Epitaxial growth of ZnO on GaN/sapphire substrate by radio-frequency magnetron sputtering

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Abstract: Zinc oxide (ZnO) thin films were grown on n-GaN/sapphire substrates by radio-frequency (RF) magnetron sputtering. The films were grown at substrate temperatures ranging from 400 to 700 ℃ for 1 h at a RF power of 80 W in pure Ar gas ambient. The effect of the substrate temperature on the structural and optical properties of these films was investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL) spectra. XRD results indicated that ZnO films exhibited wurtzite symmetry and c-axis orientation when grown epitaxially on n-GaN/sapphire. The best crystalline quality of the ZnO film is obtained at a growth temperature of 600 ℃. AFM results indicate that the growth mode and degree of epitaxy strongly depend on the substrate temperature. In PL measurement, the intensity of ultraviolet emission increased initially with the rise of the substrate temperature, and then decreased with the temperature. The highest UV intensity is obtained for the film grown at 600 ℃ with best crystallization.

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1. Introduction

As a promising candidate for future short-wavelength optoelectronic device applications, zinc oxide (ZnO) has attracted considerable interest in recent years because of its large direct bandgap (E_g = 3.37 eV) and strong exciton binding energy (60 meV). In realistic device applications such as light-emitting diodes or laser diodes, both challenging p-type conductivity and high quality films are strongly desired. For the former case, no definite answer can easily be made at present, while for the latter one, different methods have been experimentally performed to fabricate high-quality ZnO film. For instance, methods of molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD) and radio-frequency (RF) magnetron sputtering[1−8] have been mainly used to obtain high quality single crystal ZnO films, among which RF magnetron sputtering is regarded as a relative simple and economical approach for future scalable industrial production.

ZnO epitaxial films have been grown on various substrates, such as KCl, diamond, SiC, $ScMgAlO_4$, and $LiNbO_3$[9−12]. Sapphire substrates were usually employed for the growth of ZnO epitaxial films. However, the lattice mismatch between ZnO and Al_2O_3 is as large as 18.4%, which results in considerable misfit strain in ZnO films[11]. Because the lattice mismatch between ZnO and GaN is smaller (only 1.89%), GaN is a potential substrate for ZnO film. For example, Shiao[12] found that the crystalline quality of ZnO on GaN is slightly better than that of ZnO on sapphire. Meanwhile, a light-emitting diode based on ZnO/GaN hybrid growth has been reported[13]. Nevertheless, the crystal quality of ZnO grown on GaN is still not well understood. Also, the optical properties of ZnO on GaN represent many interesting research topics. Herein, a GaN buffer layer deposited on c-plane Al_2O_3 substrates was used for subsequent growth of single crystalline ZnO. In this study high quality ZnO film is grown on GaN/Al_2O_3 using the RF magnetron sputtering technique, and the microstructures and the surface morphologies are demonstrated with X-ray diffraction (XRD) and atomic force microscopy (AFM) techniques. The characteristic of photoluminescence (PL) at RT is also studied.

2. Experiment

The ZnO thin films were deposited on n-GaN/Al_2O_3 substrates using RF magnetron sputtering. A ceramic target of ZnO (99.99%) was used for sputtering. A GaN buffer layer was grown by MOCVD on a c-plane sapphire substrate. Prior to the deposition, GaN/sapphire substrates were sequentially cleaned ultrasonically using isopropyl, acetone, methanol, and de-ionized water, and then blown dry with nitrogen gas. Before deposition, the chamber was evacuated to a base pressure of 6.0×10^{-5} Pa. The target–substrate distance is set at 10 cm. In the previous report[14] we demonstrated that pure Ar growth ambient is better for getting good structural and optical quality of ZnO films; therefore, pure Ar (99.999%) is used as the sput-

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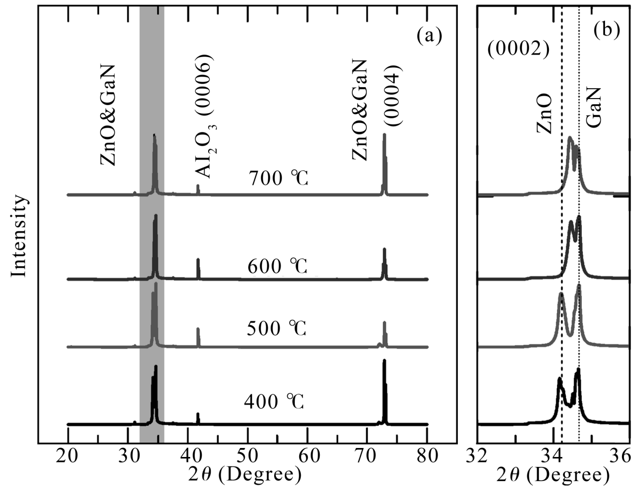

Fig. 1. (a) XRD (θ–2θ) pattern of as-grown ZnO samples at different growth temperatures. (b) The enlarged picture of the normalized intensity of ZnO (0002) and GaN (0002) diffraction peaks in Fig. 1(a).

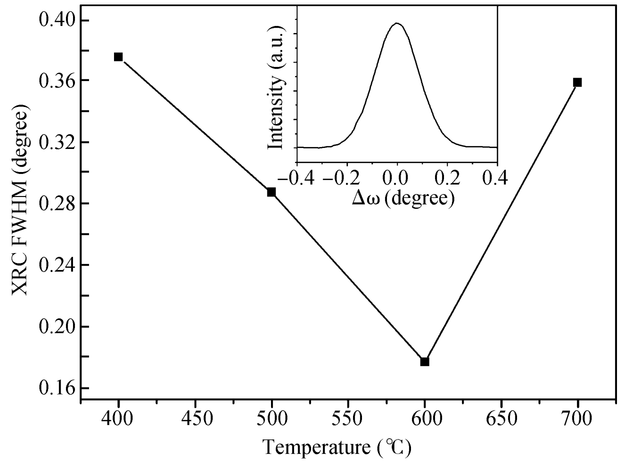

Fig. 2. Dependence of the FWHM of the ZnO (0002) XRC on substrate temperature.

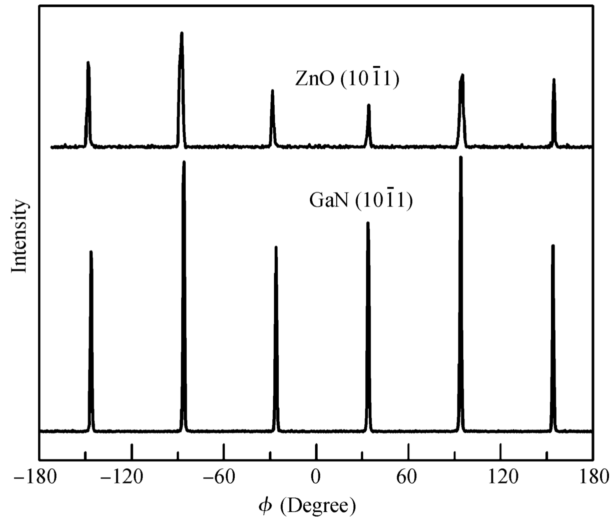

Fig. 3. XRD ϕ scans of the ZnO (10$\bar{1}$1) and GaN (10$\bar{1}$1) grown at 600 ℃.

tering gas in this work. The working pressure is maintained at 0.5 Pa by a flowing Ar stream as the sputtering gas. Prior to the film growth, the targets were pre-sputtered for 0.5 h to remove contaminants and the substrate was pre-heated at the growth temperature for 10 min to keep the temperature around the substrate constant. The substrate temperature during deposition ranged from 400 to 700 ℃ for 1 h. The RF power is 80 W. After deposition, the samples were naturally cooled to room temperature surrounded with Ar.

The crystalline structure of the ZnO films was characterized by X-ray diffraction (XRD, Panalytical X'Pert-MPD Pro) using the θ–2θ scan with CuKα (λ = 1.5405 Å) radiation operating at 40 kV and 40 mA. The rocking curve (ω scans) was also taken by a high resolution Bede-D1 diffractometer with a Ge (004) monochromator to further determine the crystalline quality of ZnO films. Epitaxial relations between ZnO films and the GaN substrate were investigated by XRD ϕ scanning. The surface roughness of the deposited films was investigated by AFM using a silicon nitride tip in contact mode. The PL of the as-deposited films was studied by using a He–Cd laser (λ = 325 nm) at room temperature. All the measurements were performed at room temperature.

3. Results and discussion

Figure 1 shows XRD θ–2θ patterns of as-grown ZnO samples for different growth temperatures. It can be seen that the XRD patterns of all four thin film samples grown on n-GaN/sapphire substrate are composed of peaks corresponding to (0002) and (0004) reflections of ZnO and GaN. The (0002) and (0004) reflection peaks from ZnO are not distinguishable from the corresponding peaks of GaN because of the very close lattice matching between ZnO and GaN. From the figure it can also be seen that all the ZnO films are of wurtzite structure, monocrystalline nature and c-axis orientation, and the features of the intensity of ZnO (0002) peaks are varied. To demonstrate this variation, the normalized intensity of ZnO (0002) and GaN (0002) diffraction peaks is presented in Fig. 1(b). The intensity of ZnO (0002) diffraction peaks increases initially and then decreases with growth temperature. The highest diffraction peak of ZnO (0002) appears at a growth temperature of 600 ℃. The alignment of the ZnO film grown on the n-GaN buffer layer at 600 ℃ was measured using the ϕ-scan of the four-circle XRD. It can be seen from the ϕ-scan pattern (Fig. 2) that the respective peaks corresponding to ZnO thin film and GaN are very much identically placed. It is to be noted that a similar ϕ-scan pattern was observed for all other samples. The (10$\bar{1}$1) plane of ZnO films showed six-fold symmetry on the GaN (10$\bar{1}$1) substrate. The (10$\bar{1}$1) planes of the GaN substrate with six-fold symmetry were also measured for comparison. The existence of such an epitaxial relationship was also noted for ZnO thin film grown on undoped GaN by other methods[12–14]. Thus from Fig. 2, it can be concluded that the ZnO film and GaN buffer layer possess hexagonal symmetry corresponding to the wurtzite structure and the epitaxial relationships between the ZnO thin film and the GaN are $(10\bar{1}1)_{ZnO}//(10\bar{1}1)_{GaN}$.

The crystalline quality of the film can also be evaluated by the X-ray rocking curve (XRC) of the ZnO (0002) peak. Figure 3 shows that the change of the full width at half maximum

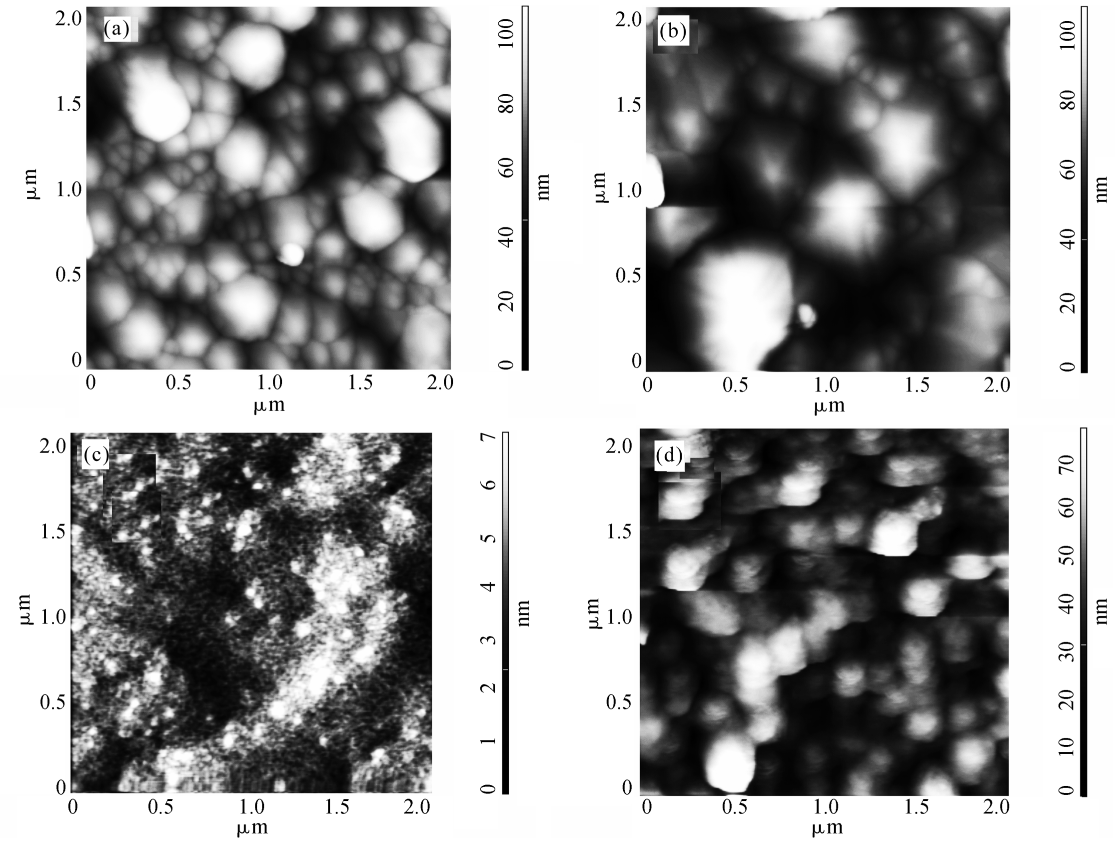

Fig. 4. AFM images of the ZnO films grown at various temperatures. (a) 400 ℃. (b) 500 ℃. (c) 600 ℃. (d) 700 ℃.

(FWHM) of the ZnO (0002) XRC is connected with the substrate temperature T_s. For the case of the ZnO film deposited at a fixed growth temperature of 600 ℃, the FWHM showed the lowest value of 0.17. The smallest FWHM is shown in the inset of Fig. 2. For higher or lower T_s, the FWHM of XRC increases. These results reveal that the crystalline quality of the film is improved with the increase of growth temperature to 600 ℃. The crystallinity of the film is also degraded when T_s increases further from 600 to 700 ℃. The probable reason for this is that, at growth temperatures lower than 600 ℃, an insufficient amount of energy is provided for the sputtered atoms to efficiently migrate on the substrate surface. For temperatures higher than 600 ℃, a rapid growth rate leads to conditions of unstable grain growth in the ZnO thin films, which degrades the crystallization of the ZnO film. These results reveal that the crystalline quality of the ZnO films improves by growth at 600 ℃. Obviously, the substrate temperature plays an important role in determining the crystalline quality.

The microstructure and surface morphology of ZnO films were also investigated by AFM. For the ZnO film grown at 400 ℃ (Fig. 4(a)), the crystal grains are dominated by a typical "honey-comb" like structure as evidenced by well-faceted hexagons, and the average grain size is around 300 nm. These features could be due to a high interfacial energy associated with the ZnO film on GaN, a high surface mobility of the Zn adatom, and a substantial desorption of Zn[13]. With increasing growing temperature, the grain size increases to around 600 nm. The grain size of the ZnO film grown at 500 ℃ is larger than that of the film deposited at 400 ℃ and the roughness increased to 18.2 nm (Fig. 4(b)). The transition towards the growth of a smooth film was found for a growth temperature of 600 ℃ (Fig. 4(c)). This change in growth mode results in a substantial reduction of RMS roughness to 3.5 nm for a flat surface. A further increase of growth temperature to 700 ℃ shows an adverse effect on the surface morphology, with irregular grains and increased roughness to about 12.3 nm.

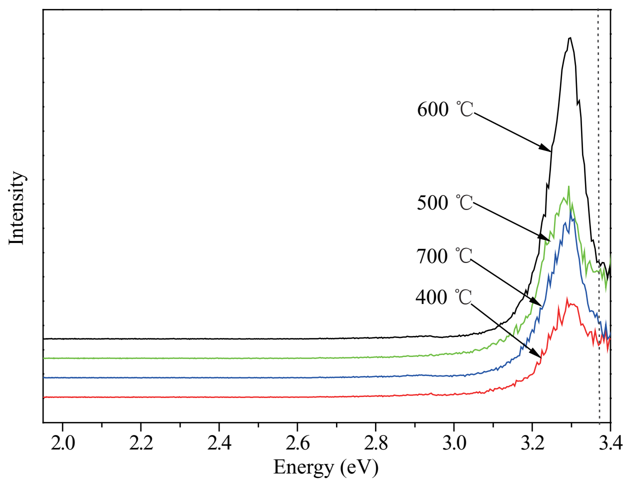

Fig. 5. Room temperature PL spectra of the ZnO films grown on sapphire at 400, 500, 600, and 700 ℃.

The room temperature PL spectra of ZnO thin films grown at different temperatures are compared in Fig. 5. The dashed line in Fig. 5 shows the emission of GaN in the ultraviolet region. The ZnO film shows a luminescent band which is a sharp near-band-edge (NBE) emission in the ultraviolet (UV) region centered at 375 nm. The peaks in this region are correlated with excitons (free or bound-exciton states). For both of the films grown at different temperatures, defect-related emission is not observed. The visible emissions have a close relation with some intrinsic defects, such as oxygen vacancies, zinc vacancies, zinc interstitials, oxygen interstitials, and/or antisite defects O_{Zn}[8−10]. The lower PL implies a low defect density in these films. From Fig. 5, it can be clearly seen that the PL are strongly dependent on the growth temperature. The intensity of the UV emissions increases initially and then decreases with increasing substrate temperature. The highest intensity of the UV emission appears at a growth temperature of 600 ℃ which is consistent with the XRD result. This implies that films deposited at lower or higher temperatures have higher crystal imperfections than that at 600 ℃, such as point defects and grain boundaries. Obviously, ZnO films with the best crystallinity can obtain the highest UV emission, implying that the crystallinity has a great influence on the UV emissions of ZnO films.

4. Conclusions

In conclusion, ZnO films with high crystalline and optical quality were grown on GaN by RF magnetron sputtering. The ZnO films can grow with high quality heteroepitaxially on GaN. The ZnO film deposited at 80 W and 600 ℃ exhibits the optimum values of XRD θ-rocking FWHM of 0.17°. Through XRD and AFM study, the PL properties of the ZnO films are found to closely relate to crystallinity.

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