Structural and optical properties of cobalt doped sprayed ZnO films

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In recent years, $Zn_{1-x}Co_xO$ has attracted special attention due to the highest solubility of Co in ZnO matrix and is expected to behave as a dilute magnetic semiconductor, which exhibits ferromagnetic properties. Thin films of cobalt doped ZnO were deposited on glass substrates by chemical spray pyrolysis at various deposition temperatures, T_s that vary in the range, 260 - 350° C. 0.1M aqueous solutions of zinc acetate (Zn $(CH_3COO)_2.2H_2O$) and cobalt acetate (Co $(CH_3COO)_2$ $.4H_2O$) were taken as precursors. The as-grown layers were characterized by different techniques to know their physical properties. The X-ray diffraction studies revealed that all the layers exhibited wurtzite structure with (002) plane as the preferred orientation. The grain size of the films was varied in the range, 20 - 40 nm. The average optical transmittance of the films was found to be > 75% in the visible region and the evaluated optical band gap of the films decreased from 3.37 eV to 3.22 eV with the increase of substrate temperature. The details of these results were reported and discussed.

(Received November 11, 2010; accepted November 29, 2010)

Keywords: ZnO, Thin films, Co doping, Spray method

1. Introduction

The dilute magnetic semiconductors (DMS) are promising materials for many device applications that include spintronics as they have charge and spin degrees of freedom in a single substance [1]. The $A^{II}_{1-x}TM_xB^{VI}$ materials are widely studied due to the higher solubility of magnetic atoms in them. Among the II–VI oxide based DMS, transition-metal-doped zinc oxide is currently attracting much attention due to its wide band gap and exhibits ferromagnetism at room temperature [2, 3]. ZnO is a wide band gap (3.37 eV) semiconductor with a high exciton binding energy of 10MeV that paves the way for an intense near-band-edge excitonic emission at room temperature and also at higher temperatures. The term DMS [4, 5] refers to the fact that some fraction of the atoms in a nonmagnetic host such as ZnO is replaced by magnetic ions. In particular, ZnO-based DMSs have been predicted to show ferromagnetic behavior with Curie temperature above room temperature and have a large magnetization, which makes them promising candidates for the next generation spintronic devices [6-7]. Co-doped ZnO films were deposited by different chemical and physical methods. In the present investigation spray pyrolysis method was used to prepare Co-doped ZnO films which are a versatile and low-cost method to prepare nanocrystalline films over large areas with controlled dimensions and surface morphology. In our earlier investigation, we have studied the effect of Co-composition on the physical properties of $Zn_{1-x}Co_xO$ films deposited by spray pyrolysis [8]. In the present study, thin films of cobalt doped ZnO were deposited on glass substrates by chemical spray pyrolysis at various deposition temperatures and the results were discussed.

2. Experimental details

$Zn_{1-x}Co_xO$ films were grown by spray pyrolysis technique at different substrate temperatures in the range, 260- 350°C on ultrasonically cleaned glass substrates at a constant Co-doping concentration of 10%. 0.1M aqueous solutions of zinc acetate, Zn $(CH_3COO)_2$. $2H_2O$ and cobalt acetate, Co $(CH_3COO)_2.4H_2O$ were taken as precursors. Compressed purified air was used as a carrier gas at a flow rate of 8 l/min and the solution was sprayed at a flow rate of 6 ml/min respectively. The substrate temperature was maintained using Eurotherm temperature controller with a Chromel-alumel thermocouple as a temperature sensor, with an accuracy of ± 5 °C. The substrate to source distance was fixed as 25cm. The spray head was moved in the horizontal plane by means of a microprocessor controlled stepper motor system in order to get uniform films on the substrate. After completion of the deposition process, the films were allowed to cool slowly to room temperature.

The structural properties of the films were measured using Siefert X-ray diffractometer while the morphological properties were evaluated using the Hitachi scanning electron microscope (SEM). The micro structural analysis was carried out by Renishaw Ramanscope 2000 micro spectrometer. The optical transmittance measurements were performed using Hitachi UV-Vis-NIR double beam spectrophotometer.

3. Results and discussion

All the grown layers were pale greenish white in colour and strongly adherent to the substrate surface.

Nearly all the layers are pin-hole free, although one or two films had few pin-holes in them.

Fig. 1 shows the XRD patterns of the cobalt doped ZnO thin films deposited at different temperatures that vary in the range, 260-350°C respectively. The XRD patterns showed that all the deposited layers were polycrystalline in nature with (002) plane as the preferred orientation. The spectra showed various peaks related to the (100), (002), (101), (102), (110) and (103) peaks that corresponds to wurtzite ZnO at 2θ values of 31.75^0, 34.44^0, 36.35^0, 47.50^0, 56.62^0 and 62.83^0 respectively. The intensity of (002) reflection increased with increase of substrate temperature, which indicated an improvement in the crystallinity of the grown layers. At lower deposition temperatures, $T_s \leq 300^\circ C$, the intensity of the (00 2) peak is low due to the incomplete reaction of the constituent chemicals in the solution, and with further increase of T_s to $350^\circ C$, the intensity of (002) peak increased, which might be due to the enhancement of horizontal mobility of adatoms and also the complete reaction of the chemicals in the solution.

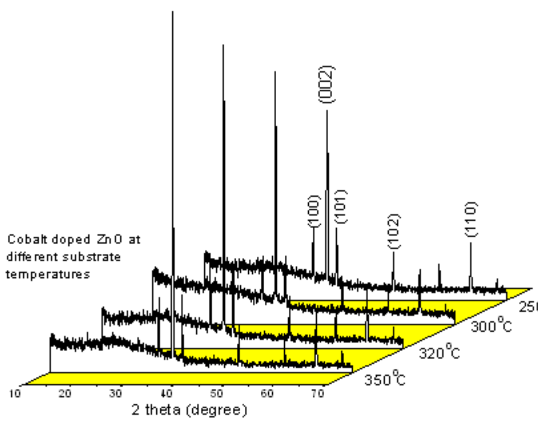

Fig.1. XRD spectra of cobalt doped ZnO films.

The average crystallite size, D was calculated using the Scherer's formula: [10]

$$D = \frac{0.94\lambda}{\beta_{2\theta}\cos\theta} \quad (1)$$

where λ is the wavelength of CuK_α radiation, θ is the Bragg angle of the diffraction peak and β is the full width at half maximum (FWHM) for the (002) orientation. The crystallite size increased from 35 nm to 52 nm with the increase of substrate temperature from 260°C to 350°C. The increase of crystallite size with substrate temperature could be attributed to the enhanced reaction kinetics among the sprayed droplets as well as improvement in the adatom mobilities that lead to a high orientation of the crystallites along the preferred direction.

Fig. 2 shows the room temperature Raman spectra of Co-doped ZnO films deposited at different substrate temperatures. The Raman band observed at 431.96 cm^{-1} is attributed to the high frequency E_2 mode [11]. The phonon frequency at 383.15 and 572.47 cm^{-1} can be ascribed to the transverse and longitudinal optical phonon modes with A_1 symmetry. The additional mode at 276.6 cm^{-1} is often observed in ZnO films deposited at 260° C. But this peak is out of present reported region. Hence we thought of that this peaks related to the intrinsic host defects and / or oxygen vacancy. The observed phonon modes are related to the wurtzite structure of ZnO with a space group of C_6 n_4 [12] and comparable with the reported data [13]. .The weak peaks A_1 (T_0) and A_1 (L_0) can be attributed to the intrinsic defects such as oxygen vacancy, interstitial zinc (or) free carriers. The analysis of Raman spectra supported the observations made from X-ray diffraction studies.

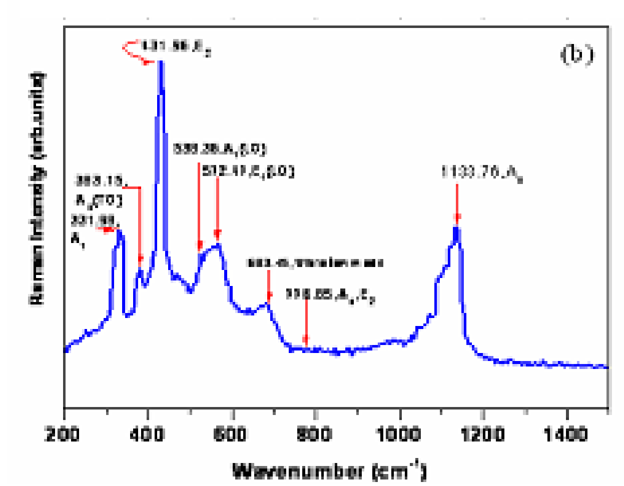

Fig. 2. Raman spectra of cobalt doped ZnO film grown at $T_S = 350^0C$.

The surface morphological studies of Co-doped ZnO films were carried out using scanning electron microscope and the SEM pictures of the layers deposited at different substrate temperatures are shown in Fig. 3. The images showed spherical grains that are uniformly distributed on the substrate surface without any voids or cracks. A gradual improvement in the crystallinity of the layers with substrate temperature was also noticed with the spherical grains turned into rod-like crystals with hexagonal face. The average grain size of the layers evaluated from SEM measurements does not matched with the crystallite size determined using XRD data.

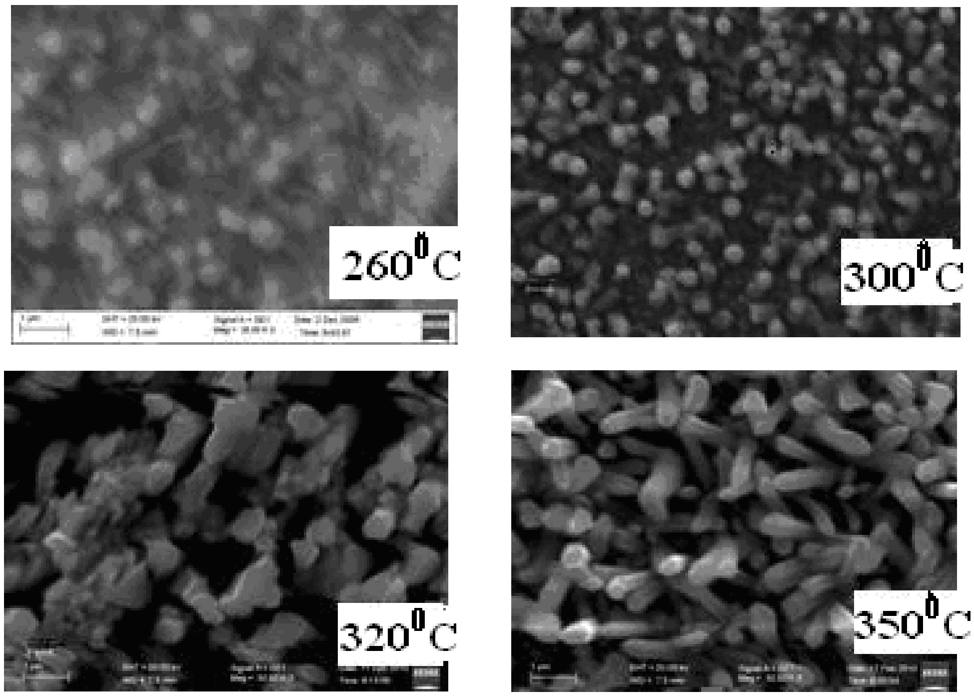

Fig. 3. SEM micrographs of Co doped ZnO films.

Fig. 4a shows the optical transmittance spectra of Co-doped ZnO films recorded in the wavelength range, 500-2500 nm. The films deposited at 260°C showed an optical transmittance of ~70% while those deposited at 350°C showed a transmittance of in 90% visible region. The high transmittance observed in the layers grown at T_s ~ 350°C was attributed to the lower optical scattering, structural homogeneity and better crystallinity whereas the less transmittance noticed in the layers grown at lower temperatures might be due to the poor crystallinity of the films.

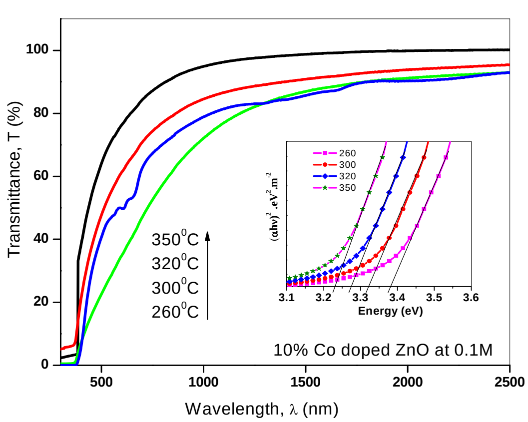

Fig. 4. Optical transmission spectra of cobalt doped ZnO films. Inset $(\alpha h\upsilon)^2$ Vs hυ plots.

The optical band gap, E_g of the films was determined from the variation of absorption coefficient (α) as a function of photon energy (hν). The optical energy band gap of the films was determined using the relation [14]

$$(\alpha h\nu) = c\,(h\nu - E_g)^{1/2} \qquad (2)$$

Where α is the absorption coefficient, hν is the photon energy. The liner dependence of $(\alpha h\nu)^2$ Vs hν plot of Co-doped ZnO films are shown in Fig.4b. The extrapolation of the linear portion of the plot on to the energy axis gives the optical energy band gap of the layers. The evaluated energy band gap of the films decreased from 3.37eV to 3.22eV with increase of substrate temperature from 260°C to 350°C. Generally in polycrystalline semiconductors, the energy band gap can be effected by the stoichiometric deviations, quantum size effect [15], dislocation density and disorder at grain boundaries [16]. In the present study, the change in band gap could be influenced by the variation of particle size with substrate temperature. Similar results were also reported by Metin et al. [17] for annealed CdS films grown by chemical bath deposition method.

4. Conclusions

Polycrystalline Co-doped ZnO films have been successfully grown by spray pyrolysis at different substrate temperatures that vary in the range, 260 - 350 °C. The structural characterization of the films showed wurtzite structure with the (002) plane as the predominant orientation. The films prepared at 350°C had an average grain size of 38nm. The Raman analysis supported the XRD observations with the intense E_2 phonon mode observed in all the samples. SEM photographs revealed that the layers grown at lower temperature showed spherical grains that are uniformly distributed on the substrate surface whereas the layers grown at higher temperatures had rod-like grains with hexagonal face and the grain size increased with substrate temperature. The films deposited at T_s>300 °C showed the highest optical transmittance of 90% in the visible region.The evaluated optical band gap of the films decreased from 3.37eV to 3.22eV with the increase of substrate temperature.

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