

# Optical properties of pulsed-laser deposited ZnO thin films

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ZnO thin films were deposited by pulsed laser deposition (PLD) technique on optical glass substrate. Structural analysis by X-ray diffraction revealed a wurtzite phase ZnO, highly textured, with (002) planes perpendicular to the growth direction. They were optically characterized by absorption and transmission spectrometry. The wavelength dependence of the refractive index was extracted from transmission data by using a numerical fitting procedure.

(Received March 2, 2009; accepted April 23, 2009)

*Keywords:* ZnO, XRD, optical properties

## 1. Introduction

Transparent conducting oxides (TCOs) are becoming increasingly critical components in applications, such as flat panel displays [1], photovoltaics [2] or transparent electronics [3]. Recently, metal oxide doped ZnO thin films have been studied as transparent conducting oxide (TCO) materials [4, and references therein]. ZnO is one of A<sup>II</sup>B<sup>VI</sup> semiconductors with a hexagonal wurtzite structure, a wide direct band gap (3.37 eV) and high optical transmittance in visible range. Particularly, because of their wide direct bandgap, low cost, non-toxic character, low sheet resistivity which can be obtained by doping, the ZnO thin films are good candidates for transparent conducting oxide semiconductors used for optoelectronic applications. Various techniques were used to produce good quality ZnO films in TCO regime (see [4] for a review).

In this paper we report on a thorough investigation on the structural and optical properties of ZnO thin films deposited by pulsed laser deposition (PLD) technique. By using a numerical fitting procedure, the spectral dependence of the refractive index in the transparency region is extracted. The procedure we used allows also for a proper determination of the band gap and the film thickness.

Details on the experimental procedure for producing the samples are given in the second section. In section 3 the theoretical model used for interpreting optical spectra is presented. The obtained results are discussed in the 4-th section. Finally, the last section of this paper summarizes the main results and conclusions.

## 2. Experimental

ZnO thin films were obtained by using a KrF excimer laser operating at 248 nm wavelength and having pulse duration of  $\approx 7$  ns. The laser was operated at a repetition rate of 20 Hz with an energy density of 2.5 J/cm<sup>2</sup>. The distance from target to substrate was 5 cm. The deposition chamber was initially evacuated to 10<sup>-6</sup> torr and the substrate was heated to 400 °C. During deposition, oxygen was used as background gas. The conditions for the deposition of the ZnO thin films are summarized in Table 1.

*Table 1. Deposition parameters for ZnO thin films samples.*

No.	Sample	Target	Substrate	T [°C]	Pressure [Pa]
1	TCO1	ZnO:Al (2%)	SiO <sub>2</sub>	400	6.5 O <sub>2</sub>
2	TCO2	ZnO	SiO <sub>2</sub>	400	1.3 O <sub>2</sub>
3	TCO3	ZnO	SiO <sub>2</sub>	400	6.5 O <sub>2</sub>
4	TCO4	ZnO	SiO <sub>2</sub>	400	1.3 O <sub>2</sub> /N <sub>2</sub> (3/1)

The crystallinity of the samples was characterized by X-Ray Diffraction (XRD), using a  $\theta - 2\theta$  diffractometer. XRD spectra were recorded by using Cu-K $\alpha$  line,  $\lambda = 1.54178$  Å. Line profiles were recorded in a step-scanning regime, with  $\Delta(2\theta) = 0.02^\circ$ .

Optical transmittance and absorption spectra were measured by using a UV-VIS spectrometer (Perkin Elmer Lambda 35).

### 3. Theoretical model

Optical characterization of ZnO thin films was performed using a method similar with that proposed in Ref. [5]. For thin films, optical quantities of interest can be obtained from the transmittance data,  $T$ , given by:

$$T = \frac{Ax}{B - Cx \cos \varphi + Dx^2} \quad (1)$$

where:  $A = 16n^2s$ ,  $B = (n+1)^3(n+s^2)$ ,  
 $C = 2(n^2-1)(n^2-s^2)$ ,  $D = (n-1)^3(n-s^2)$ ,  
 $x = \exp(-\alpha d)$ ,  $\varphi = \frac{4\pi}{\lambda}nd$ ,  $d$  and  $n$  are the thickness and the refractive index of ZnO thin films, respectively,  $s$  is the refractive index of substrate and  $\alpha$  is absorption coefficient. The analysis of the recorded data starts by constructing two envelopes around the maxima and minima of the interference fringes in the transparency region of the transmission spectrum. The interference envelopes, passing through the extreme points in the spectrum ( $\cos \varphi = \pm 1$ ), are defined by:

$$\begin{aligned} T_M &= \frac{Ax}{B - Cx + Dx^2} \text{ and} \\ T_m &= \frac{Ax}{B + Cx + Dx^2}, \end{aligned} \quad (2)$$

where  $T_M$  corresponds to maxima and  $T_m$  corresponds to minima in the spectra.

The refractive index of the ZnO thin film can be determined from the two envelopes. First, the quantity:

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A}$$

is calculated, and the refractive index can be easily extracted from it, as:

$$n = \left[ N + (N^2 - s^2)^{1/2} \right]^{1/2}, \quad (3)$$

where  $N$  is defined by  $N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}$ . Once

$n(\lambda)$  is known, all the constants  $A$ ,  $B$ ,  $C$ ,  $D$  appearing in eq. (1) can be determined.

Similarly, the optical density  $x$  of ZnO thin film can be extracted from the two envelopes, by calculating first the expression:

$$\frac{2T_M T_m}{T_M + T_m} = \frac{Ax}{B + Dx^2},$$

from which the optical density can be extracted as:

$$x = \frac{F - \left[ F^2 - (n^2 - 1)^3 (n^2 - s^4) \right]^{1/2}}{(n-1)^3 (n-s^2)}, \quad (4)$$

where  $F$  is defined by  $F = 4n^2 s \frac{T_M + T_m}{T_M T_m}$ .

Knowing the refractive index  $n$ , the film thickness  $d$  can be calculated by a linear fit procedure. The maxima (minima) positions in the transparency region are given by:

$$2nd = \left( m_0 - \frac{l}{2} \right) \lambda \quad (5)$$

where  $l = 0, 1, 2, \dots$  and  $m_0$  is the unknown order of the first interference fringe. If  $n > s$ , the first interference fringe is a maximum. By constructing the dependence of  $l/2$  as a function of  $n/\lambda$ , a straight line is obtained, its slope being twice the film thickness:

$$\frac{l}{2} = 2d \left( \frac{n}{\lambda} \right) - m_0 \quad (6)$$

The band gap of ZnO is a direct one, so the band gap value  $E_g$ , can be determined from the absorption spectra in the fundamental absorption region, where:  
 $\alpha \propto \frac{(E - E_g)^{1/2}}{E}$ , where  $E$  is the photon energy,  
 $E = hc/\lambda$ .

In the fundamental absorption region, an Urbach tail was also detected for all analyzed samples. The Urbach parameter,  $E_0$ , was extracted, its values being presented in Table 2, for all the samples.

### 4. Results and discussion

Optical and structural properties of ZnO thin films are summarized in Table 2.

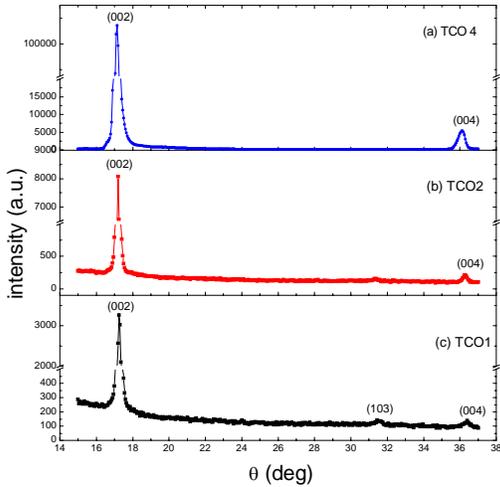
Table 2. Physical parameters that characterize the analyzed ZnO thin films.

No.	Sample	d (nm)	$E_g$ (eV)	n (500 nm)	Urbach parameter $E_0$ (meV)	$D_{\text{eff}}^{(002)}$ (nm)
1	TCO1	410	3.34	1.83	265	32
2	TCO2	1143	3.27	1.51	555	61
3	TCO3	408	3.26	1.95	106	-
4	TCO4	887	3.26	1.88	233	34

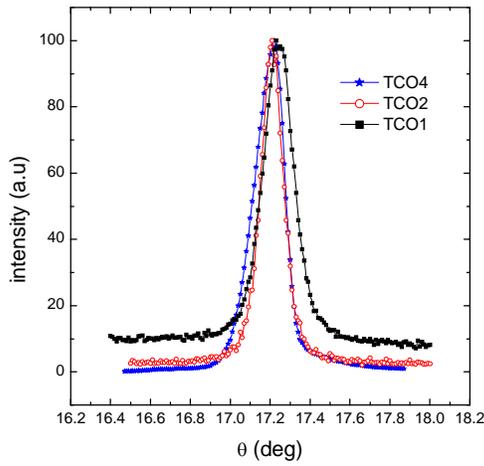
Structural analysis by X-Ray diffraction revealed a wurtzite phase ZnO, highly textured, with (002) planes perpendicular to the growth direction. XRD patterns are shown in figure 1. Crystallite sizes were determined using Scherrer formula:

$$D_{\text{eff}} = \frac{0.9 \lambda_x}{\delta \cos \theta_0} \quad (7)$$

where  $\lambda_x$  is the X-ray wavelength,  $\delta$  is the full width at half maximum corresponding peak and  $\theta_0$  is the angle where the peak occurs.



(a)



(b)

Fig. 1 Experimental X-Ray diffraction pattern of ZnO thin films (a) and enlargement of (002) peak of ZnO thin films (b).

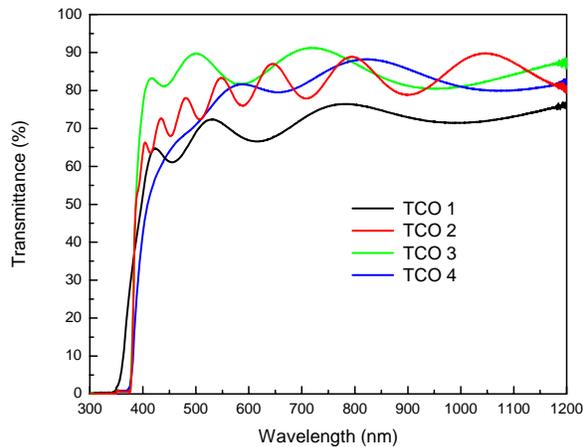


Fig. 2 Transmission spectra of ZnO thin films.

The optical transmission spectra of ZnO thin films are shown in Fig. 2, and for sample TCO2 the interference envelopes passing through the extreme points in the spectrum are shown in Fig. 3.

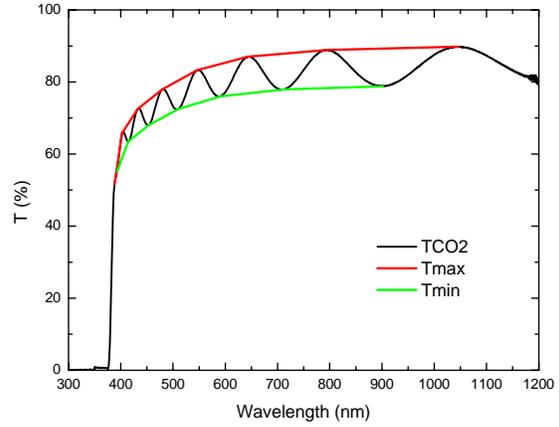


Fig. 3 Transmission curve for TCO2 sample, showing interference envelope functions  $T_M$  and  $T_m$ .

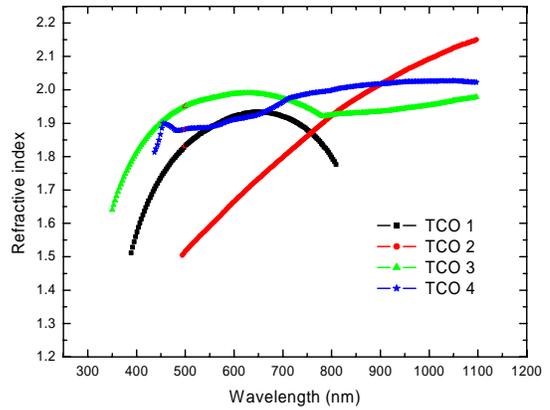


Fig. 4 Wavelength dependence of the refractive index in the transparency region

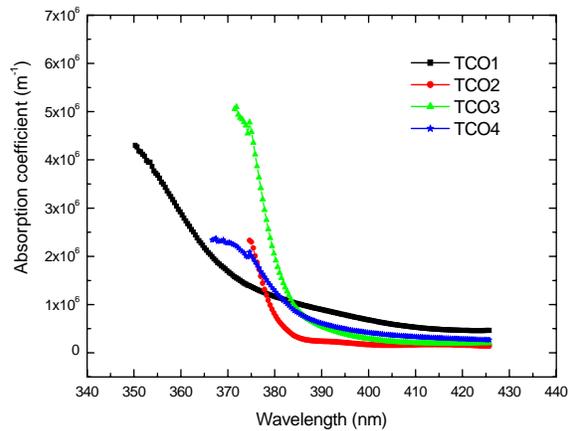


Fig. 5 Wavelength dependence of the absorption coefficient in the fundamental absorption region.

The average optical transmission in the visible region of spectrum is  $\sim 75\%$ . The wavelength dependence of the refractive index in the transparent region for ZnO thin films is shown in figure 4. This dependence was obtained using equation (3). The refractive index  $s$  was assumed to be a constant across the spectrum, because it is varying less than 5%. The wavelength dependence of the absorption coefficient in the fundamental absorption region was obtained using equation (6) and is shown in figure 5.

## 5. Conclusions

ZnO thin films in TCO regime were obtained by PLD. The deposition parameters are indicated in Table 1. Structural analysis by X-Ray diffraction revealed a wurtzite phase ZnO, highly textured, with (002) planes perpendicular to the growth direction. The transmission and absorption spectra were measured in the 1200 – 300 nm range. By using a numerical procedure, the spectral dependence of the refractive index in the transparency region was determined. The procedure we used allows also

for the determination of film thicknesses,  $d$ . The optical bandgaps,  $E_g$  and the Urbach parameter  $E_0$  characterizing the Urbach tails near the fundamental absorption region were also calculated.

## References

- [1] M. Chen, Z.L. Pei, C. Sun, J. Gong, R.F. Huang, L.S. Wen, Mater. Sci. and Eng. **B 85**, 212 (2001).
- [2] D.S. Ginley, C. Bright, MRS Bulletin **25**, 15 (2000).
- [3] K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, H. Hosono, Science 1269 (2003).
- [4] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J Cho, H. Morkoç, J. Appl. Phys. **98**, 014301-1 (2005).
- [5] R. Swanepoel, J. Phys. E: Sci. Instrum. **16**, 1214 (1983).

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