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UV ELECTRODELESS WET CHEMICAL ETCHING OF n-GaN

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ABSTRACT

Motivation for the presented work was to eliminate the necessity to use Pt counter electrode by adding an oxidizing agent of sufficient strength to the aqueous KOH solution. We studied photo-assisted electrodeless etching (ELPEC) of GaN in a $K_2S_2O_8$/KOH solution irradiated continuously with UV light. In our work we investigated the impact of mask material on GaN patterning. As mask material thin layers of Ti, Pt and Au were used. Details are given in experimental part. The ratio of mask covered surface area to uncovered one was 7:1, 1:2 and 1:5. The $K_2S_2O_8$ oxidizing agent concentration was kept in the range from 0.006 to 0.1 M, the KOH electrolyte concentration was kept in the range from 0.004 to 0.04 M.

Index Terms **–** n-GaN, ELPEC

1. INTRODUCTION

Group III-nitride semiconductors such as gallium nitride (GaN), aluminum nitride (AlN) and indium nitride (InN) offer many advantages for fabrication of electronic devices, such as Schottky diodes and high-electron mobility transistors which possess high breakdown voltages, high operating frequencies and high operation temperatures. They have opened a new era in the field of semiconductor materials and devices. They are all direct band gap materials with band gaps ranging from 0.7 eV (InN) through 3.4 eV (GaN) to 6.2 eV (AlN) and form a complete series of ternary alloys which cover the whole visible spectrum and spread into the infrared (IR) and ultraviolet (UV) region. This advantage makes them ideal candidates for the fabrication of optoelectronic devices. However, to fabricate GaN-based devices successfully, damage-free and reproducible etching processes are required. Recently, dry etching techniques have been employed to define device features with controlled profiles and etch depths. These methods generally utilize a strong physical etch components, which can lead to ion-induced damage of semiconductor and to the reduction in the selectivity between different materials when compared with wet etching technique. An alternative method to solve these problems appears to be photo-assisted wet etching (PEC) which can be an important complement to dry etching. During PEC etching supra-band gap photons are absorbed, producing electron-hole pairs. The holes drift to the semiconductor surface, where they oxidize the GaN, thus producing N_2 and Ga_2O_3 that dissolves away [1]. Electrons are swept to the Pt cathode. The process involves a variety of species, such as electrons, holes, water molecules, reactants (hydroxide ions) and products (Ga_2O_3, N_2), which affects the overall shape and morphology of the etched surface through their mass transport and reaction kinetics. By controlling the etching parameters, a smooth surface, or a whisker formation, can be achieved [2].

PEC etching of GaN in device fabrication has two disadvantages: a lateral potential gradient on the GaN film and a narrow region of operation for a smooth etched surface [3]. The lateral potential gradient was present along the distance from the conducting Pt electrode to the GaN film; etching then occurred to a non-uniform depth along the potential gradient. Electrodeless photo-assisted wet etching was developed to solve this problem, with an oxidizing agent peroxydisulfate ($S_2O_8^{2-}$) replacing the Pt electrode in PEC etching. According to Bardwell's results, the morphology of GaN etched with a SiO_2 mask showed grain boundaries and needle-like dislocations [4].

Proposed etching mechanisms for this etch chemistry of KOH + $K_2S_2O_8$ + UV is as follows [5]: the hydroxide ions ($-OH^-$) are first adsorbed on the sample surface and subsequently react with Ga atoms following the reaction:

$$2\,GaN + 3H_2O \xrightarrow{KOH} Ga_2O_3 + 2NH_3$$

KOH works as a catalyst and is a solvent for the resulting Ga_2O_3

The purpose of the UV light is to create holes which enhance the formation of Ga_2O_3. As soon as the holes are consumed, there is an excess of electrons in the semiconductor. With time, any new holes created by UV light quickly recombine with the oversupply of electrons and further etching is significantly reduced.

However, presence of $K_2S_2O_8$ enables consuming the excess of electrons [4]:

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2}-$$

Authors [6] obtained a smooth surface by using a chopped UV source in electrodeless photo electrochemical (ELPEC) etching of GaN.

2. EXPERIMENTAL

Two GaN epitaxial layers grown on a (0001)-oriented sapphire substrate by metal-organic chemical vapor deposition (MOCVD) were used in this study. One of them (A) consisted of 2.5 µm thick Si-doped (n~4×10^{17} cm^{-3}) GaN layer, the second one consisted of an undoped-GaN layer 930 – 990 nm thick covered by 20 nm thick AlN layer (B).

Non-annealed thick layer of Ti (70 nm and 100 nm), Au (110 nm) and Pt (115 nm) were used as etch masks. A 100 W filtered mercury-xenon lamp (EXFO Acticure® 40 000) with a light intensity of up to 160 mW/cm^2 was used. The light intensity was measured by wideband detector of UV radiation EXFO Radiometer R 5000. Etch depths were measured by Dektak 150 (Veeco), while the surface morphology after etching was characterised by scanning electron microscope (SEM) LEO 1550 with a resolution of 2 nm and also by optical microscope. The ELPEC etching was carried out in a standard electrochemical cell (Fig. 2). The samples were immersed in non-stirred solution incorporating $K_2S_2O_8$ and KOH. Solutions were made up freshly and all experiments were carried out at room temperature without electrical contact to the sample.

In the work we have used different ratios of covered and uncovered surface areas, namely 7:1 for mask a), 1:2 for mask c) and 1:5 for mask b), Fig. 1

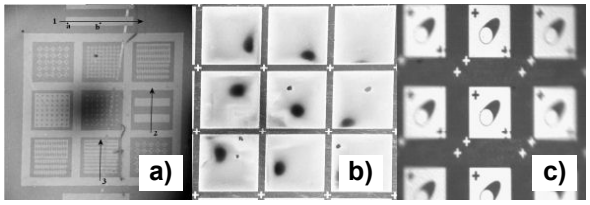

Figure 1 Mask types used in experiments. Masked area is dark in the first two parts a) and b), bright in the last one c)

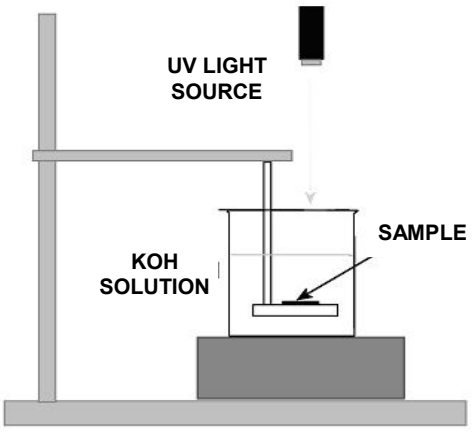

Figure 2 Workplace set-up

3. RESULTS AND DISCUSSION

To determine GaN optimal etching conditions we have used sample (A). As mask Ti (100 nm thick) was used. $K_2S_2O_8$ oxidizing agent concentration was kept in the range from 0.006 M to 0.1 M, KOH electrolyte concentration was kept constant at 0.004 M. At the source output a constant intensity of 6 mW/cm^2 was kept. We have found out that for the oxidizing agent concentrations from 0.03 M to 0.1 M homogeneous sample etching occurs. No trenches were observed in the vicinity of the mask (Fig. 3). For the oxidizing agent concentrations from 0.006 M to 0.03 M was the etched surface covered with whiskers.

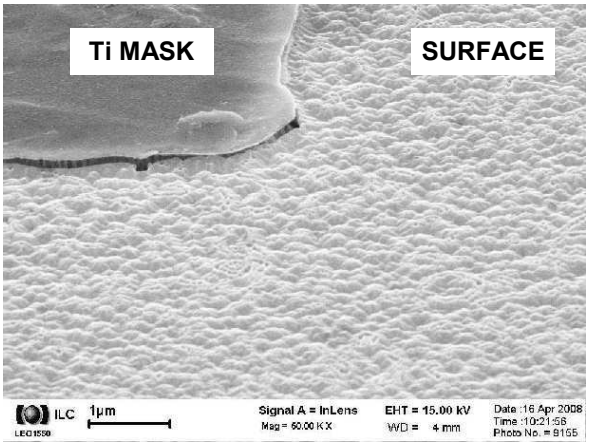

Figure 3 SEM view of sample (A) surface with Ti mask etched with 0.004 M KOH and 0.1 M $K_2S_2O_8$

3.1. Samples with other etched/unetched area ratios

Conditions achieved in previous experiments we have applied also for the sample (B). The aim was to get surface evenly etched over the whole area. Ti mask was deposited only at sample edges, therefore the covered/uncovered ratio was 1 : 4. At $K_2S_2O_8$ concentration of 0.1 M we were changing the KOH concentration in the range from 0.004 to 0.04 M. We have found out that at electrolyte concentration of 0.004 M whiskers were observed in the surface of the

sample (Fig. 4). Whiskers could be observed over the whole etched area. At electrolyte concentration of 0.04 M preferred etching of GaN could be observed near the mask. Surface at a distance of more than 100 μm was untouched.

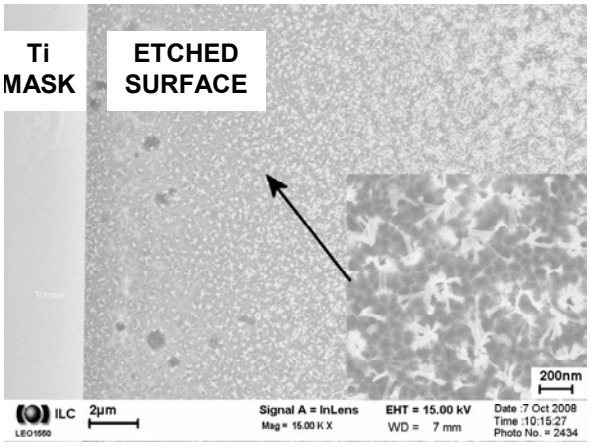

Figure 4 SEM view of sample (B) surface with Ti mask etched with 0.004 M KOH and 0.1 M $K_2S_2O_8$. The ratio masked/unmasked is 1:4

If the mask/unmasked ratio is changed to 1:5, similar results as for the previous situation of 1 : 4 are achieved (Fig. 5).

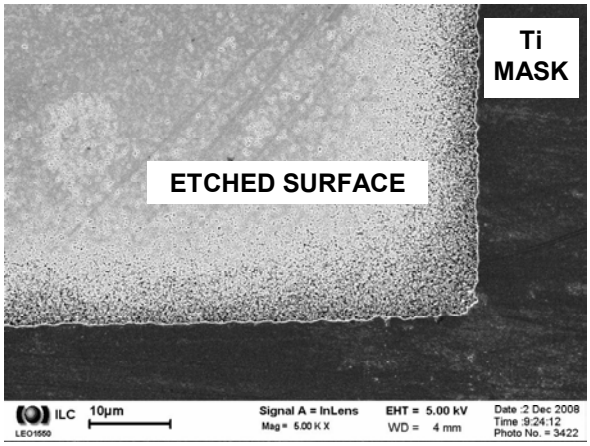

Figure 5 SEM view of sample (B) surface with Ti mask etched with 0.025 M KOH and 0.05 M $K_2S_2O_8$. The ratio masked:unmasked is 1:5

3.2. The influence of mask material on etching rate and homogenity

For etching conditions of 0.004 M of KOH and 0.05 M and 0.1 M of $K_2S_2O_8$ without stirring, sample (B) was etched with masks Ti (70 nm), Pt and Au. Mask covered to uncovered surface ratio was 1:2 (Fig. 1c). Source – sample distance was 8.5 and 4 cm with intensity at the source output of 6 mW/cm^2. Etching time was 30 min.

The lowest mask influence was observed for Ti mask. Pronounced etching took place for uncovered surface up to distance about 25 μm away from the mask edge (Fig. 6). In the area at mask edge the etching depth was about 85 nm. Uncovered surface far from the mask was etched less. Light intensity increase as the source – sample distance was decreased did cause faster etching but the 25 μm limit did not change. The $K_2S_2O_8$ concentration increase did not influence the etching rate significantly. Sample surface underneath the mask did exhibit some outgrowthed objects (Fig. 6).

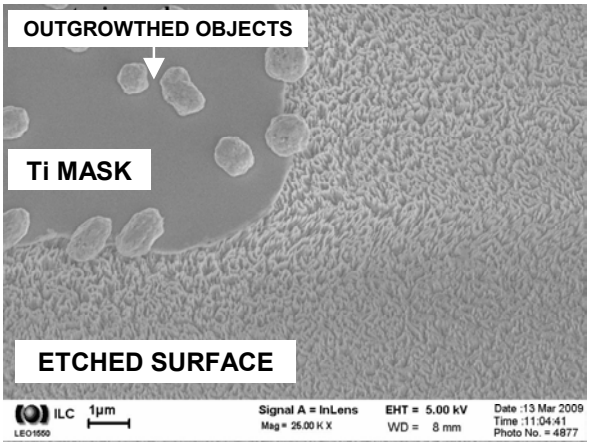

Figure 6 SEM view of sample (B) surface with Ti mask etched with 0.004 M KOH and 0.05 M $K_2S_2O_8$. The ratio masked:unmasked is 1:2

A different situation occurs when Pt and Au are used as masks. If Au as mask is used with $K_2S_2O_8$ concentration of 0.05 M and KOH concentration of 0.004 M at sample/source distance of 8.5 cm, at close vicinity to metal edge, at about 2 - 3 μm distance GaN is completely removed up to the substrate. In the range from 5 to 60 μm from the mask edge whiskers are formed, their height is comparable with GaN thickness. For larger distances the etch rate is further decreased. At a distance larger than 150 μm the surface stays unetched. Light intensity increase achieved by bringing the sample closer to radiation source causes pronounced GaN etch rate increase over the whole unmasked surface (Fig. 7).

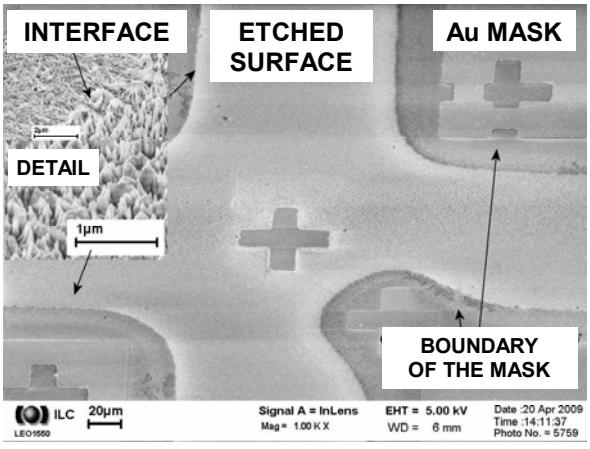

Figure 7 SEM view of sample (B) surface with Ti/Au mask etched with 0.004 M KOH and 0.1 M $K_2S_2O_8$. The ratio masked:unmasked is 1:2

Using Pt as mask the etch rate is high in the mask vicinity and sample is etched down to substrate. By distance increase (50 μm) the etching is homogenious. Further distance increase initiates whisker formation (Fig.8).

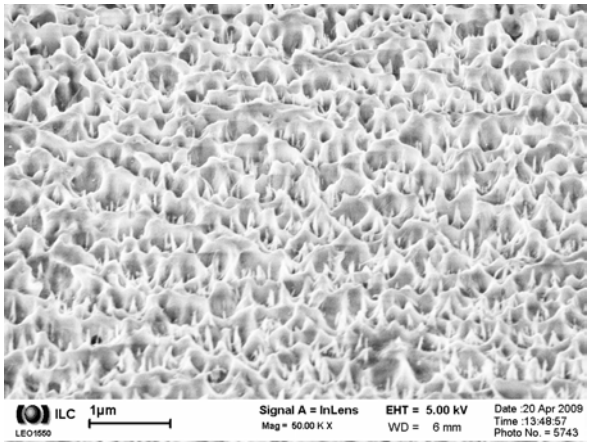

Figure 8 SEM view of sample (B) surface with Pt mask etched with 0.004 M KOH and 0.1 M $K_2S_2O_8$.

The oxidizing agent concentration increase from 0.05 M to 0.1 M does not influence etching. Whereas the radiation intensity increase does increase the etching rate.

4. CONCLUSION

In this work we have studied n-GaN and i-GaN photoenhanced chemical etching with oxidizing agent. We have found out that:

Optimal etching conditions were set with sample (A). For masked/unmasked ratio of 7 : 1 the GaN surface is etched homogeneously over the whole area. In the concentration range of the oxidizing agent from 0.03 to 0.1 M and electrolyte concentration of 0.004 M neither trenches nor whiskers are formed, defects are not highlighted. For smaller oxidizing agent concentrations, whiskers are formed where defects occur. Changing the covered/uncovered ratio to 1 : 5 or even to 1 : 2 the etched surface quality is changed. We have found out that the layer is predominantly etched in the very vicinity of the mask edge up to a distance of 50 μm. Oxidizing agent concentration for given KOH concentration does not have influence on the quality of the etched surface.

From used masks Ti, Pt a Au the less suitable was the Ti mask 70 nm thick.

Very similar results were achieved for Pt and Au masks. Mask influence was detectable for distances of up to 40 - 50 μm. Etching was faster than for Ti mask. The whole sample surface was etched. Outside the area with mask influence the etching process was slow and even, only thin layers could be removed. In the mask vicinity the etching was pronounced.

5 ACKNOWLEDGEMENTS

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