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High-quality $ZnO/GaN/Al_2O_3$ heteroepitaxial structure grown by LP–MOCVD

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Abstract

High-quality ZnO films were grown on epi-GaN predeposited on c-Al_2O_3 substrates using low-pressure metal-organic chemical vapor deposition (MOCVD). Detailed study of the X-ray diffraction spots and patterns by different diffractometers showed high structural perfection of the zinc oxide layer, which indicated that the growth of ZnO film was strongly c-oriented. The full-width at half-maximum (FWHM) of the ω-rocking curve was 0.39°. Surface morphology of the films studied by AFM showed that the growth of the ZnO film followed the regular hexagonal column structure with about 500 nm grain diameter. Zn and O elements in the deposited $ZnO/GaN/Al_2O_3$ films were investigated and compared by X-ray photoelectron spectroscopy (XPS), in which the dissociative O and Zn atom peak was hardly observed. The ratio of O/Zn atoms of the film was about 1 with O-rich. Photoluminescence spectra of the ZnO films grown on epi-GaN showed dominating exciton emission peak, and the deep-level emission which was obvious on ZnO/Al_2O_3 film had hardly been observed.
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1. Introduction

ZnO, a wide direct band gap semiconductor with a hexagonal wurtzite structure, is an attractive material for many applications, such as

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opto-electronics devices [1], SAW [2] and transparent electrode [3,4], etc. Especially the ultraviolet lasing has been observed in ZnO thin films at room temperature [5–8], which attracts much more attention in this area.

ZnO-based heteroepitaxial structures are usually grown on sapphire substrates, despite a considerable lattice mismatch: Al_2O_3 ($a = 4.754$ Å, $c = 12.99$ Å); ZnO ($a = 3.250$ Å, $c = 5.213$ Å). This shows that it is difficult to grow (0 0 0 1) oriented zinc oxide layers on the sapphire substrates by conventional methods.

Apparently, a close matching between the ZnO and GaN ($a = 3.189$ Å, $c = 5.185$ Å); crystal lattices can be used for obtaining high-quality heteroepitaxial structures of ZnO on GaN, so epitaxial GaN(epi-GaN) grown Al_2O_3 is now available as a substrate to grow ZnO films.

This paper reports the growth of high-quality ZnO layers on closely lattice-matched epi-GaN/Al_2O_3 by LP–MOCVD. We have also evaluated the structural perfection with X-ray spectra, AFM and XPS analysis. The photoluminescence (PL) spectra of the heteroepitaxial structures obtained are also studied.

2. Experimental procedure

The epitaxial layers of (0 0 0 1)GaN on (0 0 0 1)Al_2O_3 were obtained by MOCVD using a low-temperature buffer layer technique [9]. The GaN layer thickness on sapphire was about 3 μm. These structures were transferred into rotating disk vertical reactor of LP–MOCVD without preliminary cleaning and polishing procedures. The source materials are diethylzinc (DEZn) and O_2, both with high purity of 99.999%. The carrier gases were argon and nitrogen, argon (saturated with DEZn vapor) flow: 1.50 sccm, oxygen flow: 5 sccm, nitrogen flow: 10 sccm; gas pressure during growth: 0.65 Pa; After heating at 700°C for 10 min, ZnO films were then deposited at substrate temperature of 600°C for 40 min. The as-grown film was further annealed in oxygen plasma atmosphere at 700°C for 10 min. The final ZnO layer thickness was about 3 μm. For comparative analysis, ZnO film grown directly on Al_2O_3 substrate under the same condition was also prepared.

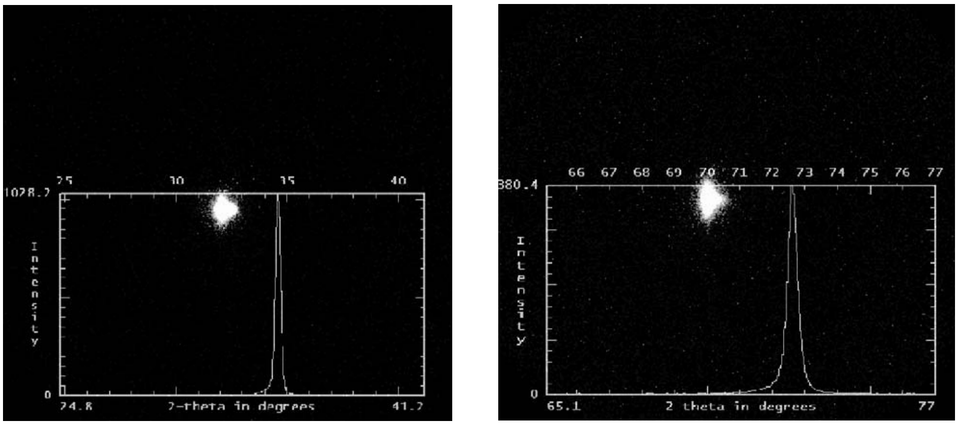
We used SIEMENS D5005 X-ray diffractometer, D8/C2 X-ray diffractometer and Rigaku DMAX 2400 X-ray diffractometer to investigate crystal quality and integrality. Surface morphology was investigated by Digital Nanoscope IIIa AFM with normal silicon nitride tip in contact mode. PL spectrum was measured by 325 nm He–Cd laser. The PL signal from the sample was filtered by a monochromator and picked up by a CCD detector. The power arriving at sample was about 3 mW with a beam diameter of 200 μm.

3. Results and discussion

X-ray diffraction measurement of $\theta - 2\theta$ scan by SIEMENS D8/C2 X-ray diffractometer was performed on ZnO film as shown in Fig. 1. Dominant diffraction spots at 2θ 34.6° which owed to ZnO (0 0 0 2) peak and 2θ 72.6° which owed to ZnO (0 0 0 4) peak could be observed, respectively. The asymmetry of the spots implied that the ZnO spot on the right-hand side and GaN spot on the left-hand side were overlapping because of the close crystal structure. The small size of the spots indicated perfect crystal quality of the ZnO/GaN/Al_2O_3 film.

Fig. 2 showed a typical diffraction pattern of the ZnO layer by SIEMENS D5005 diffractometer and Rigaku DMAX 2400 X-ray diffractometer. The spectra showed clearly pronounced (0 0 0 l) orientation in the absence of reflections characteristic of the other orientations. Note that the (0 0 0 2) ZnO and GaN peaks were not resolved because of the close crystal structures of these materials. ZnO (0 0 0 4) peak shown in inset and (0 0 0 6) peak could also be observed. The XRD $2\theta - \omega$ scan was also performed as shown in inset. Study of the rocking curve of the (0 0 0 2) reflection showed that the FWHM of the combined peak was 0.39°, which indicated that the mosaicity of the film was relatively small and better crystal quality was obtained.

The surface morphology and transverse section of the film were shown in Fig. 3. We observed many regular hexagonal grain particles in the



(a) (b)

Fig. 1. X-ray diffraction spots of $ZnO/GaN/Al_2O_3$ film by D8/C2 X-ray diffractometer. (a) ZnO (0 0 0 2) peak and (b) ZnO (0 0 0 4) peak.

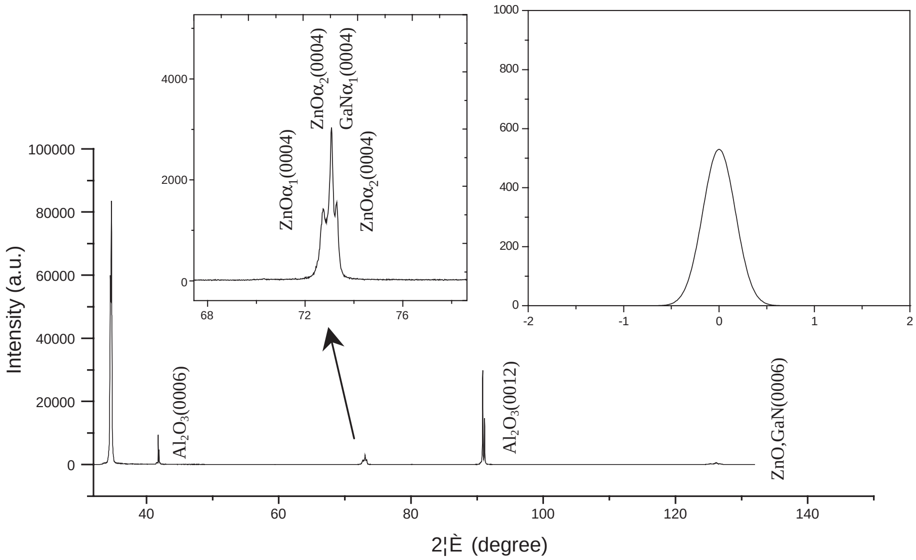


Fig. 2. X-ray diffraction spectra of $ZnO/GaN/Al_2O_3$ film by SIEMENS D5005 X-ray diffractometer. The ω-rocking curve shown in the inset by Rigaku DMAX 2400 X-ray diffractometer.

AFM image. The average grain diameter of the film was about 500 nm. It proved that the regular hexagonal column growth of the ZnO film strictly followed the hexagonal structure of the GaN epilayer. At the same time, the obvious and orderly section interface was observed by SEM image in Fig. 3(b) for our sample.

X-ray photoelectron spectra (XPS) were performed to investigate the elements and stoichiometry of ZnO film grown on epi-GaN layer. In order to avoid the influence of surface absorption in the atmosphere, Ar ion etching was performed for about 30 min with an etching rate of $0.5\,nm\,min^{-1}$. For comparative study of the composition of the ZnO film, the ZnO film directly grown on Al_2O_3 substrate with the same growth condition was tested too. Fig. 4(a) was the surface XPS spectrum of ZnO film directly grown on

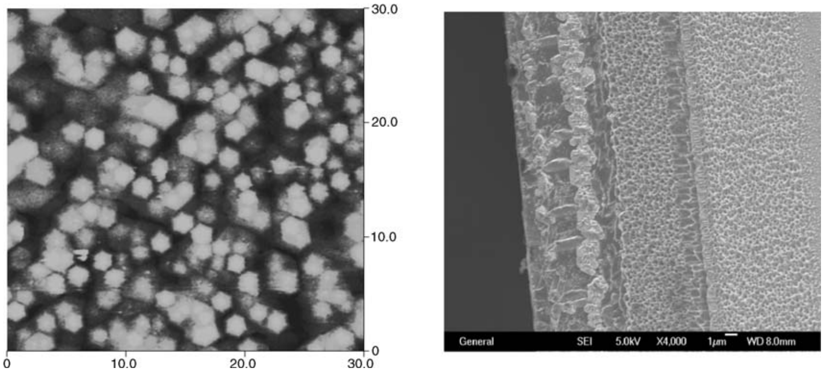


Fig. 3. The AFM image (left) and interface SEM image (right) of $ZnO/GaN/Al_2O_3$ film.

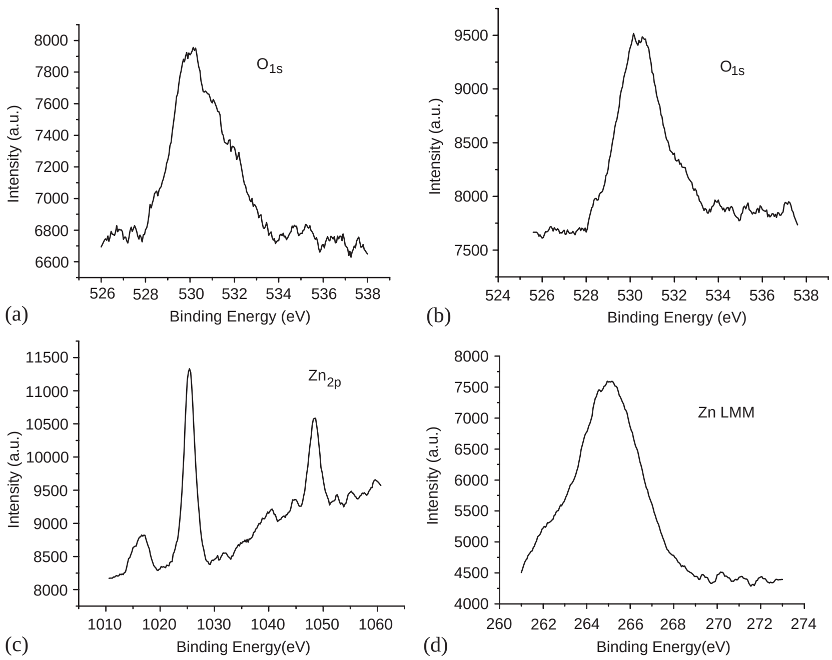


Fig. 4. XPS spectrum of ZnO film (a) O_{Is} peak of ZnO/Al_2O_3 film (b) O_{Is} peak of $ZnO/GaN/Al_2O_3$ film; (c) Zn_{2p} peak of $ZnO/GaN/Al_2O_3$ film and (d) Zn LMM peak of $ZnO/GaN/Al_2O_3$ film.

Al_2O_3 substrate. Beside the primary O_{1s} peak in 530.2 eV which owed to the O element of Zn–O bond, the dissociative or free O atom peak in 532 eV due to the interior defect was also observed, which disappeared in Fig. 4(b) for the $ZnO/GaN/Al_2O_3$ sample. Zn_{2p} peak due to Zn–O bond in 1021.6 eV was clearly seen from Fig. 4(c). In Zn LMM spectra from Fig. 4(d), except the main peak, the dissociative Zn atom or Zn interstitials peak in 262 eV was hardly observed. It implied that the Zn and O elements in ZnO film existed mostly with the Zn–O bond. From the statistical results XPS, we could obtain that atom ratio of Zn/O was near 1:1.03 which changed from Zn-rich of the previous result to O-rich [10].

Of special interest was to study the UV photoluminescence (PL) of the epitaxial ZnO layers, which could provide additional information on the crystal structure perfection of samples [11,12]. PL spectra for $ZnO/GaN/Al_2O_3$ and ZnO/

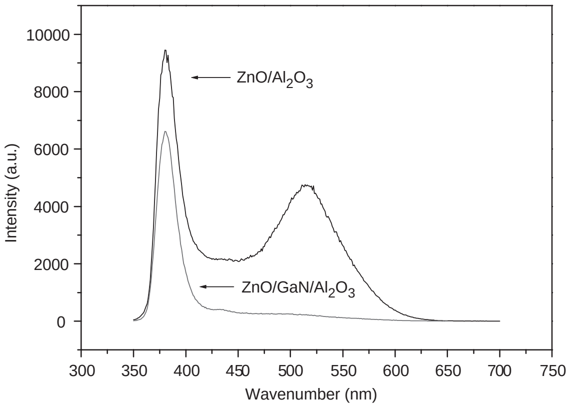


Fig. 5. Room-temperature PL spectra of $ZnO/GaN/Al_2O_3$ film and ZnO/Al_2O_3 film.

Al_2O_3 films carried out at room temperature were shown in Fig. 5. Strong ultraviolet (UV) emission coming from exciton emission could be observed in both samples. More detailed study would be carried out to analyze the exciton feature later. However, deep-level emission at 520 nm was observed in ZnO/Al_2O_3 film. In general, this deep green emission was believed to come from oxygen vacancies, interstitial zinc or zinc vacancies [13,14]. From the spectrum of $ZnO/GaN/Al_2O_3$ film, the absence of the deep-level emission peak indicated that the ZnO film grown on epi-GaN showed better optical quality and fewer interior defects. This was also in agreement with the result of our XPS analysis.

4. Conclusion

High-quality ZnO film was successfully deposited on GaN/Al_2O_3 substrate by LP-MOCVD. XRD spectra showed that ZnO films were clearly c-oriented with better crystal quality. The regular column growth mode was observed by AFM and SEM study. Through the analysis of XPS spectra, the interior dissociative O and Zn peaks for $ZnO/GaN/Al_2O_3$ film were not observed. From PL spectra, the sharp exciton emission peak near band gap was observed for our samples. Compared with the spectrum of the ZnO/Al_2O_3 film grown on the same condition, deep-level emission peak due to the interior defect disappeared. In our experiment, the structure and optical quality of ZnO film were both optimized with GaN buffer layer.

Acknowledgements

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References

[1] S. Jeong, B. Kim, B. Lee, Appl. Phys. Lett. 16 (2003) 2625.
[2] M. Kazunori, K. Yasushi, K. Yukinobu, et al., Jpn. J. Appl. Phys. 36 (11A) (1997) 1453.
[3] G. Carlotti, G. Socino, Appl. Phys. Lett. 51 (23) (1987) 1889.
[4] J. Koike, K. Shimoe, H. Ieki, et al., Jpn. J. Appl. Phys. 32 (5b) (1993) 2337.
[5] Z. Tang, G. Wong, P. Yu, et al., Appl. Phys. Lett. 72 (25) (1998) 3270.
[6] Y. Chen, D. Bagnall, Z. Zhu, et al., J. Crystal Growth 181 (1,2) (1997) 165.
[7] D. Bagnall, Y. Chen, Z. Zhu, et al., Appl. Phys. Lett. 70 (17) (1997) 2230.
[8] Y. Segawa, A. Ohtomo, M. Kawasaki, et al., Phys. Stat. Sol. 202 (2) (1997) 669.
[9] W.V. Lundin, B.V. Pushnyi, A.S. Usikov, et al., Inst. Phys. Conf. Ser. 155 (1997) 319.
[10] B.M. Ataev, A.D. Bagamadova, V.V. Mamedov, Thin Solid Films 283 (1996) 5.
[11] Y.T. Zhang, G.T. Du, D.L. Liu, et al., J. Crystal Growth 243 (2002) 439.
[12] X.Q. Wang, S.R. Yang, J.Z. Wang, et al., J. Crystal Growth 226 (2001) 123.
[13] D.C. Reynolds, D.C. Look, B. Jogni, Solid State Commun. 101 (1997) 643.
[14] K. Vanheusden, W.L. Warren, C.H. Seager, J. Appl. Phys. 79 (1996) 7983.