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Effect of Cd precursor on structure and optical properties of spin coated $Zn_{0.9}Cd_{0.1}O$ films for optoelectronics applications

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The development of transparent conducting oxide materials has gained an increased interest in the scientific community for developing efficient low cost optoelectronic devices. The effect of Cd precursor on structural and optical properties of sol-gel synthesized $Zn_{0.9}Cd_{0.1}O$ nanostructured films has been studied by using XRD, AFM, optical absorption and emission spectroscopic techniques. X-ray diffraction confirms the hexagonal wurtzite crystal structure of the deposited films and the relative intensity of diffraction peaks has been observed with different cadmium salts. The granular surface morphology of the synthesized films has been observed from AFM measurements. The optical transmission, band gap and luminescence intensity was found to change for different cadmium salts. These results are very important for developing new materials for optoelectronic applications.

Keywords: *transparent conducting oxides - TCO; thin films; sol-gel technique; structural properties; optical properties*

1. Introduction

Transparent conducting oxides (TCOs) comprise a special category of materials having huge prospects owing to their unique semiconducting properties along with very low resistivity (10^{-3} $\Omega \cdot$ cm to $10^{-4}\Omega \cdot$ cm) and high transparency in the visible region of the spectrum. A wide range of applications of TCOs includes their use as transparent electrodes in the photovoltaics [1], light emitting diodes [2], functional (protective, decorative) coatings [3] and gas sensing devices [4]. Indium tin oxide (ITO) has been identified as the most promising TCO over the past two decades due to its low resistivity of the order of $10^{-4}\Omega \cdot$ cm and its outstanding transparency in the visible spectrum. Despite of being an industry standard, ITO suffers from some prime drawbacks which include its high cost, high content of indium and its brittleness. Further, its instability to oxidation, supports the fact that there is still a room to improve. Henceforth, the search to find an alternative to ITO has become an intensive area of research from the last few decades. A number of transparent conducting oxide materials have been studied in the past, however, the attention of various research groups has been focused on ZnO as an effective TCO. Zinc oxide (ZnO) belongs to the group II-VI compound semiconductors with a stable wurtzite structure and a direct wide band gap (3.34 eV) and high excitonic binding energy (60 meV) at room temperature [5]. The presence of native defects like oxygen vacancies and zinc interstitials is responsible for its conductivity. For the further improvement of its optoelectronic properties, the doped counterparts became an interest of many scientists. Generally, Al and Ga doped zinc oxides possess excellent thermal or chemical stability as compared to that of much more common ITO [6–8].

CdO films are also a promising material as far as its TCO functionality is concerned owing to its low resistivity as compared to ITO, but its high toxicity hinders its industrial scale applications [9–11]. However, Cd as a dopant in other materials proved to be effective

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in tailoring their properties. Cd doped zinc oxide has been intensively studied by different researchers in the recent past. The study on the influence of precursor solvent on the growth of CdZnO nanostructured films revealed that 2-ethoxyethanol solvent is best suited for fabricating transparent electrodes [12]. Pathak et al. [13] reported a decrease in optical gap and electrical resistance with increasing CdO content in mixed ZnO–CdO oxide films. Ravichandran et al. [14] achieved a band gap variation from 3.1 eV to 3.6 eV by adjusting the dopant concentration in the Cd/Mg co-doped ZnO films. Many research groups have reported the physical properties of ZnO with Cd dopant variation [15–23], while the role of Cd precursor salt in optimizing the microstructure and optoelectronic properties of ZnCdO films have not been addressed anywhere in the literature. So, the role of Cd precursor type (acetate, chloride, nitrate) on structural and optical properties of sol-gel spin coated ZnO films have been reported in the present work.

2. Experimental

Polycrystalline $Zn_{0.9}Cd_{0.1}O$ thin films were deposited on well-cleaned glass substrates at room temperature by spin coating method. The precursor solution of 0.18 M of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$, CDH, 99.5 %] and 0.02 M cadmium acetate dihydrate [$Cd(CH_3COO)_2 \cdot 2H_2O$, SD Fine Chemicals, 98 %] was dissolved in 2-methoxyethanol on a magnetic stirrer with a hot plate at 60 °C for 1 h. Thereafter, the ethylenediamine [C_2H_7NO, Fisher Scientific, 98 %] was added to the above solution to achieve the metal ion concentration 1:1 ratio so that it became transparent. Then, the mixture was aged for 24 h for necessary hydrolysis process. The deposition of $Zn_{0.9}Cd_{0.1}O$ films was carried by spin coating technique (Spin NXG-P1, Apex Instruments, India) on well cleaned glass substrates at 2000 rpm for 80 s. Each deposited layer was dried at 260 °C in a hot air oven for 5 min and 15 layers were deposited to obtain films of desired thickness. The synthesized films were then finally annealed in ambient air conditions at temperature of 500 °C in a muffle furnace for 1 h.

The structural properties were examined by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany), operated at 40 kV and 40 mA using CuKα radiation ($\lambda = 1.5418$ Å). The surface morphology of the films was studied in tapping mode by atomic force microscopy (Dimension Edge, Bruker, Germany). The optical transmittance spectrum was recorded with the help of UV-Vis spectrophotometer (UV-1800, Shimadzu, JAPAN). The 370 nm line of the xenon arc lamp was used to record the photoluminescence spectra at room temperature using the fluorescence spectrophotometer (Cary Eclipse, Agilent, USA).

3. Results and discussion

3.1. Crystalline structure and surface morphology

Fig. 1 shows the X-ray diffraction patterns of the $Zn_{0.9}Cd_{0.1}O$ thin films. The deposited films have hexagonal wurtzite structure corresponding to pure zinc oxide, as the cadmium doping content is relatively small [24]. The experimental diffraction peaks occur at angles somewhat less than that of the standard, owing to the fact that the ionic radius of Cd is larger compared to that of Zn. The presence of small amount of Cd in zinc oxide gave rise to a lattice expansion resulting in a peak shift to smaller 2θ angles [25]. The peak intensity of (1 0 1) plane is maximum and minimum for the samples synthesized with cadmium nitrate and cadmium acetate, respectively. The lattice constants (a and c) for hexagonal wurtzite structure of zinc cadmium oxide films have been calculated by using the following relation:

$$\frac{1}{d^2} = \frac{4}{3}\frac{\left(h^2 + hk + l^2\right)}{a^2} + \frac{l^2}{c^2} \tag{1}$$

where d is interplanar spacing for the planes indexed by Miller indices (h k l). Three diffraction peaks (1 0 0), (0 0 2) and (1 0 1) are observed predominantly for zinc oxide structure. The calculated values of lattice constants a = 0.326 nm and c = 0.533 nm are slightly different than those of zinc oxide hexagonal wurtzite structure (a = 0.324 nm and c = 0.520 nm). This difference can be ascribed to the incorporation of cadmium in zinc oxide in ZnCdO films. The values of lattice constants (a and c) increase due to the incorporation of larger sized cadmium ions (ionic size 97 pm) replacing the smaller zinc ions (74 pm).

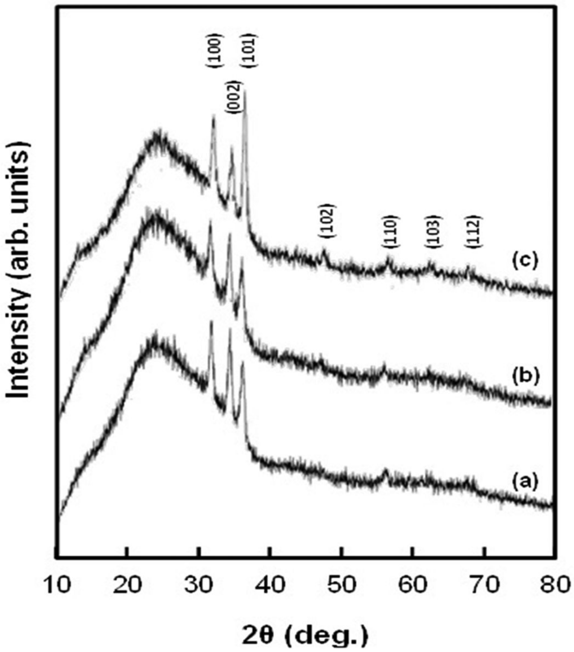

Fig. 1. X-ray diffractograms of $Zn_{0.9}Cd_{0.1}O$ thin films (a) cadmium acetate (b) cadmium chloride (c) cadmium nitrate.

The crystallite size of obtained films has also been calculated by using Scherrer formula [26]:

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \tag{2}$$

where D is the crystallite size, λ is wavelength of X-rays used (1.5406 Å), β is broadening of diffraction line measured at half of its maximum intensity (FWHM) in radians and θ is the angle of diffraction. The crystallite size has been calculated for (1 0 1) peak and given in Table 1. It has been found that the samples synthesized by using the cadmium nitrate precursor have the crystallites with the largest size (∼14.9 nm). Other parameters such as lattice strain (ϵ), dislocation density (δ) and number of crystallites per unit area (N) have been calculated using the following relations [15]:

$$\varepsilon = \frac{\beta\cos\theta}{4} \tag{3}$$

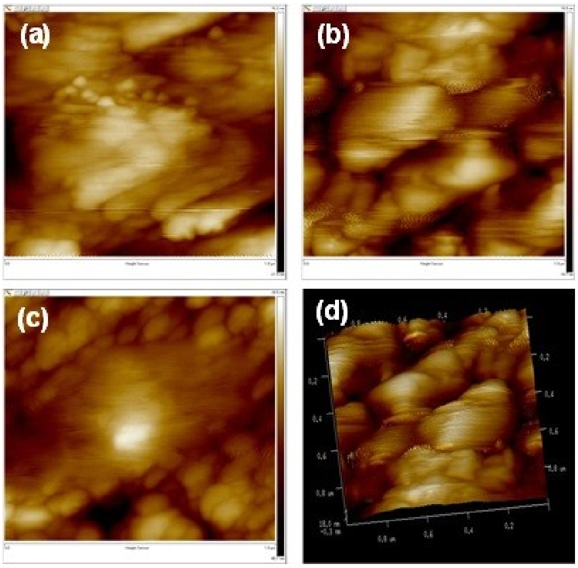

Fig. 2. 2D surface morphology of $Zn_{0.9}Cd_{0.1}O$ films synthesized using (a) acetate (b) chloride (c) nitrate and (d) 3D image for chloride precursor.

$$\delta = \frac{1}{D^2} \tag{4}$$

$$N = \frac{1}{D^3} \tag{5}$$

All the calculated parameters are tabulated in Table 1. The increased value of strain has been obtained for the cadmium acetate sample and the lowest value corresponds to the cadmium nitrate sample. The dislocation density and crystallite density are the smallest for the sample prepared with cadmium nitrate. A maximum for all the parameters (lattice strain, dislocation density, number of crystallites per unit area) has been obtained for the cadmium acetate sample.

Fig. 2 shows the 2D and 3D surface morphological view of the nanostructured $Zn_{0.9}Cd_{0.1}O$ films. As seen from the figure, the films possess granular surface morphology having some uniform as well as distorted grains of different shapes and sizes [27]. The randomly organized small and large sized grains are observed in case of acetate and nitrate samples while uniformly sized large grains are observed for the chloride sample.

Table 1. 2θ values, FWHM, average crystallite size, dislocation density, crystallite density and optical gap for the nanostructured ZnCdO films.

Sample	2θ [°]	FWHM [rad]	D [nm]	ϵ	Δ	N [g·cm^{-3}]	E_g [eV]
Acetate	35.42	0.0171	8.5	0.0041	0.0138	0.0016	3.08
Chloride	35.90	0.0159	9.13	0.0038	0.0119	0.0013	3.07
Nitrate	36.17	0.0098	14.9	0.0023	0.0045	0.0003	2.98

3.2. Optical properties

Fig. 3 shows the optical transmission spectra of $Zn_{0.9}Cd_{0.1}O$ films in the wavelength range of 200 nm to 1100 nm. All the samples show good transmission in the visible region of 400 nm to 800 nm indicating a good optical quality of the deposited films. The average transmission in visible spectrum is found to increase from 81 % to 87 % and then to 88 % for the acetate, chloride and nitrate salts of cadmium respectively. The average transmission values are in a good consent with the results reported earlier by different research groups [28]. The observed improvement in transmission may be due to the good crystal structure and surface morphology of nitrate and chloride samples as compared to the acetate sample.

The relation expressing the dependence of the absorption coefficient α on the photon energies hν for direct transition is described with equation 6 [29]:

$$(\alpha h\nu)^2 = B(h\nu - E_g) \tag{6}$$

where B is a constant and E_g is direct optical band gap energy. The variation of $(\alpha h\nu)^2$ with photon energy hν is shown in Fig. 4. The energy gap E_g values of the samples are evaluated from the intercept of the linear portion of each curve with hν on x-axis and are tabulated in Table 1. The optical band gap is found to decrease from that of ZnO (3.30 eV) with the incorporation of Cd and this decrease is found to be minimum for acetate salt (3.08 eV) while maximum for nitrate (2.98 eV) samples. Ravichandran et al. [14] have also reported a similar decrease in band gap value with Cd and Mg doping in ZnO films deposited by sol-gel technique. These results show the importance of salt type in modifying the structure-property relationships for ZnCdO films.

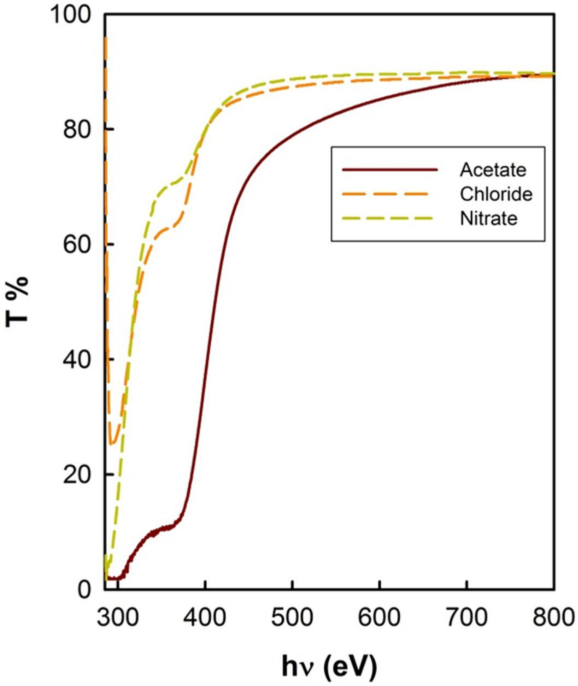

Fig. 3. Optical transmission spectra of Zn $_{0.9}$ $Cd_{0.1}O$ films with different Cd precursors.

3.3. Photoluminescence

Fig. 5 shows the room temperature photoluminescence spectra of $Zn_{0.9}Cd_{0.1}O$ films synthesized by using different Cd salts at an excitation wavelength of 310 nm. Three prominent emission peaks centred at 423 nm, 434 nm and 447 nm have been observed for all the ZnCdO films. The emission spectra of CdZnO films with a minimum doping content of cadmium resemble emission spectra of ZnO films. The native defects in zinc oxide, such as oxygen vacancies, zinc vacancies,

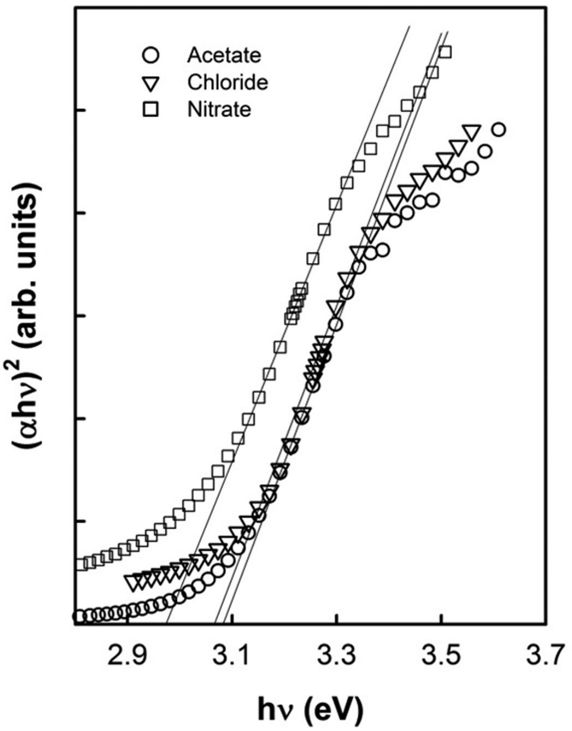

Fig. 4. Tauc plots for $Zn_{0.9}Cd_{0.1}O$ films with different Cd salt precursors.

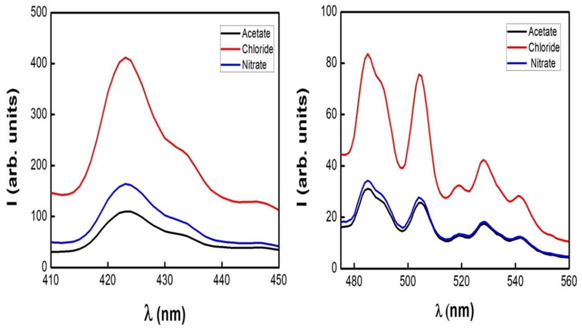

Fig. 5. Emission spectra of $Zn_{0.9}Cd_{0.1}O$ films with different Cd salt precursors.

corresponding interstitials and oxygen antisites are mainly responsible for the electrical conductivity and optical properties of zinc oxide. The existance of various instrinsic defects leads to blue, voilet, green and yellow emision peaks. The peaks positioned at 423 nm and 447 nm are attributed to the transitions of electrons from conduction band to zinc vacancy V_{Zn} and zinc interstitials Zn_i respectively while the peak at 434 nm, to the transition of electrons between zinc interstitial Zn_i and zinc vacancies V_{Zn} levels [30]. A possible shift of Fermi level towards the conduction band could result from oxygen vacancies giving rise to a low intensity peak observed at 485 nm, and the peak at 530 nm can be assigned to the oxygen antisites [31]. These results reveal that the use of chloride as precursor for the cadmium salt have resulted in an enhacement of defect related luminescence from the CdZnO films which may be very important for further development of their optoelectronic applications.

4. Conclusions

The effect of cadmium salt on the structure and optical properties of $Zn_{0.9}Cd_{0.1}O$ nanostructured films obtained by low cost sol gel spin coating technique is reported. The XRD study reveals that the ZnCdO films exhibit the hexagonal wurtzite crystal structure of pure zinc oxide. The maximum grain size along with a minimum strain and dislocation density has been observed for the Cd nitrate sample. AFM images confirm the presence of somewhat uniform and similar grains in case of Cd chloride sample as compared to the other two samples. The average optical transmission is improved for the samples prepared with nitrate. The value of optical gap varies between 2.98 eV and 3.08 eV for nitrate and acetate salts, respectively. The emission spectra reveal the presence of zinc interstitials and zinc vacancies with the main peak corresponding to the recombination of charge from the conduction band with zinc vacancies. These results suggest the importance of precursor chemicals for modifying the structure-property relationships of nanostructured ZnCdO films for developing new optoelectronic applications.

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