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Studies on zinc oxide thin films by chemical spray pyrolysis technique

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Zinc oxide (ZnO) thin films were deposited by chemical spray pyrolysis (CSP) technique using zinc acetate dihydrate solutions on microscopic glass substrates by varying the precursor concentration. The prepared films were characterized structurally and optically, using the powder X-ray diffraction (XRD) and UV analysis and Photoluminescence analysis. Crystallographic properties were analyzed through powder XRD. The XRD patterns shows a hexagonal structure with *c*-axis orientation (0 0 2) on self texturing phenomenon. Optical transmittance properties of the optimized ZnO thin films were investigated by using UV-Vis spectroscopy. The optical studies predicated a maximum transmittance in the range of above 70% with direct band gap values in the range of 2.9 to 3.2eV for the zinc oxide thin films. Under excitation of 300 nm radiations, sharp deep level emission peak at 2.506 eV dominates the photoluminescence spectra with weak deep level and near band edge emission peak at 3.026 and 3.427 eV respectively.

Key words: Transparent conducting oxide (TCO), Zinc Oxide thin film, CSP technique, X-ray diffraction (XRD), UV-Vis, Photoluminescence.

INTRODUCTION

Metal oxide semiconductor thin films have been widely researched and have received considerable attention in recent years due to their optical and electrical properties. Because they are good candidates for transparent conducting oxide (TCO) films (Hongxia et al., 2005). Zinc oxide is (ZnO) a wide direct band gap (~3.37eV at T=300 K) semiconductor (II-VI) which has been widely investigated in the past years for more literature. ZnO also has a high exciton binding energy of 60 meV which is higher than the values of other widely used wide band gap materials, such as ZnSe (20 meV) and GaN (21 meV). The large exciton binding energy can ensure efficient excitonic emission at room temperature (Zahedi and Dariani, 2012). Exciton provides a sensitive indicator of material quality. Photoluminescence (PL) is very sensitive to the quality of crystal structure and to the presence of defects (Sagar et al., 2007). ZnO has a large transparency in the visible region, high natural abundance, absence of toxicity, low cost compared to other oxide materials such as SnO_2, In_2O_3,TiO_2 (Mahalingam et al., 2003; Gaikwad et al., 2012). In generally, thin films are depends not only on the morphology of the sample, but also on the deposition parameters, thickness of the sample and grain sizes

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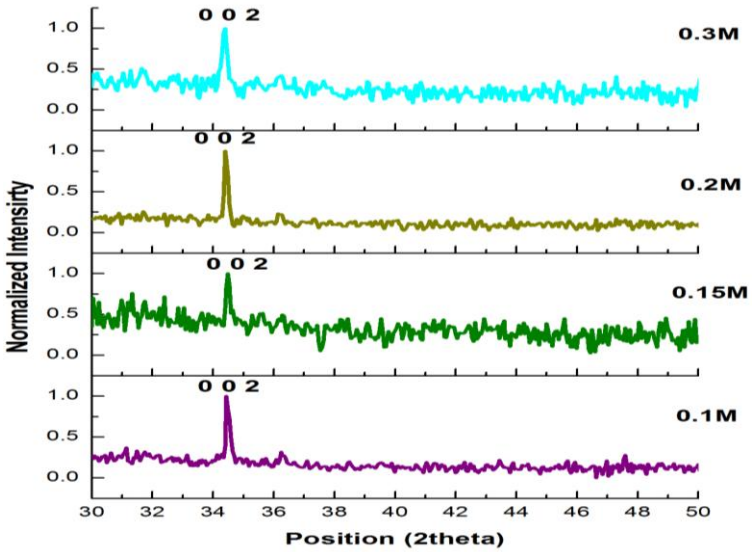

Figure 1. X-Ray pattern of ZnO thin film at (a) 0.1 M, (b) 0.15 M, (c) 0.2 M, (d) 0.3 M.

(Godbole et al., 2011). In recent years, the ZnO based films has potential applications in the field of electronic devices such as gas sensors, solar cells, optoelectronics, thin film transistors (Kuo et al., 2006; Chu et al., 2009; Van Heerden et al., 1997; Joseph et al., 1999a; Wei et al., 2007; Mani et al., 2006). Many deposition techniques have been used to prepared zinc oxide thin films in order to improve their properties such as, chemical bath deposition (CBD) (Kathirvel et al., 2009) Sol-gel spin coating (Natsume and Sakata, 2000), metal organic chemical vapour deposition (Wang et al., 2004), RF-magnetron sputtering (Shiyi et al., 2009), spray pyrolysis (Achour et al., 2007; Joseph et al., 1999a; Yoon and Cho, 2000; Ayouchi et al., 2003). Compared to the others, the spray technique has many advantages: it is easy, inexpensive, safety and the low cost of the apparatus and the raw materials, no sophisticated instrument such as vacuum systems etc., large area coating of thin film and well adopted for mass fabrication (Manouni et al., 2006; Gencyilmaz et al., 2013; Saleem et al., 2012). Furthermore, the optical, structural properties of thin films can be easily controlled by the quantity of sprayed solution in this technique. In general, the films produced with this technique are polycrystalline, stable, adherent, and hard. Spray pyrolysis has been developed as a powerful tool for preparation on various kinds of technological materials such as metals, metal oxides, superconducting materials, and nanophase materials (Saleem et al., 2012). In the present work, we report the thickness on mainly structural and optical properties involved during the effect of precursor concentration on the X-ray diffraction (XRD), UV-Visble and photoluminescence behavior of ZnO thin films deposited by chemical spray pyrolysis technique.

EXPERIMENTAL PROCEDURES

The zinc oxide films were deposited on microscopic glass substrates (Thickness 1.35 mm) at a constant temperature of 380°C with an accuracy of ±5°C by a chemical spray pyrolysis technique at various precursor concentrations. A solution of 0.1, 0.15, 0.2 and 0.3 M zinc acetate dihydrate was used as a precursor prepared by dissolving in mixture of deposited water and isopropyl alcohol (1:3) volume ratio. The nozzle was at a distance of 24 cm from the substrate during deposition. The solution flow rate was held 4±0.5 ml/min. Compressed air was used as the carrier gas. The pressure of the carrier gas should be 0.7 Kg/cm^2. The deposited films were allowed to cool down to room temperature.

The structure of the films were examined by using XPERT – PRO' X-Ray diffractometer with CuKα_1 radiation (λ=1.54056 A°). The thickness of the films was determined by stylus profilometer. The optical transmission spectroscopic measurements of the zinc oxide thin films were carried out at room temperature using SHIMADZU - 1800 Double beam Spectrophotometer in the wavelength range between 300 – 700 nm. VARAIN CARRY ECLIPSE Spectrophotometer excited with 300 nm wavelength from a xenon lamp was used to record photoluminescence spectra of the films.

RESULTS AND DISCUSSION

XRD analysis

X-Ray diffractograms of films prepared at different precursor concentration (0.1 to 0.3 M) was shown on Figure 1. All the diffractograms of the prepared films clean indicate the polycrystalline nature of zinc oxide films with prominent diffraction peak from crystal plane (0 0 2) on self-texturing phenomenon (Chougule et al., 2010) had also obtained a single peak in their XRD pattern by Sol-gel spin coating method with (0 0 2)

Table 1. XRD data of ZnO thin film.

Precursor concentration (M)	Observed values		Thickness (nm)	Grain size (nm) (k=0.9)
	2θ (deg)	lattice constant (c) A°		
0.1	34.4582	5.2013	103	70.12
0.15	34.4779	5.1986	110	46.23
0.2	34.4005	5.2098	158	84.38
0.3	34.3203	5.2216	145	11.55

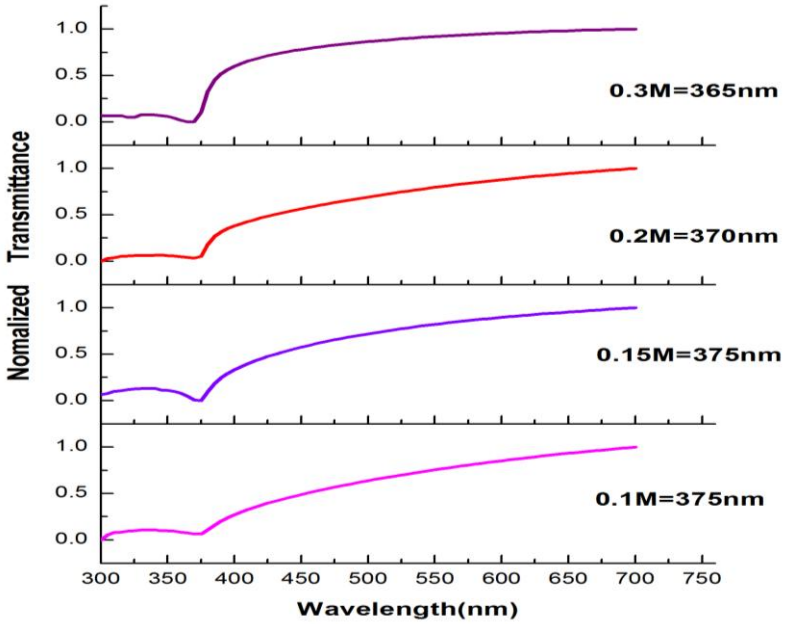

Figure 2. Transmittance spectrum of ZnO thin film.

plane reflection. The deposition of precursor concentration increased without the appearance of any new reflections. Thus no other phases were formed. The phase identification revealed that only hexagonal crystal system based zinc oxide (JCPDS File No.75-1526, 80-0075, 80-0074) was conformed. The lattice constant "C" was calculated by using the following equation:

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{L^2}{C^2} \quad (1)$$

The calculated values of the lattice constant (c) are found to be close to those of the Joint Committee on Powder Diffraction Standard (JCPDS) data reported for zinc oxide sample. The average grain size was measured using Debye-Scherer's formula (Cullity, 1978):

$$Grainsize(D) = \frac{0.9 * \lambda}{\beta \cos\theta}(nm) \quad (2)$$

Where λ is the wavelength of Cu Kα1 radiation (1.54056 A°), β is the FWHM value. The variation of film thickness, grain size, lattice constant (c), two theta with precursor concentration are shown in Table 1.

Optical properties

The transmittance spectrum of ZnO thin films in the wavelength range 300 - 800 nm are shown in the Figure 2. Optical properties of the zinc oxide thin films were studied with the help of transmission spectrum in the UV-visible region. Figure 2 shows the transmittance spectrum of zinc oxide films deposited at different precursor concentration recorded in the range 300 to 700 nm. The spectrum shows a maximum transparency of >70% in the visible region. Sharp ultraviolet absorption edges at λ=375 nm are observed with the absorption edge being shifted to shorter wavelength at higher concentration. It can be clearly seen the blue shift in band edge in Figure 3. The optical absorption coefficient can be calculated

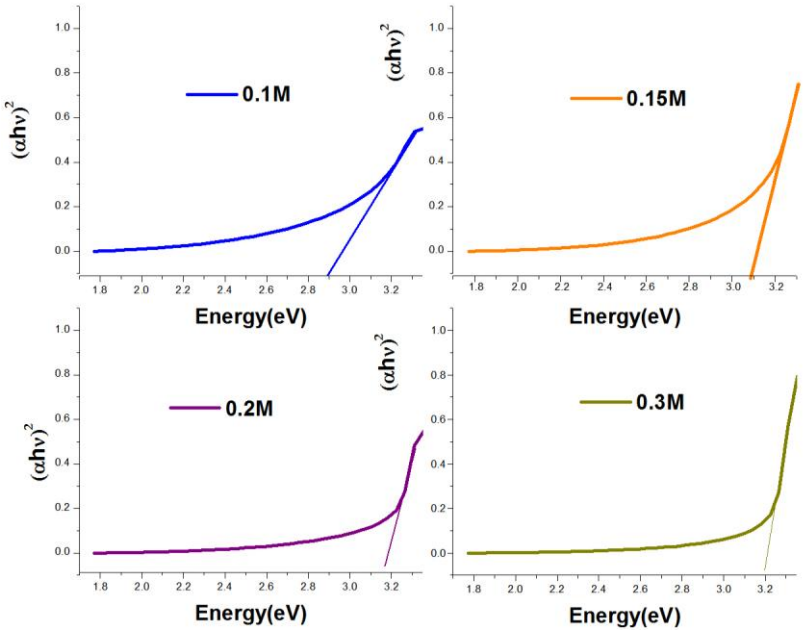

Figure 3. Variation of $(ahv)^2$ verus hv of the zinc oxide thin film.

Table 2. Transmittance at maximum, 550 nm and direct band gap for different precursor concentration.

Precursor concentration (M)	Direct band gap (eV)	Transmittance (%) T_{max}	Transmittance (%) T_{550nm}
0.1	2.9	73.345	61.88
0.15	3.1	88.603	79.93
0.2	3.18	74.602	61.51
0.3	3.20	87.372	82.78

using the Lambert law relation

$$\alpha = t * \ln\left(\frac{1}{T}\right) \quad (3)$$

where t is the thickness of the film and T the transmittance. The relation between absorption coefficient and incident photon energy can be written as:

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{\frac{1}{2}} \quad (4)$$

Where A is a constant, E is the band gap of the material and h is the planks constant. In the present case, the plot of $(\alpha hv)^2$ verus hv, indicates the direct band gap nature of the films. By extrapolating the linear portion of the curve onto the X-axis the energy band gap of the films is determined. The transmittance at maximum 700 and 550 nm, and direct band gap for different precursor concentration was shown in Table 2. Thus on increase in band gap was observed, when the concentration was changed from 0.1 to 0.3 M. This may be due to the hexagonal phase. The effect of bandgap widening is attributed primarily to the Moss-Burstein shift in semiconductors. The bandgap changes found is in good agreement with reported values 3.14 to 3.26 eV by the same spray pyrolysis technique (Joseph et al., 1999b).

The photoluminescence property of film has a close relation with the crystalline, because the density of defects in the film reduces with an improvement of the crystallinity. Room temperature PL emission spectrum for all the samples was measured in the wavelength range of 310 to 550 nm at the excitation wavelength of 300 nm. PL spectra of the zinc oxide thin films deposited on glass substrates at various precursor concentrations are shown in Figure 4. The zinc oxide emission is generally classified into two categories one is the UV emission of all zinc oxide thin films at 3.427 eV and the other is the

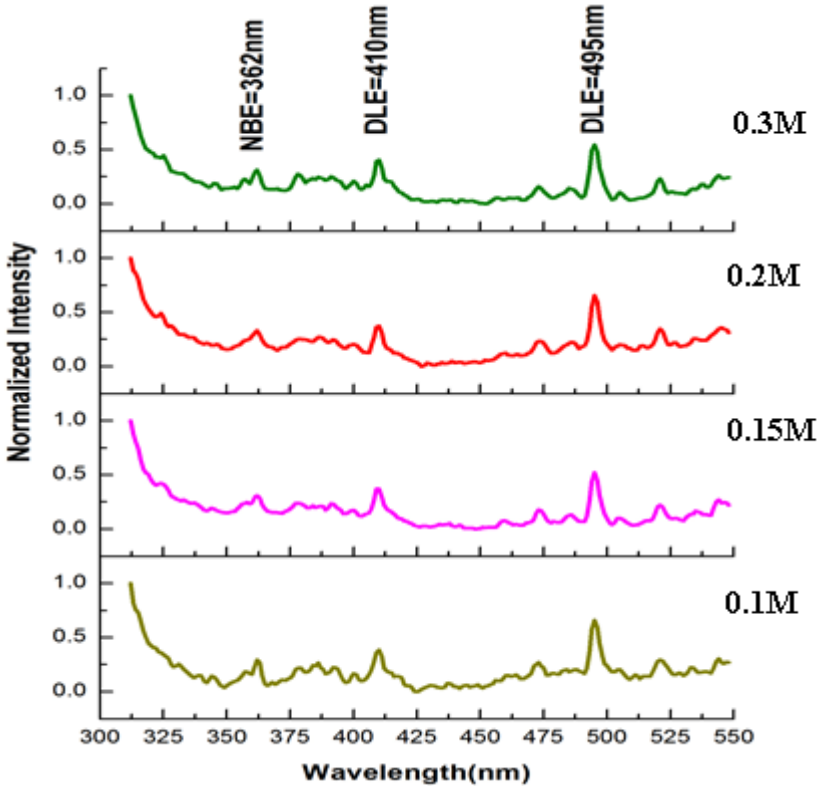

Figure 4. Comparison of the variation of peak intensity with different concentrations.

deep level (DL) emission related to the defect emission in the visible range. In the deep level emission, two emission peaks at 3.026 and 2.506 eV appear in the PL spectra shows a strong blue emission band (Gao et al., 2004) around 2.506 eV in all samples. By comparing the results from absorption spectra and PL spectra, pronounced exciton absorption peak in the UV spectra located at around 3.4 eV is assigned to the exciton effect in ZnO. It is clear that the above results exists a stokes shift between the PL spectra and the absorption spectra. The stokes shift is related to many effects such as electron–phonon coupling, lattice distortions, interface defects and point defects that may cause the blue shift of emission line from absorption edge (Sagar et al., 2007). In the case of blue shift, the filling of the conduction band by electrons will generally result in the NBE emission. The stokes shift were calculating the following equation:

$$\Delta E = E_{Abs} - E_{PL} \quad (5)$$

The stokes shifts were calculated to be much larger value respectively for increase in the molar concentration for ZnO thin films. The crystalline quality of ZnO film grain size has a larger distribution leading to PL band (Shan et al., 2006).

Conclusion

Zinc oxide thin film was deposited on the glass substrate by chemical spray pyrolysis technique. The XRD studies show that, films prepared are in nanocrystalline range. Polycrystalline nature of zinc oxide films and lattice parameter (C) has been determined which agree with the standard data. From the X-ray diffraction analysis 0.1, 0.15, 0.2 and 0.3 M films show hexagonal structure along with *c*-axis oriented (0 0 2) plane. Optical transmittance properties of the optimized ZnO thin films were investigated by using UV-Vis spectroscopy. The transmittance of above 70% in the visible region has been observed for precursor concentration and increase the concentration caused by the band gap to become broader. An intensive blue luminescence peak around 495 nm is observed at room temperature.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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