Fabrication and properties of zinc oxide thin film prepared by sol-gel dip coating method

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ZnO thin films were deposited on a glass substrate by dip coating technique using a solution of zinc acetate, ethanol and distilled water. 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. The films were found to exhibit high transmittance, low absorbance and low reflectance in the visible regions. Absorption coefficient ∝, and the thickness of the film t were calculated from interference of transmittance spectra. The direct optical band gap of the films was in the range of 3.98 to 3.54 eV and the thickness of the films was evaluated in the range of 173 to 323 nm, while the refractive index slightly varied in the range of 1.515 to 1.622 with an increase in withdrawal speed from 100 to 250 mm/s. The crystallographic structure of the films was analyzed with X-ray diffractometer. The films were amorphous in nature.

Keywords: *thin films; sol-gel; X-ray diffraction; optical properties*

1. Introduction

Zinc oxide (ZnO) is a wide band gap II – VI semiconductor which exhibits a hexagonal wurtzite structure. Transparent conductive ZnO has become the focus of attention as a substitute material for optically transparent electrodes in electronic devices. Conductive and transparent ZnO films have low electrical resistance and high optical transmittance comparable with those of indium tin oxide (ITO) films as reported by some authors [1, 2]. ZnO films are applied as alternatives to ITO electrodes for liquid crystal display (LCD) panels. Several researchers have prepared the ZnO thin films via sol-gel dip coating for studying the structural, electrical, optical properties and surface studies [3–5] because this method can be used for the production of oxide transparent films with uniform surface [6]. The dip coating is a simple method for deposition of thin films in which the films thickness can be easily controlled [7, 8].

The aim of the present project was to deposit thin films for optoelectronic applications. ZnO thin films are the most promising candidates for the Transparent Conducting Oxide (TCO) compound solar cells. Hence, in this project, thin films of ZnO were deposited by sol-gel dip coating technique and their properties were tailored by changing withdrawal speed of substrate. The withdrawal speed varied from 100 to 250 mm/s. Such values of withdrawal speed are the novelty and a characteristic feature of this project.

2. Experimental

Sol gel method was used to prepare zinc oxide thin films. Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O), absolute ethanol and distilled water (H$_2$O) were used as a starting material, solvent and stabilizer, respectively. 0.5 M solution was prepared by dissolving 1 g of zinc acetate dehydrate in 10 mL of absolute ethanol, after which the solution was stirred vigorously using a magnetic stirrer for 1 hour on a hot plate at 60 °C. Initially the solution was milky but after stirring for

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approximately 20 minutes the solution became homogeneous, transparent and stable. After stirring for about 1 hour the solution was allowed to cool, and 10 mL of water was added, drop by drop into the solution, and again the solution was stirred continuously for 3 hours at 100 °C. The water was added to keep the sol stable and clear for a period of 60 days. The sol was aged for 24 hours and then dip-coating was carried out. In this study, soda-lime glass substrates were used. The substrates were washed with a detergent and ultrasonically cleaned in acetone and then in isopropanol. Thin films of ZnO were deposited at varying withdrawal speed of 100, 150, 175, 200 and 250 mm/s. Each layer of as-prepared films was dried at 80 °C in air for 15 minutes. The dipping process was conducted 3 times after each layer cooling down to room temperature. Finally, all the films were calcined at 350 °C in air for 1 hour to ensure that all organic species were expelled from the films.

The crystal structure of the films was examined with an X-ray diffractometer Bruker XRD model D8 Discover (Germany) in the 2θ range of 30 to 60 degree. The morphology and roughness were evaluated with a scanning electron microscope (SEM) (S-3400N, Hitachi) and optical transmission spectra of ZnO films were measured with an UV-Vis spectrophotometer (UV-Vis, HITACHI U-2800) in the wavelength region of 200 to 900 nm. Transmission vs. wavelength was taken by Fourier Transform Infrared Spectroscopy (FT-IR) Model M 2000 Midac, USA.

Fig. 1. FT-IR spectrum of thin films of ZnO showing Zn–O bonding at 428.12 cm^{-1}.
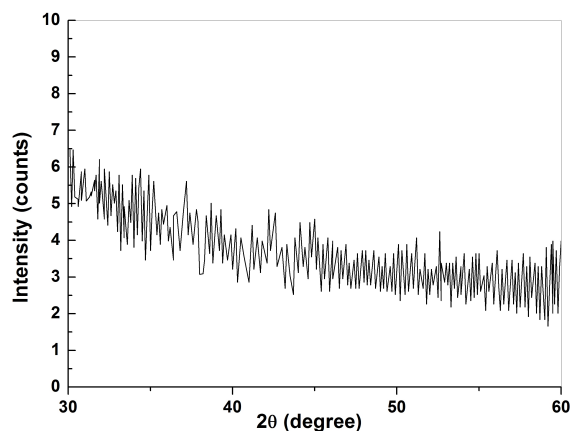
Fig. 2. XRD pattern of ZnO thin films intensity versus 2θ.

3. Results and discussion

3.1. FT-IR

An FT-IR spectrum in Fig. 1 indicates the formation of ZnO by the sol-gel method and thermal annealing treatment. Bonding between Zn–O is in the range of 400 to 700 cm^{-1}. It means that 404 and 702 cm^{-1} clearly represent the ZnO bonds. Previous researches found the ZnO peak between 464 and 419 cm^{-1} [9–11]. Bands formed at 1385 and 1602 cm^{-1} are attributed to symmetric and asymmetric C=O bonds vibrations, respectively [12]. The band at 2329 cm^{-1} is due to O=C=O mode of vibration [13].
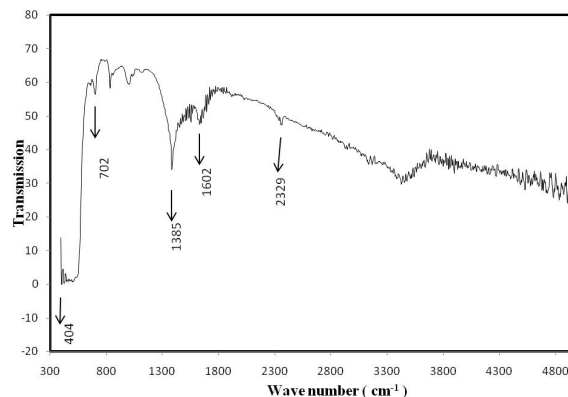
3.2. XRD analysis

XRD analysis, the results of which are shown in Fig. 2, shows amorphous nature of ZnO thin films with no Bragg peaks detected. The degree of the crystal orientation was too low to facilitate crystal growth. The vaporization of the organic solvents and the decomposition of the zinc acetate may take place almost simultaneously. Abrupt solvent vaporization and acetate decomposition which take place before the crystallization provide a chance for structural relaxation of ZnO thin films, which also disturbs the unidirectional crystal growth [14] leading to amorphous films.

3.3. Optical properties

In order to investigate the optical properties of thin films at various withdrawal speeds, the transmittance was measured as a function of wavelength in the range of 200 to 900 nm as shown in Fig. 3. The films show the transmittance higher than 95 % in the visible region at the withdrawal speed of 100 mm/s which decreases as the withdrawal speed increases. The transmission decreases because the film thickness increases with the increase in withdrawal speed. The decrease in transmittance may be due to increasing optical scattering caused by increasing grain boundary density deposited at higher withdrawal speed. Films deposited at a high speed are dense and compact, hence, having larger values of refractive indices. According to Landau and Levich relationship:

$$h = 0.94((\eta U_0)^{2/3}/\gamma_{LV}{}^{1/6}(\rho g)^{1/2} \qquad (1)$$

where η is viscosity of sol, $\gamma_{LV}{}^{1/6}$ is liquid-surface tension, ρ is the density, h is the thickness of thin films and U_0 is withdrawal speed which are directly propotional to each other. Hence, with an increase in withdrawal speed, the thickness of thin films increases.
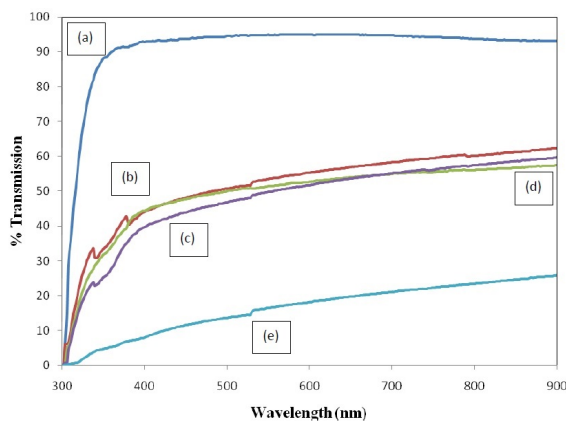

Fig. 3. Transmission spectra of ZnO thin films deposited at (a) 100, (b) 150, (c) 175, (d) 200 and (e) 250 mm/s withdrawal speed of substrate.

By interpreting the transmission curve, the thickness of the films was calculated using envelope method [15]. The optical absorption coefficient $\propto$ was calculated from equation:

$$\propto = 1/t \ln \left\{ (1-R)^2 + SQRT[(1-R)^4 + 4R^2T^2] \right\} \qquad (2)$$

where t is thickness of thin film, T is transmittance and R is reflectance.

The fundamental absorption, which corresponds to the transition from valence band to conduction band, can be used to determine the optical band gap (E_g) by the equation below:

$$\propto = A(h\nu - E_g)^n/h\nu \qquad (3)$$

where n = 0.5 for direct transition, n = 2 for indirect transition, A is a constant, h is Planck's constant (6.62×10^{-34} J·s) and ν is frequency of incident photon [16]. The ZnO is a direct band gap material and so $(\propto h\nu)^2$ vs. E (or $h\nu$) has been plotted to calculate band gap of ZnO thin films deposited at various withdrawal speeds. Table 1 shows the changes in band gap of ZnO thin films caused by changing withdrawal speed. The ZnO thin films deposited at withdrawal speeds of 100, 150, 175, 200 and 250 mm/s gave the optical band gap of 3.98, 3.97, 3.85, 3.83 and 3.54 eV, respectively, as shown in Fig. 4.

The absorption edge blue shift is due to the poor crystallinity of ZnO thin films grown at varying withdrawal speed of the substrate. The physical model of the structure can be imagined as many nano-crystalline grains fixed in an amorphous ZnO lattice. The inter-atomic distance in an amorphous structure would be longer and more disordered than in the crystalline structure, due to the lack of long-range translational periodicity. As amorphous ZnO phase increases in the films grown at increasing withdrawal speed, the extended localization in the conduction and valence bands increases. In consequence, the absorption of photon is governed by amorphous ZnO, hence, the absorption edge is blue shifted [17]. The band gap is dependent on film thickness. Band gap of thin films is a function of reciprocal of square of their thickness [18–20]. So, the band gap decreased with an increase in a film thickness (Table 1). The film thickness was found to be in the range of 173
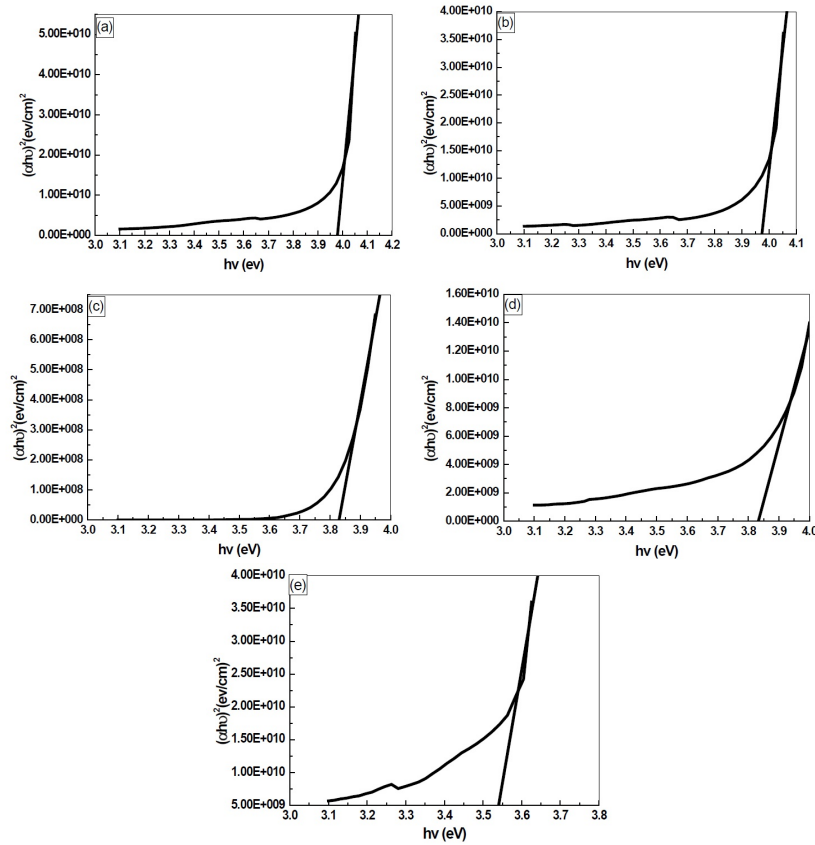
Fig. 4. The evolution of $(\propto)^2$ vs. E (or hν) curves of ZnO thin films at different withdrawal speeds (a) 100, (b) 150, (c) 175, (d) 200 and (e) 250 mm/s, respectively.
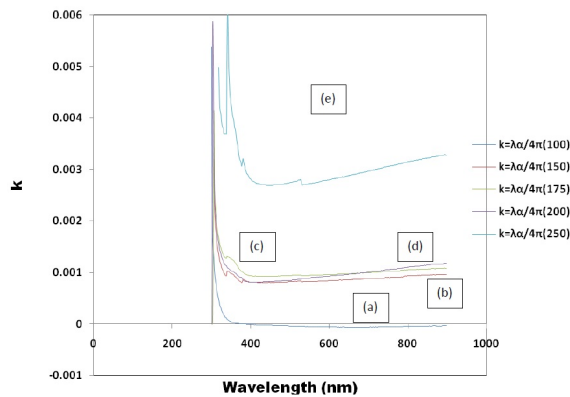

Fig. 5. Plot of extinction coefficient k as a function of photon energy for ZnO films deposited by dip-coating and withdrawn at (a) 100, (b) 150, (c) 175, (d) 200 and (e) 250 mm/s, respectively.

to 323 nm and refractive index slightly varied in the range of 1.515 to 1.622 with an increase in

withdrawal speed from 100 to 250 mm/s. Table 1 shows variations in thickness, refractive index and extinction coefficient with withdrawal speed.

The absorption coefficient α and the extinction coefficient k are related by the formula k = $\alpha\lambda/4\pi$. Extinction coefficient has been evaluated for different withdrawal speeds and the results are shown in Fig. 5. Extinction coefficient follows Sellmeier's dispersion relation and it increases with an increase in withdrawal speed of substrate. Furthermore, it displays a decrement in an ultraviolet spectral region and an increment in visible spectral region.

3.4. Surface studies

Surface morphologies of ZnO thin films prepared at different withdrawal speeds are presented in Fig. 6. Highly porous nanostructures in the ZnO films can be demonstrated by the SEM observations. The films are granular in appearance.

Table 1. Thickness and optical properties of ZnO thin films at various withdrawal speeds.

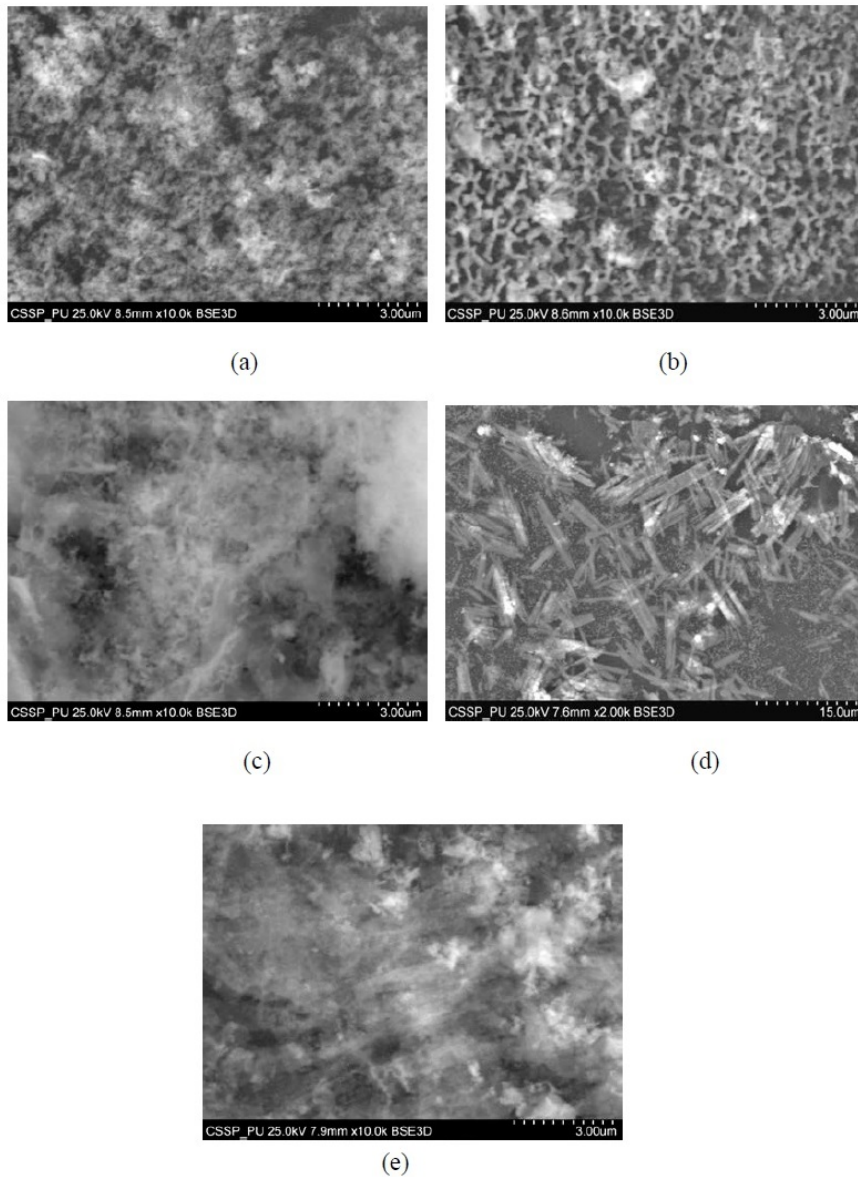| Withdrawal speed (mm/s)	Thickness nm	Refractive index n	Extinction coefficient k	Band gap E_g (eV)
100	173	1.515	0.00022	3.98
150	220	1.520	0.00095	3.97
175	243	1.591	0.00114	3.85
200	263	1.603	0.0013	3.83
250	323	1.622	0.03	3.54

(a)

(b)

(c)

(d)

(e)

Fig. 6. SEM images of thin films of ZnO deposited at a withdrawal speed of (a) 100, (b) 150, (c) 175, (d) 200 and (e) 250 mm/s, respectively.

A non-spherical shape and faceted morphology of these grains may be due to their crystallographic symmetry of the wurtzite ZnO and a preferred growth direction during deposition. At a high withdrawal speed, the liquid film has a high concentration of sol that is converted into particles which then agglomerate together during the heating process. It is why the grain size in the thin films increased from 81 to 288 nm with the increase in withdrawal speed from 100 to 250 mm/s as it is shown in Fig. 6.

4. Conclusion

The ZnO thin films were successfully prepared by sol-gel dip-coating method. All films were dipped three times, withdrawn at speeds of 100, 150, 175, 200 and 250 mm/s and calcined at 350 °C in air for 1 hour. The films exhibited amorphous structure. Moreover, these ZnO thin films had a large optical band gap of 3.98, 3.97, 3.85, 3.83 and 3.54 eV at withdrawal speeds of 100, 150, 175, 200 and 250 mm/s, respectively. These thin films are efficient UV absorbers and moderate-weak absorbers of visible light. The amorphous phase in ZnO films is considered to be the cause of the blue shift in optical band gap. Thickness and refractive index of the thin films can be tailored using suitable sol, withdrawal speed and number of dips. Therefore, the sol-gel technique and dip coating seem to be powerful means to fabricate wide gap semiconductors with unique optical properties.

References

[1] WAKEHAM J.S., THWAITES J.M., HOLTON W.B., TSAKONAS C., CRANTON M.W., KOUTSOGEORGIS C.D., RANSON R., *Thin Solid Films*, 518 (2009), 1355.

[2] SHIN H.S., SHIN H.J., PARK J.K., ISHIDA T., TABATA O., KIM H.H., *Thin Solid Films*, 341 (1999), 225.
[3] MURALI R.K., *J. Phys. Chem. Solids*, 68 (2007), 2293.
[4] KANEVA N.V., DUSHKIN C.D., *Bulg. Chem. Commun.*, 43 (2011), 259.
[5] CHENG X.L., ZHAO H., HUO L.H., GAO S., ZHAO J.G., *Sensor. Actuat. B-Chem.*, 102 (2004), 248.
[6] KLEIN C.L., *Sol-gel technology for thin films, fibres, performs, electronics, and specialty shapes*, Noyes Publications, New Jersey, 1988.
[7] LOPEZ M.T., AVNIR D., AEGERTER M., *Emerging fields in sol-gel science and technology*, Kluwer Academic Publishers, London, 2003.
[8] KAYANI N.Z., AFZAL T., RIAZ S., NASEEM S., *J. Alloy. Compd.*, 606 (2014), 177.
[9] ANNA K., NINA P., YURI K., MEINHARD M., WERNER Z., AHARON G., *Ultrason. Sonochem.*, 15 (2008), 839.
[10] LI H., WANG J., LIU H., YANG C., XU H., LI X., CUI H., *Vacuum*, 77 (2004), 57.
[11] WAHAB R., ANSARI S.G., KIM Y.S., SEO H.K., SHIN H.S., *Appl. Surf. Sci.*, 253 (2007), 7622.
[12] ALIAS S.S., ISMAIL A.B., MOHAMAD A.A., *J. Alloy. Compd.*, 499 (2010), 231.
[13] KHAN R.Z., KHAN S.M., ZULFEQUAR M., KHAN S.M., *Mater. Sci. Appl.*, 2 (2011), 340.
[14] OHYAMA M., KOZUKA H., YOKO T., *Thin Solid Films*, 306 (1997), 78.
[15] MANIFACIER C., GASIOT J., FILLARD J., *J. Phys. E*, 9 (1976), 1002.
[16] URBACH F., *Phys. Rev.*, 92 (1953), 1324.
[17] TAN T.S., CHEN J.B., SUN W.X., FAN J.W., *J. Appl. Phys.*, 98 (2005), 013505.
[18] BALASUBRAMANIAN V., SURIYANARAYANAN N., KANNAN R., *Res. J. Chem. Sci.*, 2 (2012), 51.
[19] SHINDE S.M., AHIRRAO B.P., PATIL J.I., PATIL S.R., *Indian J. Pur. Ap. Phy.*, 50 (2012), 657.
[20] OZTA M., *Chinese Phys. Lett.*, 25 (2008), 4090.