MORPHOLOGY STUDY AND CATHODOLUMINESCENCE MICROANALYSIS OF PHOTOELECTROCHEMICALLY ETCHED GaN EPILAYERS

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1. Abstract

Photoelectrochemical etching of GaN in different solutions such as KOH, $HF/H_2O_2/C_2H_5OH$ and oxalic acid was performed. The results of scanning electron microscopy cathodoluminescence analysis of the etched samples are presented.

2. Introduction

GaN and related nitrides are considered promising materials for numerous applications such as the creation of full-color display systems, data storage devices, solar-blind ultraviolet detectors, new sensor technologies, wireless communications, solid-state lighting and high-power microwave generation for radar, etc. Note that nitride-based light-emitting diodes and lasers have been successfully commercialized. Further elaboration of novel device structures on GaN and related materials depends upon the progress in growth technologies and material processing. Considerable efforts are focused nowadays to the study of etching processes in III-group nitrides, most processing being currently done by dry plasma etching. High etching rates are observed under high-density plasma conditions. There are however, important disadvantages to dry etching, including the generation of processing-induced damage and difficulties in obtaining smooth etched sidewalls, which are required for high-performance nitride-based laser diodes and other devices. Increasing attention is being paid therefore to wet etching of III-group nitrides.

Many research groups proposed different acids and bases for GaN wet etching using Hg arc lamp or HeCd laser as UV light sources. There are two mechanisms during interaction of GaN surface with solution, one of them is direct chemical reaction between dislocations and solution, the other one is gallium oxide formation on GaN surface during UV expose and its subsequent dissolution. The first mechanism seems to be highly dependent upon solution concentration and crystal orientation [1], when for the second mechanism the etch rate is dependent on the kinetics of the solution. Adjusting the UV power, it is possible to control the share of each mechanism in the etch rate and, as a result, to define the final morphology.

3. Experiment

3.1. PEC etching in KOH solution

During PEC etching using KOH as etchant solution, we use epilayers of GaN grown by low-pressure MOCVD on sapphire using trimethylgallium and ammonia as source materials. A buffer layer of about 25-nm thick GaN was first grown at 510°C, while the top n-GaN layer with 1.3-2.0 µm thickness was grown at 1100°C. The concentration of free electrons in the top n-GaN layer was $1.7\times10^{17}cm^{-3}$.

Ti/Al/Ti/Au ohmic contacts with the thickness 300/900/500/1500 A respectively were deposited by e-beam evaporation followed by rapid thermal annealing (RTA) process at 800°C for 30 seconds in nitrogen atmosphere.

The photoelectrochemical etching of samples was carried out in 0.05 M aqueous solution of KOH under in situ UV illumination provided by focusing the radiation of 50-200W Hg or Xe lamps on the GaN surface exposed to electrolyte. In experiments using Hg lamp the current between the sample and Pt electrode decreased from 4 to 0.1 mA in 10 minutes and did not depend on radiation power density, while under Xe lamp excitation the current was directly proportional to the radiation power density and was almost constant during the process. The difference between these two UV sources comes from different kinds of spectral characteristics and as a result different morphologies were obtained (Fig.1).

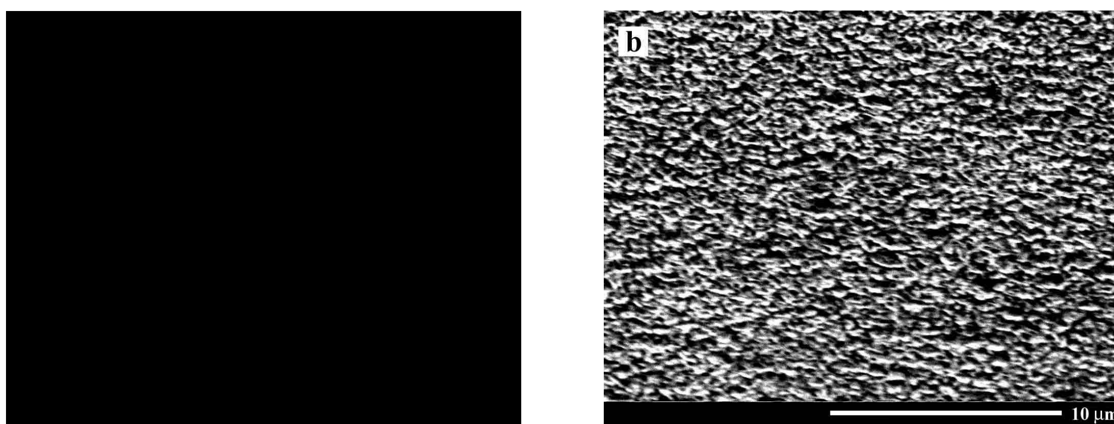

Fig.1. Samples etched for 10 min in 0.05M KOH at 100W using Hg (a) and Xe (b) lamps.

Note that the etching process using Xe lamp gives more uniform morphology near the ohmic contact and in the middle of the sample than that based on use of the Hg lamp. The I-V characteristics taken from resistive samples after PEC etching show a nonlinear behavior.

Fig. 2 shows the CL spectra of columnar and bulk GaN at 80 K. Both spectra consist of near-band-edge peaks, CL band at 3.28 eV related to non-equilibrium carrier recombination via donor acceptor pairs (DAP), phonon replicas of DAP-related band, and a broad band with the maximum at 2.15 eV (the so-called “yellow” luminescence). One can see that porosity induces an upward frequency shift of the near-band-edge peak. Apart from that, it results in a sharp diminution of the intensity of yellow emission. Monochromatic CL images taken from the same areas of the samples exhibited an anti-correlation in the spatial distribution of near-band-edge and yellow CL (Fig. 3). During irradiation exposure, attenuation of near-

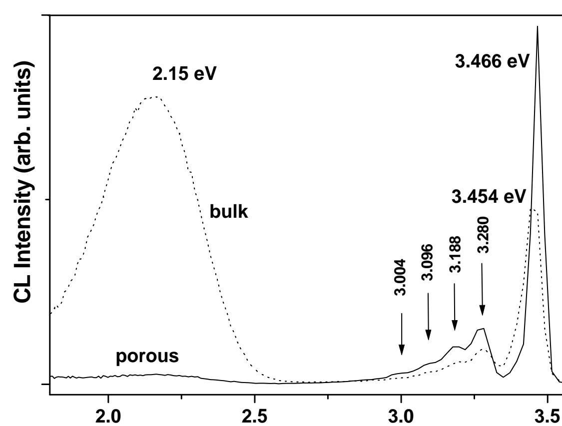

Fig. 2. CL spectra of bulk and nanostructured GaN at T = 80 K.

band-edge and visible CL by the electron beam was evidenced, the effect being more pronounced for the UV emission.

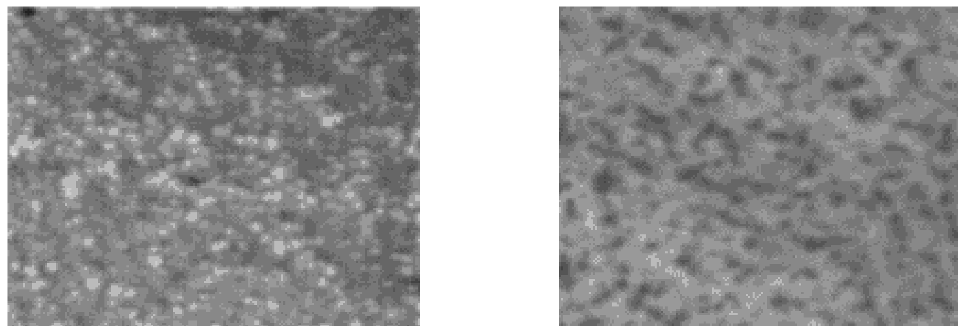

Fig. 3. UV (left) and yellow (right) monochromatic CL images taken from PEC etched GaN at T = 80 K. The image width equals 40 μm.

3.2. PEC etching in HF /H_2O_2/C_2H_5OH solution

Porous Si can be generated using Pt-assisted electroless etching in ethanol:HF:H_2O_2 (1:1:1) [2]. In this process, a thin discontinuous layer of Pt (d < 8 nm thickness) is patterned onto the surface. This approach has been used for porous GaN obtaining.

On n+n GaN layers (Si as dopant) with the thickness of 2 and 1 μm respectively with carrier concentrations of 5×10^{18} and 2×10^{17} cm^{-3} Pt islands were patterned using electrochemical deposition based on short impulses (0.1 μs duration, 1 μs period and 10V amplitude) applied during 20 seconds as a result uniform island morphology was achieved, see Fig.4.

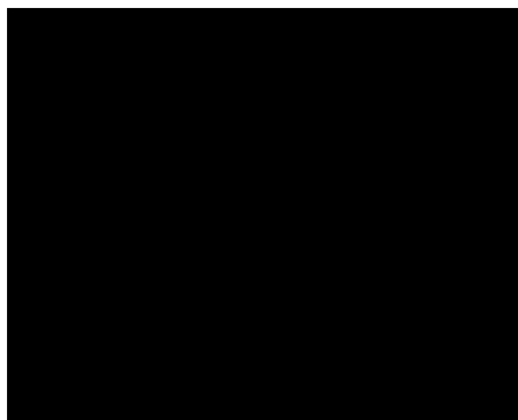

Fig.4. Pt islands on GaN surface.

Catalytic reduction of H_2O_2 at the Pt islands combined with UV illumination injects holes into the valence band, as a result local polarization is reached which initiates local etching, developing with time in a porous structure.

After precleaning procedure, the samples were dipped in a stirred solution of HF/H_2O_2/C_2H_5OH at room temperature and subjected to UV illumination from a 200W Xe lamp. No current was observed in dark so there was no chemical decomposition in HF solution. When the light is switched on, then a current of about 50 μA emerges, which drops to 10 μA after 30 minutes, at the same time, when the light is switched, the current increases up to 30 μA and then diminishes up to zero in about 10 minutes.

The fabricated porous structures were then cleaved and cross-sectional images were taken by SEM. Fig.5 shows a porous layer with the thickness of 0.8 μm exhibiting pores stretching perpendicularly to the initial surface.

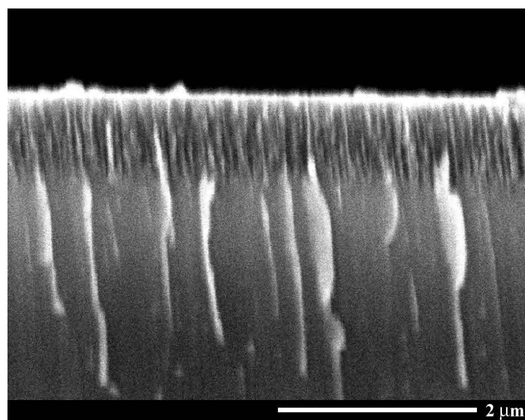

Fig.5. SEM image of porous GaN

3.3. PEC etching in oxalic acid

Oxalic acid ($H_2C_2O_4 \times 2H_2O$) can be used for GaN defect characterization [6]. Etching in this solution under UV illumination resulted in a porous structure of GaN. For the electrolyte preparation, 5 grams of oxalic acid were dissolved in 300 ml of water. Potential of 10 V was applied between the sample and Pt electrode. At room temperature and UV expose, the initial current of 120 µA increased up to 250 µA after 5 minutes and reached the value of 550 µA in 7 minutes. Intensive hydrogen bubbles were observed on GaN surface during the experiment.

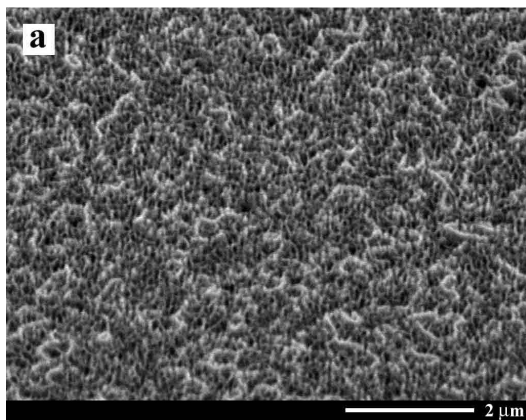

Fig.6. SEM images taken from GaN surface etched in oxalic acid, top view **(a)** and cross-sectional view **(b)**

4. Conclusion

PEC etching in KOH solution under UV Xe-lamp illumination of GaN results in smooth morphology, while columnar structures are obtained at relatively low power UV irradiation from Hg lamp when etching occurs in the same solution.

Uniform porous layers with high density of pores were obtained in $HF/H_2O_2/\ C_2H_5OH$ solution under UV irradiation.

Acknowledgements

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