Performance enhancement of crystalline quality and optical properties of GaN epilayer grown on patterned sapphire substrate

DANG-HUI WANG*, TIAN-HAN XU, FANG CHEN
College of Materials Science & Engineering of Xi'an Shiyou University, Xi'an 710065, China

In this study we have investigated optical properties of GaN epilayer grown on cone-patterned and planar c-plane sapphire substrate by low-pressure metal-organic chemical vapor deposition (LP-MOCVD) respectively. High-resolution X-ray diffraction (HRXRD), atomic force microscopy (AFM), scanning electron microscope (SEM), photoluminescence (PL) and Raman scattering measurements have been employed to study the crystal quality, surface morphology, optical properties and residual strain of GaN epifilms. Conclusions reveal that epitaxial films grown on patterned sapphire substrate can improve the crystal quality, enhance the surface morphology, and reduce the threading dislocation density. The mechanisms of growing on cone-patterned sapphire substrate to enhance the optical properties of GaN epifilms discussed from the viewpoint of residual strain state in this paper.

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1. Introduction

As a classical representative of the third generation of semiconductor materials, GaN-based materials system have already exhibited their importance in applications including green/blue, UV light-emitting diodes (LEDs) and high-brightness white LEDs in solid-state-lighting device, which are used widely in the blue/green and ultraviolet spectral regions with higher quantum efficiency [1,2,3]. InGaN/GaN multiple quantum wells (MQWs) are important active region for optoelectronic devices such as green/blue, high-brightness white LEDs and infrared detectors, which can be tuned according to In content in InGaN alloy system [4,5]. The most important issue hampering the applications and advances in solid-state lighting to LED is dislocation and residual strains existed in epililms. Owing to difficulty in fabricating bulk materials, nearly all GaN-based epifilms are heteroepitaxially grown on foreign substrates, such as sapphire, SiC, and Si substrates, which results in threading dislocations and residual strains occur greatly in GaN epifilms. For reducing the number of threading dislocation density, many of methods have been put to use for obtain higher crystalline, including a thin AlN nucleation layer or GaN buffer layer [6,7], LT-AlN nucleation layer [2,6], superlattice structure [8,9], patterned sapphire substrate [10,11], and nano-micrometer hybrid patterned substrates, which are utilized to improve the crystal quality, reduces surface roughness and eliminates the threading dislocation density. Nowadays Patterned Sapphire Substrates (PSS) are de-facto a standard for growth of III-N heterostructures for high-brightness LEDs. The main reason of LED properties improvement due to utilizing of these substrates is an improvement of light extraction efficiency, which is fine and complex, and results from interplay of a few possible mechanisms including significant modification of the initial stages of epigrowth (nucleation, growth of crystallites, and coalescence) due to existing of patterns on the surface with the height exceeding the size of the growing crystallites. However, few studies have been investigated on the crystalline quality, surface morphology, optical properties and residual strain of GaN epilayer grown on patterned sapphire substrate. In this paper, we have studied further the influence on optical properties of GaN epilayer on c-plane patterned sapphire substrates.

2. Experimental procedure

Two samples studied in this work were grown using a cold-wall showerhead low-pressure metal-organic chemical vapor deposit (LPMOCVD) system. The pressure of LPMOCVD growth system was about 5.2×10^{-3} Torr. Hydrogen was used as carrier gas, triethylgallium (TEGa) and ammonia (NH_3) were used as Ga and N source, respectively. We use c-plane sapphire (α-Al_2O_3) as substrate, and sample A and sample B were grown on a c-plane conventional unpatterned planar sapphire substrate (UPSS, denoted as Sample A) and a c-plane cone-shaped patterned sapphire substrate (CPSS, denoted as Sample B), respectively. Followed by a thin low-temperature GaN (LT-GaN) nucleation layer (about 20nm, 550℃) and a thicker GaN layer (about 5000nm, 1000℃) were grown on sapphire substrates. as shown in

Fig.1. In order to study and analyze the optical properties of blue LED grown on patterned and planar sapphire substrate, the two as-grown samples were characterized by high-resolution X-ray diffraction (HRXRD), atomic force microscopy (AFM), and Raman scattering. For the purpose to reveal and obtain a comprehensive knowledge of the threading dislocation density of sample A and sample B, we measured X-ray rocking curves (XRCs) for both symmetry and asymmetry diffraction planes by HRXRD. The HRXRD was performed using Bruker D8-discover system equipped with Ge (220) monochromator and channel-cut analyzer, delivering a pure Cu-Kα line of wavelength λ=0.15406 nm; The atomic force microscopy (AFM) was performed using an Agilent 5500 scanning probe system and the micro-Raman measurements were carried out in backscattering geometry with the Raman spectrometer Jobin Yvon LabRam HR800. An argon laser of 514-nm wavelength was used as an excitation light source and a 50× objective was used to focus the incident laser light of a power of 14.2 mW on the sample, the spectrometer was calibrated using single-crystal silicon as a reference.

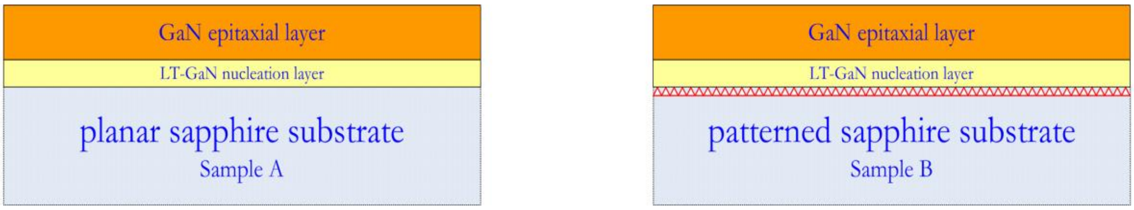


Fig. 1. Cross-section structures of Sample A and Sample B

3. Results and discussion

3. 1. High-resolution X-ray Diffraction

XRD-2θ scan profiles are shown in Fig. 2. The peak located at 34.54° and 34.59° are diffraction from the GaN (002) planes of sample A and sample B, respectively; 72.86° and 72.91° are diffraction from the GaN (004) planes of the two samples, respectively. 41.68° is diffraction from the sapphire (006) planes. The intensity of GaN (002) planes for sample B is much sharper than that of sample A indicating better crystal quality for growing on patterned sapphire substrates.

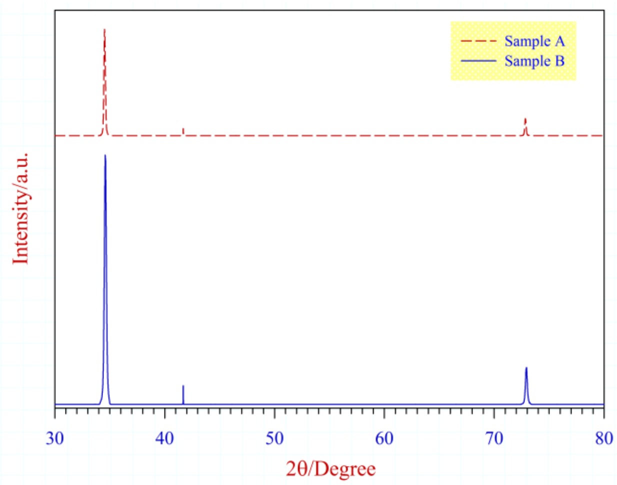


Fig. 2. XRD-2θ scan profiles for sample A and sample B

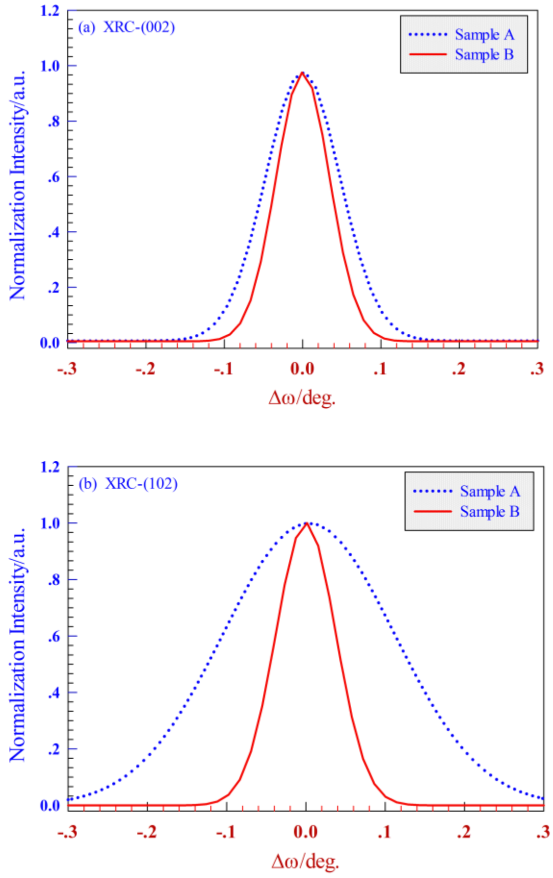
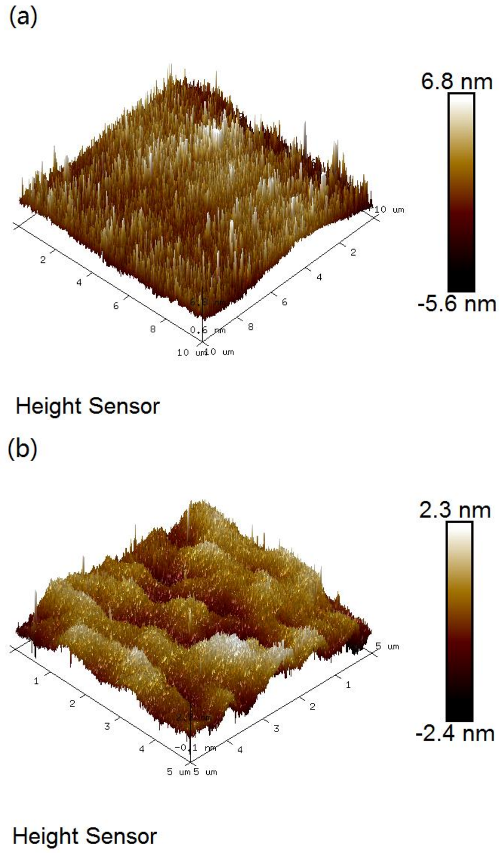


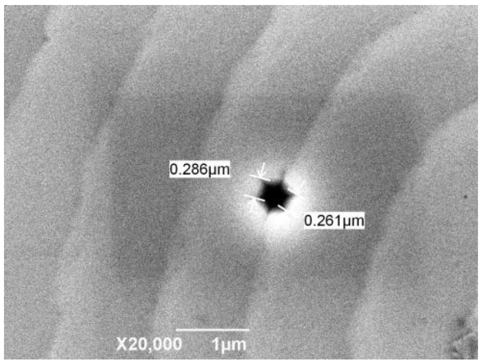
Fig. 3. X-ray rocking curve for (002) reflection for sample A and sample B. (a) is the (002) planes and (b) is the (102) planes

Furthermore, in order to study the crystalline quality of the two samples, the full-widths at half-maximum (FWHMs) of X-ray rocking curves were also measured as shown in Fig. 3. As can be seen that the FWHMs of Sample A and Sample B are 392.79 arcsec and 286.79 arcsec for (002) planes, respectively, while for (102) planes, the respective FWHMs are 919.77 arcsec and 332.38 arcsec. It is well known that the FWHMs of XRD rocking curve from (002) planes or (102) planes is related to screw or edge dislocation density [10], and the narrower FWHMs of XRD rocking curve is brought into correspondence with the lower threading dislocation density existed in the epifilms. It can be shown from Fig.3, whatever for (002) planes and (102) planes, the FWHMs of the rocking curve for sample B is smaller than sample A, which indicates that the screw or edge dislocation density existing in sample B is lower than sample A has. So we have a conclusion that, sample B grown on patterned sapphire substrate has a better crystalline quality than sample A grown on unpatterned planar sapphire substrate.

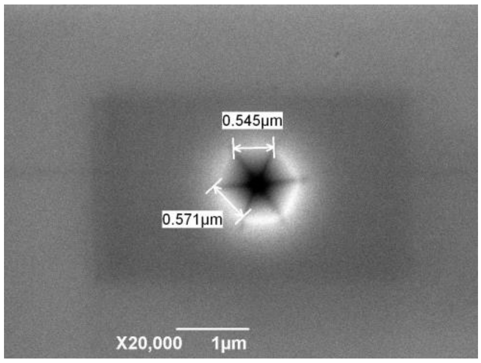
3. 2. AFM, SEM and Surface Morphology

Fig. 4 shows the $10\times 10\ \mu m^2$ AFM images of the two samples. One can see from these images that the differences in surface morphology between sample A and sample B. For comparison, the 3D surface morphology in Fig.4 (a) and (b) indicates an improvement of quality for sample A and sample B. As is seen that sample B shows clearly a lower dislocation fluctuation on the surface than sample A does. In addition, the root mean square (RMS) value is 6.20nm for sample A and 2.35nm for sample B, which indicates that sample B has a smoother surface morphology than sample A does. Furthermore, we have carried out SEM analysis in Fig.4(c) and (d). As can be shown, there appears regular hexagonal pyramid on the surface of sample A and sample B. We have marked the size of hexagonal pyramids, and found that the size of the hexagonal pyramid on sample A is smaller than that on sample B. Furthermore, one can see clearly that there exist some bent stripes induced by surface fluctuations during the process of growth owing to the differences in lattice and thermal mismatched between sapphire and epitaxial epifilms, while there isn't any stripe on the surface of sample B, indicating that there is lower RMS on the surface of Sample B, which coincides with the results of AFM analysis.





(c) SEM image of sample A



(d) SEM image of sample B

Fig. 4. 3D AFM of 10µm×10µm and SEM images (×20000) surface morphologies for sample A and sample B

4. Raman Scattering and photoluminescence

Raman scattering was performed to examine residual strain of the two samples recorded in $x(yy)x$ backscattering mode with 514nm wavelength excited from an Ar-ion laser at room temperature. According to group theory, A_1(To), E_2 (high) and A_1(LO) are active phonon modes under this geometry backscattering mode, which can be shown in Fig.5. As we known, E_2 (high) phonon peak is sensitive to residual strain existed in GaN epilayer instead of A_1(TO) or A_1(LO) phonon mode [12,13]. One can see from Fig. 5, phonon peak located at 571.16cm^{-1} and 569.99cm^{-1} are E_2 (high) phonon mode of GaN epifilm for sample A and sample B, respectively, which is caused by differences in the thermal expansion coefficient and lattice constant mismatches induced residual strain between GaN epifilm and sapphire substrate [2,14]. Raman shifts are often employed as a tool for strain assessment in mismatched epitaxial heterojunction films system. The theory phonon shift of E_2 (high) for strain-free GaN is 567.5cm^{-1} [8,15,16], so there are relative shifts of 3.66cm^{-1} and 2.49cm^{-1} relative to the theory value of E_2 (high) phonon mode for sample A and sample B, respectively, which implies that both GaN epifilms are under compressive strain. The relationship between residual strain and the relative Raman shift of E_2 (high) phonon peak is derived from the following equation: $\sigma = \Delta\omega / k$. Where σ is in-plane residual stress, $\Delta\omega$ is the relative Raman shift of E_2 (high) phonon mode, and k is the linear stress-shift coefficient (k=2.40cm^{-1}/GPa) [17] for the biaxial stress system. Thus, the smaller relative phonon shift of E_2 (high) in sample B (2.49cm^{-1}) means that the compressive strain existing in sample B is smaller than that in sample A (3.66cm^{-1}). Therefore, conclusions can be drawn that GaN epilayer grown on patterned sapphire substrate possesses superior crystalline quality than that grown on planar sapphire substrate.

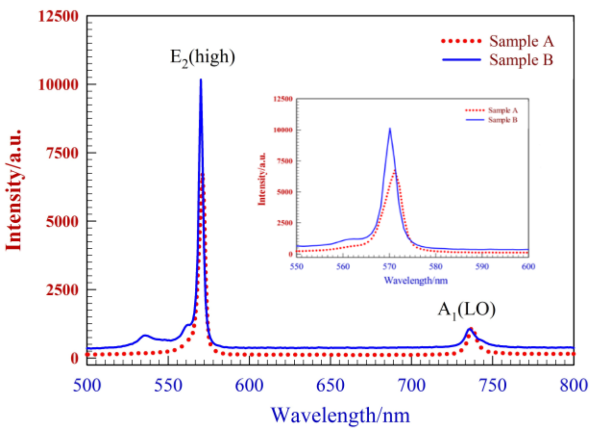


Fig. 5. Raman scattering recorded at room temperature for Sample A and Sample B

We have carried out the PL measurement to examine the optical properties of the two samples at room temperature. The PL spectral of sample A and sample B are shown in Fig. 5 for a comparison. As can be shown, a spectral peak is at 361.66 nm (3.43eV) for sample A and sample B, which is the corresponding band emission peak of GaN epifilms. The luminescence intensity of sample B is much stronger than sample A. It has been noted that a weak subsidiary peak located at 368.92 nm (3.36eV) below the main peak for sample A and sample B, which is closer to bandgap of GaN (3.42eV). Ref.[18,19] have studied and believed that the origin of subsidiary peak is probably ascribed to the inhomogeneity GaN epifilms caused by substrate temperature, V/III ratio during the growth processing at higher temperature.

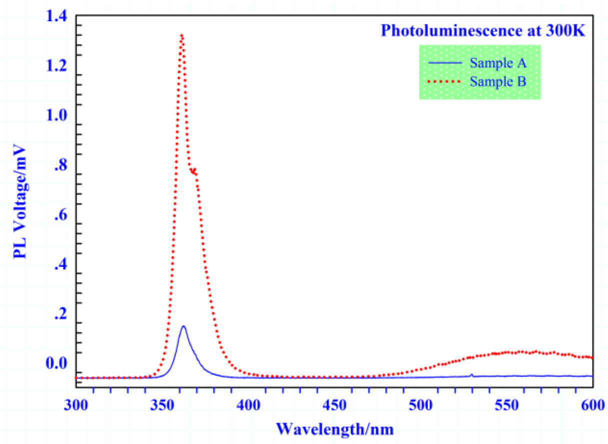


Fig. 6. PL recorded at room temperature for Sample A and Sample B

It should be noted that there exists a so-called yellow luminescence [19,20] (YL, 560nm) appeared in sample B. It is generally recognized that the origin of the YL band centered at 2.2–2.3eV in the photoluminescence spectra of GaN is associated with the vacancies, impurities and complex, and YL band was attributed to a radiative transition from a radiative process, presumably the V_{Ga} adatoms [20]. The most likely reason is the influence of the growth model (for example, GaN epifilms grown on cone-PSS substrate) to the Ga vacancies induced by residual strain in active region during the growth process of multiple quantum wells when GaN epilayer grown on different sapphires. The native Ga vacancy in GaN is reported to be the most probable candidate [21]. The migration length of the Ga adatom is long for patterned sapphire substrate, so the Ga adatom does not obtain sufficient time to achieve the lattice site where it should be, which results in the appearance of Ga vacancies and thus the enhancement of YL band. For planar sapphire substrates, the migration length of the Ga adatom is short due to the appearance of atomic steps, so the YL band of GaN epilayer on vicinal substrates is weak. Be that as it may, quantitative point of view, the photoluminescence intensity of sample B is much stronger than sample B is. So, we have a reason to believe that epitaxial films with higher crystalline quality ease obtaining when LEDs were grown on the patterned sapphire substrate. Therefore, a conclusion is reached that LED with superior optical properties active region with higher crystalline quality, lower dislocation density, smaller RMS of surface, less residual strain when LED is grown on patterned sapphire substrate.

5. Conclusion

In this paper, we have focused on the crystalline quality and luminescence property of GaN epilayer grown on planar sapphire substrate and patterned sapphire substrate. HRXRD, AFM, SEM and Raman scattering and PL have been employed to character crystal quality, surface morphology, residual strain and luminescence properties of GaN epilayer. Results indicated that crystal quality of GaN can be improved, the number of threading dislocation density and residual strain existed in GaN epifilms have reduced when GaN grown on PSS, which is consistent with optical properties.

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References

[1] T. Jiang, S. R. Xu, J. C. Zhang, Y. Xie, Y. Hao, Sci. Rep. **6**, 19955 (2016).
[2] D. H. Wang, Y. Haoe, S. R. Xu, T. H. Xu, D. C. Wang, T. Z. Yao, Y. N. Zhang, J. Alloys Compd. **555,** 311 (2013).
[3] S. R. Xu, Y. Hao, J. C. Zhang, T. Jiang, L. A. Yang, X. L. Lu, Z. Y. Lin, Nano Lett. **13**, 3654 (2013).
[4] S. N. Lee, J. Kim, H. Kim, J. Cryst. Growth **326**, 19 (2011).
[5] N. H. Niu, H. B. Wang, J. P. Liu, N. X. Liu, Y. H. Xing, J. Han, J. Deng, G. D. Shen, J. Cryst. Growth **286**, 209 (2006).
[6] Z. Y. Lin, J. C. Zhang, S. R Xu, Z. B. Chen, S. Y. Yang, T. Kun, X. J. Su, X. F. Shi, Y. Hao, Appl. Phys. Lett. **105**, 8 (2014).
[7] D. G. Zhao, D. S. Jiang, L. L. Wu, L. C. Le, L. Li, P. Chen, Z. S. Liu, J. J. Zhu, H. Wang, S. M. Zhang, J. Alloys Compd. **544**, 94 (2012).
[8] S. R. Xu, Y. Hao, J. C. Zhang, X. W. Zhou, L. A. Yang, J. F. Zhang, H. T. Duan, Z. M. Li, M. Wei, S. G. Hu, J. Cryst. Growth **311**, 3622 (2009).
[9] S. R. Xu, J. C. Zhang, Y. R. Cao, X. W. Zhou, J. S. Xue, Z. Y. Lin, J. C. Ma, F. Bao, Y. Hao, Thin Solid Films **520**, 1909 (2012).
[10] S. R. Xu, P. X. Li, J. C. Zhang, T. Jiang, J. J. Ma, Z. Y. Lin, Y. Hao, J. Alloys Compd. **614**, 360 (2014).
[11] U. Rossow, D. Fuhrmann, M. Greve, J. Bläsing, A. Krost, G. Ecke, N. Riedel, A. Hangleiter, J. Cryst. Growth **272**, 506 (2004).
[12] X. H. Wang, J. Q. Ning, S. J. Xu, H. W. Choi, J. Appl. Phys. **110**, 093111 (2011).
[13] H. C. Lin, Z. C. Feng, M. S. Chen, Z. X. Shen, I. T. Ferguson, W. J. Lu, J. Appl. Phys. **105**, 036102 (2009).
[14] G. Y. Zhang, Z. J. Yang, Y. Z. Tong, Z. X. Qin, X. D. Hu, Z. Z.Chen, X. M. Ding, M. Lu, Z. H. Li, T. J. Yu, L. Zhang, Z. Z. Gan, Y. Zhao, C. F. Yang, Optical Materials **23**, 183 (2002).
[15] M. Z. Peng, L. W. Guo, J. Zhang, X. L. Zhu, N. S. Yu, J. F. Yan, H. H. Liu, H. Q. Jia, H. Chen, J. M. Zhou, J. Cryst. Growth **310**(6), 1088 (2008).
[16] A. Hushur, M. H. Manghnani, J. Narayan, J. Appl. Phys. **106**, 54317 (2009).
[17] J. M. Wagner, F. Bechstedt, Appl. Phys. Lett. **77**, 346 (2000).
[18] Y. Guo, X. L. Liu, H. P. Song, et al. Applied Surface Science **256**, 3352 (2010).
[19] M. A. Reshchikov, Applied Physics Letters **89**, 232106 (2006).
[20] A. Reshchikov, H. Morko, Journal of Applied Physics **97**, 061301 (2005).
[21] Zhiyu Lin, Jincheng Zhang, Shengrui Xu, Zhibin Chen, Shuangyong Yang, Kun Tian, Xujun Su, Xuefang Shi, Yue Hao, Applied Physics Letters **105,** 082114 (2014).

*Corresponding author:wdhyxp@163.com