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Characteristics of undoped porous GaN prepared by UV assisted electrochemical etching

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The structural and optical characteristics of porous GaN prepared by UV assisted electrochemical etching under different etching durations were reported. SEM micrographs indicated that the average pore size for samples was around 0.33 to 0.43 μm. The AFM measurements revealed that the surface roughness increased with etching duration. PL measurements revealed that the near band edge peak of all the porous samples were red-shifted; moreover, the PL intensity enhancement was observed in the porous samples. Raman spectra exhibited the shift of E_2 (high) to the lower frequency for porous samples.

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1. Introduction

The preparation of porous semiconductors has displayed a great deal of research interest in recent years, primarily due to the potential for intentional engineering of properties not readily obtained in the corresponding crystalline precursors as well as the potential applications in optoelectronics, chemical and biochemical sensing [1-4]. When porosity is formed, these materials exhibit various special optical features, for instance, the shift of bandgap [5], luminescence intensity enhancement [6], as well as photoresponse improvement [7]. To date, porous silicon (Si) receives enormous attention and has been investigated most intensively; however the instability of physical properties has prevented it from large scale applications [8]. Thus, this leads to the development of other porous semiconductors, for instance, the conventional III–V compounds such as GaAs, GaP and InP, and the wide bandgap materials such as GaN and SiC [2, 9-17].

Porous GaN exhibit unique and superior physical properties such as the excellent thermal, mechanical and chemical stability. These special prospects robustly motivated the research in porous GaN; additionally, porous GaN can be used as intermediate layer for the reduction of substrate-induced strain [18-19]. In view of the fact that 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 ultimately lead to high density of structural defects. Comparatively, the study of porous GaN is still in the infancy stage; many fundamental properties are not well established. In this work, investigation of the structural and optical properties of porous GaN prepared by UV assisted electrochemical etching method was carried out using various post-deposition analysis.

2. Experimental

The commercial unintentionally doped n-type GaN film grown on two inches diameter sapphire substrate was used in this study. The thickness of GaN film is 6 μm with carrier concentration of ~ 6.05×10^{17} 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:HNO3) was used to etch and clean the sample. Porous GaN in this work was generated by UV assisted electrochemical etching.

For the generation of porous GaN, aluminium was first deposited at one corner of the GaN surface for front contact for all the samples by using thermal evaporator. The aluminium coated area was then contacted with copper washer and tightened with a bolt. In the anodic etching process, platinum was used as cathode electrode; the GaN sample was connected by a copper wire to power supply and biased positive with the applied voltage of 20 V. An ultra-violet (UV) lamp with 500 W and 2 % concentration of KOH electrolyte were used in this experiment for 20 and 30 minutes. Typical electrochemical cell for the generation of porous GaN are schematically shown in Fig. 1. After chemical treatment, the samples were removed from the solution and rinsed with distilled water.

Structural properties of porous GaN have been investigated by scanning electron microscope (JOEL JSM-6460LV) performed at 10 kV. Energy dispersive X-ray

analysis (EDX) was used to identify the elemental composition of the sample. Atomic force microscopy (AFM), a non-contact mode was used to determine the surface roughness of the samples. The optical quality of the films was studied by photoluminescence (PL) and Raman scattering. PL and Raman measurements were performed at room temperature by using Jobin Yvon HR800UV system.

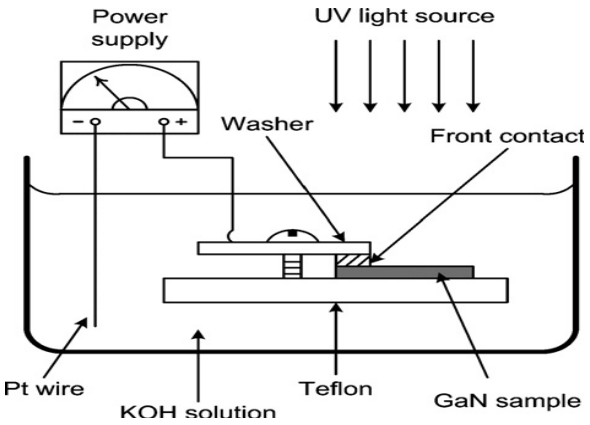

Fig. 1. Schematic of UV assisted electrochemical etching apparatus.

3. Results and discussion

SEM images of the porous GaN samples generated under different anodization durations were shown in Fig. 2. From the SEM micrographs, the pore size of all the samples was found to be varied widely, and different shapes could be observed. For the 20 min sample, the etching was in the initial stage, pores started to form, the size of the pores were relatively small therefore mostly circular shaped structures were observed. For the 30 min sample, the surface became relatively rough. SEM images revealed that the average pore size for samples were around 0.33 μm to 0.43 μm. The average pore size of the samples was found to be influenced significantly by the anodization duration. The size of the pores increased with the increase of the anodization duration. Furthermore, it can be observed that the pores are not distributed uniformly. On the other hand, it is interesting to note that the porous GaN prepared by the electrochemical etching method does not always produce similar surface morphology. Several groups [14, 20–22] fabricated porous GaN by anodic etching; porous GaN produced by Yam *et al* [14] was covered with star, elongated, triangular and squarish type of pores. Other than this, the average pore size was more sensitive to the concentration of electrolyte as compared to the applied voltage.

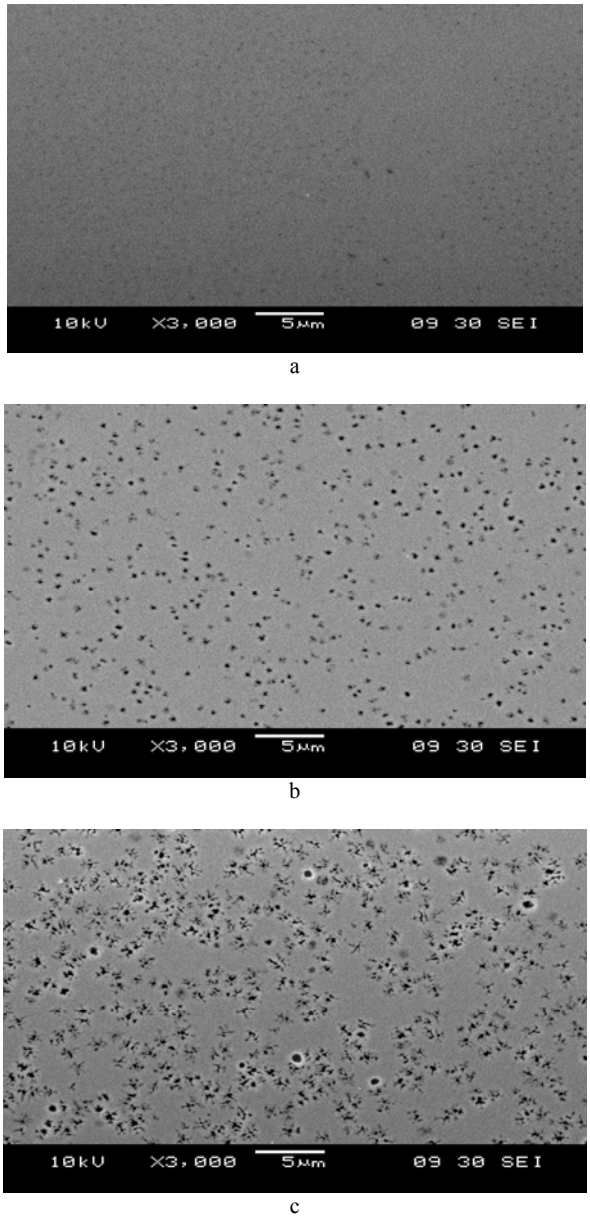

Fig. 2. SEM images of the samples etched under different durations; (a) as grown, (b) 20 min, and (c) 30 min.

Fig. 3 shows the AFM measurements of the porous GaN samples under different etching durations. The scanned area was commonly set at 5 μm × 5 μm. The surface roughness measured in root mean square (RMS) for the as grown, 20 and 30 min samples were found to be 1.95, 2.46 and 4.47 μm, respectively, indicating that the surface roughness of the porous GaN samples increased with the etching durations. These results could be further supported by SEM images as shown in Fig. 2 in which the surface morphology changed in stages with the etching durations. For the 20 min etched sample, the pores just started to form, and further for etching duration for example 30 min, the surface became relatively rough.

Thus, there were changes in the surface roughness as revealed by both SEM and AFM measurements.

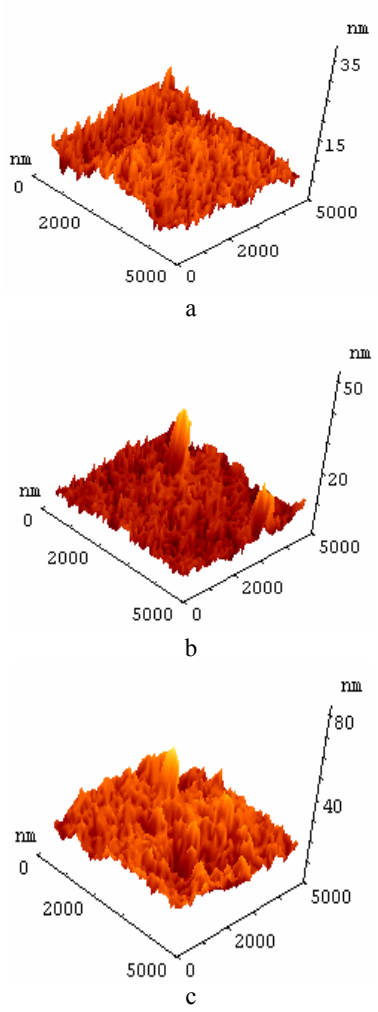

Fig. 3. AFM micrographs of the porous GaN samples etched under different durations showing different surface topography; (a) as grown, (b) 20 min and, (c) 30 min.

Fig. 4 illustrates the room temperature PL spectra recorded from the porous GaN etched under different durations and the as grown samples. The PL spectrum recorded from porous film shows a uniform PL line shape with a slight broadening toward the high-energy side. 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 red shifted relative to the as grown sample. The red shift was also ascribed the relaxation of the compressive stress in the porous samples. Yam *et al* [13] was also observed and reported similar red shift. At room temperature, a significant enhancement of PL intensity was observed from the porous GaN when compared to the as grown GaN. The improvement of PL intensity observed from the porous samples can be due to the reduction of dislocation density and extraction of strong PL by photons scattering from the sidewalls of the GaN crystallites [22], 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 [23].

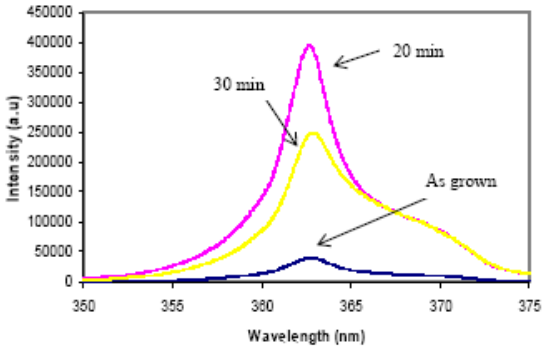

Fig. 4. The near band edge PL spectra of the samples etched under different durations measured at room temperature.

Table 1. 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	362.60	3.46	-	1.0
20 min	362.65	3.84	0.05	2.7
30 min	362.82	5.98	0.22	1.7

For appraising GaN microscopic disorder, Raman scattering is a powerful tool that can be used. Raman scattering is also effective for monitoring internal stress by measuring the frequency, polarization properties and broadening of the Raman active phonons. The Raman spectra for porous GaN and as grown sample were shown in Fig. 5. E_2(high) peak of 30 min etched sample was noted to be shifted to the lower frequency relative to the as grown sample. These revealed that stress relaxation has taken place in the 30 min sample, in which high density of pores could be found in this sample. Conversely, there was only a slight shift of E_2(high) peak for 20 min porous sample, since at 20 min, the pores just started to form and the pore density was relatively low as compared to the 30 min etched sample. In addition, there was an enhancement for the overall Raman intensity for the porous samples; however the intensity enhancement was not proportional to the anodic etching durations. Similar shift to the lower frequency was also observed and reported by Yam *et al* [13] and Vajpeyi *et al* [22].

In our study, Raman scattering experiments were carried out in the *z*(*x*, unpolarized)*z* scattering configuration, where *x* is the in-plane direction. The spectra are dominated by strong E_2(TO) and A_1(LO) phonons near 568 and 734 cm^{-1}, which are in agreement with Raman selection rules for wurtzite GaN. From the Raman spectra, A_1 transverse optical (TO) and E_1 (TO) phonon modes were found only in the 30 min sample. The presence of these two peaks shows that the change of optical properties in the porous samples has taken place, this could be attributed to the crystal disordering in the films, in which the enhancement of the scattering from the sidewalls of the porous structure eventually may transform the light polarization.

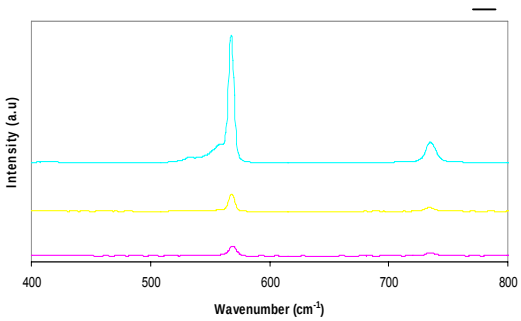

Fig. 5. The Raman spectra of the samples. (a) As grown, (b) 20 min and (c) 30 min.

Table 2. Peaks position, position of E_2 (high), A_1 (TO) and E_1 (TO) of different samples obtained from Raman spectra.

Sample	E_2 (high)			A_1 (TO)	E_1 (TO)
	Peak position (cm^{-1})	Intensity (arb. unit)	Peak shift (cm^{-1})	Peak position (cm^{-1})	Peak position (cm^{-1})
As grown	568.72	225.18	-	-	-
20 min	568.33	399.96	0.39	-	-
30 min	567.80	2695.43	0.92	535.66	561.27

4. Conclusion

The structural and optical characteristics of porous GaN prepared by electrochemical etching under different etching durations have been investigated. SEM images suggested that different etching durations have significant effect on the size and shape of the pores. AFM measurements exhibited that the surface roughness increased with etching duration. PL measurements revealed that the near band edge peak of all the porous samples were red shifted which can be associated with the development of highly anisotropic structures in the morphology. Raman study revealed the shift of E_2(high) to the low frequency relative to the as grown sample. Apart from that, A_1 transverse optical (TO) and E_1(TO) phonon modes were found only in the 30 min etched sample. The studies showed that porosity could influence the structural and optical properties of the GaN.

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