Investigation of yellow luminescence intensity of N-polar unintentionally doped GaN*

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This paper reports that the yellow luminescence intensity of N-polar GaN Epi-layers is much lower than that of Ga-polar ones due to the inverse polarity, and reduces drastically in the N-polar unintentionally-doped GaN after etching in KOH solution. The ratio of yellow luminescence intensity to band-edge emission intensity decreases sharply with the etching time. The full width at half maximum of x-ray diffraction of (10-12) plane falls sharply after etching, and the surface morphology characterized by scanning electron microscope shows a rough surface that changes with the etching time. The mechanism for the generation of the yellow luminescence are explained in details.

Keywords: N-polar GaN, yellow luminescence, KOH etching
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1. Introduction

Recently, group-III nitrides have attracted much attention, largely as a result of brilliant performance of group-III nitride-based blue light-emitting diodes and lasers.[1−4] Optical properties and electric properties are intensely studied.

In spite of considerable attention to the yellow luminescence (YL) centred around 2.2–2.4 eV in GaN, the mechanism that is responsible for this broad band emission remains unknown.[5] According to the researches done in the last decade, the origin of the YL is debating. There are three main factors which determine the intensity of the YL. A complex involving a deep acceptor ($V_{\rm Ga}$) and a shallow donor ($O_{\rm N}$) which forms a donor-acceptor-pair is widely accepted.[6,7] Carbon and oxygen impurities and edge dislocations are regarded as the other two possible reasons.[8−11]

Fewer studies on the YL of N-polar unintentionally-doped GaN are reported, while much work has done about Ga-polar GaN as mentioned above. Difference between Ga-polar GaN and N-polar GaN demonstrates that the intensity of the YL of a GaN Epi-layer is closely related to its polarity. In our work, the differences between the YL of N-polar GaN and that of Ga-polar GaN are discussed. The YL intensity attenuates obviously after etching in KOH resolution at room temperature. This phenomenon is explained in details according to the scanning electron microscopy (SEM) and the high resolution x-ray diffraction (HRXRD) measurements.

2. Experiments

Two series of samples (I, II) are prepared for this experiment. There are 2 samples in series I, a 2 μm N-polar GaN Epi-layer deposited on a nitrided c-plane sapphire substrate with a 20 nm low-temperature-GaN nucleation layer (sample A), and a 2 μm Ga-polar GaN Epi-layer deposited on a c-plane sapphire substrate without initial nitridation with a (20 nm high-temperature-AlN nucleation buffer layer sample B). In series II, a GaN film with N-polar (sample C) is fabricated under the same condition as the sample A.

3. Discussion

3.1. Effect of polarization direction on photoluminescence

Figure 1 shows normalized photoluminescence (PL) spectra of N-polar and Ga-polar bulk GaN. It

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is obvious that N-polar GaN exhibits a lower YL than that of Ga-polar. In our work the ratios of the YL to the band-edge emission ($I_{\rm YL}/I_{\rm BE}$) are 1.926 and 0.615 for Ga-polar and N-polar GaN respectively. Since the directions of polarity in N-polar and Ga-polar GaN are reversed during growth, the formed defects and incorporated impurities which act as deep acceptors in GaN buffer layer are obviously different. It is believed that GaN films of N-polar contain more oxygen but less carbon impurities than those of Ga-polar.[12] And a longer migration length of Ga atoms can be expected for the N-polar GaN during growth,[13] which indicates that GaN Epi-layer of N-polar has lower $V_{\rm Ga}$ density. The x-ray photoelectron spectroscopy (XPS) of the N-polar film and the Ga-polar film is given in Fig. 2. The integrated intensities of Ga 3d peak at 19.9 eV and N 1s peak at 397.2 eV reveal a larger Ga at% (about 49%) in the N-polar film, which demonstrates a lower $V_{\rm Ga}$ in comparison with the Ga-polar film. However, it remains unclear, which polarity of GaN has a higher total density of deep acceptors that generate the broad YL.

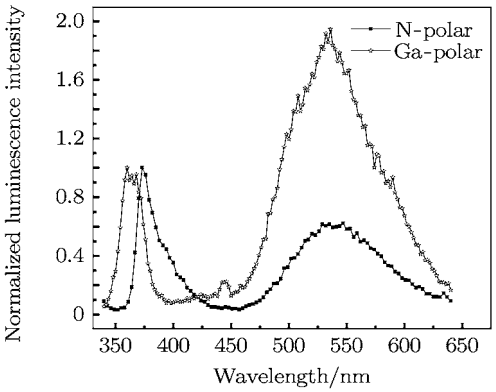


Fig. 1. Comparison of N-polar and Ga-polar GaN photoluminescence spectra at room-temperature.

We suggest that band bending is determinant to the difference of the YL intensity of different polarities. Figure 3 shows the scheme of band potentials and main transitions responsible for the YL in the N-polar and the Ga-polar GaN. We can find a downward and upward band bending at surfaces of the N-polar and the Ga-polar GaN due to the built-in electric fields induced by the polarisation in the GaN. A depletion layer ((0–X_0) in Fig. 3) formed at the surface of the Ga-polar GaN, which brings a quick separation of the photo-generated electrons and holes. A very thin 'flat-band' layer is formed as the holes accumulate (captured by deep acceptors) near the surface, where the YL is generated by the effective radiative recombination between conduction band $E_{\rm C}$ and deep acceptor or shallow donor and deep acceptor as shown in Fig. 3).[14]

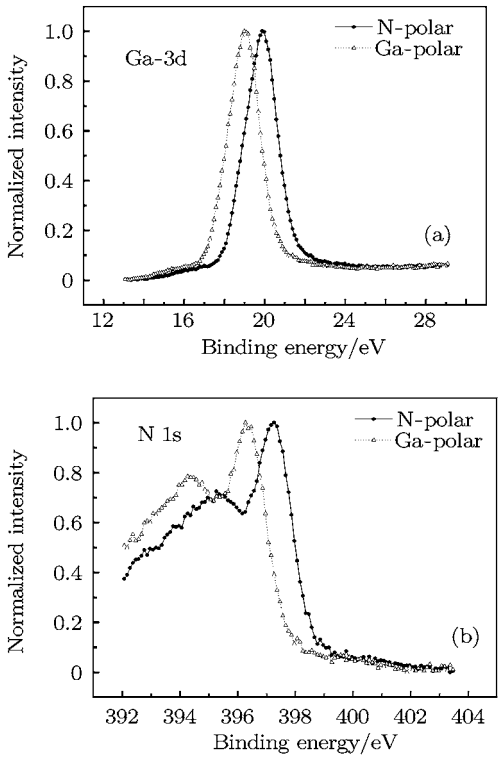


Fig. 2. Comparison of the core level between (a) Ga 3d and (b) N 1s XPS spectra of N-polar and Ga-polar GaN. The integrated intensity of Ga 3d peak and N 1s peak indicate N-polar GaN has a higher Ga atom fraction.

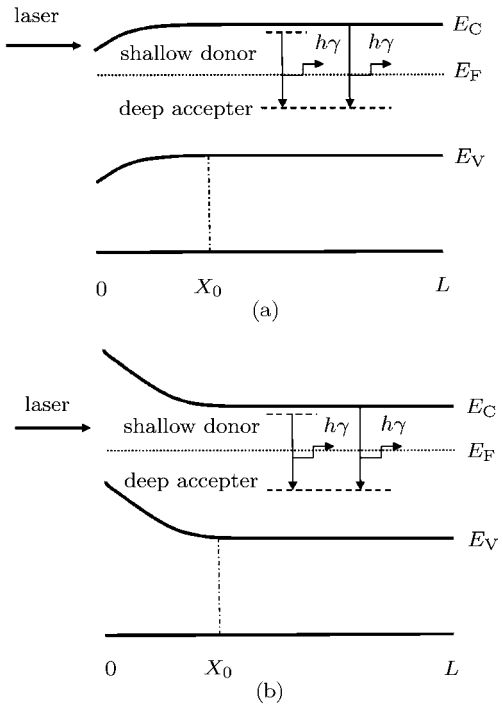


Fig. 3. Schematic diagram of energy band bending at surface and transitions between $E_{\rm C}$ and deep acceptor level (shallow donor and deep acceptor level) for the (a) N-polar and (b) Ga-polar GaN, respectively.

The Fermi-level of holes ($E_{\rm F}^{\rm P}$) becomes closer to $E_{\rm V}$, which gives a higher possibility for the holes to occupy the deep acceptor level and increases the opportunity of radiative recombination. In comparison with the indirect radiative recombination, the direct band-to-band recombination seems more sensitive to the depletion layer. Lower band-edge emissions occur since most of the photo-generated electrons and holes are swept away. This explains a higher $I_{\rm YL}/I_{\rm BE}$ in the Ga-polar GaN. In contrast, there is no such a depletion layer in the N-polar GaN, which results in more band-edge emissions and the $E_{\rm F}^{\rm P}$ becomes far away from $E_{\rm V}$. This means the holes have lower possibility to occupy the deep acceptor level and the opportunity of indirect recombination decreases, which gives a lower $I_{\rm YL}/I_{\rm BE}$ in the N-polar GaN.

Obvious red-shifts of the band-edge emission from 364 nm to 372 nm and the YL from 534 nm to 540 nm are detected in the N-polar GaN. We suggest that a stress induced band bending should be responsible for the red-shifts. As it is known, the growth of the Ga-polar GaN follows a 'two-step' method, a large compressive stress exists in the Epi-layer which broads the band and causes a higher recombination energy. In contrast, the N-polar GaN has a completely different growth procedure, especially in the early stages of the epitaxy,[15,16] which results in different stress states and leads to the red-shifts of the PL spectra of the N-polar film.

3.2. Origin of yellow luminescence

Another interesting phenomenon was discovered when the N-polar GaN was etched in KOH solution at room temperature. The N-polar GaN sample C was cut into 5 pieces, and etched in 10% KOH solution for different times: 0, 3, 30, 300 and 1200 s.

Figure 4 shows the SEM morphologies of as-grown and etched N-polar GaN (3, 30, 300, and 1200 s). It is found that the hexagonal hillocks are etched into very small and anomaly 'islands', which can be regarded as column grown GaN with a diameter of 200–300 nm.[17] In contrast with the as grown film, surfaces of all etched samples are filled with such columns. At the very initial stage of etching, the hexagonal hillocks are nearly flat with these columns stayed together (Fig. 4(b)). After 30 s, the hexagonal hillocks become rougher with those columns dispersed (Figs. 4(c)–4(e)).

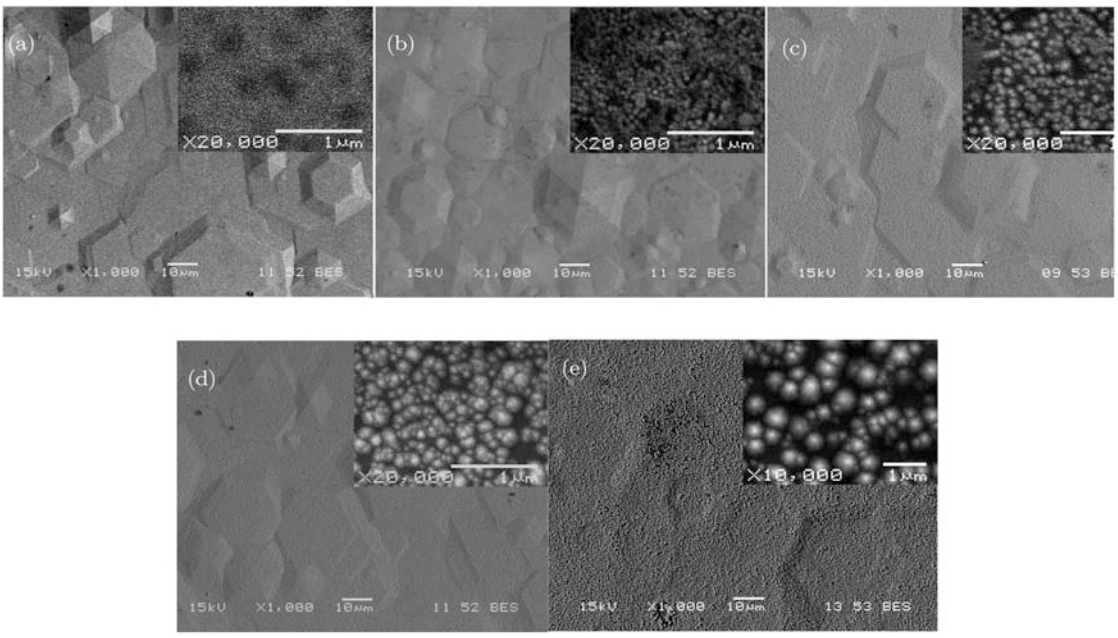


Fig. 4. The SEM surface morphology of (a) as grown N-polar GaN, (b)–(e) N-polar GaN etched for 3, 30, 300, and 1200 s in KOH solution. The insert shows details of the surface morphology at a higher resolution.

Figure 5 (a) shows the normalized PL spectra. A drastic drop of the ratio I_{YL}/I_{BE} (see Table 1 and Fig. 5(b)) and a sharp increase of the average island diameter (shown in Fig. 5(b)) versus the etching time are observed. It is necessary to explore the decrease of I_{YL}/I_{BE} by reviewing the growth and the etching process based on the SEM and the HRXRD results.

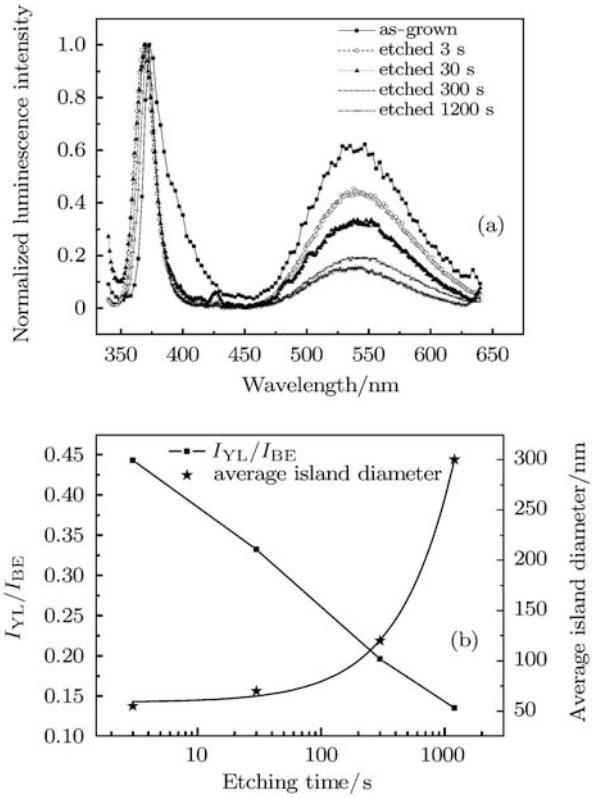


Fig. 5. (a) The PL spectra of samples in series II etched in KOH solution, and (b) the I_{YL}/I_{BE} decrease and the average island diameter increased with etching time.

Table 1. The I_{YL}/I_{BE} and the HRXRD FWHM at (10-12), (0002) planes of the N-polar GaN samples in series II.

etching time/s	I_{YL}/I_{BE}	HRXRD FWHM/arcsec	
		10–12	(0002)
0	0.627	1696	730
3	0.443	644	627
30	0.332	629	615
300	0.196	664	675
1200	0.135	649	668

At the very initial stage of etching, the HRXRD full width at half maximum (FWHM) of the (10–12) plane decreases rapidly (see Table 1 and Fig. 6(a)), while the surface remains almost flat (see Fig. 4(b)), which indicates the drop of the I_{YL}/I_{BE} correlates with the edge dislocations. A low temperature GaN nucleation layer is first deposited on a nitrided sapphire substrate. As the nucleation islands grow bigger, they coalesce and turn into quasi-two-dimensional lateral growth directly. Many edge dislocations are generated at the boundary of the islands, and abundant oxygen atoms diffuse along these edge dislocations upwards from the sapphire substrate.[18] We consider these edge dislocations, which are surrounded by oxygen atoms, form a typical shallow donor deep acceptor pairs (DAP) and serve as the origin of the YL. From the SEM morphology, it is obvious that the edge dislocations at the boundary in the N-polar GaN are easily etched than the rest of the area, as a result, most edge dislocations (act as effective radiative recombination centres) are removed after etched for a few seconds. With the decrease of the effective radiative recombination centres, the PL spectra exhibit a corresponding decreased in the I_{YL}/I_{BE} due to the decrease in the YL intensity.

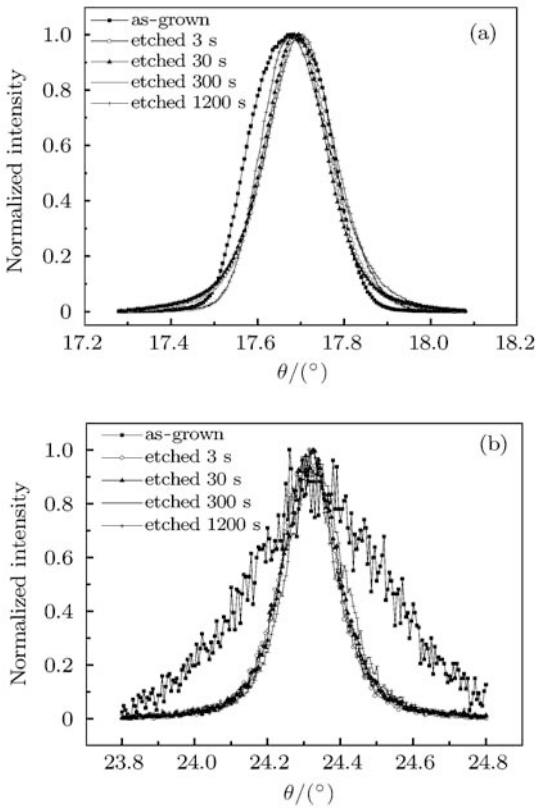


Fig. 6. (a) The XRD rocking-curve of (0002) plane of the samples in series II, and (b) the XRD rocking-curve of (10–12) plane of the samples in series II.

At the subsequent stage of etching (after 30 s), the HRXRD FWHM of the (10–12) plane remains at 630–650 arcsec (see Table 1 and Fig. 6(b)) while the surface of the hexagon becomes rougher with the increas-

ing etching time (Figs. 4(c)–4(e)), which indicates the subsequent drop of the $I_{\rm YL}/I_{\rm BE}$ correlates with the roughened surface morphology. A rougher surface can provide higher optical transmittance (equals additional emissions). As the intensity of the band-edge emission is larger than that of the YL, a stronger additional band-edge emission is expected, which result in a smaller $I_{\rm YL}/I_{\rm BE}$. The HRXRD FWHM at the (0002) plane remains around 646 arcsec, which indicates that the YL has rarely been affected by the screw dislocation.

Additionally, in the Ga-polar GaN, the epitaxy growth begins with the deposition of three dimensional islands as shown by the decrease of the reflectance at the beginning of the GaN growth process.[19] In the N-polar GaN, the epitaxy starts with a quasi-two-dimensional deposition indicated by the ideal oscillation of the reflectance at the initial growth. However, the amplitude declines during the growth process, which indicates a decrease in the grain size as the GaN Epi-layers grow thicker.[19] Therefore, an increase of the grain diameter should be expected as Epi-layers become thinner. This fact agrees well with our experiments.

4. Conclusion

In conclusion, we have made a comparision of the PL spectra of the N-polar and the Ga-polar GaN, and explained the lower $I_{\rm YL}/I_{\rm BE}$, the redshifts of the band-edge emission and the YL in the N-polar GaN. Furthermore, a drastic decrease of the $I_{\rm YL}/I_{\rm BE}$ for the N-polar GaN after etching in KOH solution at room temperature is observed. According to the HRXRD and the SEM mesurements, a decreased HRXRD FWHM of the (10–12) plane and a rougher surface morphology at different stages of etching are responsible for the decreasing $I_{\rm YL}/I_{\rm BE}$. We demonstrate that the edge dislocations, the surrounding oxygen atoms (DAP) and the surface morpology are responsible for the $I_{\rm YL}/I_{\rm BE}$.

References

[1] Strite S and Morkoç H 1992 *J. Vac. Sci. Technol.* B **10** 1237

[2] Nakamura S, Senoh M, Nagahama S, Iwasa N, Yamada T, Matsushita T, Sugimoto Y and Kiyoku H 1996 *Appl. Phys. Lett.* **69** 3034

[3] Kuramata A, Domen K, Soejima R, Horino K, Kubota S I and Tanahashi T 1997 *Jpn. J. Appl. Phys.* (Part 2) **36** 1130

[4] Fan Z, Mohammad S N, Aktas O, Botchkarev A E, Salvador A and Morkoç H 1996 *Appl. Phys. Lett.* **69** 1229

[5] Reshchikov M A and Morkoç H 2005 *J. Appl. Phys.* **97** 061301

[6] Neugebauer J and van de Walle C G 1996 *Appl. Phys. Lett.* **69** 503

[7] Colton J S, Yu P Y, Teo K L, Weber E R, Perlin P, Grzegory I and Uchida K 1999 *Appl. Phys. Lett.* **75** 3273

[8] Shi J Y, Yu L P, Wang Y Z, Zhang G Y and Zhang H 2002 *Appl. Phys. Lett.* **80** 2293

[9] Armitage R, Hong W, Yang Q, Feick H, Gebauer J and Weber E R 2003 *Appl. Phys. Lett.* **82** 3457

[10] Zhao D G, Jiang D S, Yang H, Zhu J J, Liu Z S, Zhang S M and Liang J W 2006 *Appl. Phys. Lett.* **88** 241917

[11] Zhao D G, Jiang D S, Zhu J J, Liu Z S, Wang H, Zhang S M, Wang Y T and Yang H 2009 *Appl. Phys. Lett.* **95** 041901

[12] Fichtenbaum N A, Mates T E, Keller S, Den Baars S P and Mishra U K 2008 *Journal of Crystal Growth* **310** 1124

[13] Sumiya M, Yoshimura K, Ito T, Ohtsuka K and Fuke S 2000 *J. Appl. Phys.* **88** 1158

[14] Reshchikov M A 2006 *Appl. Phys. Lett.* **89** 232106

[15] Sun Q, Cho Y S, Lee I H, Han J, Kong B H and Cho H K 2008 *Appl. Phys. Lett.* **93** 131912

[16] Sun Q, Cho Y S, Kong B H, Cho H K, Ko T S, Yerino C D, Lee I H and Han J 2009 *Journal of Crystal Growth* **311** 2948

[17] Mikroulis S, Georgakilas A, Kostopoulos A, Cimalla V and Dimakis E 2002 *Appl. Phys. Lett.* **80** 2886

[18] Zywietz T K, Neugebauer J and Scheffler M 1999 *Appl. Phys. Lett.* **74** 1695

[19] Grzegorczyka A P, Hagemana P R, Weyhera J L and Larsen P K 2005 *Journal of Crystal Growth* **283** 72