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Atmospheric pressure MOCVD growth of high-quality ZnO films on GaN/Al_2O_3 templates

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Abstract

In this paper, we present the epitaxial growth of high-quality ZnO thin films on GaN/c-Al_2O_3 templates by atmospheric pressure metal organic chemical vapor deposition (MOCVD) using deionized water (H_2O) and diethyl zinc (DEZn) as the O and Zn sources, respectively. Surface morphology of the films studied by metal-phase interference microscopy and AFM showed that the growth of the ZnO films followed the regular hexagonal columnar structure with about 19 μm grain diameter. High-resolution X-ray double-crystal diffraction was used to investigate the structural properties of the as-grown films. The FWHMs of the (0 0 0 2) and (1 0 $\bar{1}$ 2) ω-rocking curves were 182 and 358 arcsec, respectively, indicating the small mosaicity and low dislocation density of the films. The optical properties of the films were investigated by room temperature photoluminescence and temperature-dependent PL spectra. Free excitons X_A and the $n = 2$ state of FX_A can be clearly observed at 3.375 and 3.419 eV at 10 K, respectively. The domination of the free exciton and the appearance of its four replicas strongly indicate the high quality of the film.

PACS: 75.55.C; 87.64.Bx; 78.55.−m

Keywords: A1. AFM; A1. Photoluminescence; A1. X-ray diffraction; A3. MOCVD; B2. ZnO/GaN/Al_2O_3

1. Introduction

Due to its wide gap of 3.37 eV and its ultraviolet lasing at room temperature (RT) [1] and its large exciton binding energy of 60 meV [2], ZnO has many potential applications in short wavelength light-emitting devices, such as UV and blue LED/LDs. Many growth techniques for single-crystalline ZnO films have been studied, such as molecular beam epitaxy [3], metalorganic chemical vapor deposition (MOCVD) [4], RF magnetron

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sputtering [5], and pulsed laser deposition [6]. Among these techniques, MOCVD has many advantages for bulk production and has been proven to be suitable for growth of many electronic and optoelectronic materials. In addition, investigations revealed that atmospheric pressure growth of GaN films usually yield larger grain size and higher mobility than low-pressure growth [7–9]. So AP-MOCVD will be a possible way to improve the crystalline quality of ZnO film. Many growths of ZnO films grown by LP-MOCVD have been reported, but only a few investigations on AP-MOCVD growth of high-quality ZnO films have been reported [10–13].

Recently, there has been great progress in the growth of ZnO thin films. But applicable ZnO optoelectronic devices have not yet been fabricated, mainly because sufficiently effective p-type ZnO thin films have not been obtained till now. To solve the p-type doping problems, it is necessary to grow higher-quality ZnO thin films. One of the key issues to grow high-quality ZnO thin films is to find a lattice-matched substrate. Although ZnO bulk crystal can be obtained now, it is very expensive and its size is small. Therefore, heteroepitaxy is still the most used method. GaN ($a = 3.189$ Å, $c = 5.185$ Å) and ZnO ($a = 3.2498$ Å, $c = 5.2066$ Å) [14] have close lattice constants (the mismatch is less than 2%) and a small difference between the in-plane linear thermal expansion coefficients ($\alpha_{GaN} = 5.59 \times 10^{-6}$ and $\alpha_{ZnO} = 6.51 \times 10^{-6}\,K^{-1}$) [15], so GaN is possibly a suitable substrate for the growth of ZnO epitaxial layers. At present, due to the lack of low-cost GaN bulk crystal and the availability of a technique of growing high-quality GaN films on Al_2O_3 substrate, it is a feasible method to use the GaN epilayer as the buffer layers on other substrates for the growth of ZnO epitaxial layers. Since Vispute et al. [16] first reported the growth of ZnO films on epi-GaN/sapphire (0 0 0 1) by PLD, there have been a few reports on the growth of ZnO films using the GaN epilayer as the buffer layers on other substrates by RF magnetron sputtering [17], MBE [18] and MOVPE [19].

In this paper, we report the epitaxial growth of high-quality ZnO thin film on epi-GaN /c-Al_2O_3 templates by atmospheric pressure metalorganic chemical vapor deposition.

2. Experimental procedure

ZnO thin films were deposited by a home-built vertical atmospheric pressure MOCVD system with a rotating disk reactor (see Fig. 1). We have reported the epitaxial growth of ZnO thin films on c-Al_2O_3 (0 0 0 1) substrates by our home-built vertical atmospheric pressure MOCVD system [20]. The MOCVD growth of GaN/Al_2O_3 templates on 2 in. c-Al_2O_3 (0 0 0 1) substrates was performed in a Thomas Swan close-coupled showerhead (CCS) MOCVD reactor system. During the growth, trimethyl gallium (TMGa) and ammonia (NH_3) were used as the source materials of Ga and N, respectively. The thickness of the GaN layer was about 2 μm. These structures were transferred into our rotating disk vertical reactor of AP-MOCVD without the preliminary cleaning and polishing procedures. We used deionized water (H_2O) ($\rho = 18.2$ MΩ cm) and 6 N-purity DEZn as the O and Zn sources, respectively, and 7 N-purity nitrogen as the carrier gas. Before growth, the GaN/Al_2O_3 templates were thermally cleaned at 850 °C for 20 min. Typical growth conditions were as follows: the reactor-chamber pressure was 760 Torr. A two-step growth process was adopted. In the first step, a 150 Å ZnO buffer layer was grown at 200 °C using DEZn and H_2O at flow rates of 813 μmol/min and 0.039 mol/min, respectively. Then the buffer layer was processed

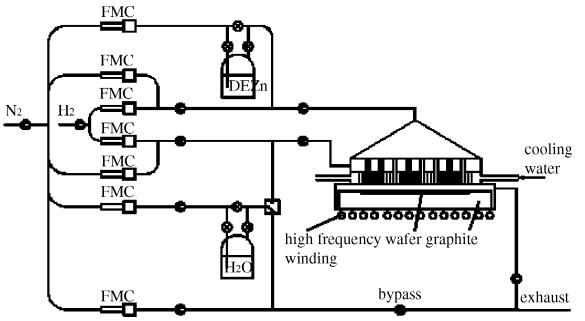

Fig. 1. Schematic sketch of the AP-MOCVD system for growth of ZnO.

at 800 °C for 5 min for re-crystallization. In the second step, the main ZnO epitaxial layer was deposited under the growth temperature of 680 °C using DEZn and H_2O at flow rates of 0.011 and 0.183 mol/min, respectively. The total carrier gas flow rate was about 15 000 sccm. The growth rate of the main ZnO layer was 4 μm/h, resulting in the total thickness of 2 μm. For comparative analysis, a ZnO film grown directly on a c-Al_2O_3 (0 0 0 1) substrate under the same conditions was also prepared.

The microscopic image of the ZnO film was observed by metal-phase interference microscopy (OLYMPUS, BX51). Surface morphology of the ZnO layers was studied by atomic force microscopy (AFM) in a contact mode using a Chinese Benyuan Nano Instrument 3100 system. Crystal perfection of the samples was examined by high-resolution double-crystal X-ray diffractometry (HRXRD) (QC200, BEDE Instruments, UK). The Cu K_α line ($\lambda = 1.54056$ Å) was used as the source, and Ge (0 0 4) was used as the monochromator. Photoluminescence (PL) of the film was measured under RT and at 10 K using the 325 nm line of a He–Cd laser (8 mW) as the excitation source.

3. Results and discussion

The as-grown films were transparent and have mirror-like surfaces. Fig. 2 shows the microscopic image of a typical ZnO film at ×200 magnification by metal-phase interference microscopy. The average grain diameter of the film was about 18 μm. We observed many regular hexagonal grain particles in the microscopic image. It proved that the regular hexagonal column growth of the ZnO film strictly followed the hexagonal structure of the GaN epilayer. Fig. 3 shows the AFM image of a typical sample for a scan area of 25 μm × 25 μm. Hexagonal-like growths can be clearly seen on the surface. The grain diameter of the film was about 19 μm, much larger than reported grain size for a ZnO film deposited by MBE [21], PLD [22] and LP-MOCVD [23]. The root mean square (RMS) roughness as determined by AFM (25 μm × 25 μm) of the film surface was about 4.5 nm.The mechanism for the formation of large grain size by AP-MOCVD has been studied by several investigations [7,8]. It is believed that the nucleation density on the substrate for AP growth is less than that for low-pressure growth. So for AP-MOCVD, the lateral growth for nucleation will proceed a long time before they coalesce, thus forming large grains.

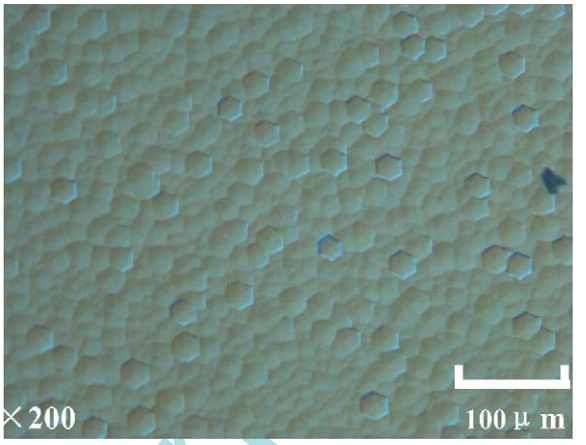

Fig. 2. Interference Micrograph of the surface of ZnO/GaN/Al_2O_3 film.

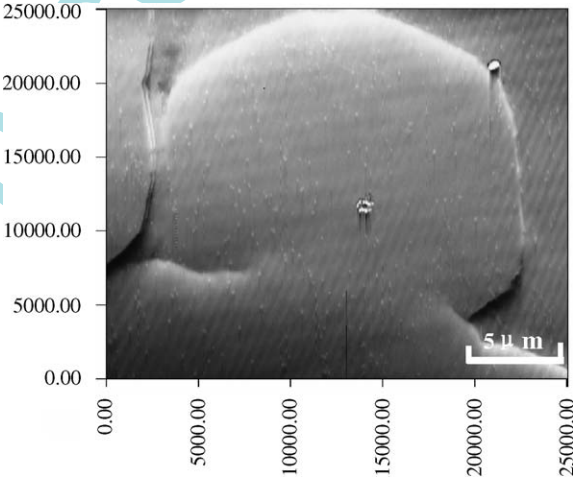

Fig. 3. AFM image of ZnO/GaN/Al_2O_3 film (25 μm × 25 μm).

It is well known that the X-ray diffraction is complementary to the transmission electron microscopy (TEM) and etch pit densites (EPD)

methods, because it is non-destructive and can be used to determine dislocation densities. The rocking curve full-width at half-maximum (FWHM) value is taken as a figure of merit for crystalline perfection. Heying et al. [24] have reported that the (0 0 0 2) rocking curve is sensitive only to the screw or mixed dislocations, while the skew (1 0 $\bar{1}$ 2) rocking curve is sensitive to all the dislocations content in the GaN films. Thus, the broadening of the skew (1 0 $\bar{1}$ 2) unsymmetrical rocking curve is a more reliable indicator of structural quality. In our experiments, FWHMs of (0 0 0 2) and skew (1 0 $\bar{1}$ 2) ω-rocking curves were used as the indicators of screw and all the dislocations, respectively. Fig. 4(a) shows the symmetric (0 0 0 2) ω-rocking curve of a typical sample of ZnO/GaN/Al_2O_3 films. The symmetry of the ω-rocking curve implied that the ZnO peak was overlapped by the GaN peak because their lattice constants are very close to each other. By Gaussian fit, we obtained a FWHM of 182 arcsec for the ZnO (0 0 0 2) ω-rocking curve, which is even smaller than the FWHM value (267 arcsec) of GaN in GaN/Al_2O_3 template. Fig. 4(b) shows the (0002) ω–2θdiffraction profile of the sample. By Gaussian fit, the FWHM values for the ZnO and GaN layers are 156 and 158 arcsec, respectively. Fig. 5 shows the skew (1 0 $\bar{1}$ 2) ω-rocking curve of a ZnO epilayer and an epi-GaN substrate. The FWHM values of the ZnO and epi-GaN layer are 358 and 320 arcsec, respectively. Heying et al. [24] have reported that the GaN sample with a (1 0 2) FWHM of 413 arcsec has a total threading dislocation density of $4 \times 10^8\,cm^{-2}$, so we estimate that the dislocation density of our ZnO sample is less than or in the range of $10^8\,cm^{-2}$. Table 1 shows the FWHM values of (0 0 0 2) and skew-(1 0 $\bar{1}$ 2) XRC in ZnO on GaN template, ZnO on c-Al_2O_3 grown at the same condition and device-grade GaN on c-Al_2O_3 grown by MOCVD. Such narrow FWHM values of ZnO films on GaN templates suggest that there were fewer threading dislocations in ZnO films on GaN templates than in ZnO films directly on c-Al_2O_3 (0 0 0 1) substrate. Moreover, these values of ZnO films on GaN templates were narrower than those of this device-grade GaN specimen which was 2 μm thick GaN grown on c-Al_2O_3 (0 0 0 1) substrate by a Thomas Swan MOCVD system in our laboratory.

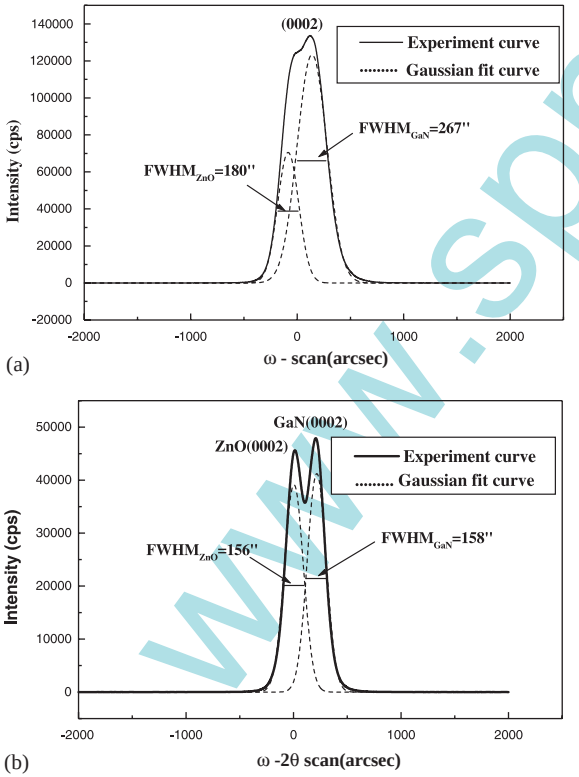

Fig. 4. The (0 0 0 2) scan curves of ZnO/GaN/Al_2O_3 film: (a) ω-scan; (b) ω–2θ scan.

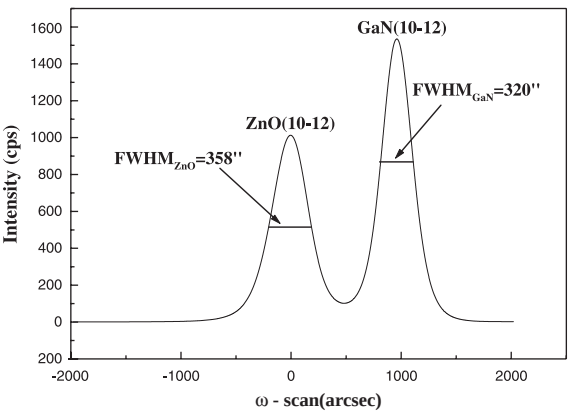

Fig. 5. The (1 0 $\bar{1}$ 2) ω-rocking curve of ZnO/GaN/Al_2O_3 film.

Table 1
FWHMs of XRD measurements in different geometries of ZnO films on various substrates and of device-grade GaN films on sapphire

Epilayer/substrate	FWHM (0 0 0 2) ω-scans (arcsec)	FWHM (0 0 0 2) ω–2θ scans (arcsec)	FWHM (1 0 $\bar{1}$ 2) ω-scans (arcsec)
ZnO/GaN/c-Al_2O_3	182	156	358
ZnO/c-Al_2O_3	386	295	650
GaN/c-Al_2O_3	365	238	410

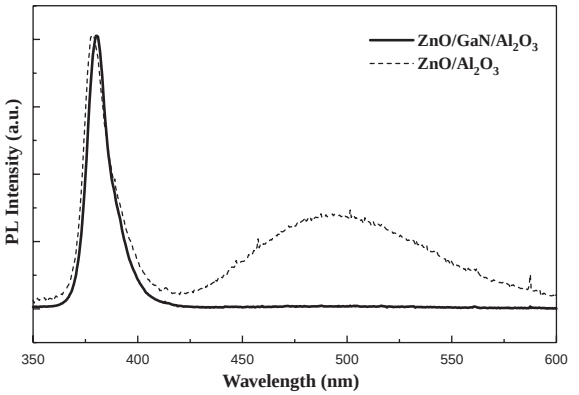

Fig. 6. Room temperature PL spectra of ZnO/GaN/Al_2O_3 film and ZnO/Al_2O_3 film.

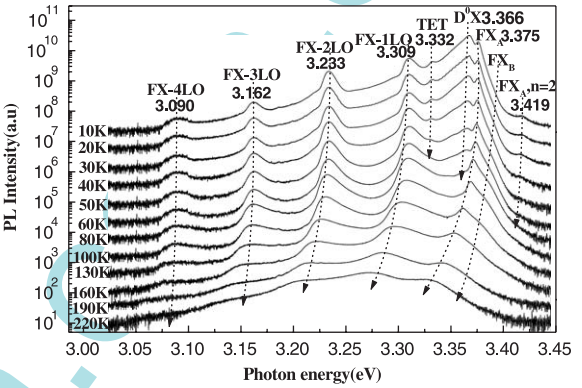

Fig. 7. Temperature-dependent PL spectra of ZnO/GaN/Al_2O_3 film from 10 K to 220 K.

PL spectra for ZnO/GaN/Al_2O_3 and ZnO/Al_2O_3 films carried out at RT are shown in Fig. 6. Strong ultraviolet (UV) emission coming from exciton emission could be observed in both samples. However, deep-level emission at 500 nm was observed in ZnO/Al_2O_3 film. The deep-level emission, which is usually defect-related, was difficult to observe in our ZnO/GaN/Al_2O_3 sample. To further study the optical properties of the film, low-temperature PL measurements at 10 K and temperature-dependent PL experiments of ZnO/GaN/Al_2O_3 film from 10 K to 220 K were performed.

Fig. 7 shows temperature-dependent PL spectra of ZnO/GaN/Al_2O_3 film from 10 K to 220 K. From the low-temperature PL spectrum of the ZnO/GaN/Al_2O_3 film collected at 10 K, we see that the energy position of the dominant peak is 3.366 eV. It can be ascribed to the exciton transition bounded to neutral donors (D^0X), since a similar peak has been observed at 3.367 eV for ZnO films on epi-GaN/ Al_2O_3 grown by MBE [25]. Another peak at 3.332 eV originates from two electron transitions (TET) [26], because the luminescence line disappears together with the BE lines with increasing temperature. The emission line at 3.375 eV can be assigned to the free exciton X_A (FX_A), and that at 3.419 eV to the $n = 2$ state of FX_A [27]. Although the $n = 2$ state of FX_A has been observed in high-quality ZnO bulk crystals [28,29] and homoepitaxial ZnO films [30], it has not been observed in heteroepitaxial ZnO films. The low-energy tail extending from the excitonic emission peaks due to the lattice deformation is much reduced, which allows the observation of the phonon replicas of the free excitons [31]. The presence of free excitons at low temperature offers evidence of the high purity and crystal quality of the ZnO epilayer. The peaks at 3.090, 3.162, 3.233 and 3.309 eV should be attributed to 1LO, 2LO, 3LO and 4LO phonon replicas of the free exciton, since these lines remain up to 220 K together with

the zero phonon line of FX_A. It should be noted that the energy difference between the zero phonon line and 1LO phonon replica line (66 meV) is somewhat smaller than the energy of a LO phonon (72 meV) calculated by Klingshirn [32], although the difference between 1LO phonon replica line and 2LO phonon replica line (76 meV) almost coincides with the theoretical value. In addition, from the temperature-dependent PL spectra of $ZnO/GaN/Al_2O_3$ film from 10 K to 220 K, we see that as the temperature increased from 10 to 80 K, the intensities of free excitons X_A transition at 3.375 eV observed at 10 K increased, while those of the bound exciton peaks at 3.366 eV decreased. The bound exciton peaks disappeared above 100 K, and only the FX_A and FX_B peaks and phonon replicas of the free exciton were observed. The domination of free exciton and the appearance of its four phonon replicas strongly indicate the high quality of the film.

4. Conclusion

In conclusion, we fabricated high quality ZnO epitaxial films with atmospheric pressure MOCVD on GaN/Al_2O_3 templates. With a growth rate of typically 4 μm/h at a growth temperature of 680 °C and a pressure of 760 Torr, the regular hexagonal column growth mode was observed by metal-phase interference microscopy and AFM. The X-ray diffraction investigations showed a single crystallinity, a wurtzite phase with a FWHM of (0 0 0 2), an ω-scan curve of 182 arcsec and a (0 0 0 2) ω–2θ scan curve of 156 arcsec.The FWHM value of skew (1 0 $\bar{1}$ 2) ω-scan curve of 358 arcsec showed that the threading dislocation density of the ZnO films was less than or on the order of $10^8\,cm^{-2}$, which is comparable to device-level GaN films. The $ZnO/GaN/Al_2O_3$ film showed very sharp near-band-edge luminescence at RT. The absence of the deep-level emission peak indicates that the ZnO films are of excellent optical quality and have few interior defects. Compared with the ZnO/Al_2O_3 film grown at the same conditions, the $ZnO/GaN/Al_2O_3$ film showed better crystalline and optical quality. From the low temperature PL spectra of ZnO thin films grown on GaN/Al_2O_3 templates, the FX_A and D^0X emissions and the $n = 2$ state of FX_A were clearly observed at 10 K, indicating high optical quality of the films. The high morphological, crystalline and optical quality of ZnO films opens broad prospects for device applications.

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