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Determination of the thickness and optical constants of transparent indium-doped ZnO thin films by the envelope method

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Transparent indium-doped ZnO thin films were deposited by the spray pyrolysis method onto glass substrates. The content of indium in the starting solution was 0.5 at. %. The crystallographic structure of the film was studied by X-ray diffraction (XRD). XRD measurement shows that the film is crystallized in the wurtzite phase and presents a preferential orientation along the *c*-axis. The texture coefficient (*TC*), grain size value and lattice constants have been calculated. The absorption coefficient and the thickness of the films were calculated from interference of transmittance spectra. Optical constants such as the refractive index *n* and extinction coefficient *k* have been determined from transmittance spectrum in the ultraviolet–visible–near infrared (UV–VIS–NIR) regions using the envelope method. The thickness of the films strongly influences the optical constants.

Key words: *ZnO; spray pyrolysis; envelope method*

1. Introduction

Recently, transparent conducting oxides (TCOs) have been widely studied. Among TCOs, zinc oxide (ZnO) is one of the most promising materials for the fabrication of the next generation of optoelectronic devices in the UV region and optical or display devices. ZnO is a wide-bandgap $A^{II}B^{VI}$ semiconductor with the bandgaps of about 3.3 eV. As a matter of fact, simultaneous occurrence of both high optical transmittance in the visible range, and low resistivity make ZnO an important material in the manufacture of heat mirrors used in gas stoves, conducting coatings in aircrafts glass avoiding surface icing, and as thin film electrodes in amorphous silicon solar cells. ZnO is a member of the hexagonal wurtzite class; it is a semiconducting, piezoelectric and optical waveguide material and has a variety of potential applications such as gas sensors [1], surface acoustic devices [2], transparent electrodes [3] and solar

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cells [4, 5]. Some of these applications are based on the simultaneous occurrence of low resistivity and high transmittance in the visible spectrum, when ZnO is manufactured in the form of thin solid films.

For many of these applications, it is very important to control the ZnO physical properties by doping. Usually, n-type doping is obtained by Al, Ga or In. On the other hand, p-type doping is not easily obtained. Various deposition techniques have been widely used to produce semiconductor thin films. However, seeking the most reliable and economic deposition technique is the main goal. The most intensively studied techniques include: RF magnetron sputtering [6], metal organic chemical vapour deposition [7], sol-gel method [8] and spray pyrolysis [9, 10]. They have been studied intensively in the last three decades due to their simplicity and economy. The chemical bath deposition, chemical spray pyrolysis and sol-gel techniques are well known methods of preparation of thin films. The spray pyrolysis is an excellent method for the deposition of thin films of metallic oxides, as is the case for the ZnO material. In this deposition technique, a starting solution, containing Zn and dopant precursors, is sprayed by means of a nozzle, assisted by a carrier gas, over a hot substrate. When the fine droplets arrive at the substrate, the solid compounds react to become a new chemical compound.

The widely used envelope method has been developed for transmittance measurements to evaluate the refractive index, extinction coefficient, and absorption coefficient. Optical characterization of thin films gives information about other physical properties, e.g. band gap energy and band structure, optically active defects etc., and therefore may be of permanent interest for several different applications. Considerable differences between optical constants of bulk material and thin films or those of films prepared under varying growth characteristics are often reported. Therefore determination of optical constants for each individual film by a non-destructive method is highly recommended.

Generally, the optical band gap (E_g) and absorption coefficient α could be evaluated from transmittance or absorbance spectra. Swanepoel [11] has improved this method to determine more accurately the thickness (t), absorption coefficient (α), etc. There are several reports on this method [12–14]. In another conventional method, the reflectance (R) and transmittance (T) spectra are used to determine α. Since α is related to the extinction coefficient k, which is defined as the imaginary part of the complex refractive index, where n is the real part of refractive index, an accurate determination of n and k is possible. But this often becomes difficult due to the presence of multiple solutions. It is necessary to have a rough idea about the thickness t and refractive index n to start with, and by a judicious adjustment of the magnitude of thickness it is possible to secure a continuous solution of n and k throughout the whole spectral range.

There are a few papers on the determination of optical constants of the ZnO thin films by using the well-known envelope method [14–18], but there is no report on the indium-doped ZnO thin film. Therefore, in this paper, the optical constants of the indium-doped ZnO thin films which have different thicknesses have been studied for the first time.

2. Experimental details

In-doped ZnO thin films of various thicknesses were deposited onto microscope glass (Objekttrager, 1×1 cm^2) substrates using the spray pyrolysis method at 350 ^oC. The experimental set-up was described elsewhere [19]. An aqueous solution of 0.1 M $Zn(CH_3CO_2)_2$ was used as a precursor, prepared from a mixture of methanol and water to a volume ratio of 3:1. The resulting solution was doped with indium by adding indium chloride ($InCl_3$) with an In/Zn ratio equal to 0.5 at. % in the starting solution. The mixture was continuously agitated until total dissolution. A small amount of acetic acid was added to obtain total dissociation of the zinc acetate. Nitrogen was used as the carrier gas, at the pressure of 0.2 bar. The ultrasonic nozzle was 28 cm distant from the substrate during deposition, the solution flow rate was held constant at 4 ml·min^{-1}. The substrate temperature was measured using an iron-constantan thermocouple.

The structural properties were studied by X-ray diffraction measurements (Rigaku Rint 2200 Series X-Ray automatic diffractometer with CuK_α radiation (λ =1.54059 Å)). The average dimensions of crystallites were determined by the Scherrer method from the broadening of the diffraction peaks taking into account the instrumental broadening.

The optical measurements of the In-doped ZnO thin films were carried out at room temperature using Shimadzu UV-VIS-NIR 3150 spectrophotometer in the wavelength range from 190 to 3200 nm. Swanepoel's envelope method was employed to evaluate the optical constants such as the refractive index n, extinction coefficient k, and absorption coefficient α from the transmittance spectra [11]. The thickness of the In-doped ZnO thin film was determined from the interference fringes of transmission data recorded over the visible range.

3. Results and discussion

3.1. Structural properties of the In-doped ZnO thin film

XRD spectrum of the In-doped ZnO thin film (t = 337 nm) is shown in Fig. 1. The peaks of the XRD pattern correspond to those of the theoretical ZnO patterns from the JCPDS data file [20], with a hexagonal wurtzite structure of the bulk and lattice constants: a = 3.24982 Å, c = 5.20661 Å. The analytical method [21] was used to calculate the lattice constants (a = 5.21580 Å, c = 3.26064 Å) for the film. The full width at half maximum (FWHM) of the (002) peak is 0.284°. Another major orientation present is (101), while other orientations like (102) and (100), are also seen with comparatively lower intensities. Therefore, the crystallites are highly oriented with their *c*-axes perpendicular to the plane of the substrate. 2θ and d values are given in Table 1.

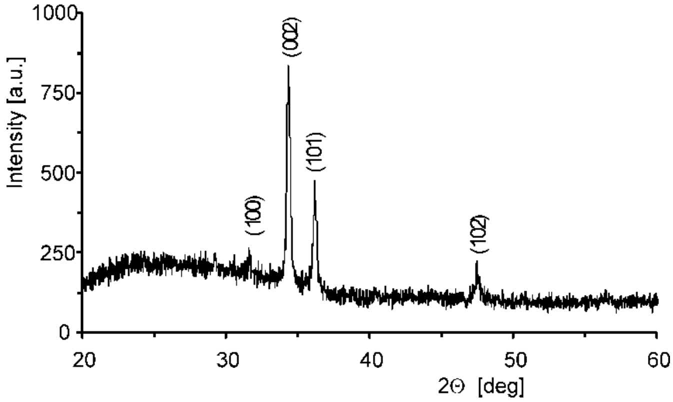

Fig. 1. XRD spectrum of the In-doped ZnO thin film

Table 1. The X-ray diffraction data results of the In-doped ZnO thin film

(*hkl*)	2θ [deg]	d [Å]	I/I_0	TC [%]
(100)	31.660	2.8238	11.5	6.58
(002)	34.360	2.6079	100.0	57.21
(101)	36.200	2.4794	48.3	27.63
(102)	47.443	1.9148	15.0	8.58

The grain size of the film from the XRD data was calculated using the Debye –Scherrer formula [21]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where D is the grain size of the crystallite, λ (1.54059 Å) is the wavelength of the X-rays used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction. The value found for the grain size is 31 nm.

The texture coefficient (*TC*) represents the texture of a particular plane, whose deviation from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation was obtained from another texture coefficient *TC*(*hkl*) defined as [22]:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\sum_n \frac{I(hkl)}{I_0(hkl)}} \times 100\% \quad (2)$$

where $I(hkl)$ is the measured relative intensity of a plane (hkl) and $I_0(hkl)$ is the standard intensity of the plane (hkl) taken from the JCPDS data. The value $TC(hkl) = 1$ represents films with randomly oriented crystallites, while higher values indicate the abundance of grains oriented in a given (hkl) direction. The variation of TC for the peaks of the wurzite lattice is presented in Table 1. It can be seen that the highest TC was in the (002) plane for In-doped ZnO thin film.

3.2. Determination of thicknesses of the In-doped ZnO thin films

An excellent surface quality and homogeneity of the film were confirmed from the appearance of interference fringes in the transmission spectra [23, 24] occurring when the film surface is reflecting without much scattering/absorption in the bulk of the film [24]. The optical constants were evaluated using the "envelope method" originally developed by Manifacier et al. [25]. Generally, outside the region of fundamental absorption ($h\nu > E_g$) or of the free-carrier absorption (for higher wavelengths), the dispersion of n and k is not very large [25]. If we assume that the film is weakly absorbing and the substrate is completely transparent, then using this method the refractive index (n), and extinction coefficient (k) of the film on a transparent substrate can be evaluated from the transmission spectra.

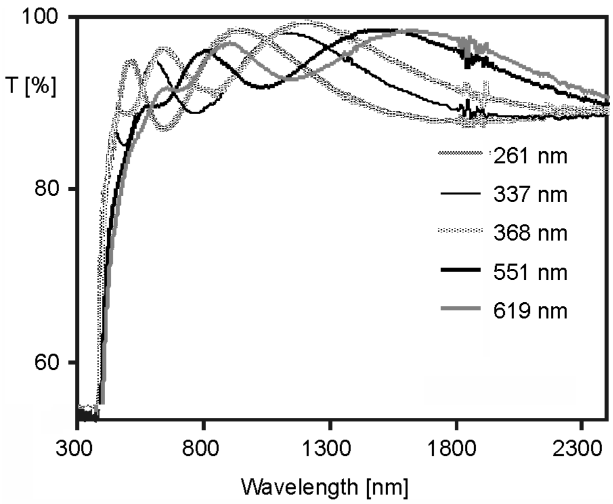

Fig. 2. Transmittance spectra of the In-doped ZnO thin films

Figure 2 shows transmittance curves for In-doped ZnO thin films at various thicknesses. These films exhibited good transparency (between 91% and 93%) in the visible and infrared region.

The refraction indices n at various wavelengths were calculated using the envelope curve for $T_{\max}$ (T_M) and $T_{\min}$ (T_m) in the transmission spectra [11]. The expression for the refractive index is given by

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

where

$$N=2n_s\frac{T_M-T_m}{T_MT_m}+\frac{n_s^2+1}{2} \tag{4}$$

and n_s is the refractive index of the substrate (n_s =1.52 for glass).

The extinction coefficient k can be calculated from the following formula [25]:

$$k=\frac{\alpha\lambda}{4\pi d} \tag{5}$$

$$\alpha=-\frac{1}{t}\ln\frac{(n-1)(n-n_s)\left(\frac{T_{\max}}{\mathrm{T}_{\min}}+1\right)^{0.5}}{(n+1)(n+n_s)\left(\frac{T_{\max}}{\mathrm{T}_{\min}}-1\right)^{0.5}} \tag{6}$$

where α is the absorption coefficient. λ_1 and λ_2 are the wavelengths at the two adjacent maxima or minima. The optical constants such as refractive index n and extinction coefficient k were determined from the transmittance spectrum by the envelope method as explained in the previous section. The variations of the refractive index n and extinction coefficient k with the wavelengths in the range 450–1800 nm are shown in Figs. 3a, b.

The thickness of the film was calculated using the equation

$$t=\frac{\lambda_1\lambda_2}{2(\lambda_1n_2-\lambda_2n_1)} \tag{7}$$

where n_1 and n_2 are the refractive indices corresponding to the wavelengths λ_1 and λ_2, respectively [11]. The thicknesses of the films are given in Table 2.

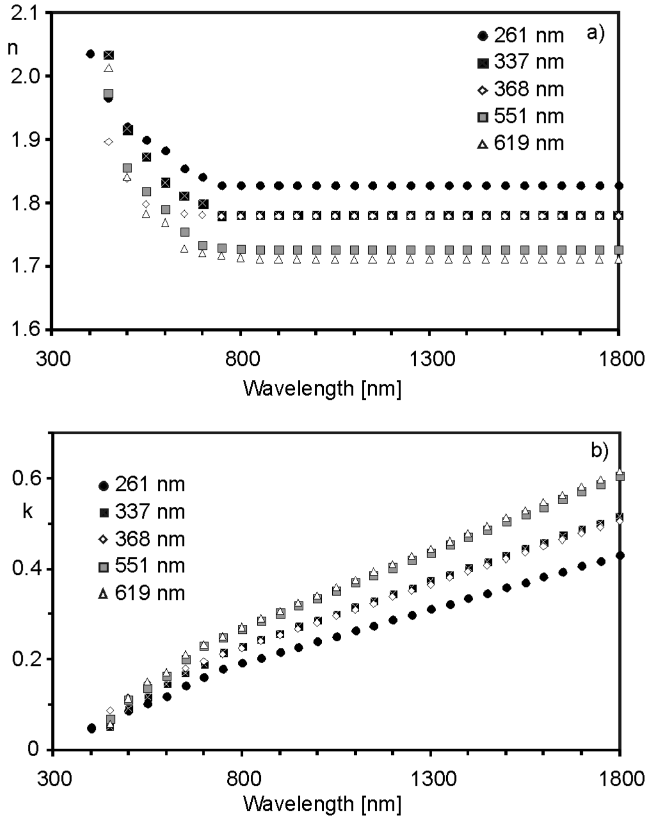

Fig. 3. Plots of refractive index (a) and extinction coefficient (b) of the In-doped ZnO thin films as a function of wavelength

Table 2. The values of the band edge sharpness B_s and optical band gap E_g of the In-doped ZnO thin films

Thickness [nm]	B_s [m^{-2}·eV^{-1}]	E_g (eV)
261	(4.57±0.04)×10^{13}	3.29±0.01
337	(6.18±0.04)×10^{13}	3.30±0.01
368	(4.78±0.04)×10^{13}	3.30±0.01
551	(7.29±0.04)×10^{13}	3.30±0.01
619	(6.84±0.04)×10^{13}	3.30±0.01

3.3. The band gap energy of the In-doped ZnO thin films

The absorption coefficient α of the In-doped ZnO thin films was determined from absorbance measurements. Since the envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient of the film in this region was performed using the following expression:

$$\alpha(\upsilon) = 2.303\frac{A}{t} \tag{8}$$

where A is the optical absorbance. The optical absorption edge was analyzed by the following equation [26],

$$\alpha h\upsilon = B(h\upsilon - E_g)^{0.5} \tag{9}$$

where B is a constant.

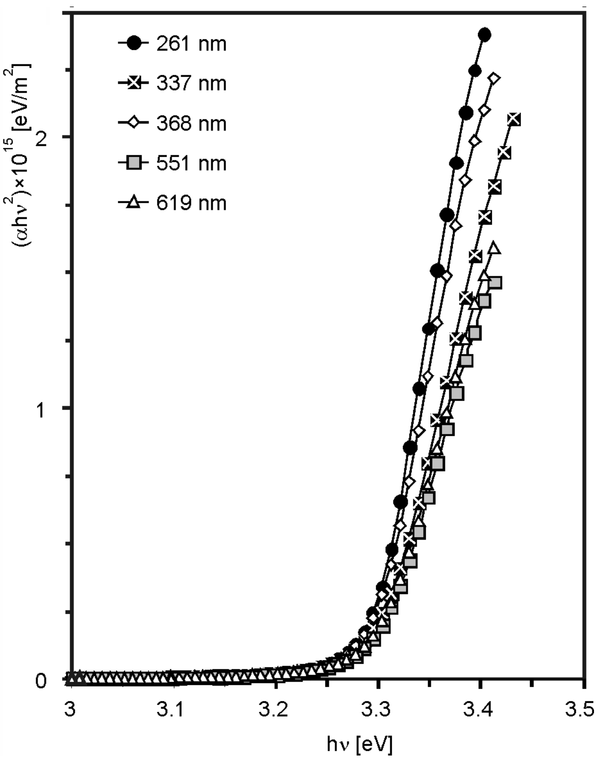

Fig. 4. Variation of $(\alpha h\nu)^2$ vs. $h\nu$ of the In-doped ZnO thin films

Figure 4 shows the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for In-doped ZnO thin films. It has been observed that the plot of $(\alpha h\nu)^2$ vs. $h\nu$ is linear over a wide range of photon energies indicating a direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis reflect the energy band gaps. The band edge sharpness value (B_s) was derived from the slope of the plot of $(\alpha h\nu)^2$ vs. $h\nu$ in the range of band-to-band absorption. The band edge sharpness B_s and optical band gap E_g

are given in Table 2. According to Table 2, a small difference occurred in the optical band gap.

4. Conclusions

In-doped ZnO thin films were deposited onto glass substrates by the spray pyrolysis method at 350 °C substrate temperature. The crystal structure and orientation of the In-doped ZnO thin film (t = 337 nm) were investigated by the XRD pattern. The X-ray diffraction pattern of this film revealed its hexagonal wurtzite structure. The films exhibited high transparency (≥ 91%) in the visible and infrared region. Optical constants such as the refractive index n and extinction coefficient k were determined from the transmittance spectra in the UV–VIS–NIR regions using the envelope method. The thicknesses of the films t were calculated from interference of the transmittance spectra. Also, E_g energy band gap values were calculated. The band gap of the films did not depend significantly on the film thickness. There was only a small change of the optical properties resulting from varying the film thickness.

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