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Photoluminescence of Nanoporous GaN Films Prepared by Electrochemical Etching *

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Nanoporous (NP) GaN is prepared by electrochemical etching on a GaN epilayer grown on a sapphire substrate by metal-organic chemical vapor deposition. Scanning electron microscopy reveals that the average pore diameter and inter-pore spacing are approximately 25 and 45 nm, respectively. The photoluminescence (PL) spectra show that in contrast to the initial as-grown GaN epilayer, the NP GaN exhibits a high near-band-edge UV intensity, significant relaxation of compressive strain, and a lower yellow luminescence intensity. Both the line shape and line width of the PL spectra are almost the same for these two samples. The high quality of the NP GaN can be explained by the enhancement of the PL extraction efficiency and the decrease of impurity and defect density after etching.

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GaN and GaN-based materials have attracted attention due to their widespread applications in light emitting diodes (LEDs), laser diodes (LDs), and other electronic devices.[1–3] The materials are generally grown on sapphire or SiC substrates. However, due to the large lattice parameter and thermal expansion coefficient mismatches between GaN and these substrate materials,[4] the GaN epilayers grown on such substrates usually exhibit a high density of dislocations and a residual strain that can impair the structural and optical qualities of the grown layers.[5–8] On the other hand, it was reported that a nanoporous (NP) GaN prepared by reducing the dimensions of the as-grown GaN epilayer to the nanoscale, exhibited a high surface area, strain relaxation, and luminescence intensity enhancement:[9–11] e.g., it could be used as a buffer layer for the growth of subsequent high quality epitaxial layers with reduced defect densities and enhanced strain relaxation.[12–14] Although NP GaN offers a good alternative for the fabrication of a high-quality GaN layer, few works have been carried out up to date. It is therefore deemed desirable to study the effects of porosity on the optical properties of GaN samples.

In this study, an NP GaN film is prepared by electrochemical etching on a GaN epilayer grown on a sapphire substrate by using metal-organic chemical vapor deposition (MOCVD). The surface morphology of the NP GaN film is investigated by using scanning electron microscopy (SEM). The temperature dependence of photoluminescence (PL) spectra in the NP and as-grown GaN films is measured and the results are analyzed.

The GaN layers were grown on c-plane (0001) sapphire substrates by MOCVD. A buffer layer of 30-nm-thick GaN was first grown at 500℃ and subsequently, a 1.5-μm-thick undoped GaN layer, followed by a 2.0-μm-thick Si-doped n-GaN layer were grown at 1050℃. The carrier concentration in the top GaN layer, as obtained by Hall measurements, was $8.2 \times 10^{18}\,\mathrm{cm}^{-3}$. The electrochemical etching procedure was conducted in a two-electrode cell at room temperature with n-type GaN as the anode and a platinum wire as the cathode. The electrolyte was prepared by adding ethanol to hydrofluoric acid (49%) at a volume ratio of 0.5:1. The anodization process was carried out in constant voltage mode (30 V) and was controlled by a Keithley 2400 source meter, while the etching current was recorded under room lighting conditions. The details of the etching procedures of the NP GaN can be found elsewhere.[15] After anodization, the sample was removed from the solution and rinsed with deionized water and dried in N_2.

The sample surface morphologies were characterized by scanning electron microscopy (Hitachi SU-70 SEM). For temperature-dependent PL measurements,

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the samples were mounted in a closed-cycle helium cryostat and the temperature was controlled from 6 K to 300 K. A 325 nm cw He-Cd laser was used as the excitation source: its spot size was approximately 150 μm and its excitation power was 3 mW. The PL signal from the sample was dispersed by a Jobin–Yven iHR320 monochromator and recorded by a thermo-electrical cooled synapse CCD detector.

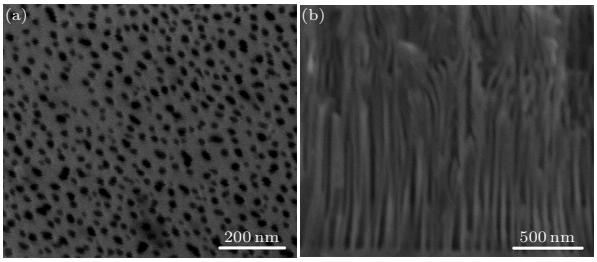


Fig. 1. Top-view (a) and plan-view (b) SEM images of NP GaN.

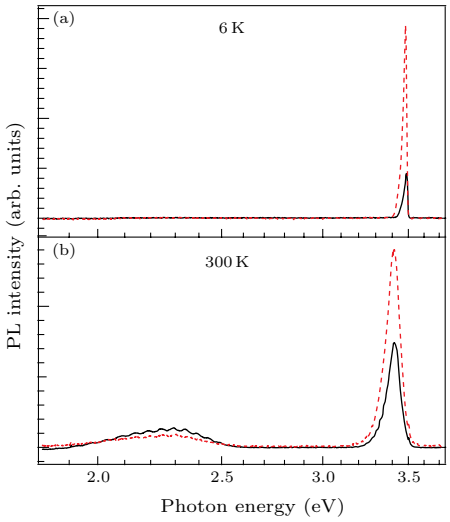


Fig. 2. PL spectra of NP GaN (dashed lines) and as-grown GaN (solid lines) at (a) 6 K and (b) 300 K.

Figure 1 shows two representative SEM images of the NP GaN. The diameter of the pores and the inter-pore spacing were approximately 25 nm and 45 nm, respectively. The distribution of the pores was practically uniform, and the density of the pores was estimated to be approximately $5.6 \times 10^{10}\,\mathrm{cm}^{-2}$.

Figure 2 shows the PL spectra of the NP and as-grown GaN layers recorded at 6 K and 300 K. At 6 K, as shown in Fig. 2(a), only one main peak at around 3.48 eV was observed in the PL spectra for both samples: this was attributed to the GaN-related near-band-edge UV transition. After increasing the temperature from 6 to 300 K, a new broad peak centered at approximately 2.30 eV for both the samples started to appear at approximately 50 K, and then gradually appeared more prominent relative to the UV peak as the temperature increased. Figure 2(b) shows the typical PL spectra of these two samples measured at 300 K. The new broad peak was assigned to the acceptor impurity- and/or defect-related yellow luminescence (denoted as YL), due to the thermal activation of the non-radiative centers such as carbon and gallium vacancies, iron impurities, and intrinsic defects strongly related to dislocations.[16–18] The oscillating structure on the YL band was attributed to intensity modulation by the Fabry–Perot cavity formed by the air-GaN and GaN-sapphire interface.

It is also found from Fig. 2 that the NP GaN shows a stronger UV intensity compared with the as-grown GaN over the temperature range measured. This improved UV intensity could be mainly attributed to the enhancement of the photon extraction efficiency due to more photons scattering from the sidewalls of the NP GaN. At the same time, it is believed that fewer impurities or defects in the NP GaN should also result from the enhancement of the UV intensity, since the electrochemical etching begins preferentially around dislocations and surface-related traps.[19–21] This speculation is confirmed further by the fact that the NP GaN shows a weaker YL intensity than the as-grown GaN at higher temperatures, as shown in Fig. 2(b).

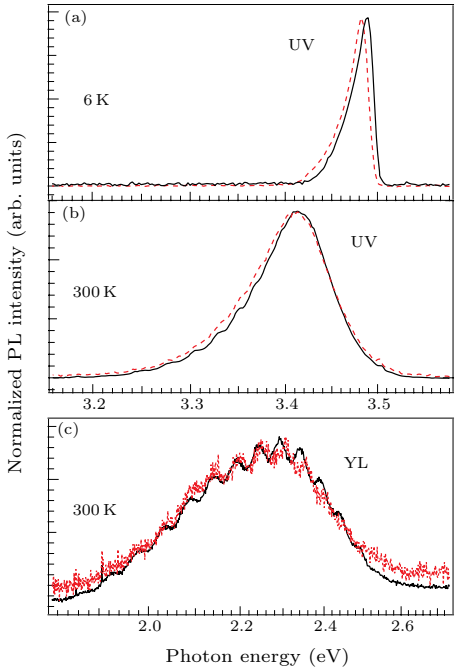


Fig. 3. Normalized PL spectra of NP GaN (dashed lines) and as-grown GaN (solid lines): (a) 6 K UV PL spectra, (b) 300 K UV PL spectra, and (c) 300 K YL spectra.

Moreover, Fig. 3 shows further the normalized UV and YL peaks of the NP and as-grown GaN at 6 K and 300 K for convenience and ease of comparison. Both the line shape and line width of the UV peak are practically the same for these two samples. This indicates that, contrary to previous reports,[22,23] the etching process in this work did not result in the incorporation of impurities or defects which result in a slight broadening of the UV band toward the low-energy side after

etching. It is consistent with the fact that the NP and as-grown GaN exhibits an almost identical line shape and line width for the YL bands (Fig. 3(c)). Together with the aforementioned stronger UV intensity and weaker YL intensity of the NP GaN, it is concluded that the NP GaN has better structural and optical qualities due to its reduced defect and impurity densities compared with the as-grown GaN.

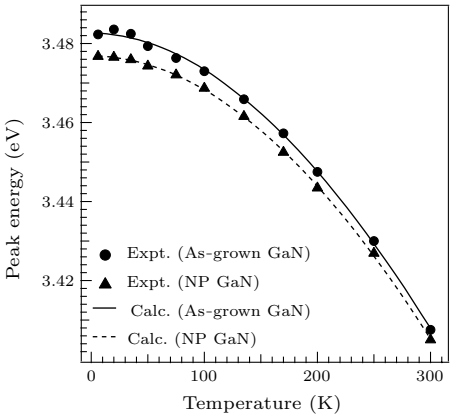


Fig. 4. Temperature dependence of the UV peak energies in NP GaN (triangles) and as-grown GaN (circles). Lines represent the least-squares fits of the experimental data according to Eq. (1).

Figure 4 shows the temperature dependence of the UV peak energy for both the samples over the temperature range from 6 to 300 K. With increasing temperature, the UV peak energies for both the samples decrease monotonically. The decreasing trend of UV peak energy with increasing temperature is considered to be associated with band-gap shrinkage, due to the fact that the temperature dependence of the UV peak energy for NP and as-grown GaN are well fitted by the phenomenological Varshni formula

$$E_{\rm g}(T) = E_{\rm g}(0) - \frac{\alpha T^2}{T+\beta}, \tag{1}$$

where $E_{\rm g}(0) = 3.477\,{\rm eV}$, $\alpha = 7.6 \times 10^{-4}\,{\rm eV\cdot K^{-1}}$, and $\beta = 1120\,{\rm K}$ for the NP GaN, and $E_g(0) = 3.482\,{\rm eV}$, $\alpha = 8.2 \times 10^{-4}\,{\rm eV\cdot K^{-1}}$, and $\beta = 1040\,{\rm K}$ for the as-grown GaN. However, it is also seen from Fig. 4 that the UV peak energy of the NP GaN demonstrates a red shift of 5.6 meV relative to that of the as-grown GaN at 6 K, while the red shift gradually weakness with increasing temperature to 300 K. The behaviors indicate that in addition to the band-gap shrinkage effect, i.e., Varshni's law, the influence on the UV peak energy of an additional strain existing in these two samples may be included, and can be explained as follows: due to the large lattice parameter and thermal expansion coefficient mismatches between GaN and sapphire, a strain and a structural defect always occur in the GaN epilayer grown on a sapphire substrate. The strain existing in the GaN epilayer is considered to be compressive and mainly caused by the difference in thermal expansion coefficients between the sapphire substrate ($\sim 7.5 \times 10^{-6}\,{\rm K^{-1}}$) and the GaN epilayer ($\sim 5.59 \times 10^{-6}\,{\rm K^{-1}}$),[24] due to the fact that the strain induced by the lattice mismatch should be almost entirely relaxed in the coherently grown GaN epilayer at a thickness of approximately 80 nm.[25] Consequently, the aforementioned red shift (5.6 meV) of the UV peak energy of the NP GaN relative to the as-grown GaN at 6 K should be associated with the partial relaxation of the compressive strain in the NP GaN induced by the electrochemical etching. The decreasing trend for the red shift with increasing temperature is attributed to the lower rate of decrease of the compressive strain in the NP GaN due to its smaller compressive strain compared with the as-grown GaN. In addition, according to the UV peak energy red shift (ΔE), the amount of stress relaxation (σ) can be estimated by $\Delta E = K\sigma$, where the value of the proportionality constant $K = 21.2 \pm 3.2\,{\rm meV/GPa}$.[6] As shown in Fig. 4, the UV peak energy red shifts of 5.6 meV and 2.6 meV at 6 K and 300 K, corresponded to stress relaxations of 0.27 ± 0.04 and $0.12 \pm 0.02\,{\rm GPa}$, respectively.

In summary, an NP GaN film was prepared by electrochemical etching on an initial GaN epilayer grown on a sapphire substrate using MOCVD. The formation of nanopores in the NP GaN film has been confirmed by SEM. PL measurements show that the NP GaN has a stronger UV intensity compared to the as-grown GaN. This improved UV intensity is mainly attributed to the enhancement of the photon extraction efficiency due to more photons scattering from the sidewalls of the NP GaN. At the same time, it is believed that fewer impurities or defects in the NP GaN should also result in an enhancement of the UV intensity, since the electrochemical etching begins preferentially around the dislocations and surface-related traps. The presence of fewer impurities or defects in the NP GaN could be confirmed further by its weaker YL intensity than that of the as-grown GaN. Furthermore, the almost identical line shape and line width of the PL peaks for these two samples indicates that the etching process does not result in the incorporation of so many impurities or defects. The red shift of the UV peak energy of the NP GaN relative to the as-grown GaN is ascribed to the relaxation of compressive stress in the NP GaN. Such strain-relaxed NP GaN could be used as a buffer, or intermediate layer, for the overgrowth of GaN layers with low stress and defect densities.

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