

## Enhancement of different illumination porous GaN using UV electrochemical etching

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### ABSTRACT

*This article reports the properties and the behavior of GaN during the photoelectrochemical etching process using four different current densities of UV illumination. The measurements show that the porosity strongly depends on the high illumination and highly affects the surface morphology of etched samples, which has been revealed by scanning electron microscopy (SEM) images. Peak intensity of the photoluminescence (PL) spectra of the porous GaN samples was observed to be enhanced and strongly depend on the illumination. Among the samples, there is a little difference in the peak position indicating that the change of porosity has little influence on the PL peak shift, while it highly affecting the peak intensity. Raman spectra of porous GaN under different current densities of UV illumination exhibit phonon mode E2 (high), A1 (LO), A1 (TO) and E2 (low). There were slight blue shifts in E2 (high) in all samples, indicating a relaxation of stress in the porous GaN surface with respect to the underlying single crystalline epitaxial GaN. Raman and PL intensities were high for samples etched in different current densities of UV illumination.*

**Keywords—** illumination; GaN; UV-electrochemical etching; Porosity.

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### I. INTRODUCTION

GaN metastable cubic phase (c-GaN) has advantages in some electrophysical and luminescent parameters over the stable hexagonal modification (h-GaN). These are, in particular, smaller effective mass and higher mobility of charge carriers at higher efficiency of acceptor impurity ionization. GaN ternary alloy system receives a great deal of attention among III-nitride compound semiconductors because of its direct band gap tuning from 0.7eV for InN to 3.4 eV for GaN, giving InGaN great potential for the design of high-efficiency optoelectronic devices that operate in the IR, visible, and UV regions of the electromagnetic spectrum [1]. Porous III-nitride compounds are considered as promising materials for optoelectronics [2] and chemical and biochemical sensors [3] because of their unique optical and electronic properties compared with bulk materials [4,5]. The formation of a porous nanostructure has been widely reported for crystalline silicon [6]. In addition to porous silicon research, attention has also been focused on other porous semiconductors, such as GaAs [7] and GaN [8-10]. Interest in porous semiconductor materials arises from the fact that these materials can act as sinks for threading dislocation and are able to accommodate strain. Porous semiconductor materials are also useful for understanding the fundamental properties of nanoscale structures for the

Development of nanotechnology. Research on porous GaN is strongly driven by the robustness of porous GaN, including its excellent thermal, mechanical, and chemical stabilities that make it highly desirable for optical applications [11]. Many researchers [4,12-14] have used the photoelectrochemical etching (PEC) technique to synthesize porous GaN. The PEC technique is more suitable and cheaper compared with other techniques for producing high-density nanostructures with controlled pore size and shape [4]. Electrolyte, current density and illumination are the main factors that affect electrochemical etching. Hydrofluoric acid (HF) is the most commonly used material in etching GaAs and GaN [15]. In the current study, the PEC technique is used to synthesize porous GaN nanostructures at various current densities. To the best of our knowledge, this study to report on the synthesis of porous GaN by using the PEC technique.

### II. EXPERIMENTAL

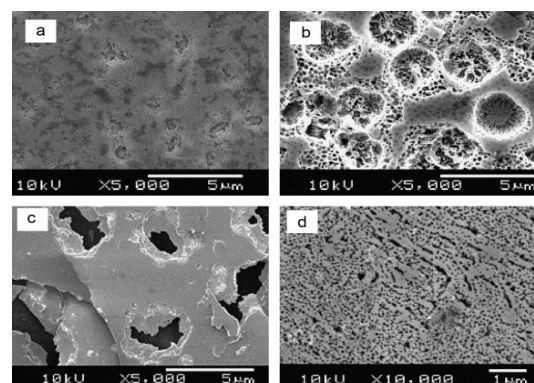
The unintentionally doped n-type GaN film grown on silicon (111) substrate was used in this study. The film growth has been performed in a Veeco Gen II molecular beam epitaxy (MBE) system. The growth was done by using high purity material sources such as gallium (7N) and aluminium (6N5), while the

nitrogen with 7N purity was channelled to RF source to generate reactive nitrogen species. First, the substrate was heated to 900°C for outgassing. Then the substrate temperature was lowered to 850°C for Ga cleaning before growth of the AlN buffer layer. Following the Ga cleaning step, an AlN buffer layer was grown at 850°C for 30 min. Next, the substrate temperature was elevated to 800°C to grow GaN layer. The growth time was about 45 min. The thickness of GaN film is about 0.6  $\mu\text{m}$  with carrier concentration of  $4 \times 10^{18} \text{ cm}^{-3}$  as determined by Hall Effect measurement. The wafer was then cleaved into few pieces. Prior to the metallization, the native oxide of the sample was removed in the 1:20  $\text{NH}_4\text{OH}:\text{H}_2\text{O}$  solution, followed by 1:50  $\text{HF}:\text{H}_2\text{O}$ . Subsequently, boiling aqua regia (3:1  $\text{HCl}:\text{HNO}_3$ ) was used to etch and clean the sample. Porous GaN in this work was generated by Pt assisted electroless etching. Two narrow stripes of Pt with thickness of about 250 nm were deposited on the GaN sample by using a sputtering system. The samples were then etched in a solution of 2:1:1  $\text{HF}:\text{CH}_3\text{OH}:\text{H}_2\text{O}_2$  under UV lamp illumination at two different current densities of 15, 25 and 50  $\text{mA}/\text{cm}^2$  for 15 min. All samples were rinsed with ethanol after the etching process, and were then dried using nitrogen gas. All experimental processes were conducted at room temperature. The optical properties of as grown and porous GaN samples were characterized by PL. PL measurement was performed at room temperature by using Jobin Yvon HR800UV system, which is an integrated confocal micro-photoluminescence spectrometer. A He-Cd laser (325nm) was used as an excitation source for PL measurement. For measurement, the incident laser power was 20 mW. To focus the laser on the sample surface, microscope objective lenses UV 40X was employed. The emitted light was dispersed by a double grating monochromator with 0.8 m focal length and equipped with 1800 grove/mm holographic plane grating. Signal were detected by a Peltier cooled CCD array detector. Before the micro-PL measurement, high quality single crystal silicon sample (with the zone-center-mode at  $520.70 \text{ cm}^{-1}$ ) was used to calibrate the system. The full width at half-maximum (FWHM) of the Si Lorentzian peak width was  $3 \text{ cm}^{-1}$ . The essential parameters peak position and full width at half maximum (FWHM) of the PL peak was determined by using curve fitting software with Gaussian and Lorentzian model.

### III. RESULTS AND DISCUSSION

Figs. 1 show the SEM images of the as-grown and etched GaN films. Fig. 1(A) shows the as-grown surface, in which can be attributed to the lattice and ridges formed on the surface. Fig. 1(B) shows the etching current density effect of 15  $\text{mA}/\text{cm}^2$  at 15 min on the surface morphology of GaN film. Irregular pores with different shapes and sizes were observed. Fig. 1(C) and Fig. 1(D) shows the etching

current density effect of 30  $\text{mA}/\text{cm}^2$  and 50  $\text{mA}/\text{cm}^2$  at 15 min on the surface morphology of GaN film. The effect of increasing the current density to 30  $\text{mA}/\text{cm}^2$  and 50  $\text{mA}/\text{cm}^2$  on the surface morphology in terms of the shape and size of the formed pores. The pores were more regular in shape and their number decreased with increasing current density, whereas average pore size increased twice with respect to Fig. 1(B). This finding indicates that pore size increases and grain size decreases when the current density is increased from 15  $\text{mA}/\text{cm}^2$  to 50  $\text{mA}/\text{cm}^2$ .



**Fig. 1** SEM images of samples etched under different current densities of UV illumination (a) as deposited, (b) 15  $\text{mA}/\text{cm}^2$ , (c) 30  $\text{mA}/\text{cm}^2$  (d) 50  $\text{mA}/\text{cm}^2$ .

Fig. 2 shows the photoluminescence (PL) spectra of the as-grown and porous films, displaying the near band-edge emission of GaN at a wavelength of 565 nm. A PL wavelength emission peak at 556 nm is related to the as-grown sample. Slight blue shifts were observed in the porous films at wavelengths of 554.3 and 553.1 nm, which correspond to the etched films at 30 and 50  $\text{mA}/\text{cm}^2$ , respectively. These shifts can be attributed to the change in current density. The PL peak intensity of the porous films was 10 times more than that of the as-grown film, indicating that porosity strongly affects peak intensity. The intensity of emitted light is known to be proportional to the number of emitted photons, and thus, the number of photons emitted by the porous film is much higher than the number emitted by the as-grown film. High porosity-induced PL intensity can be explained by the extraction of strong PL via light scattering from the sidewalls of the sample crystallites [16]. Porous films have higher surface area per unit volume compared with as-grown films, and thus, the porous GaN film provides much more exposure to the illumination of PL excitation lights for GaN molecules. This phenomenon may result in a higher number of electrons taking part in the excitation and recombination process in porous films compared with the smaller surface area of the as-grown films [13]. The relatively wide statistical size distribution of

the pores can be attributed to the broadening of the linewidth of porous films.

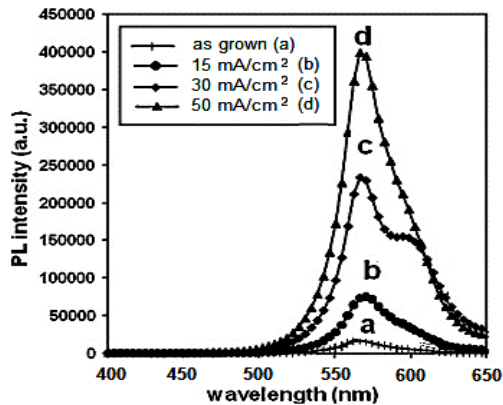


Fig. 2 PL intensity of samples etched under different current densities of UV illumination (a) as deposited, (b) 15 mA/cm<sup>2</sup>, (c) 30 mA/cm<sup>2</sup> (d) 50 mA/cm<sup>2</sup>.

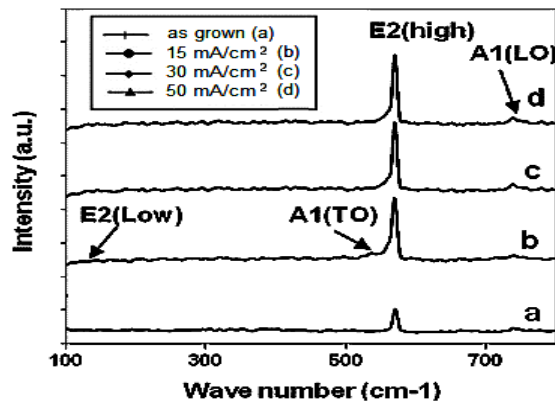


Fig. 3 The Raman spectra of samples etched under different current densities of UV illumination (a) as deposited, (b) 15 mA/cm<sup>2</sup>, (c) 30 mA/cm<sup>2</sup> (d) 50 mA/cm<sup>2</sup>.

Fig. 3 shows the Raman spectra of the as-grown and porous GaN films. One Raman phonon mode, namely, the A<sub>1</sub>(LO) at 563.6 cm<sup>-1</sup> of the as-grown film, was observed. Moreover, the porous films at 30 and 50 mA/cm<sup>2</sup> were observed to shift to higher frequencies at 566.3 and 568.6 cm<sup>-1</sup>, respectively, relative to the as-grown film. This finding can be attributed to the compressive stress. One mode behavior for A<sub>1</sub>(LO) is that the linewidth increases with increasing current density. No feature associated with the E<sub>2</sub>(high) mode was observed above the luminescence background for all samples because. The broadening of the E<sub>2</sub>(high) peak increased when the current densities of UV illumination increased. All the phonon mode peak positions of the as-grown GaN observed in our Raman study is in good agreement compare with the value obtained. For porous GaN, all the peaks of E<sub>2</sub> (low),

E<sub>2</sub> (high), and A<sub>1</sub>(LO) were observed to be shifted to illumination compare to the as-grown GaN.

#### IV. CONCLUSIONS

The porous nanostructures of the GaN layer were synthesized using the UV-assisted electrochemical etching method. These nanostructures can open a new and promising area in ternary III-nitride materials through the chosen suitable etching factors to enhance the structural and optical properties of thin films for optoelectronic devices. The pore size and roughness of the porous thin films increased with increasing current density, consequently decreasing the crystallite size and compressive stress. The change in current density had insignificant influence on the amount of peak shifting in the PL spectra, showing a clear increase in intensity. One mode behavior for A<sub>1</sub>(LO) was observed from the Raman spectra, and the linewidth increased with increasing current density, suggesting the occurrence of stress relaxation.

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