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Optical characterization of nanoporous GaN through electroless wet chemical etching

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High quality unintentionally doped n-type GaN layers were grown on Si(111) substrate, using AlN as the buffer layer, by radio frequency (RF) nitrogen molecular beam epitaxy. The present work reports on the photoluminescence (PL) studies of porous GaN prepared by ultraviolet assisted electrochemical etching in a solution of 2:1:1 HF:CH_3OH:H_2O_2 under illumination of an UV lamp with 500 W power for 10, 25 and 35 min. The optical properties of porous GaN samples were compared to the corresponding as-grown GaN. PL studies suggested that the porosity was capable of improving the lattice mismatch induced strain. Porosity induced PL intensity enhancement was found in nanoporous samples. The resulting nanoporous 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.

Key words: *photoluminescence; porous GaN; electrochemical etching; Si; RF-MBE*

1. Introduction

Porous semiconductors, especially porous silicon (PSi), exhibit properties absent in their crystalline counterparts [1]. Nonplanar structures developed by anodic etching can have specific surface areas as large as ca. 100 $m^2 \cdot g^{-1}$ [2], and quantum confinement coupled with the decreased efficiency of non-radiative recombination produce luminescence above the bulk band gap [3]. The high surface area, band gap shift, and efficient luminescence suggest uses of porous semiconductors in chemical and biochemical sensing [4, 5]. While PSi has attracted much attention, its thermal, chemical, and mechanical instability hinders its large scale application [6]. Interest in porous semiconductors as-growth templates arises from the pores acting as sinks for mismatch dislocations, accommodating elastic strain in heterostructures [7]. Since the discovery of light emitting porous silicon by Canham in 1990 [1], significant progress

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has been made on the studies of the structural, optical as well as mechanical and electrical properties of porous silicon.

In the last decade, porous semiconductors have been widely studied, 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. When porosity is formed, these materials exhibit various special optical features, for instance, a shift of band gap, luminescence intensity enhancement, as well as photoresponse improvement. Among porous semiconductors, porous silicon receives enormous attention and has been investigated most intensively; however the instability of physical properties has prevented it from large scale application. 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.

The research in porous GaN is strongly driven by its superior physical properties such as the mechanical, excellent thermal, and chemical stability, as well as the potential shift of the bandgap [8]. Moreover, it has been reported that porous GaN can be used as an intermediate layer for the reduction of substrate induced strain [9, 10]. Since bulk GaN in wafer size is not available, GaN thin film usually is grown on poor lattices and thermally mismatched foreign substrates, which will result in high residual stress and eventually lead to high density of structural defects. Research has also suggested that nanopatterned porous structures may serve as a template for nanoscale lateral epitaxial overgrowth [11]. In comparison, the study of porous GaN is still in the early stage, many fundamental properties are still not well understood.

Electroless etching is also called electrochemical oxidation without external bias. Metal-assisted electroless-chemical etching is an etching technique, developed recently, which is 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 a 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 bonds, and the dangling bonds will be attacked by nucleophilic species, resulting in material dissolution [12].

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

2. Experimental

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 model Gen II MBE system, using standard effusion sources for evaporation of Al (6N5) and Ga (7N), and

nitrogen with 7N purity was channeled by RF source to generate reactive nitrogen species. The plasma was operated at typical nitrogen pressure of 1.5×10^{-5} Torr under the discharge power of 300 W. Prior to loading into the MBE chamber, the Si(111) wafers (resistivity < 0.02 Ω·cm, n-type) were cleaned by using a standard Radio Corporation of America (RCA) method. RCA cleaning, also known as standard cleaning (SC), has been widely used in the semiconductor industry for more than twenty years.

In the preparation chamber, the substrates were outgassed for 10 min at 400 °C prior to growth. In the growth chamber, Si substrate was heated at 750 °C, and a few monolayers of Ga were deposited on the substrate for the purpose of removing SiO_2 by formation of GaO_2. A RHEED reconstruction with prominent Kikuchi lines was then observed, that turned into clean Si(111) surfaces at 750 °C. To grow an AlN buffer layer, the substrate was heated up to 850°C. Both the Al and N shutters were opened simultaneously for 30 min. Subsequently, a GaN epilayer was grown on top of the buffer layer for 15 min, with substrate temperature set at 800 °C. The unintentionally doped n-type GaN film, grown on Si(111) substrate, was used in this study. The thickness of GaN film was about 0.6 μm, with a carrier concentration of 4×10^{19} cm^{-3}, as determined by the 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 a sputtering system. The samples were then etched in a solution of 2:1:1 $HF:CH_3OH:H_2O_2$ under illumination of a 500 W UV lamp for 10, 25 and 35 min. After chemical treatment, the samples were removed from the solution and rinsed with distilled water; this was followed by the removal of the residual Pt by ultrasonic cleaning.

The optical properties of as-grown and porous GaN samples were characterized by photoluminescence (PL). PL measurements were performed at room temperature by using a Jobin Yvon HR800UV system, which is an integrated confocal microphotoluminescence spectrometer. A He-Cd laser (325 nm) was used as an excitation source. 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 a 1800 grove/mm holographic plane grating. Signals were detected by a Peltier cooled CCD array detector. Before the micro-PL measurement, a 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 ca. 3 cm^{-1}. The essential parameters (peak position and FWHM) of the PL peak were determined by using curve fitting software with Gaussian and Lorentzian models.

3. Results and discussion

The morphology of the as grown and porous GaN films was characterized by plan-view scanning electron micrographs (SEM). As seen in Fig. 1, the circular porous area is very uniform, with pore diameter in the 80–110 nm range. The etching duration has significant effect on the size and shape of the pores. For a 10 min sample, the pore sizes were observed to be around 70 to 80 nm. For a 25 min sample, the pore sizes were observed to be around 80 to 100 nm. For a 35 min sample, the pore sizes were observed to be around 100 to 110 nm. The size of the material between pores was found to be around 30–40 nm.

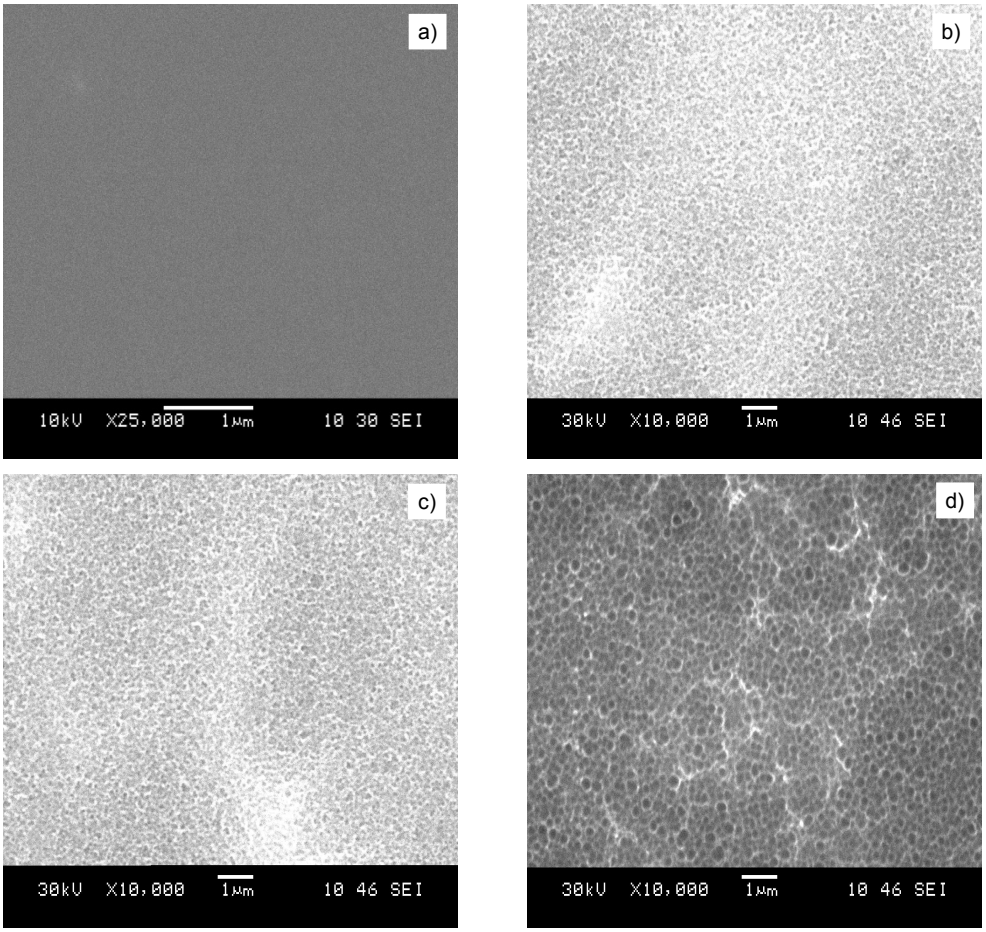

Fig. 1. SEM images of the samples: a) as-grown, b) etched for 10 min, c) etched for 25 min, d) etched for 35 min

Figure 2 illustrates the room temperature photoluminescence (PL) spectra of nanoporous GaN samples etched under different durations. The peak position, FWHM, peak shift

and the intensity of near band edge PL are given in Table 1. The spectra of the nanoporous GaN samples were observed to be blue-shifted relative to the spectra of

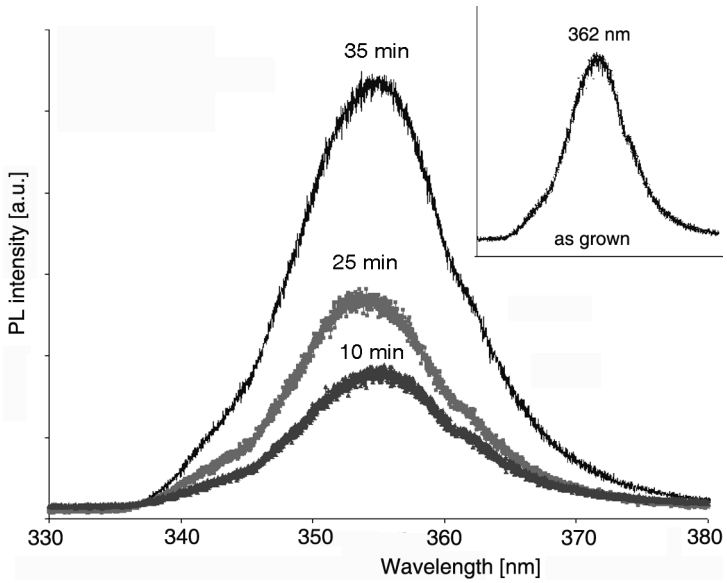

Fig. 2. The near band edge PL spectra of samples etched under various durations

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. [13] claimed that 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. [14].

Table 1. The peak positions, 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	1.4	1.20
25 min	356.50	8.8	2.0	1.64
35 min	358.13	9.9	3.1	1.80

Among the samples, there is little difference in the peak shift, and this indicates that the change of pore size has little influence on the degree of PL blue-shift. On the other hand, the PL intensity of the nanoporous samples is found to be increased. The amplification of the porosity-induced PL intensity could be explained by the reduction of surface pit density and extraction of strong PL by light scattering from the sidewalls

of the GaN crystallites [15], 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 [16], and this concept has long been applied in the fabrication of resonant cavity light emitting diodes in which the optical properties have been greatly enhanced [17].

The increase of the width of PL line of the porous samples, which is reflected in their FWHM, could be attributed to a relatively wide statistical size distribution of the pores. This shows that the luminescence spectrum of the nanoporous 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 explained by the recombination of localized excitons with strong phonon coupling.

4. Conclusion

We have used PL to characterize porous GaN samples fabricated by UV assisted electrochemical etching. PL measurements revealed that the near band edge peaks of all 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 intensities of the nanoporous samples are found to be increased. The amplification of the porosity-induced PL intensity could be explained by the reduction of surface pit density and reduction 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.

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References

[1] CANHAM L. T., Appl. Phys. Lett., 57 (1990), 1046.
[2] CULLIS A. G., CANHAM L. T., CALCOTT P. D. J., J. Appl. Phys., 82 (1997), 906.
[3] BRUS L., J. Phys. Chem., 98 (1994), 3572.
[4] SOHN H., LETANT S., SAILOR M. J., TROGLER W. C., J. Am. Chem. Soc., 122 (2000), 5393.
[5] LIN V.S.Y., MOTESHAREI K., DANCIL K.P.S., SAILOR M.J., GHADIRI M. R., Science, 278 (1997), 840.
[6] FAUCHET P.M., TSYBESKOV L., PENG C., DUTTAGUPTA S.P., BEHREN J.VON, KOSTOULAS Y., VANDYSHEV J.M.V., HIRSCHMAN K. D., IEEE J. Sel. Top. Quantum Electron., 1 (1995), 1126.
[7] SOLDATENKOV F.Y., ULIN V.P., YAKOVENKO A.A., FEDOROVA O.M., KONNIKOV S.G., KOROLKOV V. I., Tech. Phys. Lett., 25 (1999), 852.
[8] LI X., KIM Y-W, BOHN P.W., ADESIDA I., Appl. Phys. Lett., 80 (2002), 980.
[9] INOKI C.K., KUAN T.S., LEE C.D., SAGAR A., FEENSTRA R.M., Mater. Res. Soc. Symp. Proc, K1.3.1 (2002), 722.

[10] INOKI C.K., KUAN T.S., LEE C.D., SAGAR A., FEENSTRA R.M., KOLESKE D.D., DIAZ D.J., BOHN P.W., ADESIDA I., J. Electron. Mater., 32 (2003), 855.
[11] INOKI C.K., KUAN T.S., SAGAR A., LEE C.D., FEENSTRA R.M., KOLESKE D.D., DIAZ D.J., BOHN ADESIDA P.W., I., Phys. Stat. Sol. a, 11 (2003), 200.
[12] DIAZ D.J., WILLIAMSON T.J., ADESIDA I., BOHN P.W., J. Vac. Sci., Technol., B 20 (2002), 2375
[13] YAM F.K., HASSAN Z., NG S.S., Thin Solid Films 515 (2007), 3469.
[14] ADELMANN C., MARTINEZ-GUERRERO E., CHABUEL F., SIMON J., BATAILLOU B., MULA G., DANG L., PELEKANOS S., DAUDIN N.T., B., FEUILLET G., MARIETTE H., Mater. Sci. Eng., B 82 (2001), 212.
[15] VAJPEYI A.P., TRIPATHY S., CHUA S.J., FITZGERALD E.A., Physica E, 28 (2005), 141.
[16] BENISTY H., DE NEVE H., WEISBUCH C., IEEE J. Sel. Top. Quantum Electron., 34 (1998), 1612.
[17] SCHUBERT E. F., *Light-Emitting Diodes*, Cambridge University Press, Cambridge, 2003.

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