Structural and optical properties of ZnO thin films by rf magnetron sputtering with rapid thermal annealing

N. A. Suvorova,^{1,a)} I. O. Usov,¹ L. Stan,¹ R. F. DePaula,¹ A. M. Dattelbaum,¹ Q. X. Jia,^{1,b)} and A. A. Suvorova²

¹Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

²Centre for Microscopy, Characterization and Analysis, The University of Western Australia, Crawley, 6009 Western Australia, Australia

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Epitaxial ZnO thin films were grown on *c*-plane sapphire substrates by rf magnetron sputtering at room temperature followed by a rapid thermal annealing process. We found that crystallinity of the films was strongly affected by the partial oxygen pressure during deposition. Both x-ray diffraction and transmission electron microscopy studies revealed that the ZnO films grow epitaxially predominantly with aligned ZnO domains. An unresolved excitonic resonance was observed in the optical absorption spectrum. Nevertheless, refractive index and absorption edge of the ZnO films are similar to that of single crystal ZnO. © 2008 American Institute of Physics.

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Zinc oxide (ZnO), a wide band semiconductor with a direct band gap, has been extensively investigated recently due to its potential applications in the short wavelength range optoelectronics.¹ ZnO has several unique features over other conventional wide band semiconductors such as GaN. For example, ZnO shows a large exciton binding energy with a value around 60 meV, while the value for GaN is 25 meV.¹ In addition, ZnO can be grown using a fairly simple technique that can lead to a potentially reduced cost for devices. Remarkable progress has been recently made in the growth of high-quality epitaxial ZnO films.^{2–5} Aiming for a further simplification of growth processes, we have employed rf magnetron sputtering at room temperature followed by rapid thermal annealing (RTA) for the growth of epitaxial ZnO films on sapphire substrates. We have found that this post-deposition RTA process yields high-quality well-oriented ZnO films.

ZnO thin films were deposited by rf magnetron sputtering on (0001) sapphire substrates at room temperature. The target was a ZnO pellet with 99.999% purity. Prior to the deposition, sapphire substrates were cleaned ultrasonically using isopropyl, acetone, methanol, and de-ionized water. The sputtering was done in an Ar and O₂ mixture with a ratio of Ar/O₂=9/1 or 1/9 with a total pressure range of 10⁻³–10⁻² torr. The as-deposited films were treated by a rapid thermal annealing process (Heatpulse 610 RTP) in oxygen at temperatures of 800, 1000, or 1100 °C from 5 to 120 s. The ramping rate was set at 75 °C/s in all cases.

The crystal structure and the orientation relationship between the film and the substrate were examined using a Siemens D5000 x-ray diffractometer. The chemical composition was determined by Rutherford backscattering spectrometry (RBS), and the crystallinity was evaluated by RBS channeling (RBS/C) method. The interface between the film and the substrate as well as the microstructure of the film were investigated by high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction

(SAED) using a JEOL 3000F FEGTEM and JEOL 2100 TEM. The optical properties of the film were analyzed by spectroscopic ellipsometry (SE) using a rotating analyzer ellipsometer at the incident angle of 60° in the spectral range of 1.24–5.16 eV with 0.02 eV steps.

Figure 1(a) shows x-ray diffraction (XRD) patterns of ZnO films deposited on sapphire under optimized conditions (total pressure of 10⁻² torr and Ar/O₂ ratio of 9/1) and annealed at 800 and 1100 °C. A pronounced ZnO (0002) peak is present along with the Al₂O₃ (0006) peak of the substrate in both cases. Annealing at temperatures lower than 800 °C does not produce highly oriented ZnO films. X-ray diffraction ϕ scan around [10 $\bar{1}$ 1] direction and ω -rocking curve on the (0002) peak were used to determine the in-plane and out-of-plane mosaicities. The full width at half maximum (FWHM) values of the peaks were used to describe the in-plane and out-of-plane textures. Table I shows both the in-plane and the out-of-plane textures of ZnO films grown at various oxygen pressures and annealing conditions. Both in-plane and out-of-plane textures of ZnO films are strongly influenced by the partial oxygen pressure during the film deposition. This effect was reported previously for ZnO films grown on sapphire (0001) by pulsed laser deposition.⁶ The annealing temperature mostly affects the in-plane orientation of the ZnO films. The best textured ZnO film, with ϕ -FWHM of 2.91° and ω -FWHM of 0.7°, was achieved for the film grown at a total pressure of 10⁻² torr, Ar/O₂ ratio of

FIG. 1. X-ray diffraction patterns: (a) θ - 2θ scans of a ZnO thin films deposited under optimized conditions and RTA treated at different temperatures: 800 and 1100 °C; (b) ϕ scans of the ZnO (10 $\bar{1}$ 1) and Al₂O₃ (10 $\bar{1}$ 4). The peaks from the 30°-twisted domains are indicated by arrows.

^{a)}Electronic mail: natalyas@lanl.gov.

^{b)}Electronic mail: qxjia@lanl.gov.

TABLE I. In-plane and out-of-plane textures of ZnO films grown at various oxygen pressures and annealing conditions.

Growth and anneal conditions	10 ⁻³ torr Ar/O ₂ =9/1 1000 °C 5 s	10 ⁻³ torr Ar/O ₂ =9/1 1000 °C 25 s	10 ⁻² torr Ar/O ₂ =9/1 1000 °C 25 s	10 ⁻² torr Ar/O ₂ =9/1 1100 °C 25 s	10 ⁻² torr Ar/O ₂ =1/9 1000 °C 25 s	10 ⁻² torr Ar/O ₂ =1/9 1000 °C 50 s	10 ⁻² torr Ar/O ₂ =9/1 800 °C 120 s	10 ⁻² torr Ar/O ₂ =9/1 1100 °C 50 s
ω -FWHM	5.89°	4.99°	1.1°	0.86°	3.9°	3.03°	0.67°	0.7°
ϕ -FWHM	6.42°	6.19°	5.04°	3.67°	7.94°	7.0°	5.55°	2.91°

9/1, and annealed at 1100 °C for 50 s. Figure 1(b) shows the ϕ scans around ZnO [10 $\bar{1}$ 1] and Al₂O₃ [10 $\bar{1}$ 4], where the ZnO film was grown at the optimized conditions. One set of peaks with large intensity observed in Fig. 1(b) is assigned to aligned ZnO domains with an in-plane orientation relationship of ZnO[11 $\bar{2}$ 0]||Al₂O₃[10 $\bar{1}$ 0] (the unit cell of ZnO is rotated 30° with respect to that of Al₂O₃ to reduce the large lattice mismatch with the substrate). The other set of weak peaks (labeled by arrows) is from 30°-twisted domains. A very low intensity of these peaks indicates a small volume fraction (6%) of the twisted domains. These domains with an epitaxial relationship of ZnO[10 $\bar{1}$ 0]||Al₂O₃[10 $\bar{1}$ 0] was reported to be metastable due to the large lattice mismatch with the substrate (32%) and at higher growth temperature (800 °C) the twisted domains do not form.⁷ ZnO films that were rf sputtered at room temperature and RTA annealed crystallize into a multidomain structure despite the very high annealing temperature (above 1000 °C). The duration of anneal (less than 2 min) has an important influence on the crystallinity of the ZnO films on sapphire substrate.

TEM analysis reveals a columnar structure for the ZnO film with domain sizes in the range of 10–20 nm. Figure 2(a) shows a cross-sectional HRTEM image of a ZnO film on sapphire substrate recorded along the [10 $\bar{1}$ 0] zone axis of sapphire. HRTEM shows a sharp interface between the ZnO and the substrate. However, it also reveals stacking faults and dislocations [Fig. 2(a)]. Figure 2(b) shows the SAED pattern taken from ZnO film and sapphire substrate taken along the [10 $\bar{1}$ 0] zone axis of sapphire. Two sets of diffraction spots are observed in addition to those from the sapphire substrate. First, strong reflections are observed close to the (11 $\bar{2}$ 0) sapphire spots, which are identified as (10 $\bar{1}$ 0) reflections from the ZnO film. The reflections close to (0003) sapphire spots are attributed to (0002) reflections from the ZnO film. This set of reflections can be attributed to aligned ZnO domains with epitaxial orientation of ZnO[11 $\bar{2}$ 0]||Al₂O₃[10 $\bar{1}$ 0], which is typically observed in heteroepitaxial ZnO thin films. These domains are predominantly formed within the ZnO layer. Second, the diffraction pattern exhibits low intensity reflections resulting from [10 $\bar{1}$ 0] ZnO domains. The diffraction pattern in Fig. 2(b) exhibits [11 $\bar{2}$ 0] and [10 $\bar{1}$ 0] ZnO zones similar to the diffraction pattern reported by Abouzaid *et al.*^{8,9} The intensity of the diffraction spots from the [10 $\bar{1}$ 0] ZnO zone axis is weaker than the intensity of spots from [11 $\bar{2}$ 0] ZnO domains. This intensity variation can be attributed to size and concentration variations of the domains within the ZnO layer. These results are in agreement with XRD analysis where the fraction of twisted domains (defined as I_{30}/I_0 , where I_{30} and I_0 are the intensities of diffraction peaks of 30°-twisted and aligned peaks, respectively) in the film is only about 6%.

To determine the crystalline quality of ZnO films, the RBS/C was performed. The reduction of aligned backscattering yield is observed due to the channeling effect. The presence of channeling in our film and the substrate indicates that the ZnO film is epitaxially grown on sapphire using our processing conditions. Minimum backscattering yield, $\chi_{\min}$, defined as the ratio of the aligned to the random yields just below the surface peak, is a measure of a crystal's near surface region perfection.¹⁰ This ratio was found to be 28.9%. The relatively large $\chi_{\min}$ value can be attributed to a large out-of-plane mosaicity as well as to the presence of 30°-rotated domains.

Figure 3 shows the optical constants for a ZnO thin film before and after RTA treatment. The thickness, refractive index n , and extinction coefficient k of the ZnO films are extracted from SE spectra by using model based analysis. The thicknesses of a ZnO film and a roughness layer before RTA treatment are 32.7 ± 1.7 and 1.9 ± 0.8 nm, respectively, and after RTA process the values of a film and surface roughnesses are 24.6 ± 1.3 and 3.4 ± 0.7 nm, respectively. It is interesting to notice that the RTA process not only leads to densification of the film but also results in roughening of the surface. In addition, the refractive index in the visible range

FIG. 2. (a) HRTEM image of a ZnO film on sapphire. Two types of domain orientation are seen: ZnO[11 $\bar{2}$ 0]||Al₂O₃[10 $\bar{1}$ 0] and ZnO[10 $\bar{1}$ 0]||Al₂O₃[10 $\bar{1}$ 0] marked as 1 and 2, respectively. SF is stacking fault and D is dislocation between two domains. (b) SAED pattern from ZnO film and sapphire substrate taken along the [10 $\bar{1}$ 0] zone axis of sapphire. The diffraction spots from [10 $\bar{1}$ 0] ZnO zone axis indicated by arrows.

FIG. 3. Refractive index n and extinction coefficient k of ZnO film before and after RTA treatment. The inset shows the absorption coefficient of as grown and RTA annealed samples (the excitonic peak of RTA annealed sample is marked by arrow).

increases. This agrees with the densification as mentioned above. The refractive indices of the ZnO films are in the range of 1.9–2.2. An index value of 2.0 at photon energy of 1.96 eV is the same as that of a ZnO single crystal. The inset in Fig. 3 shows the absorption coefficient as a function of photon energy. The absorption coefficient α is calculated based on a relation $\alpha = 4\pi k/\lambda$, where λ is the wavelength. It must be noted that the RTA treated film has a very prominent and unresolved broad excitonic absorption feature (marked by an arrow in the inset in Fig. 3). Two distinctive excitonic peaks are commonly observed in epitaxial ZnO films.¹⁰ The unresolved exciton peak might indicate that free excitonic peaks are broadened or additional peaks, for instance defect bound excitons, are present. Several mechanisms can contribute to the excitonic broadening. Phonon interactions and lattice mismatch induced strain are likely to be the main causes that broaden the excitonic peaks. The same mechanisms broaden and shift the optical absorption edge. In order to investigate the excitonic feature of the RTA treated films and extract the band gap values, we applied the excitonic theory of Elliot¹¹ to fit the experimental absorption spectrum. The exciton density of states were described with a Lorentzian and summed with the continuum absorption above the band gap, which was fitted with a Fermi function (fit is not shown). As mentioned above, the discrete excitonic peaks in the absorption spectrum can not be distinguished, thus we only fixed the binding energy of exciton A at 63.1 meV (Ref. 12) (in annealed ZnO samples A-exciton resonance dominates the spectra), while the binding energy of the second

exciton was a fitted parameter. The band gap energy of 3.3 eV extracted from the fit is in good agreement with the value reported in the literature.¹ The resonance energy of exciton A was found to be 3.365 eV which is ~ 12 meV smaller than value measured at 4.2 K. The second resonance with energy of 3.444 eV could not be assigned to B exciton alone due to a very large energy value and broadening parameter of that peak. Therefore, the second peak may be a sum of at least two excitonic peaks: B exciton and a bound exciton on defects, which can not be resolved by room temperature measurements. In order to separate the possible reasons responsible for the broadening of the excitonic resonance energies low temperature optical measurements need to be performed.

In summary, we have demonstrated that rf sputtering at room temperature followed by a rapid thermal anneal in oxygen can be used to deposit epitaxial ZnO thin films on a sapphire substrate with good in-plane and out-of-plane textures. Oxygen partial pressure during film growth plays an essential role in determining the out-of-plane texture of the film, while annealing temperature mostly affects the in-plane orientation. Microstructures of room temperature sputtered and RTA processed ZnO films were characterized by the presence of multiple domains. The reduced crystallinity is likely to be the cause of the additional feature at the absorption edge, as well as broadening of the free excitonic peaks. However, the refractive indices and absorption band edge of the thin films have normal dispersion behavior, which is comparable with that of single crystal ZnO.

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