IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Comparative Study of Properties of $ZnO/GaN/Al_2O_3$ and ZnO/Al_2O_3 Films Grown by Low-Pressure Metal Organic Chemical Vapour Deposition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 Chinese Phys. Lett. 20 2045

(http://iopscience.iop.org/0256-307X/20/11/041)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 159.226.165.151
The article was downloaded on 05/09/2012 at 06:21

Please note that terms and conditions apply.

Comparative Study of Properties of $ZnO/GaN/Al_2O_3$ and ZnO/Al_2O_3 Films Grown by Low-Pressure Metal Organic Chemical Vapour Deposition *

ZHAO Bai-Jun(赵佰军)[1], YANG Hong-Jun(杨洪军)[1], DU Guo-Tong(杜国同), MIAO Guo-Qing(缪国庆)[2], YANG Tian-Peng(杨天鹏)[1], ZHANG Yuan-Tao(张源涛)[1], GAO Zhong-Min(高仲民)[3], WANG Jin-Zhong(王金忠)[1], FANG Xiu-Jun(方秀军)[1], LIU Da-Li(刘大力)[1], LI Wan-Cheng(李万成)[1], MA Yan(马燕)[1], YANG Xiao-Tian(杨晓天)[1], LIU Bo-Yang(刘博阳)[1]

[1] *State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jinlin University, Changchun 130023*

[2] *Open Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021*

[3] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130023*

(Received 23 June 2003)

ZnO films were deposited by low-pressure metal organic chemical vapour deposition on epi-GaN/Al_2O_3 films and c-Al_2O_3 substrates. The structure and optical properties of the $ZnO/GaN/Al_2O_3$ and ZnO/Al_2O_3 films have been investigated to determine the differences between the two substrates. ZnO films on GaN/Al_2O_3 show very strong emission features associated with exciton transitions, just as ZnO films on Al_2O_3, while the crystalline structural qualities for ZnO films on GaN/Al_2O_3 are much better than those for ZnO films directly grown on Al_2O_3 substrates. Zn and O elements in the deposited $ZnO/GaN/Al_2O_3$ and ZnO/Al_2O_3 films are investigated and compared by x-ray photoelectron spectroscopy. According to the statistical results, the Zn/O ratio changes from Zn-rich for ZnO/Al_2O_3 films to O-rich for $ZnO/GaN/Al_2O_3$ films.

PACS: 78.55.Cr, 87.64.Bx, 82.80.Pv

There is an increasing demand for photonic devices in blue and ultraviolet ranges.[1,2] ZnO, with a wide direct band-gap of 3.37 eV at room temperature, is an attractive material for many applications, such as opto-electronics devices,[3] surface acoustic wave[4] and transparent electrode,[5,6], etc. In particular, the ultraviolet lasing has been observed in ZnO thin films at room temperature,[7−10] which attracts much attention in this area.

ZnO-based heteroepitaxial structures are usually grown on sapphire substrates. Although ZnO films grown on Al_2O_3 have shown promising optical properties, the crystal quality of ZnO layers still needs improvement due to the presence of high density of defects nearly at the interface[11] as a consequence of a large lattice mismatch of 18% in the ZnO/Al_2O_3 heterostructure.

Obviously, a close matching between the ZnO and GaN 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.

In this Letter, we report the examination of relationship between the crystalline qualities and optical features determined by comparing the properties of ZnO layers on epi-GaN/Al_2O_3 and Al_2O_3 by low-pressure metal organic chemical vapour deposition (LP-MOCVD). The film properties were determined by x-ray diffraction (XRD), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) spectroscopy.

In the experiment, the epitaxial layers of (0001) GaN on (0001)Al_2O_3 were obtained by metal organic chemical vapour deposition (MOCVD) using a low-temperature buffer layer technique.[12] The GaN layer thickness on sapphire was about 3 μm. These structures were transferred into rotating disc vertical reactor of LP-MOCVD without preliminary cleaning and polishing procedures. The source materials were Diethylzinc (DEZn) and O_2, both with high purity of 99.999%, the carrier gases were argon and nitrogen. The growth condition included 1.50 sccm of argon (saturated with DEZn vapour) flow, 5sccm of oxygen flow, 10 sccm of nitrogen flow, 0.65 Pa of reactor gas pressure. After heating at 700°C for 10 min, ZnO films were then deposited at the 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, the ZnO film was grown directly on the Al_2O_3 substrate under the same growth condition.

We used a SIEMENS D8/C2 x-ray diffractometer and a Rigaku DMAX 2400 x-ray diffractometer to

* Supported by the National Natural Science Foundation of China under Grant Nos 60176026 and 60177007, and the National High Technology Program of China under Grant No 2001AA311130.

©2003 Chinese Physical Society and IOP Publishing Ltd

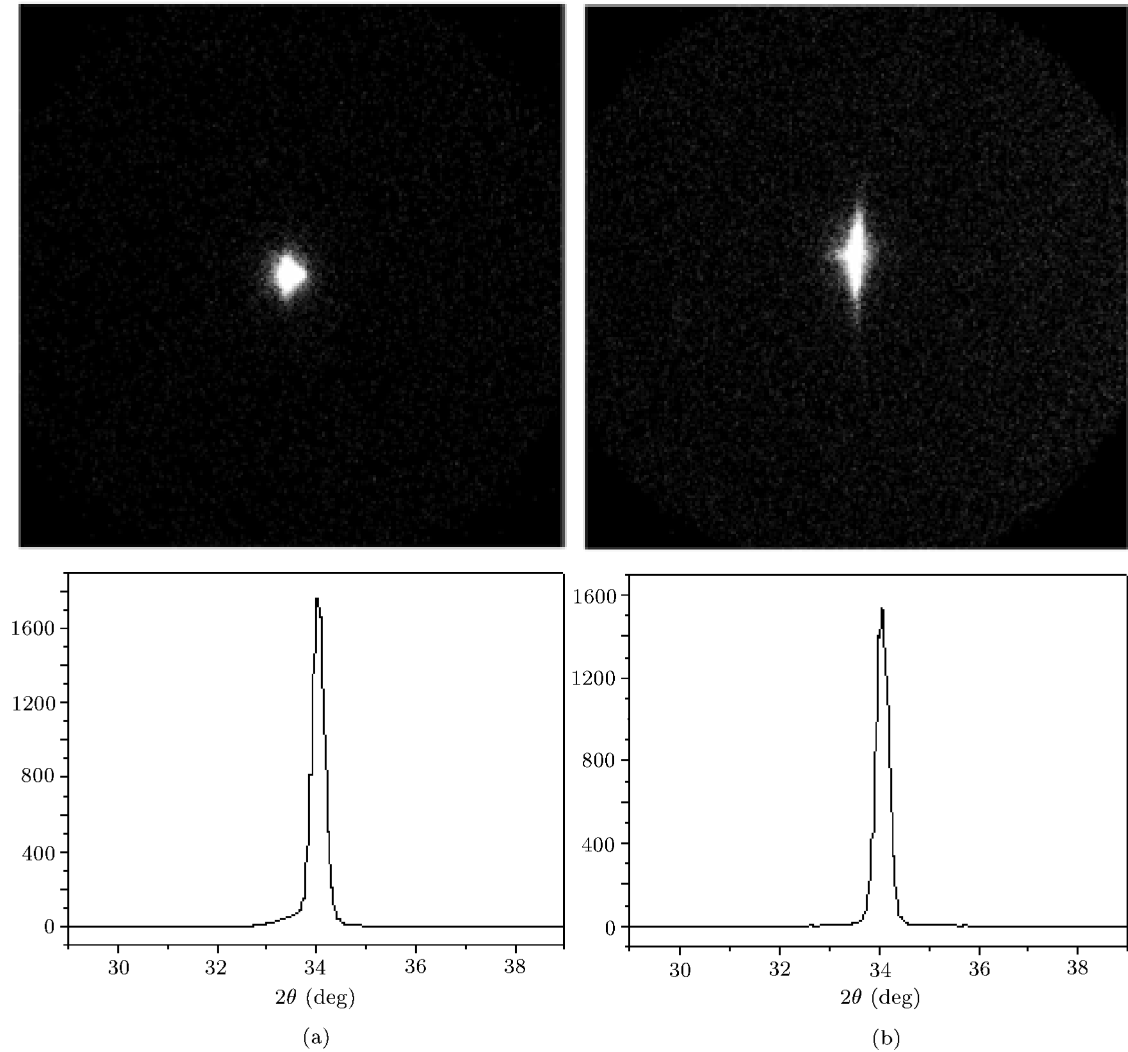

Fig. 1. XRD spectra and spots of (a) $ZnO/GaN/Al_2O_3$ film and (b) ZnO/Al_2O_3 film.

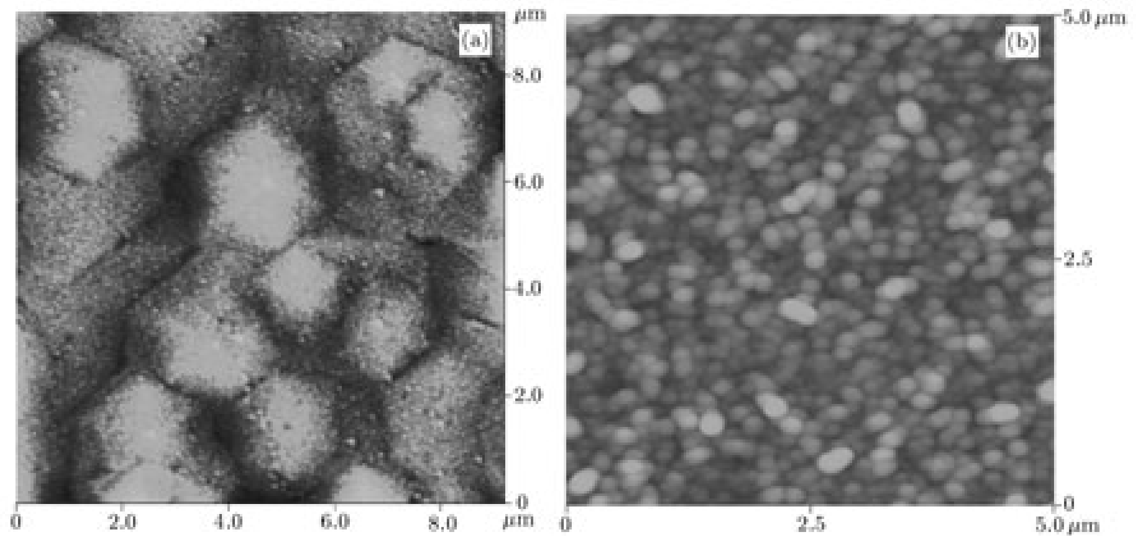

Fig. 2. Surface AFM image of (a) $ZnO/GaN/Al_2O_3$ film and (b) ZnO/Al_2O_3 film.

investigate the crystal quality and integrality. Surface morphology was investigated by Digital Nanoscope IIIa AFM with normal silicon nitride tip in the contact mode. The PL spectrum was measured by a 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 the sample was about 3 mW with a beam diameter of 200 μm. For the low-temperature measurement, the sample was mounted in a closed-cycle refrigerator.

x-ray diffraction measurement of θ–2θ scan by the SIEMENS D8/C2 diffractometer was performed on ZnO films as shown in Fig. 1. Dominant diffraction spots at $2\theta = 34.6^\circ$ due to the ZnO (0002) peak could be observed respectively. It is obvious that the spot size of the ZnO/GaN/Al_2O_3 film was smaller than that of the ZnO/Al_2O_3 film, which indicates much better crystal quality for the ZnO/GaN/Al_2O_3 film. The asymmetry of spot for the ZnO/GaN/Al_2O_3 film implies that the ZnO spot on the right-hand side and GaN spot on the left-hand side were overlapping due to the close crystal structure. The XRD $2\theta - \omega$ scan was also performed by the DMAX 2400 x-ray diffractometer. The rocking curve of the (0002) reflection showed that the FWHM of the peak was 0.39° for the ZnO/GaN/Al_2O_3 film and 0.6° for the ZnO/Al_2O_3 film, which indicates that the mosaicity of the ZnO/GaN/Al_2O_3 film was really smaller and the crystal quality was better.

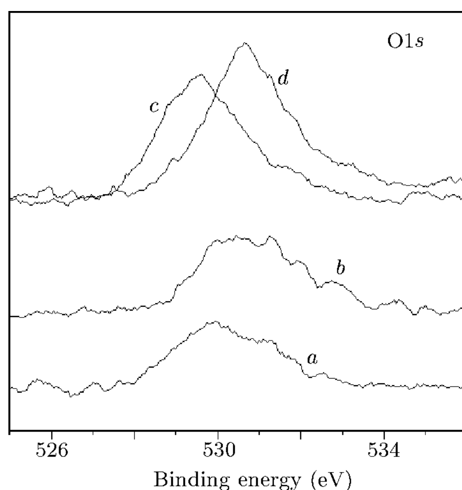

Fig. 3. XPS spectra of ZnO/GaN/Al_2O_3 film (*a*) before and (*c*) after the, etching, and ZnO/Al_2O_3 film (*b*) before and (*d*) after the, etching.

The AFM measurements were performed to study the differences between the two epitaxial ZnO films in the surface morphology. Figure 2(a) shows the AFM images for the ZnO/GaN/Al_2O_3 film scanned over an area of $10 \times 10\,\mu$m. We can find many regular hexagonal grain particles in the AFM image. The average grain diameter of the film was about 1 μm. Figure 2(b) shows the image of the ZnO/Al_2O_3 film scanned over an area of $5 \times 5\,\mu$m. The mean island shape grain particles with 50-nm sizes were found on the surface. It can be concluded that the regular hexagonal column growth of the ZnO film strictly followed the hexagonal structure of the GaN epi-layer, which was more excellent than the island growth of ZnO film on the Al_2O_3 substrate.

x-ray photoelectron spectra (XPS) were performed to investigate the elements and stoichiometry of the ZnO film grown on the epi-GaN layer and Al_2O_3. 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}. Curves *a* and *c* in Fig. 3 represent the O 1*s* spectra of the ZnO/GaN/Al_2O_3 films before and after, etching; curves *b* and *d* in Figs. 3 for ZnO/Al_2O_3 films before and after, etching. We know that the typical O 1*s* peak in the ZnO film can be considered as the combination of three nearly Gaussian peaks, centred at 530, 531.25, 532.4 eV, respectively.[13] The O 1*s* spectrum at 530 eV is attributed to O^{2-} ions on the wurtzite structure of hexagonal Zn^{2+} ion array, the O 1*s* spectrum at 531.25 eV is associated with O^{2-} ions in the oxygen deficient regions, which is related to the concentration of oxygen vacancies, and the high binding energy component located at 532.4 eV is usually attributed to the presence of loosely bound oxygen on the surface of the ZnO film. We could find from Fig. 3 that O 1*s* shifted toward the low-energy direction for the ZnO/GaN/Al_2O_3 film and the peak at 531.25 eV was difficult to be observed. This implies that the Zn and O elements in the ZnO film existed mostly with the Zn-O bond. From the statistical results XPS, we could obtain that the atomic ratio of Zn/O was nearly 1:1.03 for the ZnO/GaN/Al_2O_3 film and 1:0.95 for the ZnO/Al_2O_3 film.

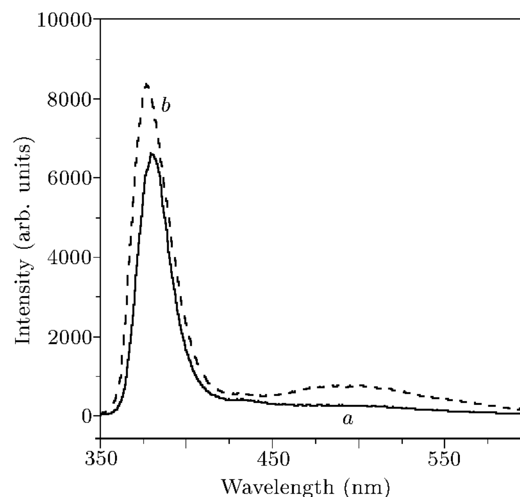

Fig. 4. PL spectrum of (*a*) ZnO/GaN/Al_2O_3 film and (*b*) ZnO/Al_2O_3 film.

Optical properties of ZnO films were characterized at room temperature by PL spectroscopy in Fig. 4. Strong ultraviolet (UV) emission coming from exciton emission could be observed in both the samples. However, the deep-level emission at 520 nm was observed in the ZnO/Al_2O_3 film. In general, this deep green emission is believed to come from oxygen vacancies, interstitial zinc or zinc vacancies.[14–16] From the spectrum of the $ZnO/GaN/Al_2O_3$ film, the absence of the deep-level emission peak indicates that the ZnO film grown on epi-GaN has better optical quality and fewer interior defects.

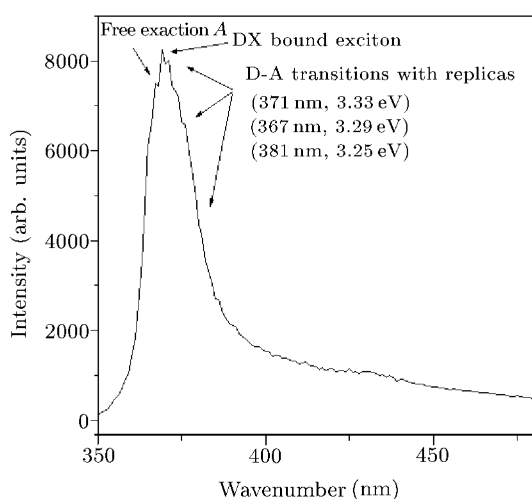

Fig. 5. Low-temperature PL spectrum of $ZnO/GaN/Al_2O_3$ film at 20 K.

For further study of the optical properties, the PL measurement at 20 K was performed on the $ZnO/GaN/Al_2O_3$ film. As shown in Fig. 5, the peak energy positions at 3.376 and 3.361 eV correspond to the A-band free exciton emission and the $D^\circ X$ bound exciton transition. The peak at 3.33 eV may pertain to the donor-acceptor pair transition while the peaks at 3.29 and 3.25 eV might be ascribed to LO phonon replicas. The observation of the A-exciton transition and its high intensity showed the better quality of the $ZnO/GaN/Al_2O_3$ film.

In summary, we have fabricated high-quality epitaxial ZnO/GaN heterostructures on sapphire. Comparative studies of XRD, AFM, XPS and PL spectra of ZnO/Al_2O_3 films implies that the $ZnO/GaN/Al_2O_3$ film shows substantial improvement in crystal quality, growth mode, defect density and luminescence properties. In addition, the matching of thermal and optical properties and the compatibility of these heterostructures provide new opportunities for the fabrication of hybrid ZnO/GaN optoelectronic devices on sapphire.

References

[1] Zhou J and Zhang G Y 2002 *Chin. Phys. Lett.* **19** 599
[2] Pan Z, Li L H, Xu Y Q, Zhang W, Lin Y W, Zhang R K, Zhong Y and Ren X M 2001 *Chin. Phys. Lett.* **18** 1249
[3] Jeong S, Kim B and Lee B 2003 *Appl. Phys. Lett.* **16** 2625
[4] Kazunori M, Yasushi K, Yukinobu K, Koji Y, Masanobu K and Azuma S 1997 *Jpn. J. Appl. Phys.* **36** 1453
[5] Carlotti G and Socino G 1987 *Appl. Phys. Lett.* **51** 1889
[6] Koike J, Shimoe K and Ieki H 1993 *Jpn. J. Appl. Phys.* **32** 2337
[7] Tang Z, Wong G, Yu P, Kawasaki M, Ohtomo A, Koinuma H and Segawa Y 1998 *Appl. Phys. Lett.* **72** 3270
[8] Chen Y, Bagnall D, Zhu Z, Sekiuchi T, Park K, Hiraga K, Yao T, Koyama S, Shen M and Goto T 1997 *J. Cryst. Growth* **181** 165
[9] Bagnall D, Chen Y, Zhu Z, Yao T, Koyama S, Shen M and Goto T 1997 *Appl. Phys. Lett.* **70** 2230
[10] Segawa Y, Ohtomo A and Kawasaki M 1997 *Phys. Status Solidi* B **202** 669
[11] Chen Y F, Bagnall D M and Ko H J 1998 *J. Appl. Phys.* **84** 3912
[12] Lundin W V, Pushnyi B V and Usikov A S 1997 *Inst. Phys. Conf. Ser.* **155** 319
[13] chen M, Wang X and Yu Y H 2000 *Appl. Surf. Sci.* **158** 134
[14] Wang X Q, Yang S R, Wang J Z, Li M T, Jiang X Y, Du G T, Liu X and Chang R 2001 *J. Cryst. Growth* **226** 123
[15] Wang J Z *et al* 2002 *Chin. Phys. Lett.* **19** 581
[16] Vanheusden K, Warren W L and Seager C H 1996 *J. Appl. Phys.* **79** 7983