap distance)</td>
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<tr>
<td>$d_d$</td>
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<td>thickness of the dielectric layer</td>
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<td>$E$</td>
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<td>V/m</td>
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<td>V/m</td>
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<td>$D$</td>
<td>C/m²</td>
<td>electric displacement field</td>
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<td>$C$</td>
<td>F</td>
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<td>$c_E$</td>
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<tr>
<td>Symbol</td>
<td>[SI-Unit]</td>
<td>Description</td>
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<tr>
<td>$c_{U}$</td>
<td>/</td>
<td>change factor of the voltage drop across the vacuum gap (development of voltage across the gap in presence of a changing dielectric layer)</td>
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<td>$I_{FN}$</td>
<td>A</td>
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</tr>
<tr>
<td>$A$</td>
<td>$m^2$</td>
<td>total area of emission</td>
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<tr>
<td>$A_{pp}$</td>
<td>$m^2$</td>
<td>area of parallel plate configuration</td>
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<tr>
<td>$\epsilon_0$</td>
<td>$C \cdot (V \cdot m)^{-1}$</td>
<td>vacuum permittivity</td>
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<td>$v(y_n), t(y_n)$</td>
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<td>special field emission elliptic functions (MG treatment)</td>
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<td>$v_t$</td>
<td>$m/s$</td>
<td>tip velocity</td>
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<td>$a$</td>
<td>$A \cdot eV \cdot V^{-2}$</td>
<td>constant applied</td>
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<tr>
<td>$b$</td>
<td>$eV^{-3/2} \cdot V \cdot m^{-1}$</td>
<td>constant applied</td>
</tr>
<tr>
<td>$c$</td>
<td>$eV \cdot V^{-1/2} \cdot m^{1/2}$</td>
<td>constant applied</td>
</tr>
<tr>
<td>$d$</td>
<td>$A \cdot eV^{-2} \cdot m^{-2}$</td>
<td>constant applied</td>
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<td>$\beta$</td>
<td>$m^{-1}$</td>
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<tr>
<td>$k$</td>
<td>/</td>
<td>geometric factor</td>
</tr>
<tr>
<td>$r_{tip}$</td>
<td>$m$</td>
<td>radius of curvature of the tip (apex)</td>
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<tr>
<td>$R_{exp}$</td>
<td>$A \cdot V^{-2}$</td>
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<td>$S_{exp}$</td>
<td>$V$</td>
<td>slope of the linear fit to the FN plotted (experimental) data</td>
</tr>
<tr>
<td>$R_t$</td>
<td>$m^2 \cdot A \cdot V^{-2}$</td>
<td>intercept of the linear fit to the FN plotted (experimental) data</td>
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<tr>
<td>$S_t$</td>
<td>$V \cdot m^{-2}$</td>
<td>slope of the linear fit to the FN plotted (experimental) data</td>
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<td>$\Gamma$</td>
<td>$eV^2$</td>
<td>exact emission area extraction function</td>
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<tr>
<td>$\alpha_{em}$</td>
<td>°</td>
<td>angle of Fowler Nordheim (FN) field emission</td>
</tr>
<tr>
<td>$w$</td>
<td>$m$</td>
<td>line width</td>
</tr>
<tr>
<td>$r_h$</td>
<td>%</td>
<td>relative humidity</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$\Omega cm$</td>
<td>electrical resistivity</td>
</tr>
<tr>
<td>$k_s$</td>
<td>$N/m$</td>
<td>spring constant of the cantilever</td>
</tr>
<tr>
<td>$\Phi_D$, $\Phi_L$, $\Phi_A$</td>
<td>$C/m$</td>
<td>dot / line / area exposure dose</td>
</tr>
<tr>
<td>$t$</td>
<td>$s$</td>
<td>exposure time (for dot / pixel exposure)</td>
</tr>
<tr>
<td>$l$</td>
<td>$m$</td>
<td>exposed line length</td>
</tr>
<tr>
<td>$A$</td>
<td>$m^2$</td>
<td>exposed area</td>
</tr>
<tr>
<td>$s$</td>
<td>$m$</td>
<td>step size (in EBL)</td>
</tr>
<tr>
<td>$p$, $hp$</td>
<td>$m$</td>
<td>pitch / half pitch of the line patterning</td>
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</tbody>
</table>