Fabrication and Characterization of Nano-porous GaN Template for Strain Relaxed GaN Growth

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Abstract **A simple and cost-effective Si-doped porous GaN is fabricated by UV-enhanced electrochemical etching. An optimum current density of 20 mA/cm^2 applied for an hour in dilute NaOH solution produces a high density of uniform pores. Cross-section TEM reveals that etching takes place along the (0001) direction. A red shift of 0.7 cm^{-1} in the E$_2$(high) phonon peak of GaN from micro-Raman indicates a relaxation of compressive stress in the porous GaN surface with respect to the underlying single crystalline epitaxial GaN. Subsequent growth of GaN layer on the porous template results in air gap formation, which is believed to serve as sinks for dislocations for reducing residual strain in the film. Reduction of FWHM of the XRD rocking curve as much as 0.033° and double intensity of the PL spectrum confirm the crystalline and optical quality improvement of the overgrown GaN layer as compared to as-grown. A red shift of ~0.4 cm^{-1} towards the stress-free GaN also indicates a relaxation of compressive stress in the overgrown GaN layer.**

Index Terms **photoelectrochemical etching, porous GaN, strain relaxation, epitaxial growth.**

I. INTRODUCTION

POROUS semiconductor materials have attracted special interest since the discovery of strong photo-luminescence in porous Si [1, 2]. The high surface area, band gap shift, and efficient luminescence suggest uses of porous semiconductor applications to extend over a wide range, from optoelectronics to chemical and biochemical sensors applications. An attractive application of porous semiconductor materials is epitaxial growth, as they retain the crystalline structure of the original material and yet is relaxed and can serve as a template for heteroepitaxial growth of lattice-mismatch materials [3, 4]. Besides the management of strain in heteroepitaxy, manipulation of the pore geometries can be used to alter quantum confinement and hence the emission properties of the materials [1].

A porous GaN template is important for GaN growth as bulk GaN substrates are not available for epitaxy, and substrates including conductive SiC, differ from GaN in lattice constant and thermal expansion coefficient [5]. Fabrication of porous GaN was first reported by Mynbaeva et al. in 1997 using n-type GaN grown by MOCVD by photo-assisted electrochemical etching in aqueous HF solution [6]. However, to date, the mechanism of pore formation in this material is still far from being clear. Exploiting the properties of porous GaN requires fabrication of porous structures with control over morphology, surface chemistry, and optoelectronic properties. Here, fabrication of nano-porous GaN structures by UV-enhanced electrochemical etching on n-GaN layer grown by MOCVD is reported.

II. EXPERIMENTAL

Si-doped GaN samples were grown by D-125 Emcore MOCVD system at 200 Torr using trimethylgallium (TMGa) and ammonia (NH$_3$) as the precursors for the Ga and N, respectively. A buffer layer of 35-nm-thick was first grown at 520°C, followed by a 0.3-μm-thick undoped-GaN and a 1.5-μm-thick Si-doped-GaN at 1015°C. The electron concentration of the Si-doped GaN is 10^{17} - 10^{18} cm^{-3} as determined by Hall measurement. When the UV light illuminates the n-GaN sample, electron-hole pairs are created. Holes oxidize the GaN, which is the anode, to a soluble form Ga$_2$O$_3$, which is then dissociated by the electrolyte. Thus etching occurs. The formation of electron and hole pairs through photoexcitation is very crucial for the etching process, and hence, the doping density. The electrolyte used for the etching is NaOH solution, and HeCd laser is used as the UV light source. The pore size and pore depth can be controlled by varying the etching conditions, mainly the etching time and applied bias between the GaN and Pt-wire. The detail of the optimization of the nano-porous structure is reported elsewhere [7]. An optimum condition of 20 mA/cm^2 current density applied for an hour in dilute NaOH solution

was obtained to produce a high density of uniform pores.

III. Results and Discussions

First, the mechanism of UV-enhanced electrochemical etching on n-GaN layer will be discussed, followed by growth of GaN on the porous template. GaN is a monocrystalline epilayer and consists of sub-grain boundaries that contain only slight twist or tilts. Discreet threading dislocations, as observed by TEM and AFM studies, define the sub-grain boundary or the columnar structure in GaN epilayers [8]. The threading dislocations serve as traps for the photo-generated carriers, creating regions of reduced etch rate [9]. Figure 1 shows a high magnification image of fabricated porous GaN by scanning electron microscope (SEM). It shows well-defined layers of pores with size ranges from < 50 to 250 nm, which gives a clear indication that the centres of the grains are attacked by a higher etch rate as compared to the grain boundaries, which contain the threading dislocations. Upon removal of the materials of the grains at the top layer, subsequent etching takes place at the sub-grains at the lower layer and so on, creating layered nano-pores structures.

Bardwell *et al*. [8] reported that when the etch rate is too large the grain boundaries are etched significantly slower than the centre of the crystals. This leads to a hexagonal, rough morphology. However, smooth surfaces can be obtained when the etch rate in the crystal centres is slow enough so the grain boundaries are etched at a sufficient rate. In other word, the final morphology of the etched surface will depend on the relative etch rate of the centres of the grains and the grain boundaries.
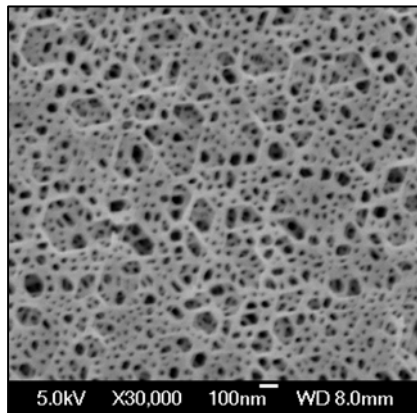

Fig. 1. High magnification SEM image of fabricated porous GaN showing well-defined layers of pores with different sizes as a result of monocrystalline epilayer structure of GaN.

Micro-Raman technique was employed to characterize the stress state of the porous GaN. It was 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 with excitation spot of about 2 μm was used as a source for Raman excitation. An average Raman response was recorded from the probing spot of the pores

area. Figure 2(A) shows the Raman spectra of as-grown and porous GaN layer collected in the $z(xx)\bar{z}$ geometry. A red shift of 0.7 cm^{-1} in the E_2(high) phonon peak of GaN from 568.4 cm^{-1} for the as-grown GaN to 567.7 cm^{-1} for porous GaN is observed. The peak shift is quite uniform when measurements were taken at several locations of the porous GaN film. The presence of surface defects did contribute to the average Raman linewidth. However, a significant amount of peak shift was detected due to presence of a lattice disorder and GaN crystallites on the surface of the porous film. These contributions lead to a relaxation of compressive stress by 0.17 ± 0.05 GPa using the proportionality factor of 4.2 cm^{-1} GPa^{-1} for hexagonal GaN [10] in the porous GaN surface with respect to the underlying single crystalline epitaxial GaN. Surface nanostructuring introduces a large increase in the scattering efficiency, resulting in a significant enhancement of the Raman intensity of the porous GaN as compared to the as-grown GaN.
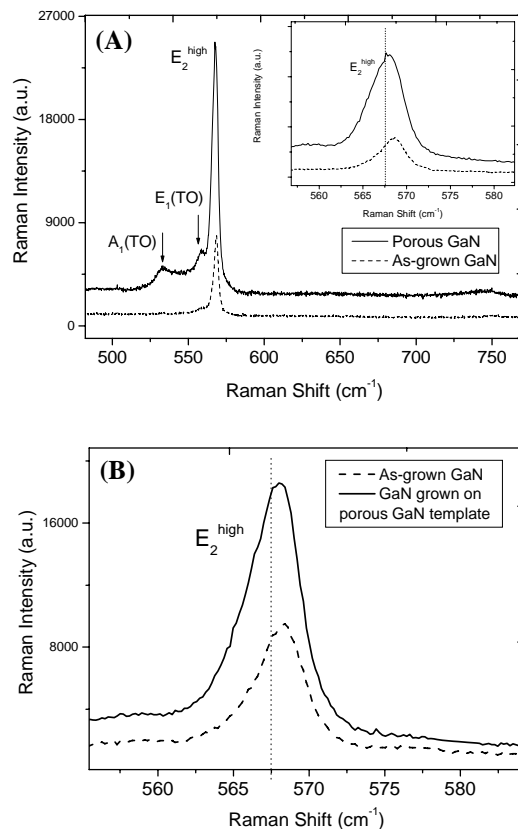

Fig. 2. (A) Micro-Raman spectra of as-grown (dash) and porous GaN (solid) epilayer. Inset shows the red shift for E_2(high) phonon from the porous GaN. (B) Micro-Raman spectra of as-grown (dash) and overgrown GaN on porous GaN template (solid) shows a red shift of 0.4 cm^{-1} in the E_2(high) phonon peak. The dotted line indicates the stress-free GaN peak at 567.5 cm^{-1}.

Next, the fabricated porous GaN is used as a template for the growth of a GaN layer. Figure 3 shows the cross-section TEM of the porous region after subsequent overgrowth of GaN layer with air being trapped inside the pores. The mechanism of this air-gap formation is not

clearly understood. However, this air-gap is believed to serve as sinks for dislocations for reducing residual strain in the film. Cross-section TEM confirms the SEM image that GaN etching results in layered nano-pores structures and also shows that etching takes place along the (0001) direction.
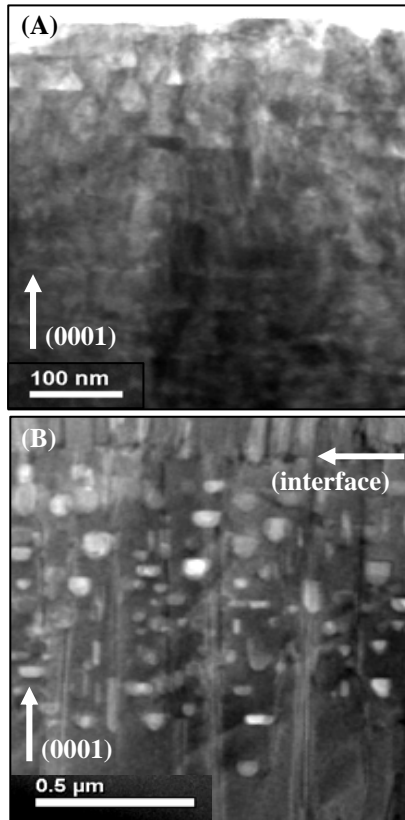

Fig. 3. Cross-section TEM of (A) the as-fabricated porous GaN and (B) the porous region after subsequent overgrowth of a GaN layer. It shows the formation of air-gap along the (0001) direction.

The Raman spectra in Fig. 2(B) shows the E_2(high) phonon peak of overgrown GaN on our porous template at 568.0 cm^{-1} and as-grown GaN at 568.4 cm^{-1}. The red shift of ~0.4 cm^{-1} towards the stress-free GaN (567.5 cm^{-1}) indicates a relaxation of compressive stress in the overgrown GaN layer. Although not shown here, it is worth to mention that there is improvement on the crystalline and optical quality of the GaN grown on the porous GaN template. The full width at half-maximum (FWHM) of the XRD rocking curve can provide information about crystalline quality. The angular distribution of the (0002) reflection planes under symmetric Bragg reflection condition shows an average reduction of FWHM as much as 0.033° for the overgrown GaN with respect to the as-grown GaN. Room temperature PL recorded using a Renishaw 2000 micro-PL setup and 325 nm line excitation from a He-Cd laser of the overgrown GaN shows double intensity than the as-grown film.

IV. CONCLUSION

The etching of Si-doped GaN by UV-enhanced electrochemical etching with current density of 20 mA/cm^2 for an hour in dilute NaOH solution results in layered nano-pores structures. A red shift of 0.7 cm^{-1} in the E_2(high) phonon peak of GaN from micro-Raman indicates a relaxation of compressive stress in the porous GaN surface with respect to the underlying single crystalline epitaxial GaN. Such a template is useful for high quality GaN growth. Subsequent growth of GaN layer on the porous template results in air gap formation, which is believed to serve as sinks for dislocations for reducing residual strain in the film. Reduction of FWHM of the XRD rocking curve as much as 0.033° and double intensity of the PL spectrum confirms the improvement on the crystalline and optical quality of the overgrown GaN on porous template as compared to as-grown. A red shift of ~0.4 cm^{-1} towards the stress-free GaN (567.5 cm^{-1}) also indicates a relaxation of compressive stress in the overgrown GaN layer.

REFERENCES

[1] L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
[2] V. Lehmann and U. Gosele, *Appl. Phys. Lett.* **58**, 856 (1991).
[3] V. Bondarenko, L. Dolgyi, N. Vorozov, V. Yakovtseva, V. Levchenko, and L. Postnova, Abstracts of NATO Advanced Research Workshop on Perspectives, Science and Technologies for Novel Silicon on Insulator Devices (kyiv), **15** (1998).
[4] S. Luryi and E. Suhir, *Appl. Phys. Lett.* **49**, 140 (1986).
[5] F. A. Ponce and D. P. Bour, *Nature (London)* **386**, 351 (1997).
[6] M. G. Mynbaeva and D. V. Tsvetkov, *Inst. Phys. Conf. Ser.* **155** (1997).
[7] H. Hartono, C. B. Soh, S. J. Chua, and E. A. Fitzgerald, *J. Electrochem. Soc.* (submitted).
[8] J. A. Bardwell, J. B. Webb, H. Tang, J. Fraser, and S. Moisa, *J. Appl. Phys.* **89**, 4142 (2001).
[9] N. G. Weimann and L. F. Eastman, *J. Appl. Phys.* **83**, 3656 (1998).
[10] C. Kisielowski, J. Kruger, S. Ruvimov, T. Suski, J. W. Ager, E. Jones, Z. Liliental, M. Rubin, and E. R. Weber, *Phys. Rev. B* **54**, 17745 (1996).