

## Stress Relaxation in Porous GaN Prepared by UV Assisted Electrochemical Etching

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**Abstract:** This study describes the stress relaxation in porous GaN grown on Al<sub>2</sub>O<sub>3</sub> substrates. The results indicate that the stress relaxation has taken place in the samples which increases by increasing the etching current. As compared to the as-grown GaN films, porous GaN exhibits substantial photoluminescence (PL) intensity enhancement with red-shifted band-edge peaks associated with the relaxation of the compressive stress. The red shifted phonon energy peak (E<sub>2</sub>) in the Raman spectra of the porous GaN films confirms further such a stress relaxation. Scanning electron microscopy (SEM) demonstrates that, the current density has significant effect on the size and shape of the pores.

**Keywords:** Stress relaxation; Porous GaN; Red shift; Raman spectroscopy.

### 1. Introduction

Among all the III-V nitrides, GaN is considerably the most intensely studied. GaN is a direct and wide band gap semiconductor (3.39 eV) at room temperature. With its superior radiation hardness and chemical stability, together with its large band gap characteristic, these properties have made GaN a suitable semiconductor material for device applications in the high-temperature and caustic environment as well as in space applications [1]. Producing and fabricating high quality electronic devices such as LEDs, LDs, photo detectors etcetera, requires growing high quality GaN doped thin films. Selecting appropriate substrate to deposit the film on it is one of the main factors that affect GaN growth techniques. The most common substrates used to grow GaN are; sapphire (Al<sub>2</sub>O<sub>3</sub>) and Si substrates. Sapphire is an interesting choice because it is a semi-insulating, high growth temperature and it is relatively cheap, but it is a large lattice mismatch (13.8%) [2], large thermal expansion coefficient mismatch (34%) and low thermal conductivity. The second choice is Si substrate which still has a large thermal expansion coefficient mismatch (56%) and large lattice mismatch (17%) [3]. The film/substrate mismatching produces high dislocation densities and high residual stress. Several techniques have been developed in order to reduce the dislocation density and residual stress including porous method.

One of the reasons for using a porous semiconductor as a substrate for depositing semiconductor layers is that, the nanopatterned porous structure can lead to a reduced extended defect density [4]. The interest in porous semiconductor arises from the fact that they can act as a sink for threading dislocations and accommodate the strain. Hence, they are widely used as a buffer or intermediate layer in epitaxial growth to obtain a subsequent layer with lowered strain and dislocation densities [5,6]. Mynbaeva et al. [7] proposed that the growth of GaN on porous GaN could lead to high-quality strain-released epilayers.

Porous GaN is a promising simple method to achieve low dislocation density and low residual stress on the whole area of a wafer. This nanostructure was first developed by Bardwell et al. by metal-assisted electroless chemical etching technique [8]. To date, several



additional techniques such as UV-assisted electrochemical etching and electrochemical etching have been developed [9-11]. In this method, the important parameters are applied voltage and current, electrolyte composition and illumination. These parameters control etch rate, morphology and optical properties.

In this work, we report the stress relaxation of GaN during etching process under different current densities of  $J = 5, 10$  and  $20 \text{ mA/cm}^2$  for 20 min. We investigated the surface morphology and the optical properties of porous GaN samples by scanning electron microscopy, and by high-spatial resolution photoluminescence and Raman spectroscopy.

## 2. Experiment

The samples used in this study were commercial (Si doped) n-GaN grown by metalorganic chemical vapor deposition (MOCVD) on  $\text{Al}_2\text{O}_3$  substrates. The electron concentration obtained by Hall measurements was  $n = 1 \times 10^{17} \text{ cm}^{-3}$ . The samples were cleaned first with acetone and methanol, then cleaned in 1:20  $\text{NH}_4\text{OH}:\text{H}_2\text{O}$  for 10 min, followed by cleaning in 1:50  $\text{HF}:\text{H}_2\text{O}$  solution to remove the surface oxides. This was followed by cleaning in 3:1  $\text{HCl}:\text{HNO}_3$  at  $80^\circ\text{C}$  for 10 min. Between the cleaning steps, the samples were rinsed in deionized water. Aluminum was then partly evaporated on the surface of GaN using a thermal evaporation system, which provided an ohmic contact. By using a homemade Teflon-cell, we fixed the GaN sample as an anode and Pt wire as a cathode (fig.1). The electrolyte was a mixture of aqueous  $\text{HF}$  49% and ethanol  $\text{C}_2\text{H}_5\text{OH}$  95%, 1:4 by volume. We used constant current densities of  $J = 5, 10$  and  $20 \text{ mA/cm}^2$  for 20 min, (supplied by a Keithly 220 programmable current source) and a UV lamp in the electrochemical etching process. After the etching, the samples were rinsed in deionized water, and dried in ambient air. The optical properties of the porous GaN samples were investigated by high-spatial resolution Raman and PL spectroscopy.

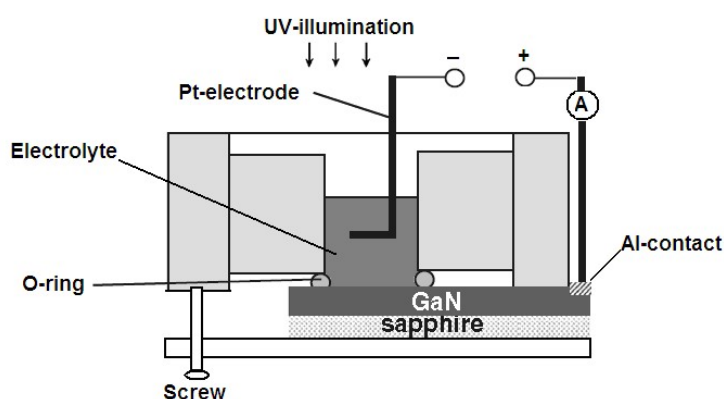
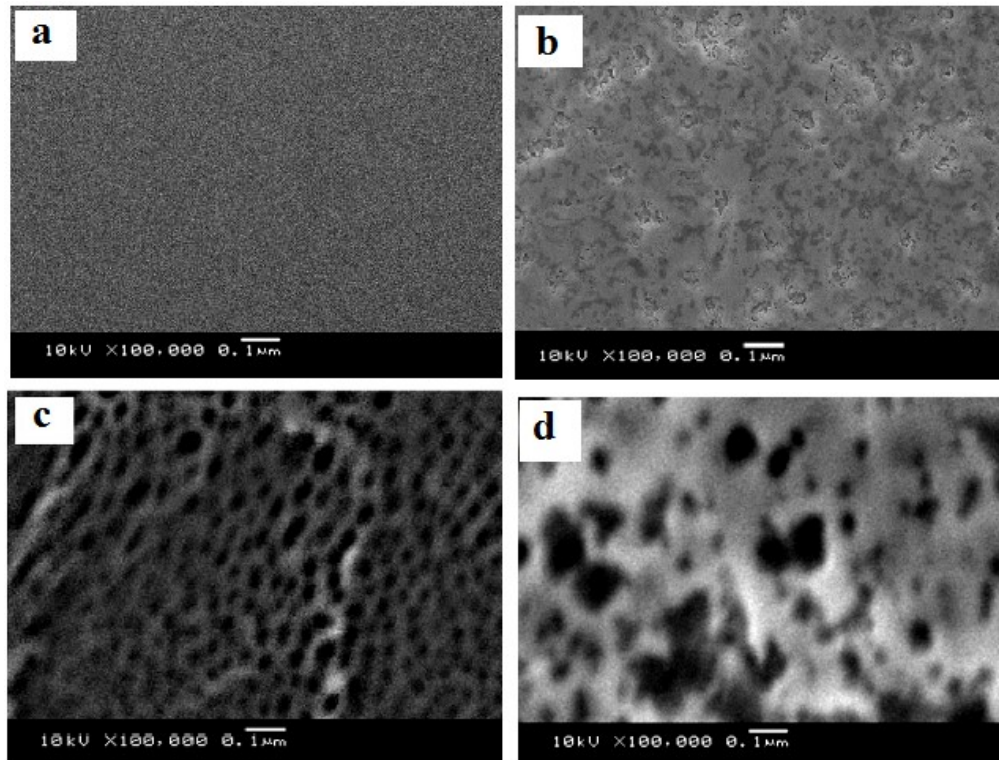


Fig. 1. The photoelectrochemical etching experimental setup used to generate porous GaN.

## 3. Results and Discussion

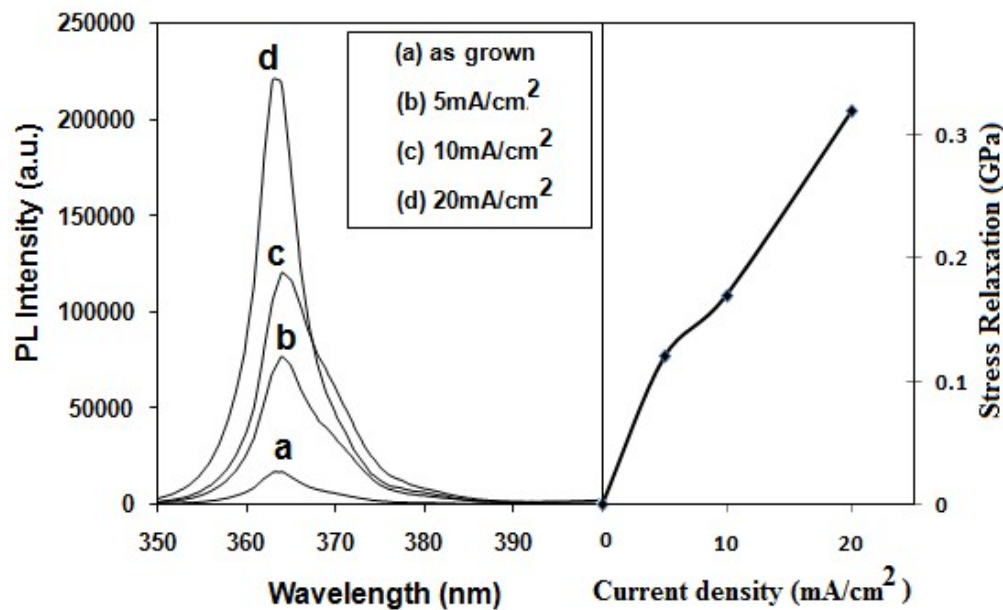
Figure 2 shows the scanning electron micrographs (SEM) of the morphology of the as-grown and porous GaN samples. The as-grown GaN possessed a smooth surface morphology (Figure. 2a). The evolution of the porous morphology with increase in etching current density is apparent from Figures 2(b-d). The figures show that the etching current density has significant effect on the size and shape of the pores. The pores started to form in the sample etched with  $5 \text{ mA/cm}^2$  as shown in Figure 2b. The sample etched with  $10 \text{ mA/cm}^2$  (Figure 2c) shows that, the pore sizes appears to be around 30 to 40 nm and the distance between

them is around 50 to 60 nm. However, the sample etched with 20 mA/cm<sup>2</sup> (Figure 2d) shows that, the pore sizes were observed to increase which become around 50 to 60 nm and some areas were destroyed, indicating that the GaN layer was very thin [11,12].



**Fig. 2.** SEM images of as-grown and porous GaN samples prepared with different etching current densities; a) as-grown b) 5 mA/cm<sup>2</sup>, c) 10 mA/cm<sup>2</sup>, and d) 20 mA/cm<sup>2</sup>.

Figure 3 shows the room temperature PL spectra and the stress relaxation of porous GaN samples etched with various current densities. The spectra were observed to be slightly red-shifted for all samples (relative to the spectrum of the as-grown sample). Similar red-shifted PL from porous GaN has been reported before [13]. The red-shift can be attributed to the relaxation of the compressive stress in the porous samples. The energy shift between porous and the as-grown GaN sample can be used to quantify the amount of stress relaxation. The amount of stress relaxation can be calculated using the expression:  $\Delta = K\sigma$ , where  $K$  is the proportionality factor and  $\sigma$  is the stress. Using the  $K$  value reported in literature, i.e.,  $K = 21.273.2$  meV/GPa [14], using this value of the proportionality factor for the stress-induced PL peak shift, a compressive stress relaxation of about 0.12, 0.17 and 0.32 GPa is estimated in 5, 10 and 20 mA/cm<sup>2</sup> respectively.

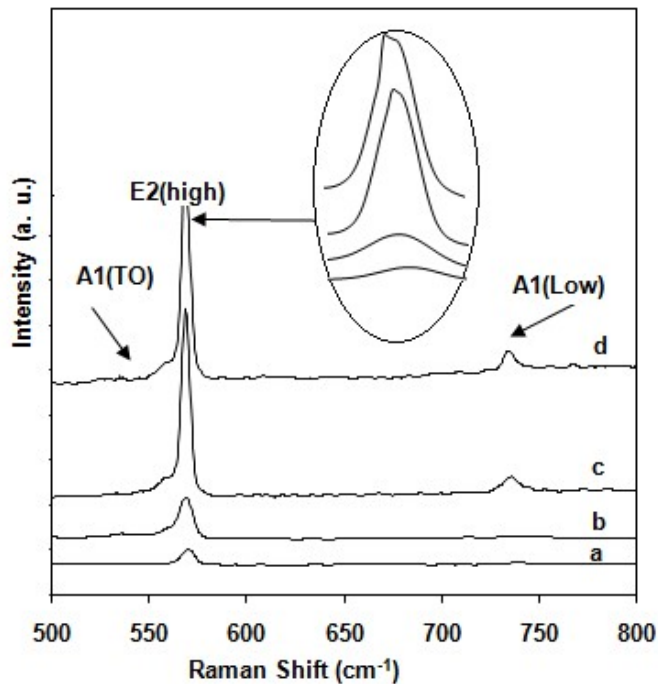


**Fig. 3.** Photoluminescence spectra and stress relaxation of porous GaN etched with different current densities: (a) as-grown, (b) 5 mA/cm<sup>2</sup>, (c) 10 mA/cm<sup>2</sup> and (d) 20 mA/cm<sup>2</sup>.

Small deviations in the peaks position indicating that the change of pore size has no considerable influence on the PL peak shift. However, the PL peak intensity of the porous samples has increased compared to that of the as-grown sample. The PL spectra for porous GaN samples show an increase in the intensity while increasing the current density. For example, at 10 mA/cm<sup>2</sup> and 20 mA/cm<sup>2</sup> current densities, the PL peak intensity was improved by factor of about 7 and 13, respectively, compared to that for the as-grown sample. The intensity of emitted light is proportional to the number of photons emitted. This means that the number of photons emitted is much higher in porous GaN than that in as-grown GaN. This could be attributed to the increase in the anti-reflectivity due to the roughening of the surface and the high surface area of porous structure.

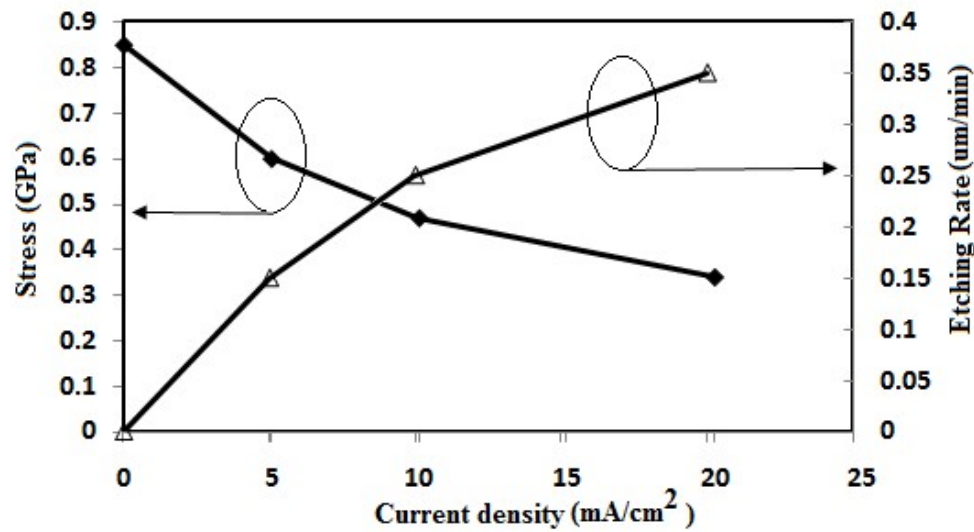
Figure 4 shows Raman spectra of the as-grown and the porous GaN samples. The spectra exhibit silent phonon mode  $E_2$  (high) and transverse optical mode  $A_1$  (LO), and relatively small peak of  $A_1$  (TO), also figure shows the increase in peaks intensity with etching current density. The frequencies of all the observed modes were in good agreement with the results of other researchers [15-17]. The phonon peak position, intensity and peak shift for GaN samples etched with different current densities are summarized in Table 1.

Circle inset in figure 4 shows the Raman spectra on  $E_2$  (high) together with that of the as-grown one. Moreover, the  $E_2$  Raman mode of as grown GaN appears at an identical wave number of 566.2 cm<sup>-1</sup>. We take this number as a reference for unstressed films.



**Fig. 4.** Raman spectra of samples etched with different current densities; as-grown GaN, 5 mA/cm<sup>2</sup>, 10 mA/cm<sup>2</sup> and 20 mA/cm<sup>2</sup>, indicated by (a), (b), (c) and (d) respectively. (circle inset showing the small shift of  $E_2$  (high) for porous samples compared to that of as-grown.

All the porous samples prepared with etching current densities of 5, 10 and 20 mA/cm<sup>2</sup> show an  $E_2$  (high) shifted to slightly lower frequency than that of the as-grown one. Using the proportionality factor of 4.2 cm<sup>-1</sup>/GPa for hexagonal GaN [16,18], the total stress in the as-grown GaN is 0.85 GPa compared to the unstressed sample (free stress). While the relaxation of stress took place in the porous sample, and by using the same proportionality factor, the relaxation of stress was found to be 0.25 GPa for the 5 mA/cm<sup>2</sup> sample, 0.38 GPa for the 10 mA/cm<sup>2</sup> sample and 0.51 GPa for the 20 mA/cm<sup>2</sup> sample. These results indicate the stress relaxation has taken place in the samples and it increases by increasing the etching current density as seen in Figure 5.



**Fig. 5.** The stress and the etching rate as a function of the current density.

Figure 5 also shows the dependence of the etching rate with respect to the current density. From this figure, we can conclude that the etch rate increases with the current density by an exponential proportionality. Another conclusion is that we can obtain from Figure 5 that, for high current densities, the higher etch rate hinders the fine control of the layer thickness in the case of thin layer.

**Table 1.** The phonon modes detected in the Raman spectra.

Phonon mode		$E_2(\text{low})$	$A_1(\text{TO})$	$A_1(\text{LO})$	$E_2(\text{high})$	FWHM of $E_2(\text{high})$ ( $\text{cm}^{-1}$ )
as-grown	Peak position ( $\text{cm}^{-1}$ )	147.474	523.897	738.366	569.794	5.850
	Intensity (a.u)	41.377	37.222	45.742	102.757	
5 mA/cm <sup>2</sup>	Peak position ( $\text{cm}^{-1}$ )	143.517	536.200	738.880	568.734	5.570
	Intensity (a.u)	49.878	70.927	62.857	233.544	
	Shift ( $\text{cm}^{-1}$ )	-3.960	12.300	0.514	-1.060	
10 mA/cm <sup>2</sup>	Peak position ( $\text{cm}^{-1}$ )	142.950	532.990	735.742	568.199	2.990
	Intensity(a.u)	40.484	51.185	126.711	871.553	
	Shift ( $\text{cm}^{-1}$ )	-4.524	9.090	-2.624	-1.595	
20 mA/cm <sup>2</sup>	Peak position ( $\text{cm}^{-1}$ )	143.517	535.669	734.690	567.688	2.900
	Intensity (a.u)	65.000	163.712	283.981	1039.340	



Shift (cm <sup>-1</sup> )	-3.960	11.772	-3.676	-2.126
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The full width at half maximum (FWHM) value of  $E_2$  phonon for the as-grown and the porous samples at 5, 10 and 20 mA/cm<sup>2</sup> are also shown in Table 1, indicating decreasing FWHM value with increasing etching current density. The lower value of the FWHM represents good crystalline quality. This suggests an improvement in the crystalline structure of porous GaN with increasing etching current density [19].

Generally, the porous samples exhibited broader FWHM than the as grown sample for (0002) a diffraction planes, this could be due to the relatively wide statistical size distribution of the pores, however for porous samples, no relation between the FWHM and the average pore size was observed.

#### 4. Conclusions

Porous n-GaN was prepared by photoelectrochemical etching under ultraviolet light using various current densities in electrolytes consisting of aqueous HF and ethanol electrolyte at room temperature. All porous samples showed increased PL and Raman intensities compared with that of the as-grown. PL and Raman results confirms that porous GaN layer possess less compressive stress than that for the as-grown GaN layer and the quality of the porous sample is as good as the as-grown sample. The peaks of  $E_2$  (high) in Raman spectra for all the porous samples suggest that the crystallite quality and stress relaxation increases with increasing the current density. The relaxation of stress is 0.25 GPa for the 5 mA/cm<sup>2</sup> sample, 0.38 GPa for the 10 mA/cm<sup>2</sup> sample and 0.51 GPa for the 20 mA/cm<sup>2</sup> sample. These results indicate that the stress relaxation has taken place in the samples and increasing with higher etching current density. This indicates that, it is possible to fabricate high quality porous GaN layer with tunable stress, suitable for growing or depositing further high quality active layers with minimized lattice mismatch.

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