Morphology and luminescence properties of porous $Al_{0.09}Ga_{0.91}N$ generated via Pt-assisted electroless etching

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(Received 26 December 2007)

High quality unintentionally doped n-type $Al_{0.09}Ga_{0.91}N$ layers were grown on Si(111) substrate using AlN as buffer layer by radio frequency (RF) nitrogen plasma-assisted molecular beam epitaxy (PAMBE). This paper presents the structural and optical studies of porous $Al_{0.09}Ga_{0.91}N$ sample as compared to the corresponding as grown AlGaN. The porous $Al_{0.09}Ga_{0.91}N$ was prepared by Pt assisted electroless chemical etching using HF solution as an electrolyte. To assess the optical quality and morphology of these porous films, scanning electron microscopy (SEM), high resolution x-ray diffraction (HRXRD), and photoluminescence (PL) techniques have been employed. The porous area is very uniform, with pore diameter in the range of 100-150 nm. XRD measurements showed that the (0002) diffraction plane peak width of porous samples was slightly broader than the as grown sample. As compared to the as grown film, the porous layer exhibits a slight increase in PL intensity.

I. INTRODUCTION

$Al_xGa_{1-x}N$ alloys are extremely important materials with widespread applications for optoelectronic devices because they have a direct wide energy bandgap, which ranges from 6.2 to 3.4 eV. Due to their wide band gap range, the alloys are very attractive materials for applications in ultraviolet (UV) laser diodes (LD's), light emitting diodes (LED's) and photodetectors [1-3].

A great deal of the interest displayed in porous semiconductors in recent years is motivated by the prospects that they could be applied in optoelectronics, chemical and biochemical sensors, and as matrices for characterization of macromolecules. Porous SiC and GaN have recently been explored as promising substrates to grow epitaxial SiC or GaN with reduced dislocation density [4-6]. It has been speculated that a porous surface may serve as a template for nano-scale lateral epitaxial overgrowth, and that a porous substrate layer may be compliant to any lattice and thermal mismatch strains [5]. Porous Si (PSi) has been widely studied since the first report of visible luminescence in 1990 [7]. However, the nonideal thermal, mechanical, and chemical properties of PSi are challenges to its large scale application, spurring research into other porous materials, including the III-V nitrides [8].

Porous GaN is often generated by dry etching [9] or photoelectrochemical (PEC) methods [10]. Dry etching techniques suffer from the disadvantage that they may induce surface damage, and they lack the desired selectivity towards morphology, dopant, and composition [11]. PEC etching of GaN and other semiconductors offers advantages over dry etching methods, allowing for anisotropic, dopant-selective etching, preparation of porous or smooth surfaces, and selective etching of areas between dislocations. Unfortunately PEC requires electrical contact to the sample making this method impractical for large scale production. Electroless methods for the etching of GaN have been recently developed by Bardwell [12]. Bardwell and co-workers developed an approach based on the chemical oxidation of GaN by peroxydisulfate in KOH under UV illumination.

Similar to porous GaN, porous AlGaN can be used as a buffer or intermediate layer to reduce substrate-induced stress. Such a regrowth method may reduce the defect density in the epitaxial layer leading to high quality stress free layer on porous template. In this work, the investigation of porous $Al_{0.09}Ga_{0.91}N$ prepared by Pt assisted electroless chemical etching has been performed. The simplicity of the electroless etching technique is attractive, because it is compatible with large-scale production.

II. MATERIAL AND METHODS

Unintentionally doped n-type $Al_{0.09}Ga_{0.91}N$ film grown on Si(111) substrate was used in this study. Sample nominally consisted of 0.20 µm AlN followed by 0.23 µm AlGaN with carrier concentration of $\sim 4\times10^{19}$ cm^{-3} as determined by Hall Effect measurement. The wafer was then cleaved into few pieces. Prior to the platinum (Pt) metallization, the native oxide of the sample was removed in the 1:20 NH_4OH:H_2O solution, followed by 1:50 HF: H_2O. Subsequently boiling aqua regia (3:1 HCl: HNO_3) was used to etch and clean the sample.

Porous $Al_{0.09}Ga_{0.91}N$ in this work was generated by Pt assisted electroless etching. Two narrow stripes of Pt

with thickness of about 400 nm were deposited on the $Al_{0.09}Ga_{0.91}N$ sample by using sputtering system. The samples were then etched in a solution of 4:1:1 $HF:CH_3OH:H_2O_2$ under illumination of an UV lamp with 500 W power for 10 minutes. The Pt films used to catalyze etching of AlGaN are still present even after long etch times. After chemical treatment, the samples were removed from the solution and rinsed with distilled water; followed by the removal of the residual Pt by ultrasonic cleaning.

Precleaning to remove any pre-existing surface contaminant adlayer is imperative to obtain reproducible etching. An adlayer would adversely affect hole injection across the Pt-$Al_{0.09}Ga_{0.91}N$ interface and lead to irreproducible etching due to the increased Schottky barrier height for Pt-$Al_{0.09}Ga_{0.91}N$ [13,14]. Etching of the $Al_{0.09}Ga_{0.91}N$ samples, as evidenced by evolution of gas around the narrow stripes of Pt and by changes in the visual appearance of the substrate, commenced immediately upon immersion of samples that were precleaned and sputtered with Pt into the $HF:CH_3OH:H_2O_2$ etchant solution. $Al_{0.09}Ga_{0.91}N$ samples etched without Pt, or etched with Pt but without UV illumination did not produce porous $Al_{0.09}Ga_{0.91}N$, yielding samples that were virtually indistinguishable from unetched $Al_{0.09}Ga_{0.91}N$.

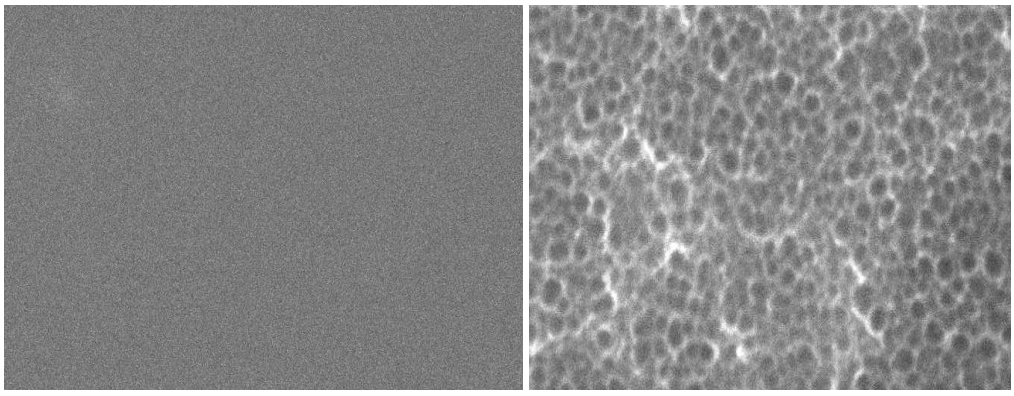
The morphological, structural and optical properties of as grown and porous $Al_{0.09}Ga_{0.91}N$ samples were characterized by SEM, HRXRD, and PL. PL measurement was performed at room temperature by using a Jobin Yvon HR800UV system. A He-Cd laser (325 nm) with 20 mW power was used as an excitation source for PL.

III. RESULTS AND DISCUSSION

The morphology of the as grown and porous AlGaN films was characterized by plan-view scanning electron micrographs (SEM). As seen in Fig. 1, the porous (dark) area is very uniform, with pore diameter in the range of 100-150 nm. Diaz prepared their porous GaN samples by platinum assisted electroless etching, and found that, at short etch time (< 15 min), a rich network of small pores were formed. However for longer etch times; a ridge-valley-like morphology was obtained [15,16].

In order to examine the quality of the films, $\omega/2\theta$ scan of HRXRD rocking curve (RC) for (0002) plane was carried out. Fig. 2 shows the $\omega/2\theta$ scan of the HRXRD RC of (0002) plane for the as grown and porous AlGaN/Si(111). Porous samples exhibited broader peak width than the as grown sample for (0002) diffraction plane. The full width at half-maximum (FWHM) of the RC for the as grown sample and porous AlGaN sample are 19.15 arcmin and 22.20 arcmin, respectively. On the other hand, the peak shift of (0002) diffraction plane for the etched samples relative to the as-grown sample was observed; however change of peak positions was relatively small about 0.03 deg.

Fig. 3 illustrates the room temperature PL spectra of as grown and porous AlGaN samples. The slight amplification of porosity induced PL intensity could be explained by the extraction of strong PL by light scattering from the sidewalls of the GaN crystallites [17]. However, it also could be ascribed to the optical microcavity effect which is inherent to porous GaN areas characterized by strong light scattering. It has been known that optical mode density could be altered by interference due to the optical environment [18].



(a) (b)

FIG. 1. SEM images of the samples (a) As grown, (b) Etched for 10 min.

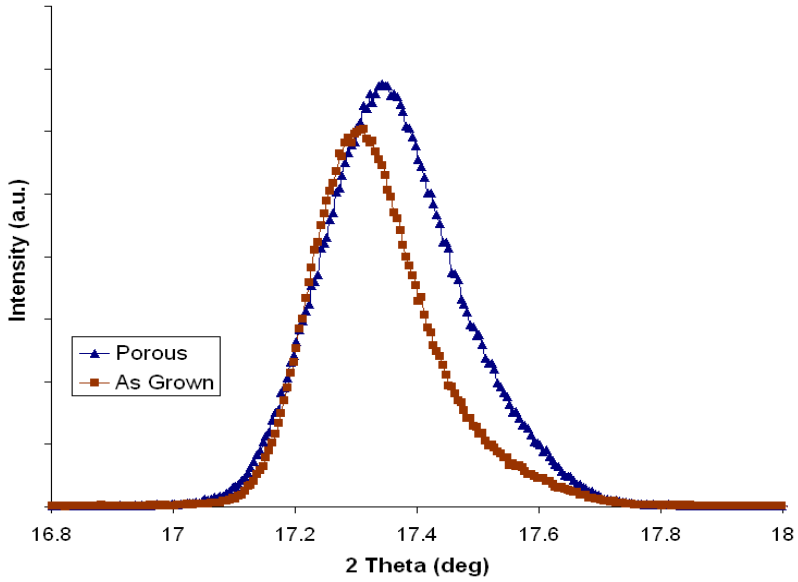


FIG. 2. HRXRD RC of (0002) plane for as grown and porous AlGaN grown on Si(111) substrates.

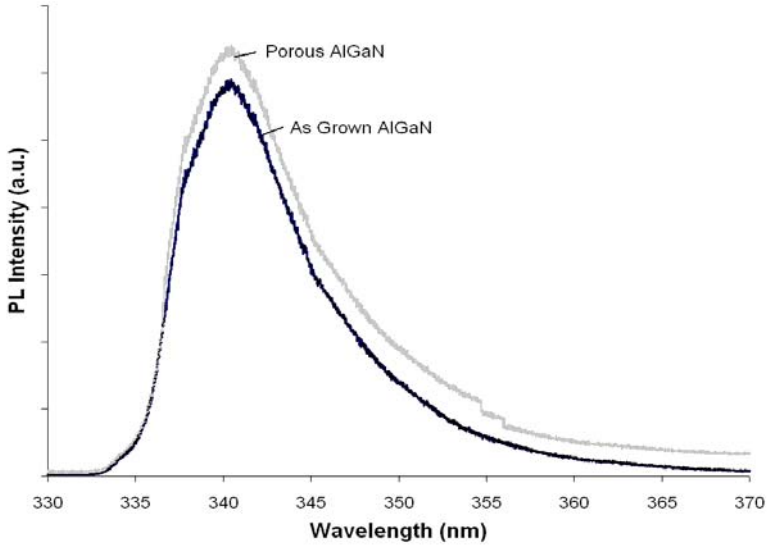


FIG. 3. The near band edge PL spectra of the samples measured at room temperature.

IV. CONCLUSION

The structural and optical characteristics of porous AlGaN prepared by Pt assisted electroless etching have been investigated. SEM images indicated that the porous area is very uniform. XRD measurements show an increase in the FWHM of (0002) diffraction peak as compared to the corresponding as grown AlGaN. PL intensity in porous AlGaN shows intensity enhancement at room temperature.

ACKNOWLEDGMENTS

The authors highly acknowledge the support from Short Term grant and Universiti Sains Malaysia. The authors would like to thank Madam Ee Bee Choo for the SEM measurements

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