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Short communication

Comparisons of structural and optical properties of ZnO films grown on (0 0 0 1) sapphire and GaN/(0 0 0 1) sapphire template by atmospheric-pressure MOCVD

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Abstract

In this paper, we compare the properties of ZnO thin films on (0 0 0 1) sapphire and GaN/c-Al_2O_3 templates by atmospheric pressure metal–organic chemical vapor deposition (AP-MOCVD) using deionized water (H_2O) and diethylzinc (DEZn) as the O and Zn precursors, respectively. The atomic force microscopy (AFM) images exhibited that ZnO films grown on GaN/c-Al_2O_3 template had a regular hexagonal columnar and smooth morphology, and the ZnO grown on c-Al_2O_3 film had the hexagonal pyramid morphology. The full widths at half maximum (FWHMs) of the (0 0 0 2) and (10–12) ω-rocking curves of ZnO film grown on GaN/c-Al_2O_3 template were 182 and 358 arcs, respectively, indicating the smaller mosaicity and lower dislocation density of the film compared to ZnO film grown on c-Al_2O_3. The room temperature PL spectra showed that the PL intensity ratio of the band-edge emission (BEE) to the deep-level emission (DLE) for the ZnO film on GaN/c-Al_2O_3 template was larger than that of the film on c-Al_2O_3. Besides, the FX_C (or the first excited state of A exciton) and four phonon replicas could be clearly observed in ZnO film on GaN/c-Al_2O_3 template at 10 K compared to ZnO film on c-Al_2O_3.

Keywords: MOCVD; ZnO/GaN/Al_2O_3; AFM; X-ray diffraction; Photoluminescence

1. Introduction

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

To obtain high quality layers, various substrates have been used to grow ZnO including Al_2O_3 [7], Si [8], spinel [9], CaF_2 [10], GaAs [11] and so on. One of the recent attempts to improve the crystal quality of the ZnO films is to use the epitaxial GaN (epi-GaN) as the buffer layer on other substrates for the growth of ZnO epitaxial layers since GaN ($a = 3.189$ Å, $c = 5.185$ Å) and ZnO ($a = 3.2498$ Å, $c = 5.2066$ Å) [12] have close lattice constants (the mismatch is less than 2%) and a small difference between the in-plane linear thermal expansion coefficients ($\alpha_{GaN} = 5.59 \times 10^{-6}\,K^{-1}$ and $\alpha_{ZnO} = 6.51 \times 10^{-6}\,K^{-1}$) [13]. Since Vispute et al. [14] first reported the growth of ZnO films on epi-GaN/(0 0 0 1) sapphire template by PLD, there has been a few reports about the growth of ZnO films using the GaN epilayer as the buffer layers on other substrates by RF magnetron sputtering [15], MBE [16], MOVPE [17]. However, there have been few reports on the comparative studies on structural and optical properties of ZnO films on (0 0 0 1) sapphire and GaN/(0 0 0 1) sapphire template.

In this paper, we report the fabrication of ZnO films by AP-MOCVD on (0 0 0 1) sapphire and GaN/(0 0 0 1) sapphire template and compare the surface morphology, the structural property and the optical property of two kinds of ZnO films. It

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was found that significant differences of structural and optical properties of them.

2. Experimental procedure

ZnO thin films were deposited by a home-built vertical atmospheric pressure MOCVD system with a rotating disk reactor. 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 [18,19]. The MOCVD growth of GaN/Al_2O_3 templates on 2-in. c-Al_2O_3(0 0 0 1) substrates was performed in the Thomas Swan close-coupled showerhead (CCS) MOCVD reactor system. During the growth, trimethylgallium (TMGa) and ammonia (NH_3) were used as Ga and N precursors, 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 preliminary cleaning and polishing procedures. We used deionized water (H_2O) (ρ = 18.2 MΩ cm) and 6N-purity diethylzinc (DEZn) as the O and Zn precursors, respectively, and 7N-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 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 for 30 min 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. Typical growth rates of the main ZnO layers were about 3.5–4 μm/h. For comparative analysis, a ZnO film grown directly on c-Al_2O_3(0 0 0 1) substrate under the same condition was also prepared.

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 Kα line (λ = 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 on (0 0 0 1) sapphire and GaN/(0 0 0 1) sapphire template were transparent and have mirror-like surfaces. Fig. 1 shows the AFM images of ZnO films grown on c-Al_2O_3 (ZnO/Al_2O_3) and (ZnO/GaN/Al_2O_3) template for a scan area of 25 μm × 25 μm. From the figure, it was observed that the ZnO/GaN/Al_2O_3 film had a regular hexagonal columnar morphology (Fig. 1a), and the ZnO/Al_2O_3 film had the hexagonal pyramid morphology (Fig. 1b). It proved that the regular hexagonal column growth of the ZnO film grown on GaN/c-Al_2O_3 template strictly followed the hexagonal structure of the

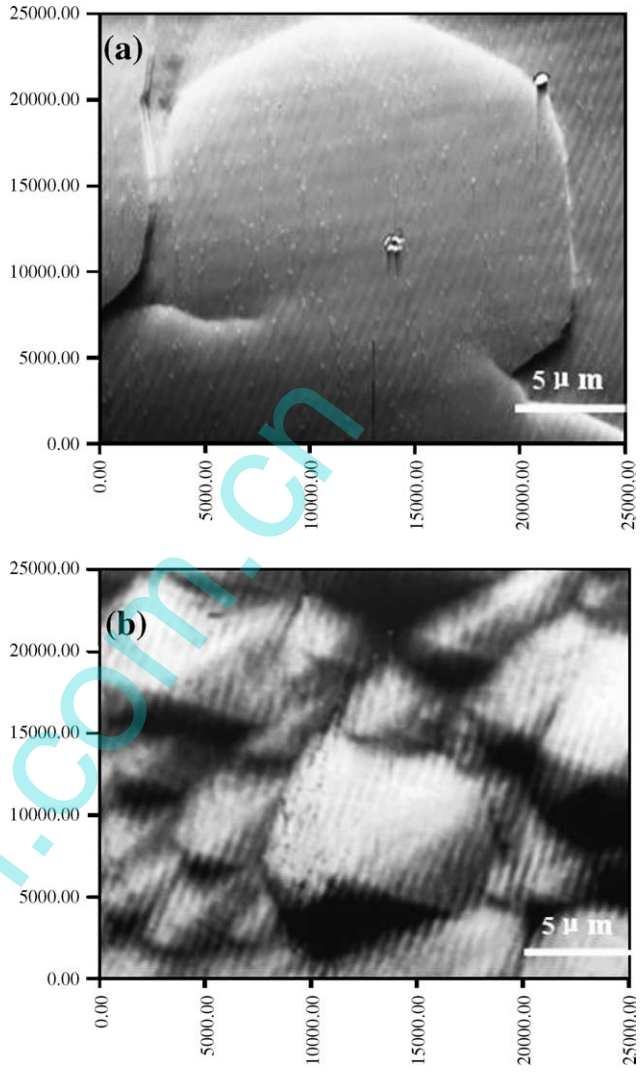

Fig. 1. AFM image of ZnO films (25 μm × 25 μm): (a) ZnO/GaN/Al_2O_3; (b) ZnO/Al_2O_3.

GaN epilayer. The root mean square (rms) roughness as determined by AFM (25 μm × 25 μm) of the ZnO film surface grown on GaN/c-Al_2O_3 template was about 3.5 nm, and the rms of the ZnO film surface grown on c-Al_2O_3 was about 7.9 nm. The result suggested that the larger grains were obtained and the rms roughness decreased in the ZnO film after using GaN/Al_2O_3 as the template. *It should be noted that the origin of the difference in morphology is not known at present and will be the focus of future work*.

It is well known that the X-ray diffraction is complementary to the transmission electron microscopy (TEM) and etch pit densities (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. [20] have reported that the (0 0 0 2) rocking curve is sensitive only to the screw or mixed dislocations, while the skew (10–12) rocking curve is sensitive to all the dislocations content in the GaN films. Thus, the broadening of the skew (10–12) unsymmetrical rocking curve is a more reliable indicator of structural quality. In our experiments,

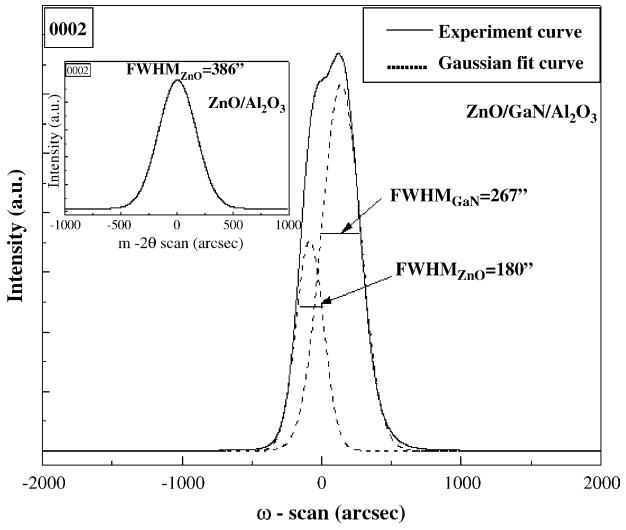

Fig. 2. The (0 0 0 2) ω-scan curve of ZnO/GaN/Al_2O_3 film. The inset shows the (0 0 0 2) ω-scan curve of ZnO/Al_2O_3 film.

FWHMs of (0 0 0 2) and skew (10–12) ω-rocking curves were used as the indicators of screw and all the dislocations, respectively. Fig. 2 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 arcs for the ZnO(0 0 0 2) ω-rocking curve, which is even smaller than the FWHM value (267 arcs) of GaN in GaN/Al_2O_3 template. Fig. 3 shows the (0 0 0 2) ω–2θ diffraction profile of the sample. By Gaussian fit, the FWHM values for the ZnO and GaN layers are 156 and 158 arcs, respectively. Fig. 4 shows the skew (10–12) 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 arcs, respectively. Heying et al. [20] have reported that the GaN sample with a (1 0 2) FWHM of 413 arcs has the total

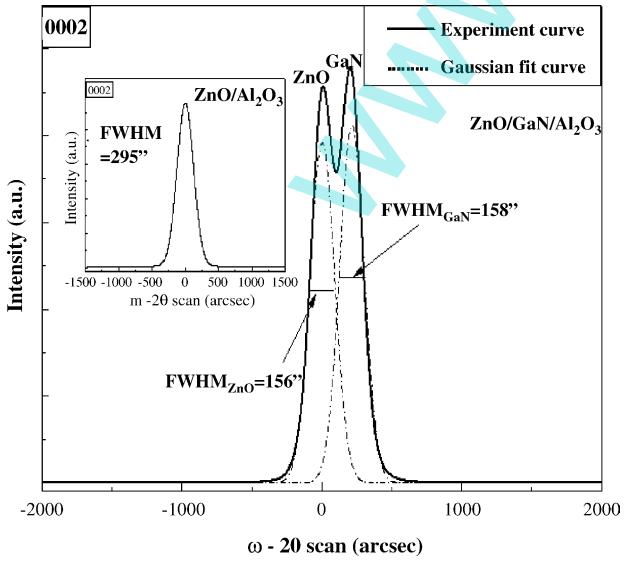

Fig. 3. The (0 0 0 2) ω–2θ scan curve of ZnO/GaN/Al_2O_3 film. The inset shows the (0 0 0 2) ω–2θ scan curve of ZnO/Al_2O_3 film.

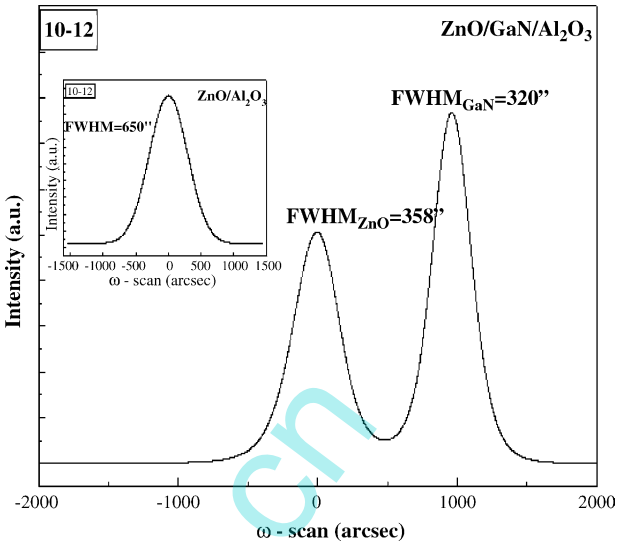

Fig. 4. The (10–12) ω-scan curve of ZnO/GaN/Al_2O_3 film. The inset shows the (10–12) ω-scan curve of ZnO/Al_2O_3 film.

threading dislocation density of 4×10^8 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}. Such narrower 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 by the same condition.

PL spectra for ZnO/GaN/Al_2O_3 and ZnO/Al_2O_3 films carried out at room temperature (RT) are shown in Fig. 5. Strong ultraviolet (UV) emission coming from exciton emission could be observed in both samples, which indicated that the two films have a good optical quality. The deep-level emission, which is usually defect-related was difficult to observe in our ZnO/GaN/Al_2O_3 sample. But, the deep-level emission at 500 nm was obviously observed in ZnO/Al_2O_3 film. The PL intensity ratios of the band-edge emission (BEE) to the deep-level emission (DLE) were 58:1 and 8:1, respectively, which indicated that ZnO/GaN/Al_2O_3 sample had a better optical quality than ZnO/Al_2O_3 sample.

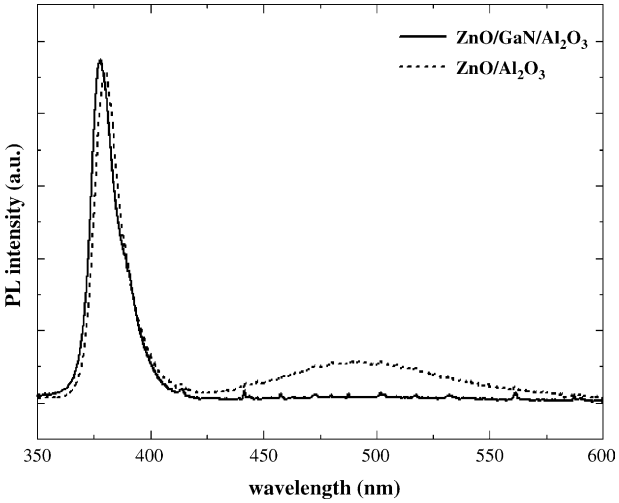

Fig. 5. Room temperature PL spectra of ZnO/GaN/Al_2O_3 film and ZnO/Al_2O_3 film.

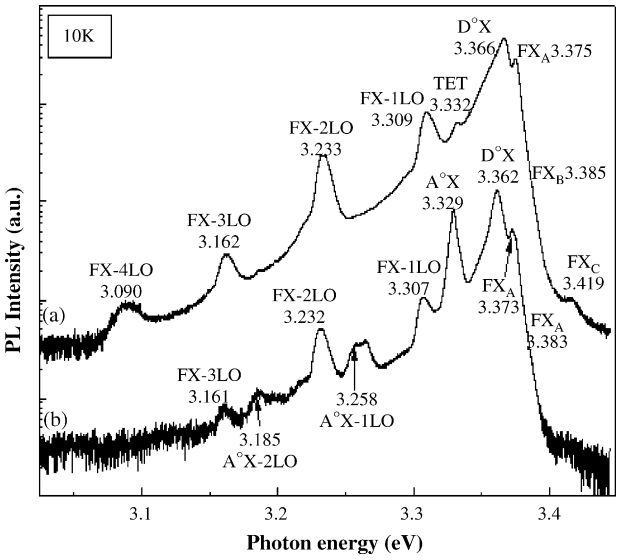

Fig. 6. Low temperature PL spectrum of ZnO/GaN/Al_2O_3 and ZnO/Al_2O_3 films measured at 10 K: (a) ZnO/GaN/Al$_2$O; (b) ZnO/Al_2O_3.

To further study the optical properties of the films, it was carried out that the low temperature PL measurement at 10 K. Fig. 6 shows the low-temperature PL spectrums of ZnO/Al_2O_3 and ZnO/GaN/Al_2O_3 films collected at 10 K. The peaks at 3.366 eV, 3.362 dominate both the spectra of ZnO/Al_2O_3 and ZnO/GaN/Al_2O_3 films, respectively. They can be ascribed to the exciton transition bounded to neutral donors (D^0X) since a similar peak has been observed in ZnO films [21,22]. At the higher energy side, three peaks are shown clearly at 3.375, 3.385 and 3.419 eV, respectively, in ZnO/GaN/Al_2O_3 film (Fig. 6a). The peak at about 3.385 eV shows only a shoulder so the position is a roughly estimated one. The energy positions of these three peaks are very close to the A, B and C free excitons observed in optical reflectance spectra of bulk ZnO crystal [23]. So they are tentatively attributed to the free A, B and C excitons. The little red shift of these peaks compared to bulk ZnO can be explained by a tensile strain in the films. It should be noted that the peak at 3.419 eV could also be attributed to the first excited state of A exciton. So a more detailed analysis is needed to clarify the origin of this peak. The presence of free excitons at low temperature offers evidence of the high purity and crystal quality of the epilayer. The ZnO/Al_2O_3 sample (Fig. 6b) shows two peaks at the higher energy side. Two peaks at 3.373 and 3.383 eV are tentatively attributed to the free A and B excitons according to the above. The little red shift of the two peaks compared to ZnO/GaN/Al_2O_3 sample proves that there is a bigger tensile strain in the ZnO/Al_2O_3 sample. 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 bound exciton and free excitons [24]. At the lower energy side, the ZnO/GaN/Al_2O_3 sample shows five peaks. The peak at 3.332 eV originates from two electron transitions (TET) [25]. 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 A free exciton's since the energy difference of each neighbor is close to LO phonon energy (72 meV) of ZnO calculated by Klingshirn [26]. 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, although the difference between 1LO phonon replica line and 2LO phonon replica line (76 meV) which almost coincides with the theoretical value. For the ZnO/Al_2O_3 sample, there are six peaks in the lower energy side. The peaks at 3.307, 3.232 and 3.161 eV should be attributed to 1LO, 2LO and 3LO phonon replicas of the A free exciton's. Another peak at 3.329 eV is tentatively attributed to the exciton transition bound to neutral acceptors (A^0X). The two weak peaks at 3.258 and 3.185 eV are attributed to the 1LO and 2LO phonon replicas of the bound exciton (A^0X).

4. Conclusion

In conclusion, we compare the properties of ZnO thin films on (0 0 0 1) sapphire and GaN/c-Al_2O_3 template by atmospheric pressure metal–organic chemical vapor deposition (AP-MOCVD). The ZnO/GaN/Al_2O_3 film had a regular hexagonal columnar and smooth morphology, and the ZnO/Al_2O_3 film had the hexagonal pyramid morphology. The X-ray diffraction investigations showed ZnO/GaN/Al_2O_3 film had fewer threading dislocation density than that of the ZnO/Al_2O_3 film. Both of the ZnO/GaN/Al_2O_3 and ZnO/Al_2O_3 films showed very sharp near band-edge luminescence at room temperature. The PL intensity ratios of the band-edge emission (BEE) to the deep-level emission (DLE) indicated the ZnO/GaN/Al_2O_3 film had a better optical quality. From the low temperature PL spectra of both films, the FX_A, FX_B emissions were clearly observed at 10 K in both samples, indicating high optical quality of the ZnO films. The little red shift of the FX_A, FX_B emission peaks in ZnO/Al_2O_3 sample compared to ZnO/GaN/Al_2O_3 sample proves that there was a bigger tensile strain in the ZnO/Al_2O_3 sample. In addition, compared to ZnO/Al_2O_3 film the FX_C (or the first excited state of A exciton) and four phonon replicas could be clearly observed in ZnO/GaN/Al_2O_3 film. The appearance of either the C exciton or the excited A exciton and four phonon replicas strongly suggest the high quality of the ZnO/GaN/Al_2O_3 film.

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