ELECTRODELESS WET ETCHING OF n-GaN ASSISTED WITH ULTRAVIOLET LIGHT

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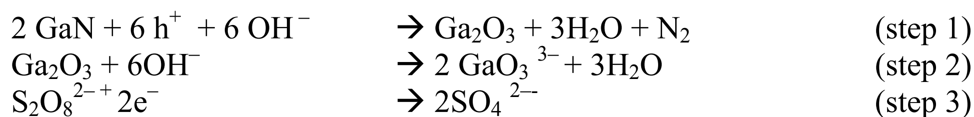
1. Introduction

Recently, GaN-based materials have been the subject for both optoelectronic and high-temperature/high-power electronic devices. They have opened a new era in the field of semiconductor materials and devices. However, to fabricate GaN-based devices successfully, damage-free and reproducible etching processes are required. Dry etching techniques have been employed to define device features with controlled profiles and etch depths, but 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. This technique uses a weak electrolyte as part of an electrochemical cell. Ultra-violet light is used to create electron-hole pairs inside the semiconductor. Assuming a pinned surface potential and the resulting band bending at the surface, holes are forced toward the surface in an n-type semiconductor. Excess holes at the surface are essentially broken chemical bonds, making the semiconductor susceptible to the etch solution. By controlling the etching parameters, a smooth surface, or a whisker formation, can be achieved [1,2].

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]. A promising improvement of the above mentioned method was obtained by adding the KOH solution potassium peroxydisulphate ($K_2S_2O_8$). An oxidizing agent peroxydisulfate ($S_2O_8^{2-}$) replaces the Pt electrode in PEC etching.

Proposed etching mechanism for this etch chemistry of KOH + $K_2S_2O_8$ + UV is as follows [4]:



$2\,GaN + 6\,h^{+} + 6\,OH^{-} \rightarrow Ga_2O_3 + 3H_2O + N_2$ (step 1)
$Ga_2O_3 + 6OH^{-} \rightarrow 2\,GaO_3^{\,3-} + 3H_2O$ (step 2)
$S_2O_8^{\,2-} + 2e^{-} \rightarrow 2SO_4^{\,2-}$ (step 3)

Authors [5] used a chopped UV source in the ELPEC etching to suppress the recombination current at dislocations.

In this paper we studied photo-assisted electrodeless etching (ELPEC) of n-GaN in a $K_2S_2O_8$/KOH solution irradiated continuously with UV light. We investigated the impact of mask material on n-GaN patterning. As mask material thin layers of Ti, Pt and Au were used. 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.

2. Experimental

The GaN used in this study was n-type, Si doped with a carrier concentration $n\sim4\times10^{17}$ cm^{-3} and undoped, grown on a (0001)-oriented sapphire substrate by metal-organic chemical vapor deposition (MOCVD). One of them (A) consisted of 2.5 μm thick Si-doped 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. 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.

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. 1). For the oxidizing agent concentrations from 0.006 M to 0.03 M the etched surface was covered with whiskers.

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. 2). 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.

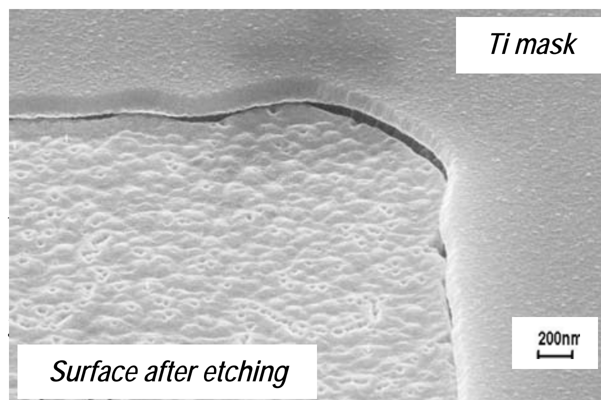


Fig. 1: *SEM view of sample (A) surface with Ti mask etched with 0.004 M KOH and 0.1 M $K_2S_2O_8$*

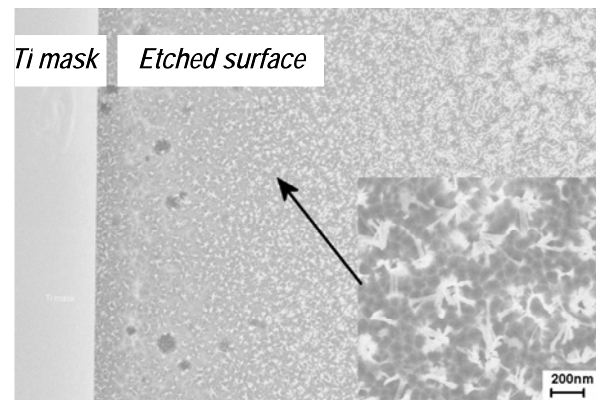


Fig. 2: *SEM view of sample (B) surface with Ti mask etched with 0.004 M KOH and 0.1 M $K_2S_2O_8$. The ratio masked/unmasked is 1:4*

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

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

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. 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. 3). 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.

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. 3a)

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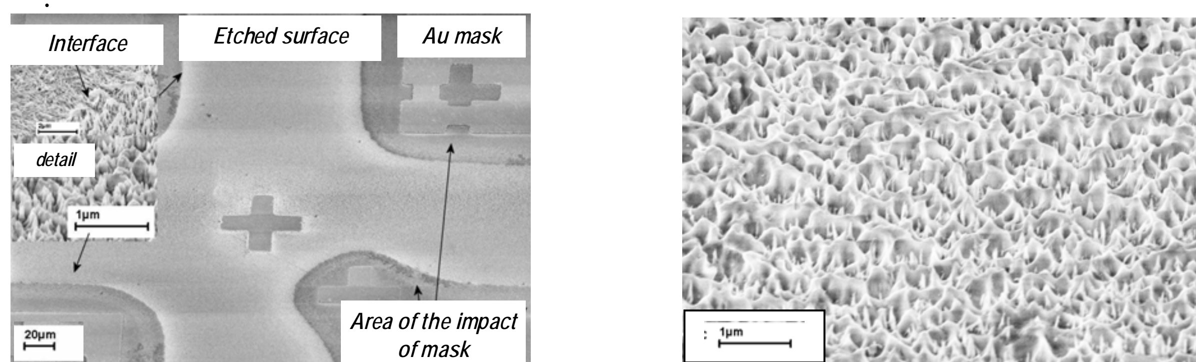

Figure 3a,b: *SEM view of sample (B) surface with Ti/Au and* Pt *mask etched with 0.004 M KOH and 0.1 M* $K_2S_2O_8$.

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 homogeneous. Further distance increase initiates whisker formation (Fig.3b).

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. Conclusions

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.

Acknowledgements
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