

Deposition and Characterizations of ZnO Thin Films on Al₂O₃ (0001) Substrates with III-Arsenide Intermediating Layers

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Abstract: ZnO thin films have been grown by radio-frequency magnetron sputtering on c-plane sapphire substrates with III-V (i.e., GaAs and InAs) intermediate layers. The intermediate layers were grown by molecular beam epitaxy. Structural and optical properties were studied by X-ray diffraction (XRD) and Raman scatterings. The growth orientations of the ZnO/III-V/c-sapphire heterostructures were determined by off-axis XRD, i.e., x-ray pole-figure mapping. It is found that the crystalline quality of the III-V intermediate layers play an important role in the growth of ZnO. The 30-degree in-plane rotation that usually occurs in the growth of ZnO on a c-sapphire substrate is absent due to the insertion of III-V intermediate layers. Raman scattering, together with the XRD, reveals the relaxation of the tensile strain in the GaAs interlayer after the ZnO thin film deposition, while the strain relaxation did not occur in the InAs interlayer.

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Keywords: ZnO thin film, III-V intermediate layers, RF-magnetron sputtering, XRD, and Raman scattering.

1. INTRODUCTION

ZnO has been attracting intensive attentions due to its large exciton binding energy (60 meV) [1]. The direct and wide band gap (~ 3.37 eV at room temperature) of ZnO, together with its large exciton binding energy, makes it suitable for the fabrication of short-wavelength optoelectronic devices such as light emitting diodes, ultraviolet detectors, and solar cells [2]. The easy chemical etching and the potential low-cost fabrication of ZnO-based devices also contribute to the advantages of ZnO over GaN as the next generation of solid-state lighting semiconductor. Unfortunately, p-type doping of ZnO, which is required in the fabrication of high performance ZnO-based devices, is still remaining a challenge in various crystal growth technologies such as metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and pulse laser deposition (PLD).

Growth of ZnO on III-V substrate, e.g., GaAs and InP, followed by thermal annealing has been reported as a promising method to produce p-type ZnO [3-6]. However, the processing conditions are critical and the interfacial atom reactions may lead to recrystallization of new phase [7]. Meanwhile, the mechanism of the p-type doping is still under debate [3-6]. To minimize the interfacial interactions and to investigate the p-type doping mechanisms via post-growth thermal annealing using III-V material as the doping sources, we designed the ZnO/III-V/c-sapphire sandwich structures,

where the III/V ratio in the III-V compound can be modified by controlling the growth temperatures as well as the III/V flux ratio on the growing surface. More importantly, the doping level of III-V elements in the ZnO thin film can be controlled by the thickness of the III-V intermediate layers.

In terms of III- and V-elements co-doping in ZnO, post-growth thermal annealing of the ZnO/III-V/Sapphire sandwiched structures is desired but seldom reported in the literature. In this work, we presented our studies on growths of ZnO by radio-frequency (RF) magnetron sputtering on III-V intermediate layers, i.e., GaAs and InAs that were grown on c-sapphire substrates by MBE. The crystal quality, growth orientation, strain building and relaxation were characterized by x-ray diffractions (XRD) and Raman scattering. The results obtained may be helpful in consequence post-growth thermal annealing for generating p-type ZnO films via III and V co-doping.

2. EXPERIMENTS

To prepare the GaAs and InAs intermediate layers, epitaxial c-sapphire, i.e., Al₂O₃ (0001) substrate, was heat-treated at 800°C in a MBE (Riber-32P) growth chamber for ~ two hours. The substrate temperature was then ramping down to 540°C to grow GaAs and InAs thin films. The same III/V ratio, i.e., 0.05 was used in the growth of GaAs and InAs. The film thicknesses are also similar for GaAs and InAs (~ 500 nm). After growth the samples were loaded into a RF-magnetron sputtering chamber for the growth of ZnO [8]. For the sake of brevity, hereafter, ZnO samples grown on GaAs/c-Sapphire and InAs/c-Sapphire substrates are referred to as samples A and B, respectively. For both samples A and B the growth parameters are the same: the substrate

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temperature is 350°C, which is lower than the growth temperature of the III-V intermediate layers. The RF-power applied on the ZnO target is 60 W and the working gas is pure argon, setting at 5 mTorr with a flow rate of 10 sccm.

The XRD ($\text{Cu}_{K\alpha 1}$) measurements were carried out in a Philips X'pert-MRD high-resolution x-ray diffractometer. For the pole-figure mappings, an x-ray mirror and a parallel plate collimator were mounted in the incident and the diffracted beams, respectively. Raman scattering was conducted at room temperature in a micro-Raman system: a 532-nm He-Ne laser was used as the excitation light source, the scattered light was dispersed through a JY-T64000 triple-monochromator attached to a liquid-nitrogen-cooled charge-coupled-device (CCD) detector.

3. RESULTS AND DISCUSSION

Figs. (1a and 1b) show the high-resolution XRD patterns measured from samples A and B, respectively. As a comparison, the XRD spectra from the GaAs/c-sapphire and the InAs/c-sapphire substrates (without growing ZnO thin films) are also presented. It is seen that after the growth of ZnO the GaAs (111) peaks is slightly shifted to smaller angle, corresponding to an increased compressive strain or a reduced tensile strain built in the GaAs intermediate layer, while that of InAs (111) is kept intact. Since the growth temperature of ZnO by sputtering is lower than that of GaAs and InAs by MBE, the thermal anneal-induced strain relaxation is neglected. It is known that the lattice strain built in an epitaxially grown film for a certain thickness depends on the lattice mismatch between the substrate and the epilayer, which is also observed in sputtering growth of ZnO thin films. Fig. (1c) presents the comparison of ZnO thin films grown under the same conditions on a c-sapphire and a GaAs (111) epi-ready substrates. The lattice mismatch between ZnO and c-sapphire is supposed to be 18.4% due to the 30-degree in-plane rotation while that between ZnO and GaAs (111) is -18.6% [8]. As a result, one can see that the ZnO (0002) XRD peak measured from the ZnO/c-sapphire sample is smaller than that measured from ZnO/GaAs(111), indicating the larger compressive (smaller tensile) strain built in the ZnO thin film grown on the c-sapphire [GaAs (111)] substrate. Likewise, the ZnO (0002) diffraction peak in sample A Fig. (1a) is slightly smaller than that in sample B Fig. (1b) due to the smaller lattice constant of GaAs than that of InAs and, thus, the smaller tensile mismatch between ZnO/GaAs (-18.6%) than that of ZnO/InAs (-24.1%). The small angular shift of the GaAs (111) peak caused by the growth of ZnO may indicate the tensile strain relaxation in the GaAs intermediate layer since the tensile lattice mismatch between GaAs and c-sapphire is -15.9%, larger than that between InAs and c-sapphire, -9.9%.

Fig. (2) shows the pole-figure mapping measured from samples A Fig. (2 d-f) and B Fig. (2 g-i) as well as those from a ZnO/GaAs(111) sample Fig. (2 b-c) grown under the same conditions as those of samples A and B. Fig. (2a) is a schematic diagram showing the mapping configuration. from Figs. (2b and 2c) one can see that the growth of ZnO on the epi-ready GaAs (111) substrate is epitaxy, and the growth relationships are ZnO(0001)//GaAs(111) and ZnO[10-10]//GaAs[110]. The epitaxial growth of ZnO is also observed in sample B Fig. (2 h-i), where the InAs intermediate layer is

epitaxially grown on the c-sapphire substrate Fig. (2 g-h). The epitaxial relationships of sample B are revealed to be ZnO(0001)//InAs(111)//Al₂O₃(0001) and ZnO[10-10]//InAs [110]//Al₂O₃[10-10]. The 30-degree in-plane rotation, which usually occurs in epitaxial growth of ZnO/c-sapphire, is absent in sample B due to the insertion of InAs layer. However, Fig. (2d and 2e) show that the GaAs interlayer grown on c-sapphire is a polycrystal with GaAs(111)// Al₂O₃(0001) and GaAs[110]//Al₂O₃[10-10] as the dominant growth orientation. The pole-figure mapping around the ZnO (10-11) atom planes of sample A see Fig. (2f) shows a high-intensity distribution at $\phi \approx 60^\circ$, which is an indicative of the c-axis preferred growth direction of ZnO. However, the mapping does not show any preferred intensity distribution in the ϕ scans. These results imply that the ZnO thin film grown on the GaAs polycrystal intermediate layer is mainly formed in a fiber textured structure, similar to that grown on a GaAs (001) epi-ready substrate [8].

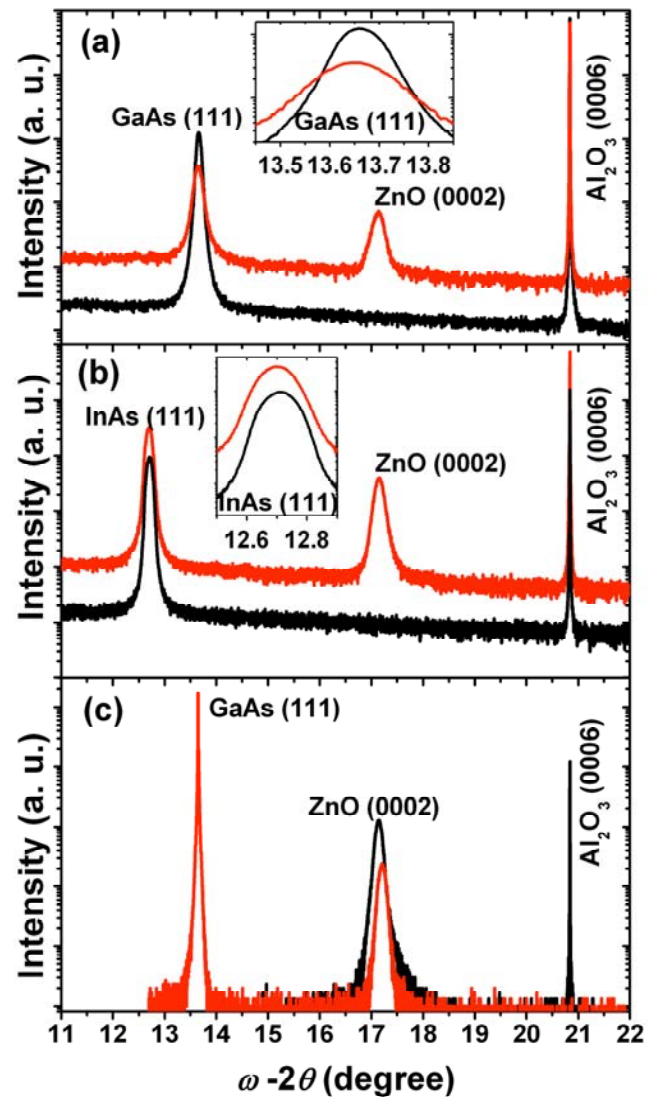


Fig. (1). XRD spectra measured from (a) sample A on GaAs/c-sapphire, (b) sample B on InAs/c-sapphire, and (c) ZnO grown on GaAs(111) and c-sapphire epi-ready substrates. For simple comparison, the XRD spectra from GaAs/c-sapphire and InAs/c-sapphire substrates are also presented in (a) and (b), respectively.

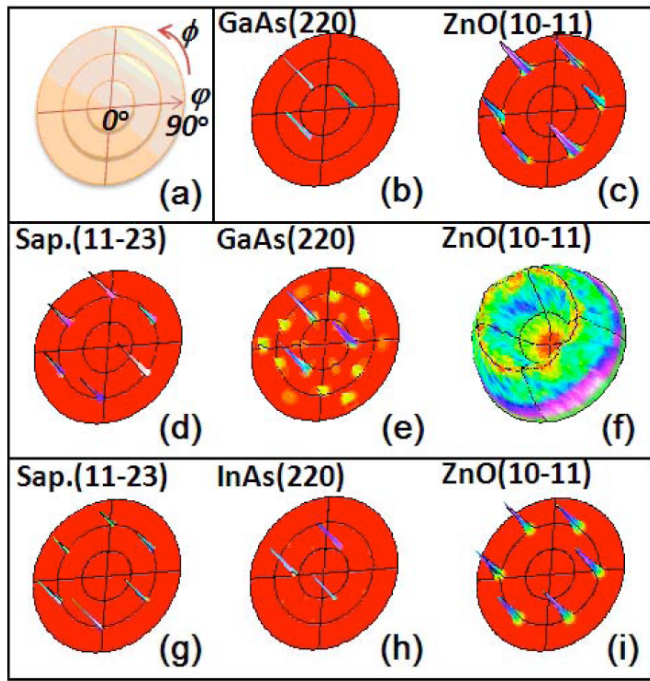


Fig. (2). XRD pole-figure mappings with (a) the configuration measured from (b-c) ZnO/GaAs(111), (d-f) sample A on GaAs/c-sapphire, and (g-i) sample B on InAs/c-sapphire.

Fig. (3a and 3b) shows the Raman scattering spectra recorded from samples A and B with a comparison to those recorded from the III-V/c-sapphire substrates before the growth of ZnO thin films. The enlarged spectra of the first-order Raman features of the III-V intermediate layers are shown in the insets. Where, one can see that the transverse optical (TO) phonon mode of GaAs is blue shifted after the growth of ZnO while that of InAs does not show any shift. It is well known that in a backscattering configuration the TO mode of the zinc blende crystal is sensitive to the biaxial strain remained in the crystal. The blueshift of the GaAs TO mode indicates the increased compressive strain or reduced tensile strain that remained in the GaAs intermediate layer after the growth of ZnO thin film, and the none-shift of the TO mode of InAs indicates no strain change. These results are in good agreement with the XRD measurements.

The E_2^{high} mode of ZnO in sample A is clearly seen at $\sim 438 \text{ cm}^{-1}$ while that of $A_1(\text{LO})$ falls in the second-order Raman features of GaAs. Likewise, the $A_1(\text{LO})$ of the ZnO in sample B is at $\sim 581 \text{ cm}^{-1}$ while that of E_2^{high} falls in the second-order Raman features of InAs. The enlarged spectra of the second-order Raman features of the GaAs and InAs intermediate layers are shown in Fig. (3a' and 3b'), respectively. The comparison between the Raman spectra before and after the ZnO thin films growth reveals that the $A_1(\text{LO})$ of sample A is $\sim 582 \text{ cm}^{-1}$ and the E_2^{high} of sample B is $\sim 437 \text{ cm}^{-1}$. The slightly smaller Raman shift of the E_2^{high} mode in sample B than that in sample A is also in agreement that the

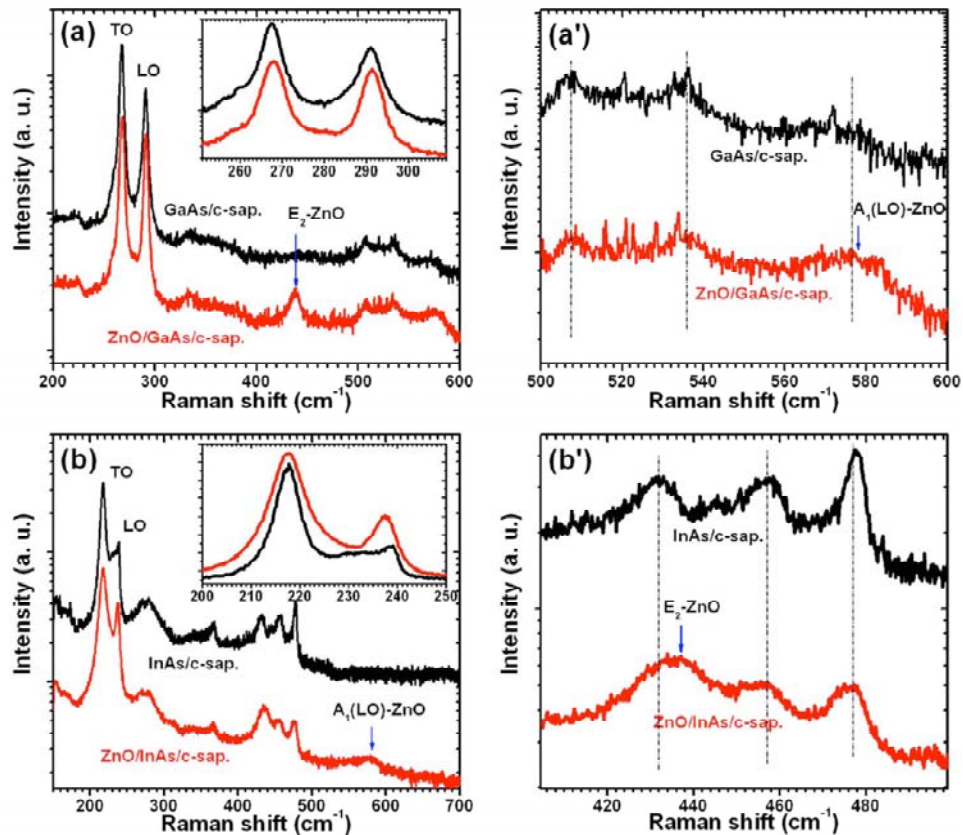


Fig. (3). Raman spectra recorded from (a) sample A on GaAs/c-sapphire and (b) sample B on InAs/c-sapphire substrate. The Raman spectra measured from the GaAs/c-sapphire and InAs/c-sapphire substrates are also presented in (a) and (b), respectively, for comparison. The insets of (a) and (b) are the enlarged spectra of the first-order Raman spectra while (a') and (b') are the enlarged spectra of the second-order Raman spectra.

XRD results, however, which is in conflict with the in-plane lattice mismatches since the in-plane lattice mismatch between ZnO and GaAs is tensile (-18.6%) and smaller than that between ZnO and InAs (-24.1%). The exact physics of this conflict is not clear at this stage, but it could be related to the atoms diffusion from the III-V intermediate layers into the ZnO thin films, especially the group III atoms [9], during the sputtering growth of ZnO. The smaller frequency difference between $A_1(\text{LO})$ and E_2^{high} of sample A ($\sim 143 \text{ cm}^{-1}$) than that of sample B ($\sim 145 \text{ cm}^{-1}$) implies the larger defects incorporated in the ZnO thin film of sample A [10, 11]. Finally, it is interesting to note that the Raman intensity changes in the first-order Raman scattering range of InAs, especially at about 230 and 239 cm^{-1} [See the inset of Fig. (3b)], after the growth of ZnO could be due to the elimination of the surface polaritons effect in the InAs/c-sapphire layered structure [12].

4. CONCLUSION

ZnO thin films have been grown by RF-magnetron sputtering on GaAs- and InAs-intermediated c-sapphire substrates. The in-plane lattice constants of the III-V interlayers are smaller than the c-sapphire substrates but larger than the ZnO thin film, and the insertion of the lattice grade interlayers leads to the absence of the 30-degree in-plane rotation between ZnO and the c-sapphire substrate. The larger tensile in-plane lattice constant mismatch of GaAs/c-sapphire leads to the polycrystal GaAs growth on the c-sapphire substrate. For InAs intermediate layer, the reduced tensile in-plane lattice mismatch between InAs and c-sapphire leads to the single crystal growth of InAs and, hence, the single crystal growth of the ZnO thin film. The tensile in-plane lattice mismatch between ZnO and the interlayers leads to the reduced tensile strain or increased compressive remained in the GaAs interlayer. However, the strain remained in the InAs interlayer does not show any significant change before and

after the growth of ZnO thin film. Atoms diffusion from the intermediate layers into the ZnO thin films could be the physical origin that affect the lattice constant and hence the strain remained in the ZnO thin film.

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