High Optical Quality Nanoporous GaN Prepared by Photoelectrochemical Etching

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***Abstract*— — Nanoporous GaN films are prepared by UV assisted electrochemical etching using HF solution as an electrolyte. To assess the optical quality and morphology of these nanoporous films, micro-photoluminescence (PL), micro-Raman scattering, scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques have been employed. SEM and AFM measurements revealed an average pore size of about 85-90 nm with a transverse dimension of 70-75 nm. As compared to the as-grown GaN film, the porous layer exhibits a substantial photoluminescence intensity enhancement with a partial relaxation of compressive stress. Such a stress relaxation is further confirmed by the red shifted E_2(TO) phonon peak in the Raman spectrum of porous GaN**.

Introduction:

Porous semiconductors have been widely studied in the last decade due to their unique optical properties compared to the bulk materials. Porous semiconductors successfully prepared from Si,[1,2] GaAs,[3] GaP,[4,5] and InP[6] exhibit tunable properties that can be explored to fabricate new sensing devices. The main objective of this research direction was to control the emission properties of the porous semiconductors by controlling the pore dimension. Porous layer can also be used as a buffer or intermediate layer for strain management during epitaxial regrowth. Such growth method may reduce the defect density in the epitaxial layer leading to high quality stress free layer on porous template. GaN and its related nitrides are generally grown on sapphire (13.6% lattice mismatch) or SiC substrates (4% lattice mismatch), where larger lattice mismatch degrades the layer quality. However, reducing the dimensions of these structures to nanoscale can extend the range of properties of nitride materials. For example, nanostructured GaN can have a reduced defect density and enhanced strain relaxation as compared to epitaxial GaN films, and the optical properties of such materials can be tailored to suit various device requirements.

It is reported that GaN grown on nanoporous SiC and nanoporous GaN shows improved chemical and optical quality.[7-9] Although porous GaN offers a good alternate to grow high quality stress free over layer, yet very little work has been done. Recently, few studies on the bandgap and morphology control in porous GaN through electroless wet chemical and photoelectrochemical etching are reported.[10-14] A method to prepare ordered nanopores in GaN films by inductively coupled plasma (ICP) etching using anodic alumina templates as etching mask is also demonstrated recently.[15] Photoelectrochemical etching would be more suitable as a cost effective method to produce high-density nanopores with pore size < 100 nm. The pore size, etching depth or the transverse dimension of the pores can be easily controlled by varying the etching/anodization conditions. If much higher PL signal can be extracted from porous GaN compared to the as grown material, then such porous template would be suitable as a pumping source or suitable host for multiple light emitting layers that emit emission energy lower than the bandgap of GaN. Apart from improved optical pumping, such template will reduce the dislocation density of the layers to be grown on top of it via nano-ELO process.[8,9] In this letter, we report fabrication and properties of nanoporous GaN prepared by UV-assisted electrochemical etching using HF solution as an electrolyte. A significant photoluminescence (PL) intensity enhancement is observed from porous GaN films. The red-shifted PL emission observed from porous GaN when compared with the as grown epilayer indicates a relaxation of compressive stress. This is further confirmed by micro-Raman spectroscopy.

Experiment:

The GaN layers were grown by low pressure MOCVD on sapphire (0001) substrates. A buffer layer of 25 nm thick GaN was first grown at 500°C and subsequently, a 0.5 micron thick undoped GaN layer followed by a 2.0 μm Si doped n-GaN layer were grown at 1050 ^{o}C. The carrier concentration in the upper layer was 1.2×10^{18} cm^{-3} as determined by Hall measurement. For a comparative study, we have also taken an unintentionally doped 2.5 μm thick GaN with a carrier concentration of 1.2×10^{16} cm^{-3}. These GaN layers were subjected to UV assisted electrochemical etching using 49 % (HF: H2O = 2: 1) buffered HF solution as an electrolyte. Al
films were evaporated to the GaN surface for contact and Pt electrode was used during various anodization conditions. The anodization current was varied from 20 mA/cm^2 – 50mA/cm^2

for different samples with a constant etch time of 60 mins. The optical quality of the porous GaN samples prepared by this method was investigated by high-spatial resolution PL and Raman microscopy. PL spectra were recorded using a Renishaw 2000 micro-PL set up and using 325 nm line excitation from a He-Cd laser. Micro-Raman measurements were carried out using a JYT64000 triple spectrograph attached to a liquid nitrogen cooled CCD camera for spectral imaging. The 514.5 nm line of an Ar^+ laser was used as a source for Raman excitation. The spatial and spectral resolution of the Raman set up is 1.0 and 0.2 cm^{-1}, respectively.

Results and Discussion:

Figure 1 shows the top view SEM image of the porous GaN surface prepared using varying etching conditions.

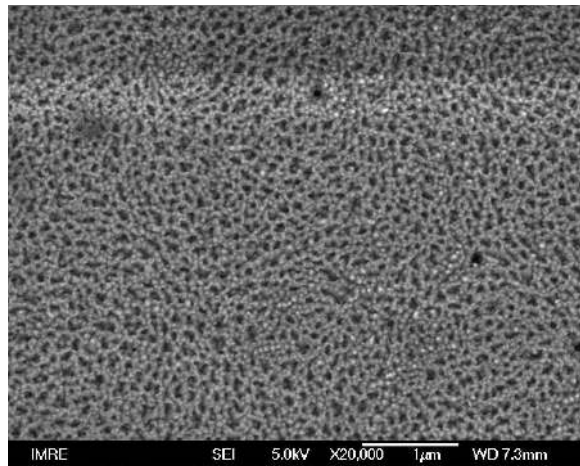

Fig 1a. Low magnification SEM micrograph of porous GaN prepared with 49% HF solution ($HF:H_2O$ = 2:1), anodization current density 20mA/cm^2

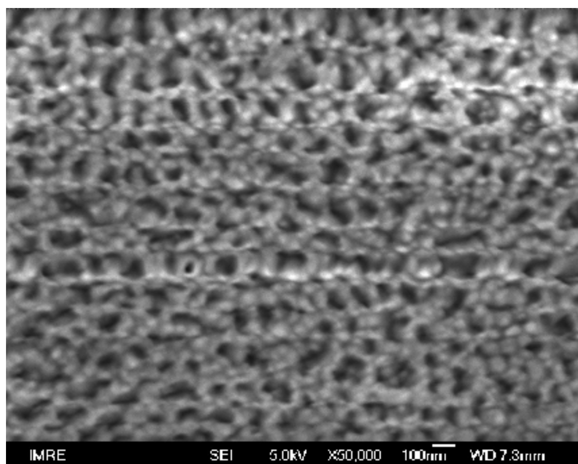

Fig 1(b) High magnification SEM image of the porous sample (a)

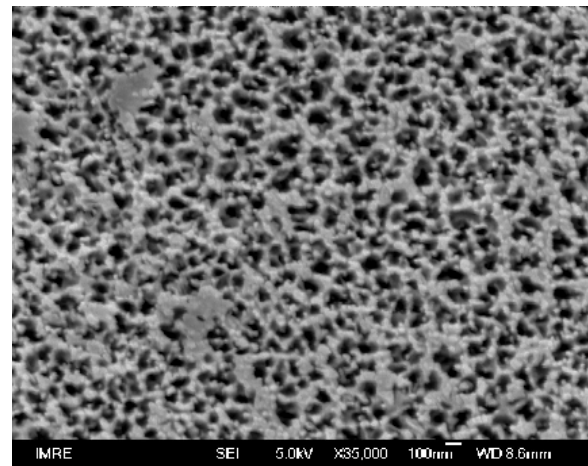

Fig 1c. High magnification image of porous layer prepared from unintentionally doped GaN with 49% HF solution ($HF:H_2O$ = 2:1) anodization current density 50 mA/cm^2.

The average pore and the GaN crystallite size are < 100 nm. Optimized etching conditions in n-GaN layer gave an average pore size of about 85 – 90 nm with a transverse dimension of 70 – 75 nm. In the unintentionally doped GaN sample, the pore depth was found to be only 30 nm even if using a higher anodization current density

Figure 2 shows the 3D-AFM topography of the porous GaN using a Digital Nanoscope III set up.

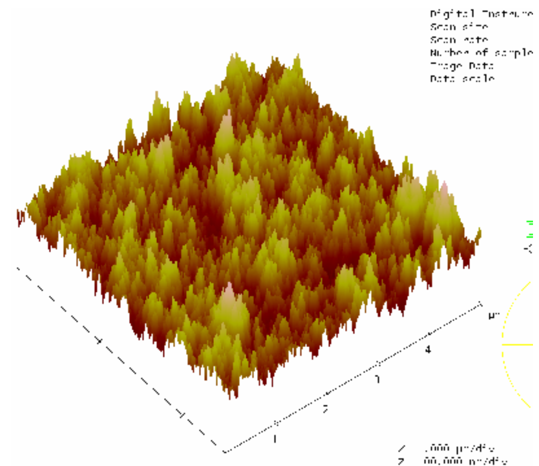

Fig 2. 5.0μm×5.0μm 3D-AFM micrograph of nanoporous GaN.

The surface rms roughness of the porous film is 24 nm. From cross-sectional line scan, we estimate an average pore depth of about 75 nm. The density of the nanopores is much higher as evident from the SEM image. Such large area nanoporous GaN prepared by this method would be suitable for regrowth of GaN and high Al content AlGaN based device layers

Fig. 3 shows the room temperature micro-PL spectra recorded from the nanoporous GaN and the as-grown GaN

epilayer.

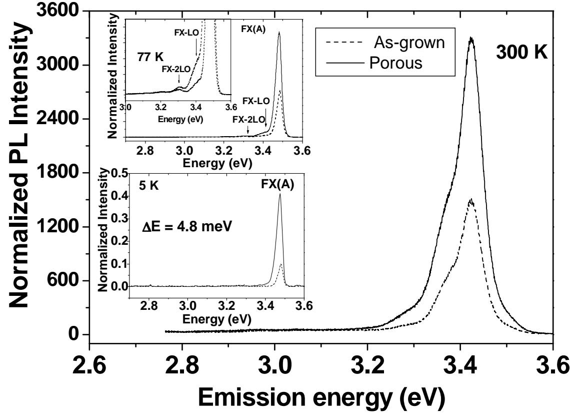

Fig 3. Micro-PL spectra of porous GaN and as grown GaN. Inset shows spectra recorded at 77 and 5 K.

The room temperature near-band-edge PL peaks are centered around 3.42 eV. The PL spectrum recorded from porous film shows a uniform PL lineshape with a slight broadening toward the low-energy side. The slight amount of broadening relative to the GaN epilayer emission could be due to incorporation of impurity-induced disorder or surface defects during etching. At room temperature, a significant enhancement of PL intensity was observed from the porous GaN when compared to the as-grown GaN epilayer. To confirm the improved emission properties of nanoporous GaN, we have also carried out low-temperature PL measurements. Fig. 1 also shows PL spectra recorded at 77 K and 5 K from the porous GaN and the as-grown epilayer where a dominated free-excitonic transition 'FX(A)' is observed from both the samples. A two-fold intensity enhancement is clearly observed for the free exciton (FX(A): 3.476 eV at 5 K) lines from nanoporous film. A red shift of about 4.8 ± 0.5 meV is observed for the FX(A) transition from the nanoporous GaN when compared to the as-grown GaN epilayer. Such a red-shifted emission can be associated with partial relaxation of compressive stress in the nanoporous film. The improved PL intensity observed from porous GaN can be attributed to the reduction of dislocation density and extraction of more photons by scattering off the sidewalls of the GaN crystallites. Etching through the dislocation cores and surface related traps could also lead to an enhancement of band-edge PL. In addition, we have also observed phonon replicas of FX(A) line such as FX-LO and FX-2LO peaks from 77 K micro-PL spectrum. The donor-acceptor pair emissions are also absent in the PL spectra. Yellow luminescence (YL), which is commonly observed in the PL spectrum of defective GaN around 2.2-2.3 eV, was also very weak in both porous and as grown film. Etching can lead to a nonstoichiometric GaN surface with C_N and O_N related vacancy-impurity complexes at the surfaces. Therefore, the actual PL intensity may be quenched somewhat due to etching and creation of surface defects. The high optical quality of the nanoporous film indicates that they such template have good potential for GaN based luminescent or sensing devices.

We have also studied the evolution of integrated FX(A) PL intensity in porous GaN with temperature. The experimental data point were fitted according to Arrhenius equation,

$$I(T) = \frac{I(0)}{1 + C\exp(-E_A / kT)} \qquad (1)$$

where $I(T)$ is the intensity at temperature T, $I(0)$ is the intensity at 0 K and E_A is the activation energy. From nanoporous GaN, activation energy of 26 meV is estimated from the best-fitted curve for temperature range 5 K – 300 K. For the as grown film, the activation energy is same as the porous film. Such observation agrees well with the reported value of activation energy of GaN nanocoloumns prepared by photoelectrochemical etching.[14] The temperature dependence of the emission energy for porous and the as grown GaN are well fitted by Varshni's equation[16]

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{\beta + T} \qquad (2)$$

where $E_g(0)$ is the FX(A) energy at 0 K and α, and β are the Varshni's thermal coefficients. For nanoporous GaN, the best fitted values obtained from least square fitting are given by $E(0)$ = 3.484 eV, $\alpha = 7.0 \times 10^{-4}$ and β = 700 K, whereas for as-grown GaN, the parameters are given by $E(0)$ = 3.490 eV, $\alpha = 7.6\times10^{-4}$ and β = 680 K. Since Varshni coefficient β is associated with the Debye temperature, there is no significant change in the Debye temperature expected from porous GaN. The energy shift between porous and as-grown GaN sample can be used to quantify the amount of stress relaxation. Using the value of the proportionality factor K = 21.2 ± 3.2 meV/GPa[17] for the stress-induced PL peak shift, a compressive stress relaxation of about 0.22 ± 0.02 GPa is estimated. This observation also agrees well with micro-Raman analyses of the porous GaN.

Fig. 2 shows the Raman spectra of porous and as grown epilayer in the $z(xx)\bar{z}$ geometry.

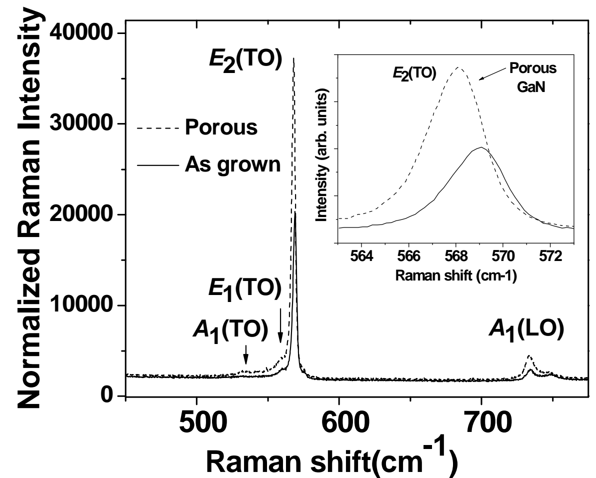

Fig. 4. Micro-Raman spectra recorded from as grown and porous GaN epilayer. Inset shows the observed red shift for E_2(TO) phonon from porous film.

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. As compared to the Raman spectrum of the as-grown film, a large increase in the scattering efficiency is clearly observed from the porous sample. An increase in the scattering signal has been observed previously for GaN nanocolumns.[18] Due to multiple scattering of light and more efficient coupling of the scattered radiation due to presence of surface disorder introduced by the surface nanostructuring, a significant enhancement of the Raman intensity is observed from porous film. In GaN, the E_2(TO) phonon linewidth can be used to monitor the crystalline quality, while its frequency can be used to monitor the stress in the film. The E_2 phonon lines of GaN are observed at 569.2 and 568.1 cm^{-1} for the as grown and the porous sample, respectively. The red shift of 1.1 ± 0.2 cm^{-1} in the peak phonon frequency confirms the stress relaxation in porous GaN. This shift corresponds to a relaxation of compressive stress by 0.25 ± 0.05 GPa using the proportionality factor of 4.2 cm^{-1} GPa^{-1} for hexagonal GaN.[19] These observations show that stress relaxation estimated from PL and Raman shift agrees quite well. The full width at half maximum (FWHM) value of E_2 phonon for as-grown and porous sample was 3.2 and 3.0 cm^{-1}, respectively, which shows that there is no difference in the phonon linewidth considering the spectral resolution of our Raman set up. Furthermore, such a lower value of the FWHM represents good crystalline quality. Anodization of the sample results in slight break down of the polarization selection rules, due to which very weak E_1(TO) and A_1(TO) modes also appeared in the spectrum recorded from porous film.

Conclusion

PL, and micro-Raman result confirms that porous GaN layer possess less compressive stress than as-grown GaN layer and the quality of the porous sample is as good as the as-grown sample. PL intensity in porous GaN shows intensity enhancement at room temperature and a much higher intensity enhancement at low temperature, which is a direct evidence of the surface quality. Since band-edge PL is more surface-sensitive, presence of point defects or disorder in the top porous surface could lower the actual PL efficiency. From this study, we can conclude that such strain released nanoporous GaN films prepared by photoelectrochemical etching can be used as an intermediate layer for overgrowth of GaN/InGaN/AlGaN layers for high luminescent device applications.

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