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The determination of the thickness and optical constants of the ZnO crystalline thin film by using envelope method

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ZnO crystalline thin film has been deposited onto glass substrates by the spray pyrolysis method. The crystallographic structure of the film and the size of the crystallites in the film were studied by X-ray diffraction. XRD measurement shows that the film is crystallized in the wurtzite phase and presents a preferential orientation along the c-axis. Only one peak, corresponding to the $(0\ 0\ 2)$ phase (2θ=34.760^{o}), appears on the diffractograms. An envelope method, based on the optical reflection spectrum taken at normal incidence, has been successfully applied to the geometrical–optical characterization of thin films having significant surface roughness. Such a method allows the determination of the average thickness and the refractive index of the films with accuracies better than 1%, as well as the average amplitude of the surface roughness with an accuracy of about 2%. Optical constants such as refractive index *n* and extinction coefficient *k*, were determined from transmittance spectrum in the ultraviolet-visible-near infrared (UV-VIS-NIR) regions using envelope methods. Absorption coefficient α, and the thickness of the film *t* were calculated from interference of transmittance spectra. The energy band gap, and the thickness of the films were evaluated as 3.283 eV and 635 nm, respectively.

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1. Introduction

Transparent conducting oxides (TCOs) have long been a subject of various investigations due to its unique physical properties and applications in commercial devices. These transparent, metallic oxides include, in part, indium-oxide, tin-oxide, indium-tin-oxide, zinc-oxide, cadmium–indium-oxide and cadmium-tin-oxide. Among TCOs, Zinc oxide (ZnO) belongs to a member of hexagonal wurtzite class, it is an 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 cells [4, 5]. ZnO has been intensively studied as a promising material for blue and ultraviolet light emitting devices because of its wide-band gap of 3.3 eV and large exciton binding energy (60 meV).

Many techniques have been employed to produce zinc oxide, sputtering [6], metal organic chemical vapour deposition [7], sol gel [8] and spray pyrolysis [9, 10]. Dikovska et al. [11] have deposited high quality ZnO films by pulsed laser deposition. Among these techniques, spray pyrolysis has proved to be a simple and inexpensive method, particularly useful for large area applications. The sprayed solution are usually $ZnCl_2$ or $Zn(CH_3CO_2)_2$ diluted in an alcoholic solution.

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. The widely used envelop method has been developed for transmittance measurements to evaluate the refractive index, extinction coefficient and absorption coefficient.

Generally, the optical band gap (E_g) and absorption coefficient α could be evaluated from transmittance or absorbance spectra. Swanepoel [12] to determine more accurately the thickness (*t*), absorption coefficient (α) etc. has improved this method. There is another conventional method where the reflectance (*R*) and transmittance (*T*) spectra have been 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.

In this paper, the optical properties of the crystalline ZnO thin film prepared by spray pyrolysis method using both the above techniques are reported.

2. Experimental details

The crystalline ZnO thin film was deposited onto glass slices using the spray pyrolysis method at 350 ^{o}C substrate temperature. 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 mixture was continuously agitated until total dissolution. A small amount of acetic acid was added to obtain a total dissociation of the zinc acetate. Nitrogen was used as the carrier gas, pressure at 0.2 kgcm^{-2}. The ultrasonic nozzle to substrate distance was 28 cm and during deposition, solution flow rate was held constant at 4ml 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$_\alpha$ (λ=1.54059 Å) radiation). The average dimension of crystallites was determined by the Scherrer method from the broadening of the diffraction peaks taking into account the instrumental broadening.

The optical measurements of the crystalline ZnO thin film were carried out at room temperature using Shimadzu UV-VIS-NIR 3150 scanning 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 transmittance spectra [12]. The thickness of the crystalline ZnO thin film was determined from interference fringes of transmission data measured over the visible range.

3. Results and discussion

3.1. Structural properties of the crystalline ZnO thin film

The crystal structure and orientation of the ZnO thin film were investigated by X-ray diffraction (XRD) pattern. The X-ray diffraction spectrum for the crystalline ZnO thin film shown in Fig. 1, indicate that the film is of polycrystalline nature. The X-ray diffraction pattern of the crystalline ZnO thin film reveal that the existence of a ZnO single-phase with a hexagonal wurtzite structure. The XRD pattern consists of a $(0\ 0\ 2)$ main peak, which is due to ZnO crystals that grow along the c-axis. The full width half maximum (FWHM) of the $(0\ 0\ 2)$ peak was 0.189 for the crystalline ZnO thin film. Another major orientation present is $(1\ 0\ 1)$, while other orientations like $(1\ 0\ 0)$, $(1\ 0\ 3)$, $(1\ 0\ 2)$ and $(1\ 1\ 0)$, 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.

The lattice constants for hexagonal ZnO film are reported in JCPDS standard data a=3.24982 Å and c=5.20661 Å [13]. The analytical method [14] was used to calculate lattice constants a and c for ZnO film. The calculated values of a and c were found to be 3.21907 Å and 5.15760 Å, respectively. These calculated values are in agreement with JCPDS data.

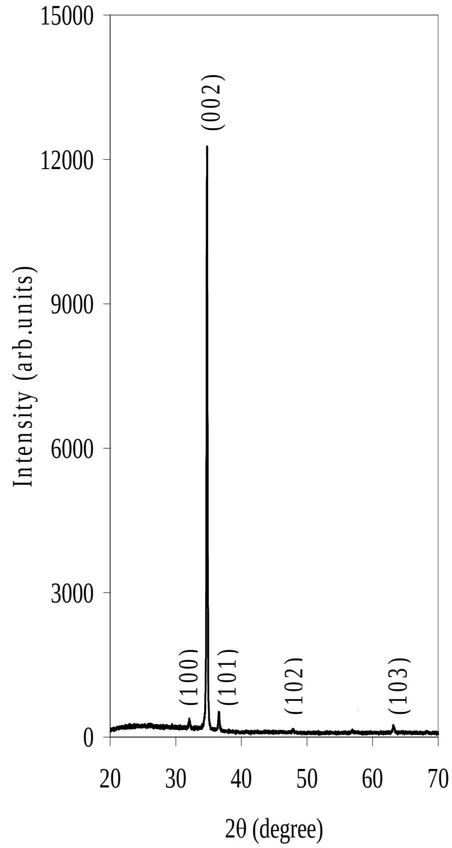


Fig. 1. XRD spectrum of the crystalline ZnO thin film.

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

(h k l)	2θ	d(Å)	I/Io	TC(hkl)
(1 0 0)	32.080	2.7878	1.4	0.0788
(0 0 2)	34.760	2.5788	100	5.6285
(1 0 1)	36.580	2.4546	3.0	0.1689
(1 0 2)	47.879	1.8984	0.5	0.0281
(1 1 0)	56.919	1.6164	0.4	0.0225
(1 0 3)	63.159	1.4709	1.3	0.0732

The grain size of crystallites was calculated using a well-known Scherrer's formula [14]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the grain size of crystallite, λ (=1.5405 Å) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The value found for the grain size is 46 nm.

The texture coefficient (TC) represents the texture of the particular plane, deviation of which from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation was obtained from the different texture coefficient $TC(hkl)$ defined as [15]

$$TC(hkl)=\frac{I(hkl)/I_o(hkl)}{N^{-1}\sum_n I(hkl)/I_o(hkl)} \qquad (2)$$

where *I(hkl)* is the measured relative intensity of a plane *(hkl)*, $I_o(hkl)$ is the standard intensity of the plane *(hkl)* taken from the JCPDS data, *N* is the reflection number and *n* is the number of diffraction peaks. A sample with randomly oriented crystallite presents *TC(hkl)*=1, while the larger this value, the larger abundance of crystallites oriented at the *(hkl)* direction. The calculated texture coefficients are presented in Table 1. It can be seen that the highest *TC* was in $(0\ 0\ 2)$ plane for ZnO thin film.

3.2. Optical properties of the crystalline ZnO thin film

Fig. 2 shows transmittance and reflectance curves for the crystalline ZnO thin film, where the film due to interference phenomena between the wave fronts generated at the two interfaces (air and substrate) defines the sinusoidal behaviour of the curves' transmittance vs. wavelength of light. ZnO thin film showed interference fringe pattern in transmission spectrum. This revealed the smooth reflecting surfaces of the film and there was not much scattering loss at the surface. In transparent metal oxides, metal to oxygen ratio decides the percentage of transmittance. A metal rich film usually exhibits less transparency.

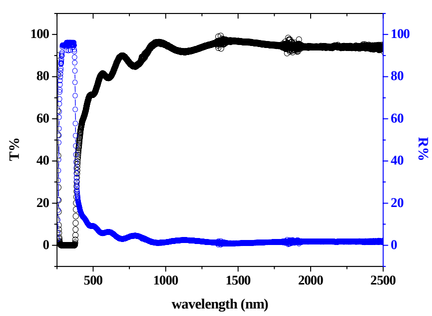


Fig. 2. Transmittance and reflectance spectra of the crystalline ZnO thin film.

The excellent surface quality and homogeneity of the film were confirmed from the appearance of interference fringes in the transmission spectra. This occurs when the film surface is reflecting without much scattering/absorption in the bulk of the film. The films exhibited good transparency in the visible and infrared region (~95%). The index of refraction *n* at different wavelengths was calculated using the envelope curve for T_{max} (T_M) and T_{min} (T_m) in the transmission spectra [12]. The expression for refractive index is given by

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

where

$$N=2n_s\frac{T_M-T_m}{T_M T_m}+\frac{n_s^{\,2}+1}{2} \qquad (4)$$

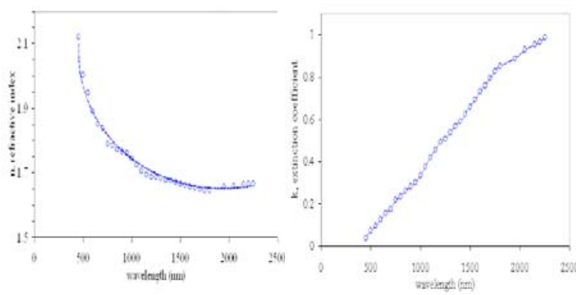
and n_s is the refractive index of the substrate (in our case n_s =1.52 (glass)).

The extinction coefficient *k* can be obtained from the experimental expression [16]:

$$k=\frac{\alpha\lambda}{4\pi d} \qquad (5)$$

$$\alpha=-\frac{1}{t}\ln\frac{(n-1)(n-n_s)\left(\left(T_{max}/T_{min}\right)+1\right)^{0.5}}{(n+1)(n+n_s)\left(\left(T_{max}/T_{min}\right)-1\right)^{0.5}}$$

where α is the absorption coefficient and *t* is the film thickness. The optical constants such as refractive index *n* and extinction coefficient *k* were determined from a transmittance spectrum by envelope method as explained in the previous section. The variations of refractive index *n* and extinction coefficient *k* with wavelength in the region 450 nm-2250 nm are shown in Figs. 3a and b. Although extinction coefficient values increase with the increasing of the wavelength, refractive index values decrease.



a) b)

Fig. 3. Plots of refractive index (a) and extintion coefficient (b) as a function of wavelength of the crystalline ZnO thin film.

The thickness of the films was calculated using the equation

$$t=\frac{\lambda_1\lambda_2}{2(\lambda_1 n_2-\lambda_2 n_1)} \qquad (6)$$

where n_1 and n_2 are the refractive indices corresponding to wavelengths λ_1 and λ_2, respectively [12]. The thickness of the film was found to be 635 nm.

The absorption coefficient α of the ZnO film was determined from transmittance measurements. Since envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient of the film in this region was calculated using the following expression:

$$\alpha(\upsilon)=2.303(A/t) \qquad (7)$$

where *A* is the optical absorbance. The optical absorption edge was analyzed by the following equation [17],

$$\alpha h\upsilon=B(h\upsilon-E_g)^{0.5} \qquad (8)$$

where *B* is a constant. The variation of $(\alpha h\upsilon)^2$ with photon energy $h\upsilon$ for the ZnO thin film is shown in Fig. 4. It has been observed that the plots of $(\alpha h\upsilon)^2$

versus $h\upsilon$ are linear over a wide range of photon energies indicating the direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the energy band gaps. From this drawing, the band gap, E_g=3.283 eV is deduced.

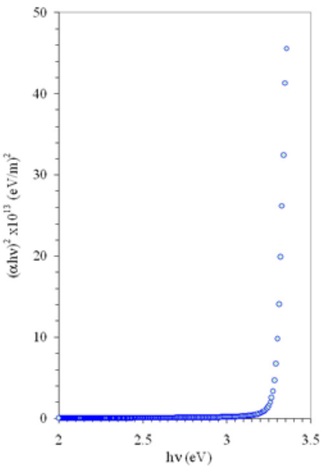


Fig. 4. Variation of $(\alpha h\nu)^2$ vs. $h\nu$ of the crystalline ZnO thin film.

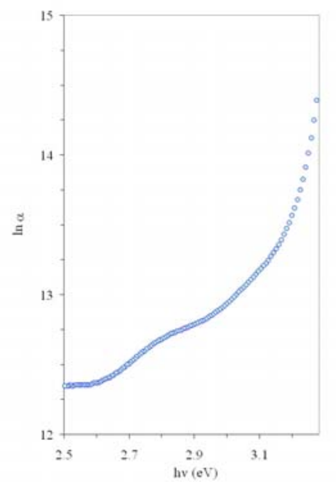


Fig. 5. Urbach plot of the crystalline ZnO thin film.

It is also assumed that the absorption coefficient near the band edge shows an exponential dependence on photon energy and this dependence is given as follows [18],

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_u}\right) \quad (9)$$

where α_o is a constant and E_u is Urbach energy interpreted as the width of the tails of localized states, associated with the amorphous state, in the forbidden gap. The $ln(\alpha)$ vs. photon energy plots for the ZnO thin film is shown in Fig. 5. The value of E_u obtained from this figure is 71.88 meV.

4. Conclusions

ZnO crystalline thin film has been deposited onto glass substrates by the spray pyrolysis method at 350 ^oC substrate temperature. The crystal structure and orientation of the ZnO thin film were investigated by XRD pattern. The X-ray diffraction pattern of the crystalline ZnO thin film reveal that the existence of a ZnO single-phase with a hexagonal wurtzite structure. The XRD pattern consists of a $(0\ 0\ 2)$ main peak, which is due to ZnO crystals that grow along the c-axis. Optical constants such as refractive index *n* and extinction coefficient *k* were determined from transmittance spectrum in the UV-VIS-NIR regions using envelope method. The thickness of the film *t* was calculated from interference of transmittance spectra. Also, E_g energy band gap value and E_u Urbach energy were calculated. In conclusion, it may be considered that the deposited crystalline ZnO thin film was suitable for many optical devices, such as solar cells, gas sensors, surface acoustic devices, transparent electrodes, etc., because of well-crystallized, high transmittance (~95%) and wide-band gap value (3.283 eV). Furthermore, we consider that the electrical properties of the deposited ZnO thin films will also give good results for these applications and studies on this matter are in progress.

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