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Evaluation of the optical characteristics of *c*-axis oriented zinc oxide thin films grown by sol gel spin coating technique

K. Baisakh[1], S.Behera[1] and S.Pati[2]*

[1]Department of physics, School of Applied Science, CUTM, Bhubaneswar, 752050, India.
[2]Department of Physics, N. C. (Auto.) College, Jajpur, 755001, India

Abstract. In this work we have systematically studied the optical characteristics of synthesized wurzite zinc oxide thin films exhibiting (002) orientation. Using sol gel spin coating technique zinc oxide thin films are grown on pre cleaned fused quartz substrates. Structural properties of the films are studied using X-ray diffraction analysis. Micro structural analysis and thickness of the grown samples are analyzed using field emission scanning electron microscopy. With an aim to investigate the optical characteristics of the grown zinc oxide thin films the transmission and reflection spectra are evaluated in the ultraviolet-visible (UV-VIS) range. Using envelope method, the refractive index, extinction coefficient, absorption coefficient, band gap energy and the thickness of the synthesized films are estimated from the recorded UV-VIS spectra. An attempt has also been made to study the influence of crystallographic orientation on the optical characteristics of the grown films.

Keywords: Crystal texture; Grain growth; Optical property; Envelope method

*Corresponding author: Sumatipati.11@gmail.com, Phone-+919438855121

1. Introduction

The optical characteristics of metal oxide films are greatly influenced by their crystallographic orientation. The influence of preferential orientation on the optical characteristics of the thin films has scarcely been reported in the literature. As explained by F. Paraguay-Delgado, et al. texture has strong influence on the optical properties of the tin oxide thin films [1]. Various techniques have been used to grow such oriented thin films. This includes CVD (chemical vapor deposition), radio frequency sputtering, ion-beam evaporation, MBE (molecular beam epitaxy), spray pyrolysis, and so on [2-3]. Usually these techniques are expensive and also need special approach for the growth. In these methods careful regulation of various parameters during growth facilitates the growth of films with desired orientations. However, in the literature there are hardly any reports on the synthesis of thin films by simple and cost effective sol gel spin coating technique [4]. In this method the growth along specific directions depends on several factors, such as the concentration and viscosity of the sol, speed of the spin coater unit, drying and annealing schedule, etc. Hence using this method, precise control of all these parameters and acquiring a metal oxide thin film with desired orientation is really a

challenging issue. Among metal oxides, zinc oxide is considered to be an efficient candidate in optoelectronic applications [5]. In this work, *c*-axis oriented zinc oxide thin films have been synthesized by the cost effective sol gel spin coating technique. The phase formation behaviour and the microstructure evolution of the samples are investigated by X-ray diffraction (XRD) pattern and field emission scanning electron microscopy (FESEM) analyses, respectively. The optical characteristics are analyzed from the measured transmission and reflection spectra using UV-Vis spectroscopy. From these spectra, the values of the refractive index (n), extinction coefficient (k), absorption coefficient (α), band gap energy (E_g) and the thickness (d) of the films are estimated. An attempt has also been made to study the influence of crystallographic orientation of the grown films with their optical properties.

2. Material synthesis and characterization

With an aim to synthesize zinc oxide thin films with specific (002) orientation precursor sol was prepared by adding 2-methoxyethanol with Zn $(CH_3CO_2)_2 \cdot 2H_2O$. Mono-ethanolamine was used as stabilizer. The solution was stirred for 2 h at 60 ^{0}C and is used as precursor sol. In a spin coater unit the precursor sol was put onto pre cleaned quartz substrates and required heat treatment is provided. The structural properties of the synthesized films are studied by X-ray diffraction (XRD) analyses using Cu Kα radiation. The micro structural properties of the films were analyzed by field emission scanning electron microscopy (FESEM) analysis. The optical characteristics of the films were evaluated from the recorded transmission and reflection spectra using UV-VIS absorption spectrometer (Lambda 750, Perkin Elmer, USA).

3. Results with discussion

3.1 Structural and micro structural properties

X-ray diffraction (XRD) pattern of the synthesized zinc oxide thin films is shown in Fig. 1. As observed from the figure it shows only one peak along (002) plane. This textured behavior of the film indicates the *c*-axis orientation of the grains i.e., along the normal to the substrate. As reflected in the literature, since in zinc oxide the surface energy is minimum along (002) plane hence there is a preferential growth along this direction [6].

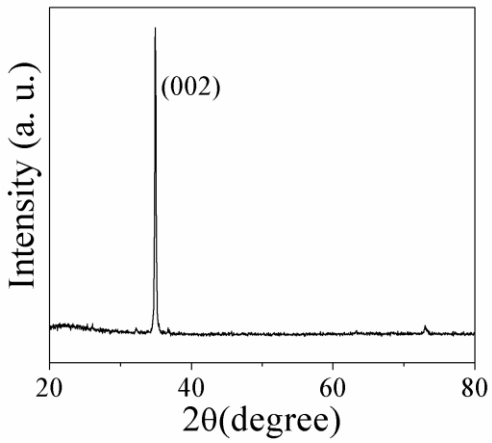

Fig.1. X-ray diffraction pattern of zinc oxide thin films synthesized by sol gel spin coating method, on fused quartz substrate.

From the studied X-ray diffraction pattern the average crystallite size (D) is estimated to be 46.5 nm using the well known Debye-Scherer formula [6], which is $D = 0.9\lambda / \beta\cos\theta$, where λ = 0.154 nm, is the wavelength of the used X-ray radiation, 2θ is the diffraction angle of the (002) peak and β is the full width at half maximum (FWHM) of the diffraction peak at 2θ measured in radian.

Fig. 2 shows a typical micro structure of the synthesized zinc oxide thin films. From this figure the continuous and uniform nature of the film is observed, thus indicating the good quality of the film.

The cross section of the same sample is shown in the inset of fig. 2. From the cross section the thickness of the film is estimated to be ~418nm. In addition, the orientation of the grains perpendicular to the substrate is clearly observed from the figure, which could be the effect of annealing. Thus both the structural and micro structural properties indicate the *c*-axis orientation of the thin films.

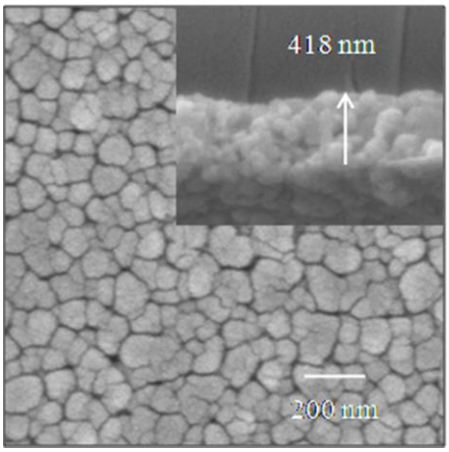

Fig.2. FESEM image of zinc oxide thin films synthesized by sol gel spin coating method, on fused quartz substrate. The inset shows the cross sectional view indicating the thickness of the film.

3.2 Optical characterization

The optical transmission and reflection spectra of the synthesized zinc oxide thin films, in the wavelength (λ) range 200 – 800 nm, is shown in Fig. 3. As the maxima in the transmission spectra matches well with the minima of the reflection spectra and vice versa, so "envelope method" is suitable for evaluation of its optical constants. This method was originally developed by Manifacier et al. [7] and latter modified by Swanepoel [8].

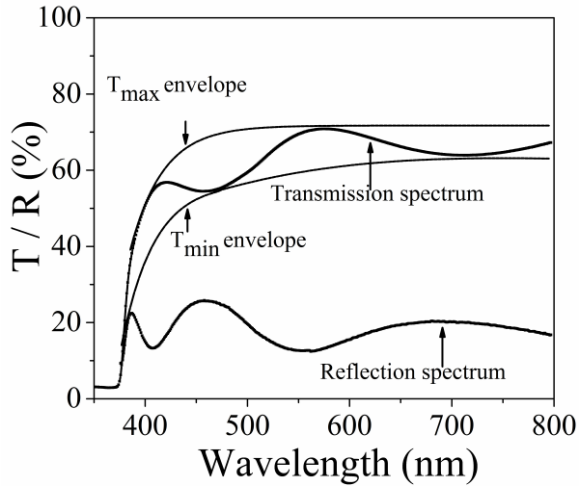

Fig.3. The transmission and reflection spectra of the synthesized zinc oxide thin films and the envelope drawn on the transmission spectra

Using this we have calculated the optical constants like refractive index(*n)*, extinction coefficient(*k)*, absorption coefficient*(*α*)*, band gap energy (*E_g*)*, and thickness (*d)* of the grown films from the transmission spectra. Using the model proposed by Manifacier et al. [7] α of the film is given by

$\alpha = -lnx/d$ (1)

and is related to *k* and λ by $k = \frac{\alpha\lambda}{4\pi}$ (2)

and *n* is expressed as $n = [N + (N^2 - n_s^2)^{0.5}]^{0.5}$ (3)

where $N = 0.5(1 + n_s^2) + 2n_s \frac{(T_{max} - T_{min})}{(T_{max} T_{min})}$ (4)

Using the expression given below the value of refractive index of fused quartz (n_s) as a function of λ in the range 200 – 6700 nm can be estimated

$$n_s = 1 + \left[\frac{0.6961663\lambda^2}{\lambda^2 - (0.684043)^2}\right] + \left[\frac{0.4079426\lambda^2}{\lambda^2 - (0.1162414)^2}\right] + \left[\frac{0.8974794\lambda^2}{\lambda^2 - (9.896161)^2}\right] \quad (5)$$

Where λ is in micron [9]. Knowing the value of *n*, *x* can be found using the following equation

$$x = \frac{C_1\left[(T_{max} - T_{min})^{1/2} - 1\right]}{C_2\left[(T_{max} - T_{min})^{1/2} + 1\right]} = \frac{(n+1)(n_s+1)\left[(T_{max}/T_{min})^{1/2} - 1\right]}{(n-1)(n_s-1)\left[(T_{max}/T_{min})^{1/2} + 1\right]} \quad (6)$$

3.2.1 Determination of thickness (d) of the film

The value of *d* of the film can be calculated using the following relation [8]:

$$d = \frac{\lambda_1\lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \quad (7)$$

Where $n(\lambda_1)$ and $n(\lambda_2)$ are the refractive indices at two adjacent maxima (or minima) in the transmittance spectrum at λ_1 and λ_2, respectively.

Table 1. Determination of thickness *(d)* of the ZnO thin film using "envelope method"

Composition	λ (nm)	*n*	*d′* (nm)	$d'_{av}m'$ (nm)	*m*	*d*	d_{av} (nm)	*d* (FESEM) (nm)	(nm)
ZnO	417 (p)	2.35	482	454	5.12	5	443	437	418
	571 (p)	2.03			3.24	3	420		
	440 (v)	2.26	426		4.66	4.5	438		
	695 (v)	1.94			2.53	2.5	447		

p = peak position, v = valley position

Using Eq. (7) different values of *d* are obtained for different positions of interference maxima and minima in the transmittance spectra and their average (d_{av}) is calculated. Then from the formula for interference fringes

$$2nd = m'\lambda \quad (8)$$

m' values are obtained using the value of d_{av} in place of *d*. The obtained values of m' are rounded off to the nearest integer for maxima and half integer for minima and the values thus obtained is denoted by m. Now again using Eq. (8), different values of *d* are obtained using the values of m (in place of m'), λ and *n* and their average is taken to get the value of *d* of the film.

3.2.2 Evaluation of α and k of the film

Using the value of *x* as obtained from Eq. (6) and *d* value, α and *k* of the film can be calculated from Eq. (1) and (2), respectively. The value of band gap energy (E_g) is estimated from Fig. 4 (c) by extrapolating the linear portion of the graph using the expression given below [6]:

$$\alpha h\nu^2 = B\left(h\nu - E_g\right)^n \quad (9)$$

where *hν* is the energy of photon and *B* is a constant. In case of direct band gap materials, such as zinc oxide, *n* = ½. The value of E_g can be estimated from the intercept of this plot on the energy axis.

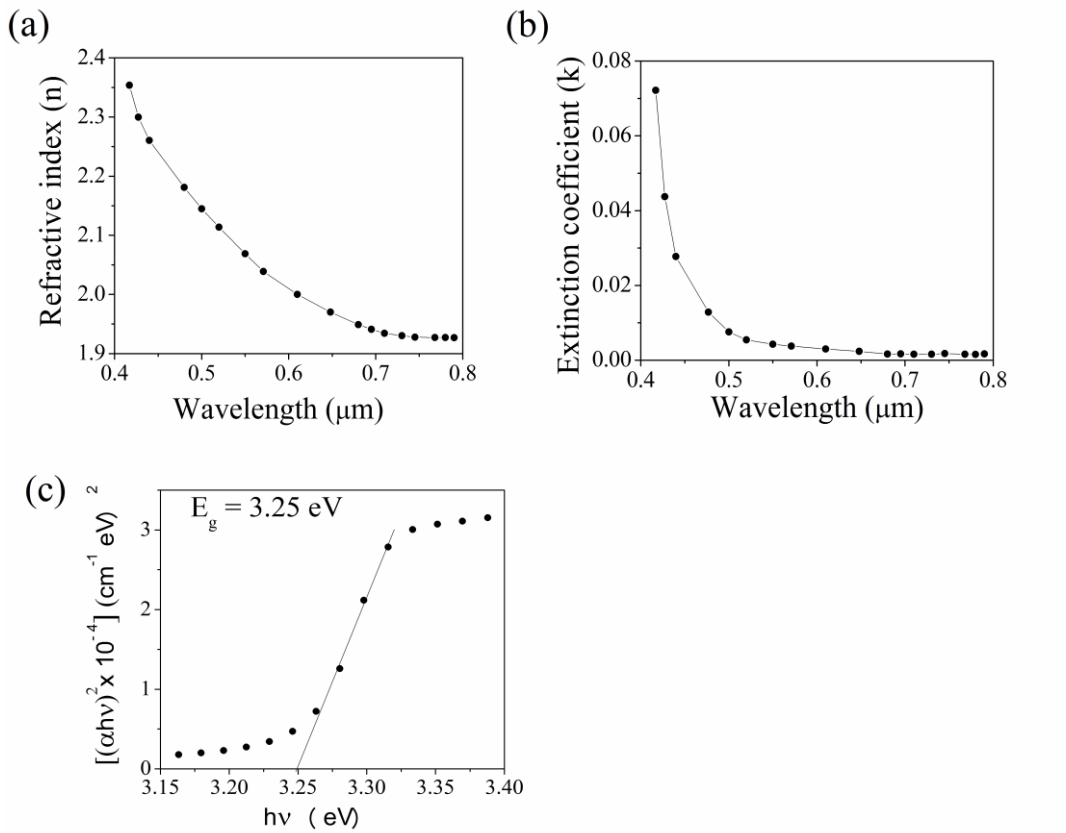

Fig. 4.Optical characteristics of the synthesized zinc oxide thin films, (a) refractive index (*n*) verses wavelength (λ), (b) Extinction coefficient (*k*) verses wavelength (λ), and (c) $(\alpha h\nu)^2$ *vs* $h\nu$ plot (Tauc plot).

As shown in Fig. 3 two envelopes T_{max} and T_{min} are drawn taking the maxima and minima points of the transmittance spectra. Then the value of *n* of the film as a function of λ is calculated using Eq. (3) and is plotted in Fig. 4(a). As observed from the figure the value of *n* decreases with increasing λ. Table 1 summarizes the procedure for determination of thickness (*d*) of the film using the obtained values of *n*. This value of *d* is used to calculate the value of *k* of the film with the variation of λ using Eq. (1), (2) and (6) and is shown in Fig.4 (b). Higher value of *n* and lower value of *k* than the reported value [10] signifies the good optical quality of the film. Fig.4 (c) shows the plot of $(\alpha h\nu)^2$ versus $h\nu$. Then using Eq. (9) the value of E_g is calculated to be 3.25 eV, and is near to the band gap of zinc oxide.

The values of optical parameters thus obtained are compared with the reported values. For example, Gaspera et al. reported the value of *n* of ZnO thin film at 600 nm as 1.65 [11] and Suvorova et al. reported the *n* value of 2 at 632 nm which is same as that of single crystal [12]. In our study we obtained the value of *n* as 1.95 at the wavelength 632 nm. The higher value of *n* than that reported by Gaspera et al. [11] could be due to the textured behavior of the thin film, as the value of *n* depends on the direction of propagation of light, which in turn changes with the crystallographic orientation. Moreover, it can be seen that our value of *n* almost equal to that of Ref. 12, which is same as that of single crystal and may be attributed to the *c*-axis orientation of the grains in the thin film.

4. Conclusion

In the present work, *c*-axis orientated zinc oxide thin films are grown on fused quartz substrates using sol gel spin coating method. The surface morphology, micro structural analysis and optical properties of the grown films are investigated. The films are textured along (002) planes with

an average grain size of 46.5 nm. Optical constants such as refractive index, extinction coefficient and film thickness are evaluated from transmission and reflection spectra using the envelope method. The lower value of extinction coefficient and higher value of refractive index than the reported value suggest good surface quality of the films and is attributed to the *c*-axis orientation of the films. The thickness of the films estimated from the optical characteristics (437 nm) is in consistent with that obtained from the FESEM image (418 nm). The film is found to have optical band gap energy of 3.25 eV which is near to the band gap energy of zinc oxide. Finally, the optical properties are correlated with the crystallographic orientation of the zinc oxide thin films.

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