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Doping concentration and annealing temperature effects on the properties of nanostructured ternary CdZnO thin films towards optoelectronic applications

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ABSTRACT

Nanostructured ternary CdZnO thin films with zinc concentrations (0, 2, 4, 6 and 8 wt%) were prepared by spray pyrolysis technique using perfume atomizer on glass substrates at 375 °C. The effect of doping concentration on the structural, morphological, optical and electrical properties of the films was studied and from the results obtained it is observed that the CdZnO film with 6 wt% Zn doping concentration has better physical properties and this film is subjected to post annealing in air at different temperatures. The effect of thermal annealing on the properties of the deposited films was systematically studied. The XRD patterns reveal that the films are polycrystalline in nature with cubic structure and are highly textured along (1 1 1) preferential orientation. The SEM and AFM images confirmed these results and showed more crystallization up to 300 °C annealing temperature. Film transparency decreases with annealing temperature. Analysis of the absorption edge revealed that the optical band gap energies of the films was red shifted with annealing temperature. The annealed films have a resistivity in the order of 10^1 Ω cm. Increased transparency and reduced resistivity observed for the CdZnO films make them suitable for optoelectronic device applications especially as window layer in solar cells.

1. Introduction

Cadmium oxide (CdO), an n-type degenerate semiconductor is an important transparent conducting oxide (TCO) material which finds applications as transparent electrodes in flat-panel displays, solar cells, gas sensors and smart windows [1–4]. CdO has been remained less scared due to the toxicity of Cd and its narrow band gap of 2.27 eV. But the studies on photovoltaic solar cells showed that CdO is an important material for CdTe and CIS hetero-junction as the window material [5]. CdO crystallizes in cubic structure of Fm3m space group of 6-coordination with a lattice constant of 0.4695 nm, and relatively low electrical resistivity (10^{-2} – 10^{-4} Ω cm). The concentration of oxygen vacancies plays a vital role for the resistivity of undoped CdO and too much oxygen vacancies can also deteriorate the quality of the doped film [6]. It has been reported earlier that the opto electrical properties of CdO could be controlled by doping with different elements like In [7], Zn [8], F [9], Li [10], Al [11] etc. It is experimentally established that doping CdO with ions having a smaller ionic radius than that of Cd^{2+} can improve its electrical conductivity and optical band gap, which is explained through the Moss – Burstein (MB) effect [12]. Zinc is an important transition element having ionic radius (0.74 Å) smaller than that of cadmium (0.97 Å) and hence could be an ideal doping candidate for CdO which can improve its opto-electrical properties. However, only a very meagre amount of work on the synthesis and characterization of sprayed Zn-doped CdO thin films are available in the literature, which describes the limited effectiveness of this well-deserved n-type TCO material. Also, the effect of thermal annealing on the properties of Zn-doped CdO films is very scarce. Motivated by this fact, in this study, CdZnO thin films were deposited by spray pyrolysis technique with different Zn doping concentrations, and investigation on their physical properties was made. Among them, the best candidate with improved structural, morphological, optical and electrical properties is selected and subjected to thermal annealing in air at temperatures (100, 200, 300 and 400 °C) and the modifications observed in the properties of the films were reported. Spray pyrolysis is adopted here due to its simplicity,

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Table 1
Structural parameters of Zn-doped CdO thin films.

Zn concentration (wt%)	$2\theta_{(111)}$ (°)	d-spacing $_{(111)}$ (Å)	Lattice parameter ‘a’ (Å)	Crystallite size, D (nm)	Strain, $\varepsilon \times 10^{-4}$	Dislocation density, $\delta \times 10^{15}$ lines/m^2	Electrical resistivity, $\rho \times 10^1$ Ω cm
0	33.070	2.7116	4.6966	31.88	0.397	0.984	1.63
2	33.076	2.7061	4.6871	34.55	0.352	0.838	1.56
4	33.097	2.7045	4.6843	36.05	0.339	0.770	1.33
6	33.099	2.7044	4.6842	36.50	0.333	0.704	0.794
8	33.105	2.7038	4.6831	33.17	0.406	0.909	0.944

in-expensiveness, non-vacuum requirement and capability of large area coatings [13]. Also, the glazing acquired by spray pyrolysis technique is naturally homogeneous with very large surface-to-volume ratio and is capable of coating nano-structured materials.

2. Experimental details

Spray pyrolysis technique deals with a chemical reaction stimulated between cluster/clusters of liquid or vapour atoms consisting of different chemical species. It involves aqueous spraying solution, containing soluble salts of the desired compound on to preheated substrates. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic (endothermic) decomposition and forms a single crystalline or cluster of crystallites as a product on the substrate. Deposition of CdO and Zn-doped CdO (CdZnO) thin films takes place by spraying an aqueous solution (50 ml in volume) of cadmium acetate (0.05 M) and zinc acetate with different concentrations (0, 2, 4, 6 and 8 wt% Zn) on preheated glass substrates kept at 375 °C. The precursor salts used were of analytical reagent grade with purity 99.9% supplied by Qualigens. Prior to the deposition, the glass substrates supplied by Labtech, Mumbai, were initially boiled in hot water for 10 min, washed with acetone and again washed with double distilled water, followed by ultrasonic cleaning for 15 min. X-ray diffractometry (PW diffractometer ‘XPERT – PRO’) was used to determine the structure, crystallinity and phase of the CdO and CdZnO thin films. The surface morphology was characterized by a scanning electron microscope (HITACHI S – 3000H). Atomic force microscopy was carried out using the AFM, digital instrument, nanoscope III at room temperature. The optical transmittance measurements were carried out using a PerkinElmer UV – vis – NIR double beam spectrophotometer (Lambda-35). The resistivity (ρ) measurements were carried out by a standard four point probe technique.

3. Results and discussion

3.1. Effect of doping concentration

Fig. 1 shows the XRD patterns of the Zn-doped CdO films deposited with different Zn concentrations (0, 2, 4, 6 and 8 wt%). All the films are characterized by five diffraction peaks at 2θ values of approximately 33°, 38°, 55°, 65° and 69° corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes, respectively. By comparison with the data from JCPDS card No. 05-0640, all diffraction peaks can be indexed to cubic structure of pure CdO. The narrow peaks show that the material has good crystallinity. All the films show a preferential growth along the (1 1 1) plane irrespective of Zn doping level. The preferential orientation along the (1 1 1) plane observed here exactly matches with the results reported by Manjula et al. [14] for CdO thin films prepared by spray technique using a perfume atomizer. No peaks corresponding to cadmium hydroxide or zinc compounds were detected in the XRD patterns even for the highest Zn doping concentration, suggesting that incorporation of Zn ions in the host CdO lattice does not affect its crystal structure. The 2θ and the lattice constant ‘a’ values calculated for the (1 1 1) peak form the Bragg formula: $d = \frac{2\lambda}{\sin\theta}$ as a function of Zn doping concentration are shown in Table 1.[1]

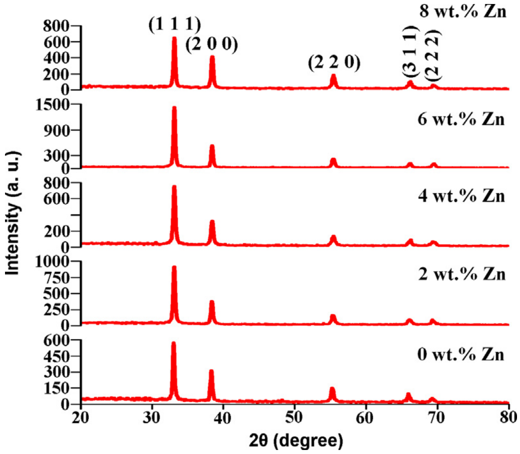

Fig. 1. XRD patterns of CdO:Zn thin films coated with different Zn doping concentrations.

Fig. 1 also shows that the doping of Zn induces a variation of the film growth texture. The texture of a particular plane can be represented by the texture coefficient TC (hkl), which can be calculated from X-ray data using the formula [15]:

$$\mathrm{TC}(hkl) = \frac{I(hkl)/I_o(hkl)}{N^{-1}\sum_{N} I(hkl)/I_o(hkl)} \tag{1}$$

where, $I(hkl)$ is the measured relative intensity of the plane (h k l), I_0(h k l) is the standard intensity of the plane (hkl) taken from the JCPDS data and N is the reflection number. Any deviation of the calculated TC value from unity implies the preferred growth. The texture coefficient with varied Zn concentration calculated for the diffraction peak (1 1 1) are plotted in Fig. 2. It is observed that the texture coefficient increases with Zn concentration attaining a maximum value for the CdO film coated with 6 wt% Zn concentration and for further increase in doping concentration it decreases. The increased TC values observed up to 6 wt% Zn concentration might be due to the fact that Zn^{2+} ions successfully replace Cd^{2+} ions in the host lattice. However, at higher Zn doping concentration, apart from replacing Cd^{2+} ions, Zn^{2+} ions occupies the interstitial positions in the CdO lattice and hence the TC value decreases. This is in accordance with the results reported by Deokate et al.

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[1] It is seen from Table 1, that there is a slight shift of 2θ in (1 1 1) diffraction peak toward higher Bragg angle as the Zn doping concentration increases, which implies that doping Zn substituting Cd position in CdO crystal induces the lattice shrinkage since the ionic radius of Zn^{2+} ions (0.74 Å) is slightly smaller than that of Cd^{2+} (0.95 Å) and thus they have high diffusivity and low activation energy. The dissolution of Zn^{2+} ions in CdO lattice can proceed mainly by substitution for some host Cd^{2+} and by location in the interstitial positions. It can also be observed from Table 1, that the value of interatomic spacing decreases linearly with increase in Zn concentration which infers that Zn^{2+} ions successfully replace Cd^{2+} ions in the host lattice substitutionally.