Surface Morphology and Formation of Nanostructured Porous GaN by UV-assisted Electrochemical Etching

L. S. Chuah, Z. Hassan, C. W. Chin, and H. Abu Hassan

Abstract—This article reports on the studies of porous GaN prepared by ultra-violet (UV) assisted electrochemical etching in a solution of 4:1:1 HF: CH3OH:H2O2 under illumination of an UV lamp with 500 W power for 10, 25 and 35 minutes. The optical properties of porous GaN sample were compared to the corresponding as grown GaN. Porosity induced photoluminescence (PL) intensity enhancement was found in these samples. The resulting porous GaN displays blue shifted PL spectra compared to the as-grown GaN. Appearance of the blue shifted emission is correlated with the development of highly anisotropic structures in the morphology. An estimate of the size of the GaN nanostructure can be obtained with the help of a quantized state effective mass theory.

Keywords—Photoluminescence, porous GaN, electrochemical etching, Si, RF-MBE.

I. INTRODUCTION

POROUS semiconductors have been widely studied, primarily due to the potential for intentional engineering of properties not readily obtained in the corresponding crystalline bulk solids [1-3]. These materials exhibit unique chemical and physical properties due to their extremely small size and large surface to volume ratio, therefore it opens alternative possibilities for their various potential applications in optoelectronics, chemical and biochemical sensing. When porosity is formed, these materials exhibit various special optical features, for instances, the shift of band gap, luminescence intensity enhancement, as well as photo response improvement. Porous layer can be used as a buffer or intermediate layer for strain management during epitaxial regrowth.

Among porous semiconductors, porous silicon receives enormous attention and has been investigated most intensively;

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however the instability of physical properties has prevented it from large scale application. This leads to the development of other porous semiconductors, for instances, the conventional III-V compounds such as GaAs, GaP and InP; and the wide band gap materials such as GaN and SiC [4-7].

Since bulk GaN in wafer size is not available, GaN thin film usually is grown on poor lattice and thermal mismatch foreign substrates which will result in high residual stress and eventually lead to high density of structural defects [8]. Researches have also suggested that nanopatterned porous structures may serve as a template for nano-scale lateral epitaxial overgrowth [9-10]. Comparatively, the study of porous GaN is still in the early stage, many fundamental properties are not well established.

Electroless etching is also called electrochemical oxidation without external bias. Metal-assisted electroless-chemical etching was an etching technique developed recently which was proven to be efficient in generating porous semiconductors (especially GaN). In this process, a discontinuous layer of Pt is deposited on the semiconductor surface before immersing into solution containing CH_3OH, HF, and an oxidant, H_2O_2. Etching proceeds as the H_2O_2 is catalytically reduced at the surface of the Pt, thereby injecting mobile holes into the valence band. Similar to anodic etching, the holes will induce dangling bond, and the dangling bonds will be attacked by nucleophilic species, resulting in material dissolution.

The observation of visible photoluminescence (PL) in a variety of semiconductor nanocrystallites has fueled a large body of research work in the past decade [11]. A material which has attracted considerable attention is porous silicon, which is a disordered collection of silicon nanocrystallites with varying sizes. The PL spectra from such system are broad, and often asymmetric about the peak energy. To compute the parameters of emission, or, equivalently, the spectral line shape from an ensemble of semiconductor nanocrystallites, one needs to consider the distribution of crystallite sizes in the system [12-15]. The luminescence depends on the energy gap, the oscillator strength, the exciton binding energy, among others. All these factors exhibit a dependence on the size of the nanocrystallite.

In this work, porous GaN structures were formed from crystalline GaN grown on conducting Si substrate using metal-assisted UV electroless etching in $HF/CH_3OH/H_2O_2$. The surface morphology and optical properties of porous GaN samples were characterized by scanning electron microscopy (SEM), and photoluminescence (PL) spectroscopy

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respectively. An estimate of the size of the GaN nanostructure required to produce PL can be obtained from effective mass theory.

II. EXPERIMENTAL METHOD

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 channeled to RF source to generate reactive nitrogen species. First, the substrate was heated to $900^{o}C$ for outgassing. Then the substrate temperature was lowered to $850^{o}C$ for Ga cleaning before growth of the AlN buffer layer. Following the Ga cleaning step, an AlN buffer layer was grown at $850^{o}C$ for 30 min. Next, the substrate temperature was elevated to $800^{o}C$ to grow GaN layer. The growth time was about 45 min. The thickness of GaN film is about 0.6 μm with carrier concentration of 4×10^{18} 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 $NH_4OH:H_2O$ 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 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 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, 25 and 35 minutes (Fig. 1). 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.
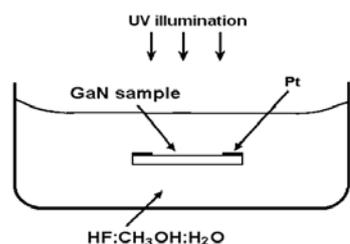
Fig. 1 The electroless chemical etching experimental set up used to generate porous GaN

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 (325 nm) 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 cm^{-1}) was used to calibrate the system. The full width at half-maximum (FWHM) of the Si Lorentzian peak width was ~ 3 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

The surface morphology of the as grown and porous GaN films was studied by scanning electron micrographs. As seen in Fig. 2, the circular porous area is very uniform, with pore diameter in the range of 80-110 nm. For 10 min sample, the pore sizes were found to be around 70 to 80 nm. For 25 min sample, the pore sizes were observed around 80 to 100 nm and for 35 min sample, the pore sizes were around 100 to 110 nm. The etching duration has significant effect on the size and shape of the pores.
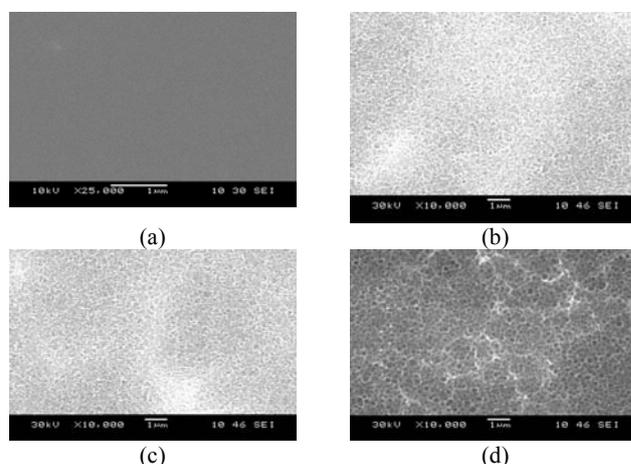
Fig. 2 SEM images of the samples. (a) as grown, (b) etched for 10 min, (c) etched for 25 min, (d) etched for 35 min

PL is one of the properties of nanostructured materials. In order to explain the broad PL band, it is assumed that the porous GaN contain wide distribution of nanocrystallites with different sizes. This means that the position and shape of PL band also depends on the sizes distribution of the nanocrystallites. Fig. 3 illustrates the room temperature photoluminescence (PL) spectra of porous GaN samples etched under different durations. The peak position, FWHM, peak shift (as compared to as grown GaN) and the intensity of near band edge PL are summarized and shown in Table 1. The spectra of the porous GaN samples were observed to be blue shifted relative to the as grown sample. Appearance of the blue-shifted PL emission is correlated with the development of highly anisotropic structures in the morphology. On the other hand, Yam et al [16] claimed that the porous GaN samples were observed to be PL red shifted relative to the as grown sample. Their finding was generally different from our result. Similar blue shifted PL was also observed and reported by Adelmann et al [17].

Among the samples, there is difference in the peak shift, and this indicates that the change of pore size has little influence on

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the amount of PL blue shifting. On the other hand, the PL intensity of the porous samples is found to be increased. The amplification of the porosity induced PL intensity could be explained as the reduction of surface pit density and extraction of strong PL by light scattering from the sidewalls of the GaN crystallites [18], however, it could be also 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 [19] and this concept has long been applied in the fabrication of resonant cavities light emitting diodes in which the optical properties have been greatly enhanced [20]. According to the quantum confinement luminescence mode, the shorter peak wavelength of luminescence is due to increase in band gap energy of the porous material. The strength of PL output become stronger as the porosity increased. It means that, the intensity of the PL is proportional to the number of photons emitted by the porous surface. The higher energy is dominated by surface-state recombinations and low energy emission originates from the quantum confinement effect.
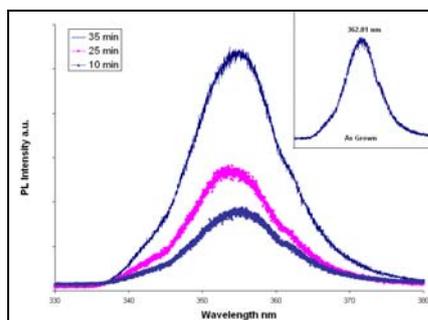
Fig. 3 The near band edge PL spectra of samples etched under different durations

TABLE I
THE PEAK POSITION, FWHM, PEAK SHIFT AND THE RELATIVE INTENSITY OF NEAR BAND EDGE PL OF DIFFERENT SAMPLES

Sample	Peak Position (nm)	FWHM (nm)	Peak Shift (nm)	Relative Intensity
As grown	362.01	6.8	-	1.00
10 min	357.63	8.5	4.38	1.20
25 min	356.50	8.8	5.51	1.64
35 min	358.13	9.9	3.88	1.80

The increase of the PL line width of the porous samples which is reflected in their FWHM shows that the luminescence spectrum of the porous GaN is broader for the sample prepared under longer chemical etching time. The broad luminescence band of the porous GaN with the feature of the homogeneous line shape is understood from the recombination of localized excitons with strong phonon coupling [21].

An estimate of the size of the GaN nanostructure required to produce PL can be obtained from effective mass theory.

Assuming infinite potential barriers, the energy gap E for three-dimensionally confined GaN should vary as [22]

$$E = E_g + \frac{h^2}{8d^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \qquad (1)$$

where E_g is the bulk GaN energy gap, d is the diameter of the spherical particle, and m_e^* and m_h^* are the electron and hole effective mass, respectively. At 300 K, E_g = 3.42 eV, m_e^*=0.20 m_0 and hole m_h^*=1.0 m_0 (see Ref. [23]). With these values Eq (1) become E (eV) = 3.42 + 14.08/d^2 with d in nanometer. Therefore, we can estimate that the observed PL peak at 357.63 nm (10 min) was due to GaN nanocrystallites of radius of about 14.5 nm. For 25 min sample, the GaN nanocrystallites were found to be around 13.4 nm. The GaN nanocrystallites were found to be around 15.0 nm for 35 min sample.

High resolution XRD was used to measure and determine the lattice parameters and structural quality of the samples. However, relatively large variation of the peak intensities was found for the porous samples, this indicated the slight change of the crystalline quality after etching. For the hexagonal structure, the d value which characterizes the distance between adjacent planes in the set of planes with Miller-Bravais indices (hkil), where $i = -(h+k)$ is given by the following relation (Verma, 1981):

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2+hk+k^2}{a^2} + \left(\frac{l}{c}\right)^2 \qquad (2)$$

Thus, equation (2) can be used to calculate the values of the lattice constants a and c, which will give an indication on the strain present in the sample.

The XRD measurements performed on the symmetric (0002) and asymmetric ($10\bar{1}2$) plane further confirmed the change of crystalline quality of the porous samples which was reflected in the FWHM of the peaks as shown in Table II. The porous samples exhibited broader FWHM than the as grown sample for both (0002) and ($10\bar{1}2$) diffraction planes, however for porous samples, no strong relation between FWHM and average pore size was observed.

From the XRD measurements, the lattice constants, c and a were also obtained and derived from peak position of (0002) and ($10\bar{1}2$) based on the Eq. (2). The calculated lattice constants were also presented in Table II. For lattice constant c, all the porous samples were found to have a bigger c relative to the as grown sample; however, for in-plane lattice constant, all the porous samples were found to have smaller a as compared to the as grown sample. The change of lattice constants c and a indirectly measures the degree of distortion of the hexagonal cell, this could be observed from the change of the c/a ratio.

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TABLE II
PEAK POSITIONS AND LATTICE CONSTANTS OF DIFFERENT SAMPLES DERIVED FROM XRD MEASUREMENTS

Sample	(0002)		$(10\bar{1}2)$		Lattice constant (Å)		
	Peak (°)	FWHM (arcmin)	Peak (°)	FWHM (arcmin)	c	a	c/a ratio
As grown	17.287	22.87	24.059	89.69	5.1844	3.1869	1.627
PG 1	17.258	24.97	24.147	90.94	5.1929	3.1583	1.644
PG 2	17.206	25.40	24.006	91.23	5.2081	3.1851	1.635
PG 3	17.264	26.10	24.049	90.30	5.1911	3.1847	1.630

Inoki (Inoki, et al 2003) studied the growth of GaN on porous GaN layer. The GaN seed layer was grown by hydride vapor phase epitaxy (HVPE), and the porous samples of HVPE GaN was prepared by electroless etching technique. XRD was used to measure the crystalline quality of porous and unetched seed samples from both the symmetric (0002) and asymmetric $(10\bar{1}2)$ planes. For (0002) symmetric plane, one of the etched samples was observed to have a smaller FWHM than the unetched sample, on the hand, for $(10\bar{1}2)$ asymmetric plane, the etched samples was observed to have a smaller FWHM than the unetched sample, furthermore, the variation of FWHM for etched and unetched samples were relatively small for both (0002) and $(10\bar{1}2)$ planes. Their studies showed that the crystalline quality was not strongly affected by the etching.

IV. CONCLUSION

In summary, nanostructured porous GaN has been obtained using UV-assisted electrochemical etching. PL measurements revealed that the near band edge peak of all the porous samples were blue shifted which was ascribed to the relaxation of the tensile stress in the porous samples. On the other hand, the PL intensity of the porous samples is found to be increased. The amplification of the porosity induced PL intensity could be explained as the reduction of surface pit density and extraction of strong PL by light scattering from the sidewalls of the GaN crystallites. The studies showed that porosity could influence the optical properties of the GaN. From the effective mass theory, the nanostructured porous GaN were found to have crystallite sizes between 13.4 nm and 15.0 nm.

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