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Thin film epitaxy and structure property correlations for non-polar ZnO films

P. Pant [a,*], J.D. Budai [b], R. Aggarwal [a], Roger J. Narayan [a,c], J. Narayan [a]

[a] Department of Materials Science and Engineering, EB-I, Centennial Campus, North Carolina State University, Raleigh, NC 27695-7907, USA
[b] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6030, USA
[c] Joint Department of Biomedical Engineering, University of North Carolina, Chapel Hill, NC 27599, USA

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Abstract

Heteroepitaxial growth and strain relaxation were investigated in non-polar *a*-plane (1 1 −2 0)ZnO films grown on *r*-plane (1 0 −1 2)sapphire substrates in the temperature range 200–700 °C by pulsed laser deposition. The lattice misfit in the plane of the film for this orientation varied from −1.26% in [0 0 0 1] to −18.52% in the [−1 1 0 0] direction. The alignment of (1 1 −2 0)ZnO planes parallel to (1 0 −1 2)sapphire planes was confirmed by X-ray diffraction $\theta-2\theta$ scans over the entire temperature range. X-ray ϕ-scans revealed the epitaxial relationship:[0 0 0 1]ZnO‖[−1 1 0 1]sap; [−1 1 0 0]ZnO‖[−1 −1 2 0]sap. Depending on the growth temperature, variations in the structural, optical and electrical properties were observed in the grown films. Room temperature photoluminescence for films grown at 700 °C shows a strong band-edge emission. The ratio of the band-edge emission to green band emission is 135:1, indicating reduced defects and excellent optical quality of the films. The resistivity data for the films grown at 700 °C shows semiconducting behavior with room temperature resistivity of 2.2×10^{-3} Ω-cm.
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1. Introduction

With a direct bandgap of 3.32 eV and an exciton binding energy of 60 meV, ZnO is considered to be an attractive alternative to GaN for a host of optical devices, including blue or UV light-emitting diodes (LEDs), laser diodes and optical sensors [1,2]. However, most of the work reported so far has focused on polar ZnO grown on *c*-sapphire. Polar heterostructures experience strong spontaneous and piezoelectric polarization fields which reduce the overlap between the electron and the hole wave functions and thus reduce the luminous efficiency of LEDs. It has been demonstrated that the growth of non-polar films can eliminate the polarization effects and in turn increase the quantum efficiency of LEDs. In the case of GaN-based LEDs, the internal quantum efficiency has increased from 35% in polar heterostructures to 50% in LEDs grown on non-polar substrates.

This paper reports the growth of non-polar *a*-plane ZnO(*a*-ZnO) films on *r*-plane sapphire substrates via pulsed laser deposition (PLD) over the temperature range 200–700 °C, and focuses on the details of epitaxial growth in the orthogonal in-plane directions where the anisotropic lattice misfit changes from −1.26% in [0 0 0 1] to −18.52% in the [−1 1 0 0] direction. There have been earlier reports on the growth of *a*-plane ZnO films on *r*-plane sapphire by MOCVD [3–5] and MBE [6–9]. These reports determined epitaxial relationships, but did not address the details of strain relaxation and epitaxy under large misfit conditions. In addition, misfit anisotropy in the thin film plane was not considered. The in-plane misfit anisotropy can play an important role in strain relaxation of *a*-ZnO on *r*-plane sapphire substrates, as $\frac{\varepsilon_{zz}}{\varepsilon_{yy}+\varepsilon_{xx}} = f(\nu)$, where ε_{xx} and ε_{yy} are the in-plane strains, ε_{zz} is the strain along the

* Corresponding author. Tel.: +1 919 515 7219; fax: +1 919 515 7724.
E-mail address: ppant@ncsu.edu (P. Pant).

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film normal, and ν is Poisson's ratio. By invoking positive and negative in-plane strains, it is possible to minimize the overall strain in the film. Strain relaxation in thin films under large anisotropic misfit conditions becomes significant for device applications of non-polar films. The present work addresses the issue of strain relaxation for films <300 nm thick and grown in the temperature range 200–700 °C. Low temperature growth and strain relaxation are of special significance for the growth of thin films on temperature-sensitive substrates. The primary focus of this study is on the management of strain, characteristics of epitaxy and defect microstructure as a function of growth temperature to establish the structure–property correlation of these films. The details of the epitaxial growth of *a*-plane ZnO films on *r*-plane sapphire have been investigated by high-resolution X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The electrical and optical properties of the ZnO films were studied to establish structure–property correlations and assess their potential for device structures. This work shows that, though the films grow epitaxially over the temperature range 200–700 °C, the film growth variables, namely the oxygen partial pressure, growth temperature and film thickness, strongly influence the microstructure of the films and its correlation with the electrical and optical properties of the films needed for device applications.

2. Experimental

The *a*-plane ZnO films were grown on *r*-plane sapphire substrates by PLD. The ZnO target was prepared by the solid-state reaction technique. A pulsed KrF excimer laser

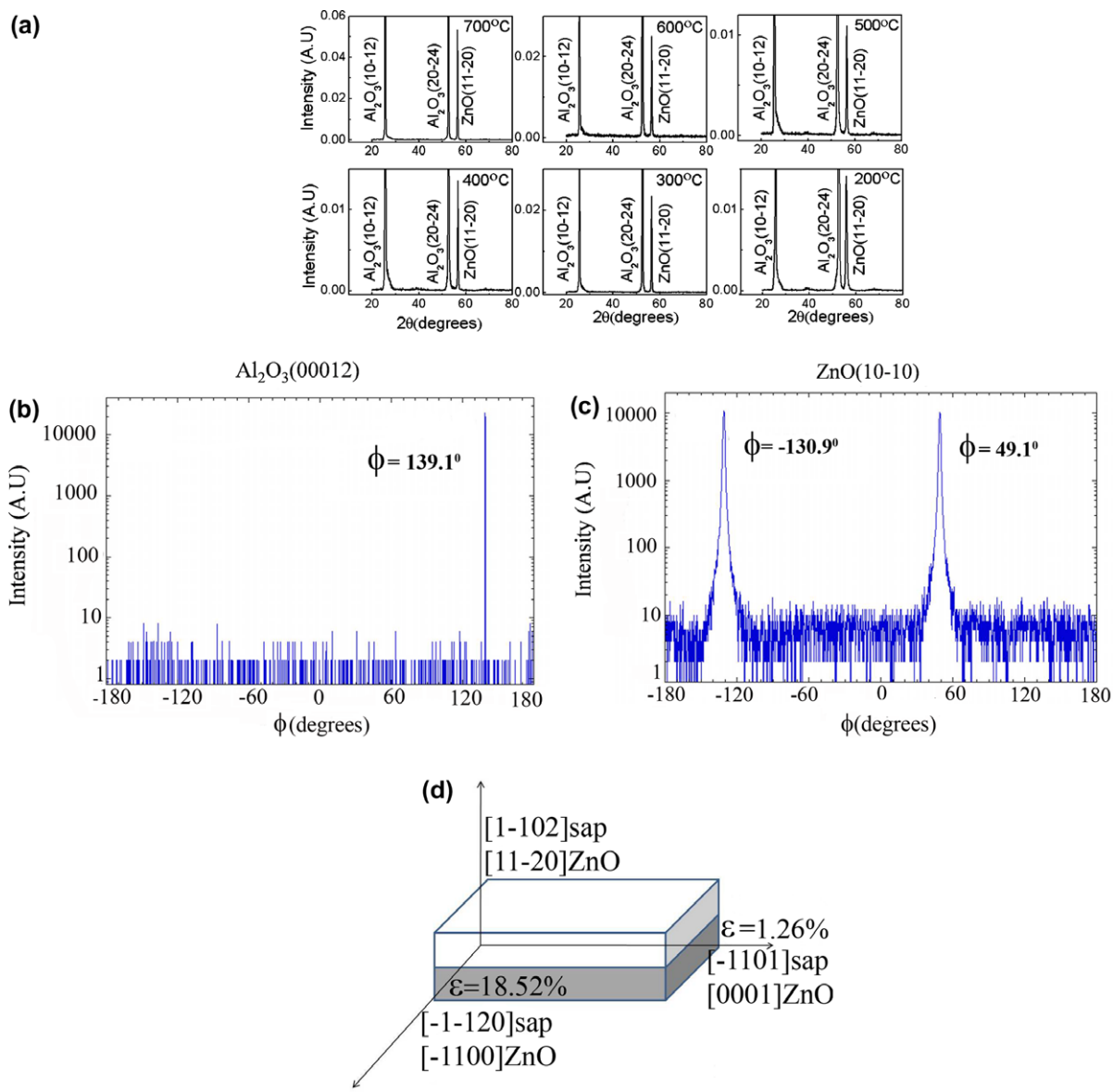

Fig. 1. (a) XRD $\theta-2\theta$ scan of *a*-plane ZnO films grown on *r*-sapphire in the temperature range 700–200 °C. XRD ϕ-scans of (b) sapphire(0 0 0 1 2) reflection, (c) ZnO(1 0 −1 0) reflections. (d) Schematic showing a lattice misfit of −1.26% along the in-plane *c*-axis of ZnO and a misfit of −18.52% along the in-plane *m*-axis of ZnO.

with a wavelength of 248 nm and pulse duration 25 ns was used for ablation. The energy density of the laser beam was 2–3 J cm^{-2} with a repetition rate of 5 Hz. The base pressure of the chamber prior to deposition was 7×10^{-7} torr, and deposition was carried at an oxygen partial pressure of $\sim 2 \times 10^{-4}$ torr over the temperature range 200–700 °C. For a comparison of properties, the ZnO films were also grown on *c*-sapphire substrates. The XRD (θ–2θ) scans were measured using a Rigaku X-ray diffractometer with Cu Kα radiation and a Ni filter. Transmission electron microscopy (TEM) using a JEOL 2010 field emission microscope and JEOL 2000FX were used to perform the detailed studies of epitaxial characteristics and the nature of defects and interfaces for structure–property correlations. The surface morphology of the films was studied by atomic force microscopy (AFM) using a JEOL 5200 microscope. The photoluminescence (PL) optical measurements were made using a Hitachi U-2500 fluorescence spectrophotometer. The electrical resistivity measurements were carried out using the Agilent 4155B semiconductor parameter analyzer. These measurements were made by the van der Pauw technique using indium contacts and gold wires.

3. Results and discussion

Fig. 1a shows the X-ray θ–2θ scans for ZnO films grown on *r*-plane sapphire substrate in the temperature range 200–700 °C. The scans show (1 0 −1 2), (2 0 −2 4) peaks of sapphire and the (1 1 −2 0) peak of ZnO establishing an out of plane growth orientation relationship of (1 1 −2 0)ZnO‖(1 0 −1 2)sapphire. This orientation relationship was found to be stable over the temperature range 200–700 °C. From the scans, it was found that the films grown at 700 °C showed the maximum intensity for the 2θ peak and the narrowest FWHM ~0.29°, indicating improved crystallinity of the film. Off-axis diffraction peaks were used to determine the in-plane orientation of the ZnO film with respect to the substrate. Fig. 1b and c shows ϕ-scans for sapphire(0 0 0 1 2) and ZnO(1 0 −1 0) reflections. The 180° separation for the (1 0 −1 0)ZnO peaks indicates twofold symmetry of these planes in the *a*-plane. From the correlation between the φ positions of the ZnO and sapphire peaks, the following epitaxial relationship was derived: (1 1 −2 0)ZnO‖(1 0 −1 2)sap, [0 0 0 1]ZnO‖[−1 1 0 1]sap, which is in concurrence with the epitaxial relationship reported in the literature for growth of *a*-ZnO on *r*-sapphire by other growth techniques [5,6]. The results on epitaxial growth of (1 1 −2 0)ZnO films on (1 0 −1 2)sap substrate are summarized in Fig. 1d with an in-plane orientation relationship: [0 0 0 1]ZnO‖[−1 1 0 1]sap and [−1 1 0 0]ZnO‖[−1 −1 2 0]sap. The figure shows that the calculated value of the lattice mismatch along in-plane *c*-axis of ZnO is only −1.26%, while the lattice mismatch along the in-plane *m*-axis of ZnO is −18.52%. The observed in-plane epitaxial relationship with a small misfit along the *c*-axis of ZnO and a large misfit along the *m*-axis of ZnO can be explained by the paradigm of domain matching epitaxy [10], where matching of domains of lattice planes is considered along the film–substrate interface. For the projection along the [0 0 0 1] direction of ZnO, the 18.52% misfit can be accommodated by matching two alternating domains. In one domain, five ZnO(1 −1 0 0) planes match six sap(1 1 −2 0) planes. In the other domain, six ZnO(1 −1 0 0) planes match seven sap(1 1 −2 0) planes. The misfit will be completely relaxed if these domains alternate with a frequency of 3:2. The 1.26% misfit for the projection along the [−1 1 0 0] direction of ZnO can be accommodated by matching ZnO(0 0 0 1) planes with sap(−1 1 0 1) planes.

The strain in a film has three components: (a) lattice misfit, (b) thermal misfit, and (c) defect-related strain. These strains are additive and can be measured by XRD analysis. According to Poisson's relationship, these strains are related by the expression $\frac{\varepsilon_{zz}}{\varepsilon_{yy}+\varepsilon_{xx}} = f(v)$, where ε_{zz} is the strain in the growth direction, that is [1 1 −2 0] ZnO, ε_{yy} and ε_{xx} are the strain in the in-plane directions, that is [−1 1 0 0]ZnO and [0 0 0 1]ZnO, respectively, and v is Poisson's ratio. For the growth of *a*-ZnO on *r*-sapphire, if one considers relaxed values of lattice parameters for the film and the substrate, the lattice parameters for the film and the substrate along [0 0 0 1]ZnO are $c_{\mathrm{ZnO}} = 0.5206$ nm and $\sqrt{(3a_{\mathrm{sap}}^2 + c_{\mathrm{sap}}^2)} = 1.5384$ nm. The lattice spacing of sapphire is three times the lattice spacing of ZnO and gives a compressive lattice misfit of 1.26% along [0 0 0 1]ZnO. The lattice parameters along [−1 1 0 0]ZnO are calculated as $\sqrt{3}a_{ZnO} = 0.5627$ nm and $a_{\mathrm{sap}} = 0.4758$ nm and also give a compressive lattice misfit of 18.52% between the film and the substrate. The values of thermal coefficient of expansion in the *a* and *c* directions for ZnO and sapphire available in the literature for the temperature range 200–700 °C predict the presence of a compressive thermal strain in the film. The calculated value of ε_{zz} from θ–2θ scans in the [1 1 −2 0] direction, which is the growth direction of the film, indicates the variation of strain with growth temperature. The observed variation in strain with growth temperature could be explained by the defect strain, which is a function of the growth ambient and can be compressive or tensile, depending upon the nature of the defects present in the film [11]. In a recent work, Saraf et al. [12] reported a net compressive strain ε_{xx} in the film along [0 0 0 1]ZnO and a net tensile strain ε_{yy} in the film along [−1 1 0 0]ZnO. They showed that, with increasing film thickness, ε_{yy} relaxes faster than ε_{xx} does because of the larger misfit of −18.52% along [−1 1 0 0]ZnO. Previous in situ XRD (using synchrotron) studies [10] on ZnO/*c*-plane sapphire showed that large misfit strains ~15.44% are relaxed rapidly within 1–2 monolayers. Because of the large misfit of −18.52% along [−1 1 0 0]ZnO, a complete relaxation of lattice strain in the film along this direction is proposed, and the measured strain is attributed to the thermal strain and defect strain. Film relaxation along [−1 1 0 0]ZnO can

also be explained by the nucleation and glide of dislocations, because slip systems can be easily activated along this direction. The smaller strain measured along [0 0 0 1]ZnO is harder to relax because of nucleation and propagation barriers for dislocations, as the resolved shear stress along [0 0 0 1] is zero, and slip systems cannot be activated. The strain along [0 0 0 1] must therefore have three components: lattice, thermal and defect strain.

Cross-sectional TEM imaging was done to study the epitaxial relationship and the structure of the interface between ZnO and sapphire. The inset in Fig. 2 shows the selected area diffraction pattern at the ZnO–sapphire interface from a cross-section sample for the film grown at 700 °C. The zone axes for ZnO and sapphire are identified as [1 0 −1 1]ZnO and [2 −2 0 1]sapphire, giving an epitaxial relationship of [1 0 −1 1]ZnO||[2 −2 0 1]sap. The diffraction pattern shows that the (0 −1 1 −2) plane of sapphire is parallel to the (1 −2 1 0) plane of ZnO. During the alignment of the zone axes, it was observed that the film and the substrate zone axis were off by ∼4–5°. This offset in the zone axes is evident in the diffraction pattern where the corresponding film and the substrate planes are not exactly parallel, but are tilted with respect to each other by 4–5°. The misorientation between the film and substrate zone axes is explained by the 86° rhombic symmetry of the sapphire (1 0 −1 2) crystal planes [13]. As a result, the electron beam in a cross-section sample is along the direction perpendicular to the (0 −1 1 −2) plane, which is equivalent to an angle of 86° to the substrate surface. Fig. 2 shows the HRTEM image of the film–substrate interface taken in the [1 0 −1 1] zone axis of the film for a film grown at 700 °C. The image shows that the interface between the film and the substrate is atomically sharp and shows planar matching between the film and substrate planes across the interface. Also no stacking faults are seen in this orientation.

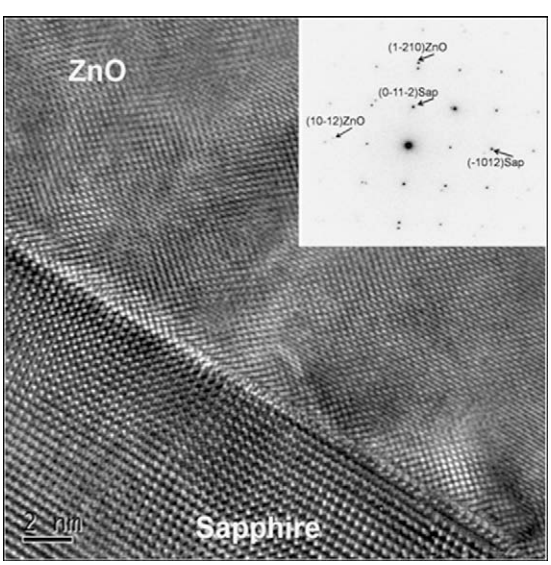

Fig. 2. HRTEM micrograph showing a sharp interface for the epitaxial growth of *a*-plane ZnO film on *r*-plane sapphire. The inset shows the selected area diffraction pattern from the interface region taken along the [1 0 −1 1] zone axis of ZnO.

Fig. 3 shows the AFM images of films grown at 700 °C and at 400 °C. The measured RMS roughness of the films grown at 700 °C and at 400 °C is 4 nm and 3 nm, respectively, from a 5 × 5 μm scan area. These values indicate that the films have a relatively smooth surface and that the surface roughness is a function of the growth temperature. The surface morphology of the film shows an elongated, stepped growth along one direction, indicating the presence of an in-plane anisotropy. The elongated growth direction is identified as the [0 0 0 1] direction, as it is the kinetically favored growth direction in wurtzite structures. The steps are wider for the films grown at 700 °C than for the film grown at 400 °C, and illustrate the effect of temperature on film growth, with a larger grain size being observed at higher growth temperatures.

The quality of the films grown at different temperatures was further studied by measuring the optical and electrical properties of the films. Fig. 4a shows the PL data for 225-nm-thick films. Films grown at 700 °C show a strong near band-edge emission, whereas the near band-edge emission intensity drops sharply for films grown in the temperature range 400–600 °C. From the PL data shown in Fig. 4b, it can be seen that the ratio of the band edge to the green band emission is approximately the same (∼3:1) for the films grown in the temperature range 300–600 °C, and it increases to 135:1 for films grown at 700 °C. Fig. 4c shows the effect of thickness and oxygen partial pressure on the PL spectra. In both cases, a drop in the PL band-edge emission intensity was observed. These results show that the optical quality of the film is a function of the growth temperature and oxygen partial pressure. Undoped ZnO is characterized by the presence of native point defects, namely donors and acceptors which influence its electrical and optical properties [2]. The presence of green band luminescence indicates that the mid-gap state defects are higher for films grown at temperatures 600 °C and below compared with films grown at 700 °C. The increase in the band-edge emission intensity which indicates an increase in the radiative recombination across the bandgap and the narrow FWHM of the PL curve are indicators that the film has fewer defect states and is of good optical quality. The PL data also show that the films grown at 700 °C show a red emission which is not seen for films grown at 600 °C and below. This is attributed to double diffraction effects of the near band-edge and is observed for the case where the intensity of the band edge is high but is not seen in the samples where the intensity is low.

Fig. 5 shows the resistivity measurements in the temperature range 15–300 K for films grown at 700 °C and 400 °C. The films grown at 700 °C show a negative temperature coefficient of resistivity which is characteristic of semiconducting behavior. For films grown at 400 °C, a drop in resistivity is observed in the temperature range 50–170 K, while for temperatures >170 K the resistivity continues to increase up to room temperature. This transi-

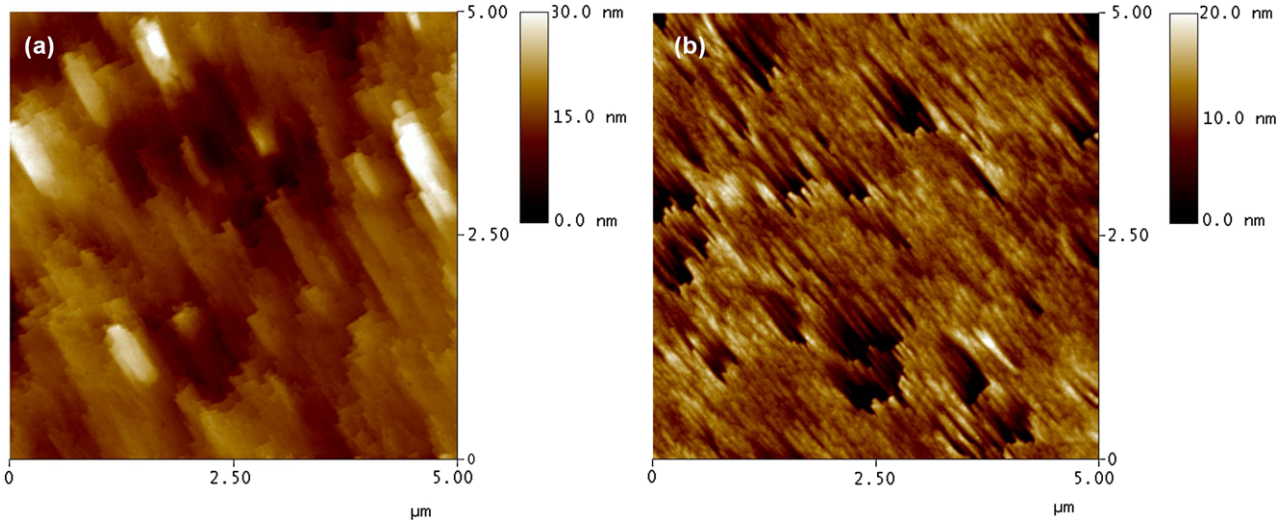

Fig. 3. AFM images showing the elongated stepped growth morphology of *a*-plane ZnO films on *r*-plane sapphire at: (a) 700 °C and (b) 400 °C.

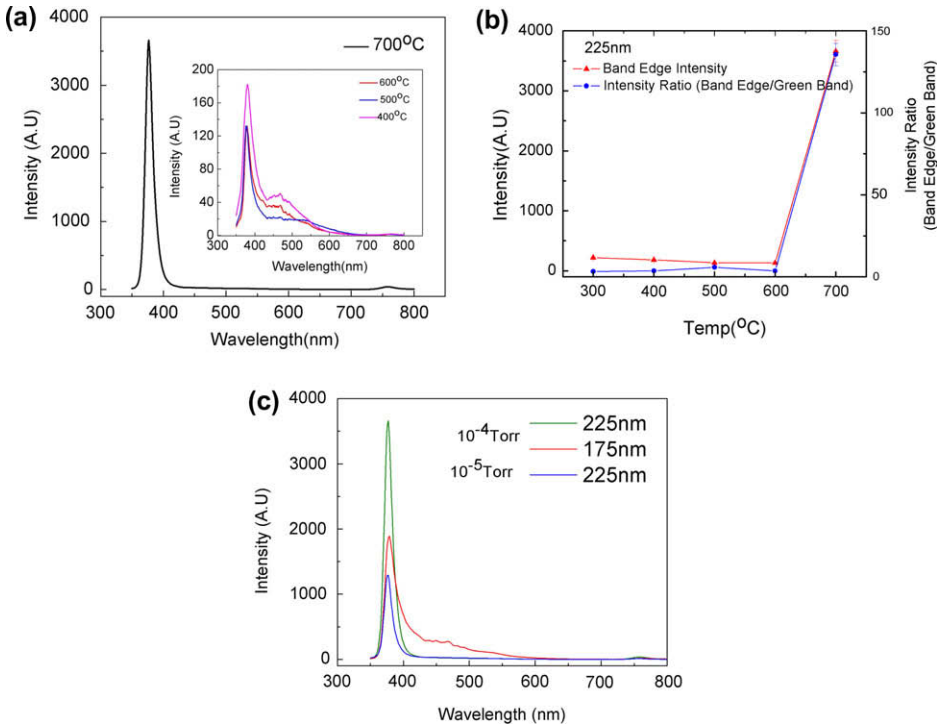

Fig. 4. Room temperature PL spectra of *a*-plane ZnO grown on *r*-plane sapphire obtained using the 300 nm wavelength from a Xe lamp source for excitation (a) at 700 °C, the inset shows the PL for films grown at 600 °C, 500 °C and 400 °C. (b) Variation in the near-band edge PL intensity and intensity ratio of band-edge emission to green band emission with growth temperature. (c) Effect of film thickness and oxygen partial pressure on the PL spectra for ZnO films grown at 700 °C.

tion in resistivity was not observed in the case of undoped ZnO films grown under similar conditions on *c*-plane sapphire substrates. It is also seen that the resistivity of the films grown at 400 °C is four times higher than that of the films grown at 700 °C. The initial decrease in resistivity at low temperatures in this sample can be explained by contributions to electrical transport from shallow donor states, and the subsequent increase in resistivity can be explained by the thermal activation of deep level defect states or shallow acceptor states, which leads to increased scattering. It is interesting to note that a similar transition in resistivity has been reported by Brilis et al. [14] for undoped ZnO thin films grown on Si(1 0 0). They have, however, reported a change in the conductivity from *n*-type at low temperatures to *p*-type at temperatures >270 K.

In summary, the epitaxial growth of *a*-ZnO films on *r*-sapphire was established in the temperature range 200–700 °C by PLD. The epitaxial relationship between the film and the substrate was determined as (1 1 −2 0)ZnO‖(1 0 −1 2)sap, [0 0 0 1]ZnO‖[−1 1 0 1]sap. From X-ray

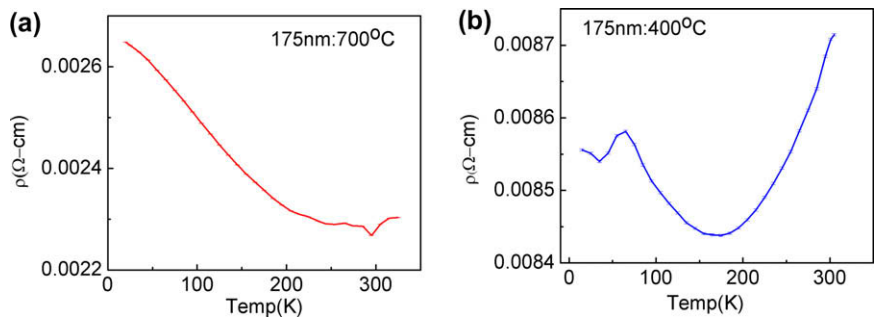

Fig. 5. Van der Pauw resistivity measurements for *a*-plane ZnO films grown on *r*-plane sapphire at: (a) 700 °C and (b) 400 °C.

scans, it was found that the epitaxial quality of the films improved with growth temperature for films grown at 700 °C showing the maximum peak intensity and minimum value of FWHM. The surface morphology of the films shows a preferred in-plane growth along the *c*-axis and indicates the presence of an in-plane anisotropy. The observed in-plane anisotropy which is associated with strain in the film requires further analysis by detailed XRD measurements to study its effect on electrical and optical properties. The high value of the band edge to green band emission ratio of 135:1 for films grown at 700 °C indicated improved optical quality of the film and suggests the potential of these films for optoelectronics with improved efficiency.

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