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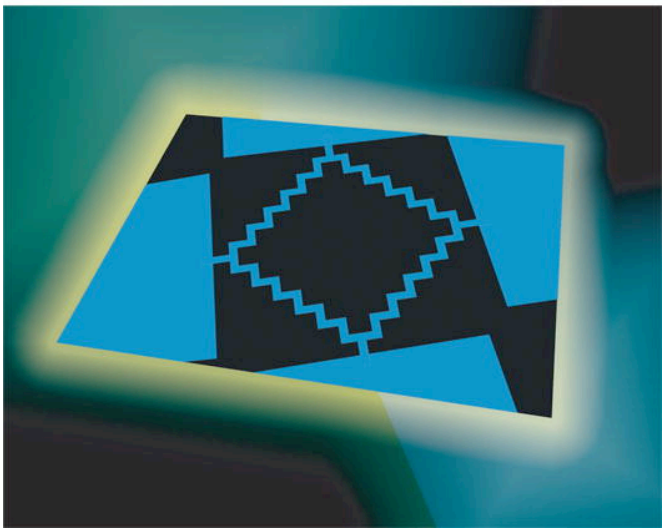

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ZnO films grown by laser ablation with and without oxygen CVD

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Abstract

In the present work we have studied the properties of zinc oxide (ZnO) thin films grown by laser ablation of ZnO targets under different substrate temperature and background oxygen conditions. The ZnO layers were deposited with a Pulsed Laser Deposition (PLD) system on pre-nitrided (0001) sapphire (Al_2O_3), using the base line of a Nd:YAG laser at 1064 nm. The films were characterized by different structural and optical methods, including X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmission spectroscopy, and steady-state photoluminescence (PL). XRD analysis with rocking curves and θ–2θ scans indicates preferential growth along the *c*-axis direction with a full width at half maximum (FWHM) smaller than 1.5°. Low-temperature photoluminescence (PL) showed strong excitonic emission near 3.36 eV between 9 and 65 K.

Keywords: Pulsed laser deposition; Zinc oxide; X-ray analysis

1. Introduction

Due to their wide direct band gap of about 3.3 eV at room temperature (RT) and their high electrical conductivity, thin films of zinc oxide (ZnO) are widely used in practical applications

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such as transparent conducting oxides for flat panel displays and solar cells [1]. Very recently, improvement of material quality and in particular the difficulties in p-doping of ZnO has initiated intense research into two directions: (1) ZnO has nearly perfect lattice match to gallium nitride (GaN) and could serve as a substrate for applications of GaN-based devices; (2) high-purity ZnO films have recently shown room-temperature lasing and are therefore promising candidates for blue-violet emission LEDs and lasers [2]. ZnO is similar to GaN with respect to its piezoelectric properties, but exhibits an advantage for optical applications due to its large exciton binding energy of 60 meV.

In the present work we report the structural, morphological, and optical properties of ZnO thin films prepared by a hybrid CVD-PLD method with and without background oxygen.

2. Experimental

All the ZnO films studied in this work were grown by PLD on *c*-plane sapphire. A *Q*-switched Nd:YAG laser, operating at a wavelength of 1064 nm with a variable pulse energy of up to 100 mJ and a pulse duration of 5 ns is used to ablate the target in a frequency ranging from 2 to 10 Hz. The laser beam is introduced into the chamber via a quartz window at an incidence angle of 30° to the target and focused on the zinc oxide target through a quartz lens to a typical elliptical spot of size $200 \times 400\ \mu m^2$. ZnO targets were made from zinc oxide powder (purity 99.99%). The target-to-substrate distance was about 3 cm. Samples A, B, and C were deposited at 25 °C, 400 °C, and 600 °C, respectively. Film A was exposed to oxygen background gas during ablation, whereas the other films were deposited under vacuum. Film B′ was deposited under identical parameters as film B and used for PL analysis.

To examine film structure, X-ray diffraction studies were carried out on a Siemens D5000 diffractometer using Cu Kα radiation at 40 kV. Optical properties were measured on films grown on (001) sapphire substrates. Transmission spectra were recorded in the range 250–800 nm. The observation of surface morphology was performed using a scanning electron microscope (SEM, JEOL model JSM5300). PL measurements were carried out with a 325 nm HeCd laser and the excitation power density was typically less than 0.6 W/cm^2.

3. Results and discussion

3.1. Structural characterization

The crystal structure and orientation of the as-deposited ZnO thin films were investigated by means of the X-ray diffraction (XRD) method. Fig. 1(a) shows the XRD θ–2θ scans corresponding to ZnO thin films prepared with (upper curve) and without (lower curve) oxygen background atmosphere. Two peaks were detected in the range between 30° and 45°. The first peak, located at about 34°, can be assigned to the (002) crystallographic plane family in hexagonal ZnO [3], whereas the second peak at 41.68° is attributed to the (006) diffraction line of the sapphire substrate [4]. The observation of only the (002) peak indicates that both films were grown with a *c*-axis orientation normal to the substrate surface.

To investigate the degree of alignment of the ZnO crystallites with respect to the normal to the surface, rocking curve (RC) measurements were also performed for the (002) reflection. Fig. 1(b) shows the rocking curves of both samples; FWHM values of 1.21° and 1.55° were determined for the samples prepared with and without oxygen atmosphere, respectively. These small values indicate that both samples are strongly textured along the *c*-axis [5], although there exists some

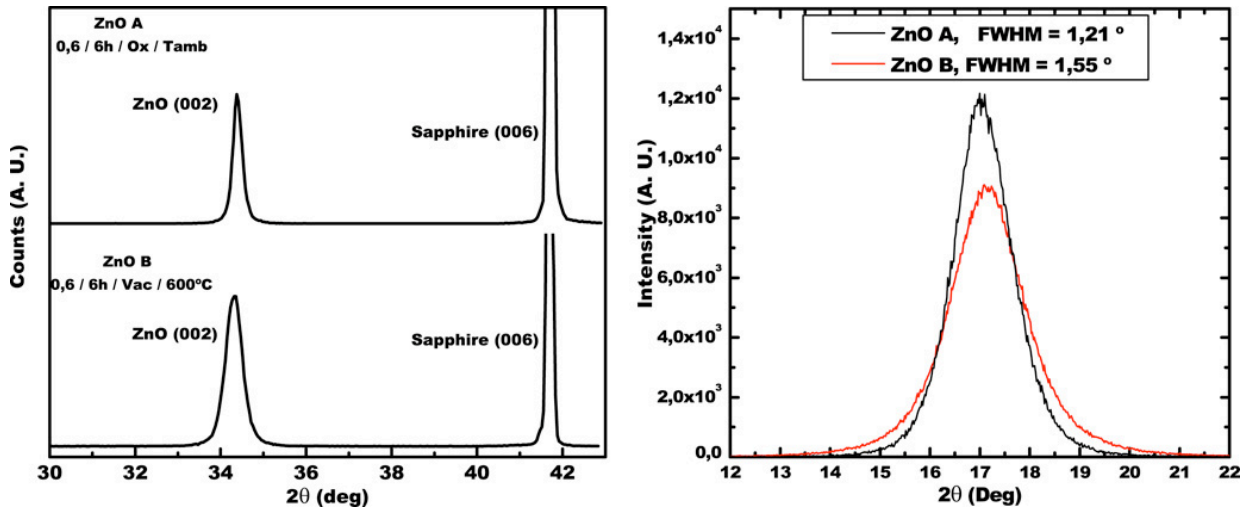

Fig. 1. XRD analysis of samples A and B: (a) θ–2θ XRD pattern; (b) (002) rocking curves.

Table 1
XRD peak position, c-parameter value, average crystallite size, and calculated stress in three different ZnO films

Sample	Back-ground gas	Substrate temperature (°C)	Peak position (deg)	c-parameter (nm)	Crystallite size (nm)	Stress (GPa)
A (ZnO-12)	O_2	23 (RT)	17.197	0.5209	19	−0.12
B (ZnO-6)	Vac	400	17.142	0.5225	17	− 0.85
C (ZnO-7)	Vac	600	17.144	0.5226	17	− 0.83

degree of misorientation among the crystallites. Because crystal quality usually improves as the growth temperature increases, a narrower RC should be expected for sample B. The higher FWHM value obtained for the latter sample indicates that oxygen favours the orientation of the crystallites.

Additional information on structural properties can be obtained from the *residual* stress measurements. Based on the biaxial strain model, the strain can be calculated as in [6]:

$$\sigma = -233 * (c(\text{film}) - c(\text{bulk}))/c(\text{bulk}) \text{ (GPa)}. \quad (1)$$

Table 1 shows the peak position, c-parameter value, average crystallite size and the calculated stress using the above equation for the three samples, A, B, and C. As expected for ZnO thin films grown on sapphire by the PLD method, compressive stresses are calculated for all films, with a higher value obtained at 600 °C. This higher value appears in the film during cooling due to the large difference between ZnO and sapphire thermal expansion coefficients.

3.2. Morphological characterization

SEM images of the surfaces of samples A and B are presented in Fig. 2. In the SEM micrograph corresponding to sample A, particles with diameters of around 40–100 nm are observed, together with some particulates which are themselves formed by very fine particles. Sample B shows a very smooth and continuous surface with a high density of particles with diameters ranging from 100 nm to about 500 nm. We have checked by energy-dispersive X-ray analysis (EDX) that, indeed, in the dark areas of micrograph B a compact Zn-containing film was present.

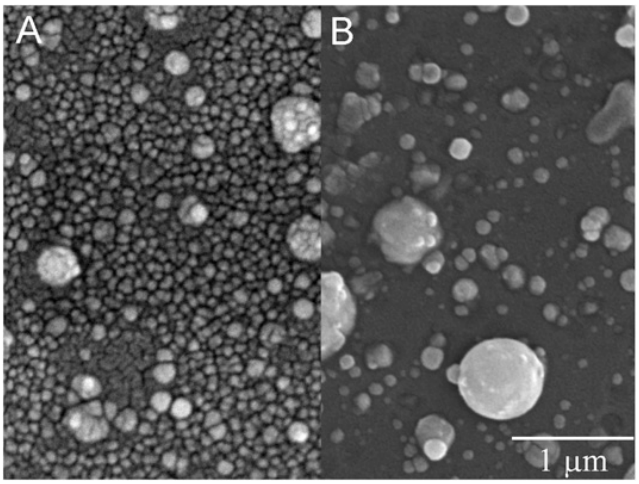

Fig. 2. SEM micrographs of samples A and B.

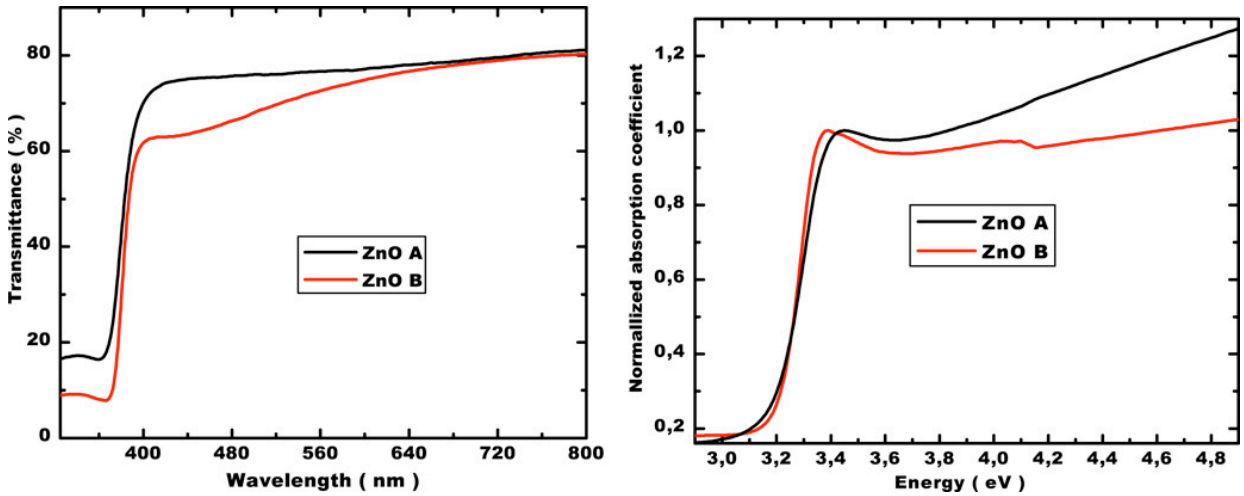

Fig. 3. Optical transmission (a) and normalized optical coefficient (b).

Table 2
Film thickness and optical properties

Sample	Back-ground gas	Substrate temperature (°C)	Film thickness (nm)	Band gap (eV)	Urbach tail (meV)
A (ZnO-12)	O_2	23 (RT)	155	3.25	121 ± 5
B (ZnO-6)	Vac	400	285	3.24	89 ± 5
C (ZnO-7)	Vac	600	195	–	70 ± 5

3.3. Optical properties

Fig. 3(a) shows the RT optical transmittance spectra of two ZnO thin films in the wavelength range between 320 and 800 nm. Both samples exhibit high transmittance in the visible region (about 90 and 70% for the samples A and B, respectively) and high absorption in the UV region.

The absorption coefficient curves shown in Fig. 3(b) were calculated from the transmission data according to Beer's law. Both samples exhibit typical excitonic structure on the high-energy side, with discrete exciton peaks at photon energies of 3.44 and 3.39 eV for sample A and B, respectively. The optical direct band gaps E_g, given in Table 2, are evaluated according to the

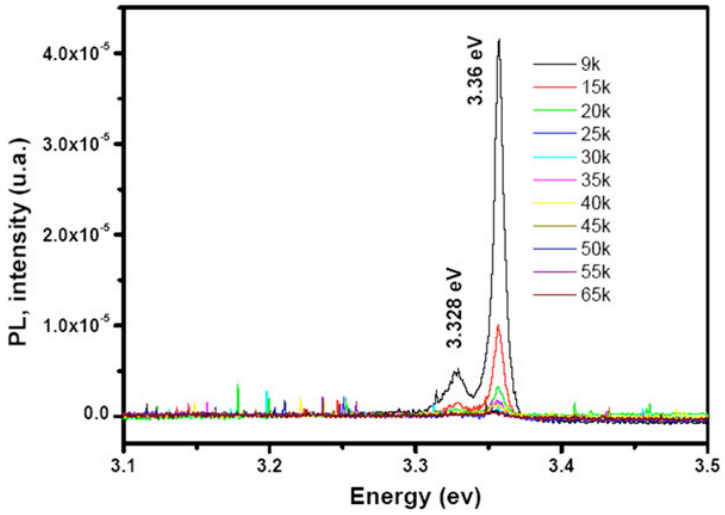

Fig. 4. Evolution of steady-state photoluminescence as a function of temperature for sample B′ prepared under identical conditions as sample B.

general formula $(\alpha h\nu)^2 = B(h\nu - E_g)$, where B is a constant [7]. The absorption coefficient $\alpha(h\nu)$ in the energy range just below the gap follows the well-known exponential law, that is the Urbach tail, expressed by:

$$\alpha(h\nu) = \alpha_0 \exp(h\nu/E_0) \tag{2}$$

where α_0 is a constant, and E_0 is the width of the tail of localized states in the band gap. The E_0 values given in Table 2 are lowest for samples prepared at 600 °C, indicating that increasing the substrate temperature improves the optical quality and the film stoichiometry.

For both samples, the band gap energy that is obtained is lower than the tabulated value of 3.37 eV in stoichiometric ZnO. This is consistent with the influence of the excitonic peak near the band edge, as seen in Fig. 3(b).

Fig. 4 shows typical steady-state photoluminescence spectra corresponding to a ZnO thin film prepared at 400 °C in vacuum, measured in the range between 9 and 65 K. This film, B′, was deposited under identical deposition conditions as sample B given in Tables 1 and 2. The photoluminescence is dominated by the emission at 3.36 eV (D0X), with an associated smaller peak at 3.328 eV [8]. As the temperature is increased, the intensity of the main peak at 3.36 eV is decreased, showing that the same optically active defects are present as in as-grown ZnO single crystals [8].

4. Conclusions

In the present work, we showed that it is possible to grow ZnO thin films with good structural, morphological, and optical properties using the PLD technique. Room-temperature deposition leads to highly c-axis oriented films, as seen by X-ray analysis, but the optical data indicates a high defect density, as evidenced by a wide Urbach tail. The film quality is improved at larger deposition temperatures.

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References

[1] C.H. Agashe, O. Kluth, G. Schöpe, H. Siekmann, J. Hüpkes, B. Rech, Thin Solid Films 442 (2003) 167.
[2] Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270.
[3] JCPDS database, file card no 36-1451.
[4] JCPDS database, file card no 42-1468.
[5] A. Ohtomo, A. Tsukazaki, Semicond. Sci. Technol. 20 (2005) 1.
[6] J. Mass, P. Bhattacharya, R.S. Katiyar, Mater. Sci. Eng. B 103 (2003) 9.
[7] R. Ayouchi, F. Martin, D. Leinen, J.R. Ramos-Barrado, J. Cryst. Growth 247 (2003) 497.
[8] T. Monteiro, A.J Neves, M.C. Carmo, M.J. Soares, M. Peres, E. Alves, E. Rita, U. Wahl, Superlatt. Microstruct. 39 (2006) 202.