

Nanoporous GaN by UV assisted electroless etching for sensor applications

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Introduction

GaN-based devices have demonstrated excellent performance for electronics and optoelectronics applications. In particular, these devices exhibit very good performance when operated at high temperatures and in harsh environments when compared to similar devices fabricated with conventional material systems. The good stability, durability and biocompatibility of the nitrides have also led to the development of GaN based chemical and biological gas sensors. These devices have been developed using Schottky diodes with platinum or palladium contacts on GaN and AlGaIn/GaN structures [1-3] and showed high sensitivity. However, the response may be further improved if the effective surface area is increased, allowing a more efficient accumulation of the gas induced dipole layer [4]. In this paper fabrication and characterization of nanoporous GaN is presented as a first step for the fabrication of improved GaN gas sensors.

Experimental

The nanoporous GaN layers (nP-GaN) were fabricated using n-type GaN substrates (silicon doping concentration $\sim 10^{18}$ atm/cm³) grown by HVPE on sapphire. The samples were subjected to an etching procedure in order to induce the formation of pores. The etching was photo-assisted with a 365 nm UV light beam with power density up to 0.8 W/cm² (Hamamatsu L9566-01), and directed on the sample using a quartz light guide and a collimator (Hamamatsu E5147-06). The etching was performed in an in-house made electrochemical chamber with an illumination window. In this work, no external bias was applied between the sample and the electrolyte.

Prior to the etching, the GaN samples were cleaned in a standard organic procedure (hot 2-metil-pirrolidone followed by hot acetone and rinsed in methanol) and a 10% HF bath for 30 seconds. After the cleaning procedure some of the samples were covered with 3 nm thin platinum islands of different sizes. Different HF:H₂O₂ based electrolytes were investigated for this procedure using different concentrations and diluents (mainly H₂O and CH₃OH).

SEM, PL and wetting angle measurements were performed in order to characterise the fabricated material. An He-Cd (above bandgap illumination with $\lambda = 325$ nm) pumping laser was used for the PL measurements.

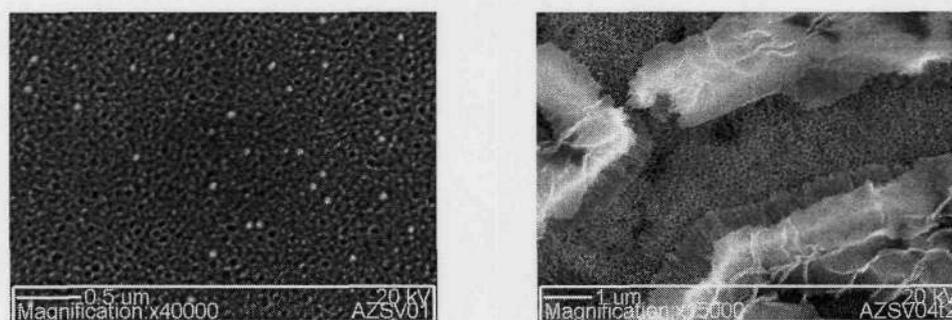


Fig. 1. SEM image of two nP-GaN layers formed by an electroless etching in CH₃OH:HF:H₂O₂ (1:4:1) with $P_{UV} = 0.8$ W/cm² for $\lambda = 365$ nm. The only difference between these layers is that a 3 nm Pt deposition was performed on the sample on the right prior to the etching.

Results

The best defined porous layers were obtained using the $\text{CH}_3\text{OH}:\text{HF}:\text{H}_2\text{O}_2$ (1:4:1) electrolyte with a UV illumination power of 0.8 W/cm^2 . The average diameter of the pores, which formed a dense network (see Fig. 1), was $\sim 50 \text{ nm}$. For the Pt assisted etching (samples with 3 nm Pt metallization) the formation of the pores was very fast, and partial etching of the material was observed to occur. The porous layer had higher affinity to water as observed in DI H_2O wetting experiments. This increased affinity leads to a higher chemical sensitivity which may be exploited in sensing applications.

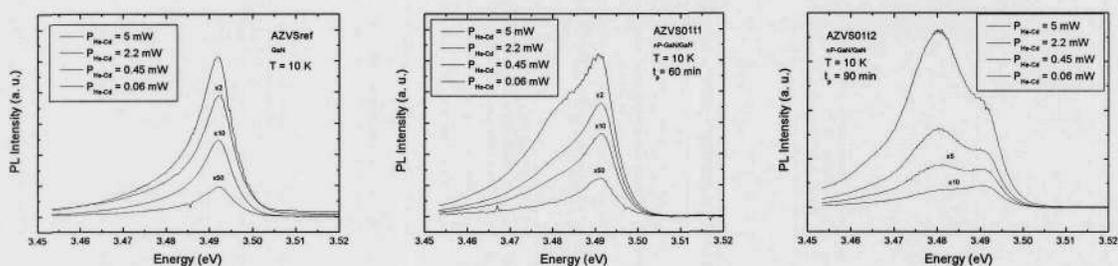


Fig. 2. PL spectra of a reference GaN layer and two nP-GaN/GaN layers prepared in $\text{CH}_3\text{OH}:\text{HF}:\text{H}_2\text{O}_2$ (1:4:1) with etching times (t_p) of 60 min and 90 min, at several optic powers.

In addition to the peak around 3.492 observed in the GaN reference, the PL spectra of the nP-GaN samples show a red-shifted peak related with the porous layer. Its energy suggests that the shift is originated due to the relaxation of the residual stress in the material [5-7]. The samples etched with $\text{CH}_3\text{OH}:\text{HF}:\text{H}_2\text{O}_2$ (1:4:1) electrolytes show the stronger intensity of this peak.

The relative intensity of the nP-GaN peak to the GaN peak decreases as the pumping power is reduced, due to the large surface recombination in the nP-GaN layers. For those layers prepared using a Pt assisted etching, this dependence with the pumping laser power is weaker, and the peaks are narrower; therefore, this etching procedure is useful to reduce surface effects in porous layers.

Finally, the nP-GaN layers were subjected to several chemical sensitivity experiments. The more relevant results were obtained using a 5M KOH@50° C etching. A c-direction etch rate of 6 nm/min was measured and inverted hexagonal pyramid-like structures were detected by SEM and AFM imaging. Meanwhile, the reference GaN layers had no measurable etching. This high sensitivity to KOH is due to the exposure of a large surface with different crystal orientations in the nP-GaN.

Conclusions

Nanoporous GaN layers have been fabricated using UV assisted electroless etching. The electrolyte which provided the higher pore density and better definition was $\text{CH}_3\text{OH}:\text{HF}:\text{H}_2\text{O}_2$ (1:4:1). It has been proved that pores with 50 nm diameter can be achieved; the porous layers exhibit strain relaxation and an increase in the chemical sensitivity. Therefore this material is a suitable candidate for chemical sensors based on surface interactions. Schottky diode sensors are currently being developed.

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