Structural, Optical, and Electrical Properties of Zn-Doped CdO Thin Films Fabricated by a Simplified Spray Pyrolysis Technique

K. Usharani · A. R. Balu

Received: 14 March 2014/Revised: 20 July 2014/Published online: 16 November 2014
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Abstract Thin films of zinc-doped cadmium oxide with different Zn-doping levels (0, 2, 4, 6, and 8 at%) were deposited on glass substrates by employing an inexpensive, simplified spray technique using perfume atomizer at relatively low substrate temperature (375 °C) compared with the conventional spray method. The effect of Zn doping on the structural, morphological, optical, and electrical properties of the films was investigated. XRD patterns revealed that all the films are polycrystalline in nature having cubic crystal structure with a preferential orientation along the (1 1 1) plane irrespective of Zn-doping level. Zn-doping level causes a slight shift in the (1 1 1) diffraction peak toward higher angle. The crystallite size of the films was found to be in the range of 28–37 nm. The band gap value increases with Zn doping and reaches a maximum of 2.65 eV for the film coated with 6 at% Zn doping and for further higher doping concentration it decreases. Electrical studies indicate that Zn doping causes a reduction in the resistivity of the films and a minimum resistivity of 15.69 Ω cm is observed for the film coated with 6 at% Zn.

KEY WORDS: Semiconductors; Thin films; Crystal structure; Optical properties; X-ray diffraction

1 Introduction

Metal oxide thin films have a variety of uses in optical, thermal, electronic, and solar energy devices. Transparent conducting oxide (TCO) films have found a wide application in the field of optoelectronic devices, and among these TCOs, cadmium oxide (CdO) is widely used for its high electrical conductivity and optical transparency [1]. CdO thin films can be used as transparent contacts and

windows instead of tin oxide (SnO_2) and cadmium sulfide (CdS) in the $\text{SnO}_2/n\text{-CdS}/p\text{-cadmium telluride (CdTe)}$ heterostructure solar cells [2, 3]. CdO is a *n*-type semiconductor with band gap nearly equal to 2.5 eV [4]. Due to its low optical band gap, CdO is not widely used in optoelectronics and photovoltaics, although CdO thin films show low resistivity due to defects of oxygen vacancies and cadmium interstitials [1]. There are few reports on the improvement of optical band of CdO thin films by doping. Saha et al. [4] have reported an improvement in optical band gap of CdO by titanium incorporation. Yan et al. [5] have observed that the optical band gap of tin-doped CdO films increases up to 6.2 at% tin doping and then decreases with further doping. It is found that when CdO is doped with metallic ions having ionic radius less than Cd^{2+} , its electrical conductivity is improved and optical band gap is increased [6]. Shah et al. [7] have reported that the band gap of the CdO thin films deposited by radio frequency magnetron sputtering decreases with increase in aluminum doping level. Deokate et al. [8] reported that fluorine

Available online at <http://link.springer.com/journal/40195>

K. Usharani · A. R. Balu
PG and Research Department of Physics, AVVM Sri Pushpam
College, Poondi 613 503, Tamilnadu, India

A. R. Balu (✉)
PG and Research Department of Physics, AVVM Sri Pushpam
College, 757 MIG Colony, New Housing Unit,
Thanjavur 613 005, Tamilnadu, India
e-mail: arbalu757@gmail.com

doping increases the band gap of CdO films. To use in optoelectronics and photovoltaic applications, the optical band gap of pure CdO must be made wide besides its improved structural and electrical properties. To obtain CdO thin films with wide optical band gap and improved electrical conductivity, other suitable dopant which does not alter the CdO crystal structure should be identified. It is well known that Zn is an important transition metal element having an ionic radius of 0.074 nm, which is slightly less than that of Cd^{2+} (0.095 nm) and hence Zn^{2+} ions can easily penetrate into the CdO crystal lattice and substitute Cd^{2+} position in the crystal. So it can be expected that Zn ions substituting Cd ions in the CdO crystalline structure should improve its electrical and optical properties. Different chemical and physical deposition techniques such as SILAR, spray pyrolysis, laser deposition, magnetron sputtering, chemical vapor deposition, chemical bath deposition, etc. have been employed to prepare undoped and doped CdO thin films. Salunkhe et al. [9] reported the effect of film thickness on liquefied petroleum gas (LPG) sensing properties of SILAR-deposited CdO thin films. They observed that the CdO thin film deposited at 698 K by this technique with 1.5 μm thickness showed a maximum gas response of 18.75%. Bhosale et al. [10] reported the structural, optical, and electrical properties of chemically sprayed CdO thin films. Saha et al. [7] reported the electrical and optical properties of Al-doped cadmium oxide thin films deposited by radio frequency magnetron sputtering. They measured the actual doping percentages of aluminum present in the CdO films from X-ray photoelectron spectroscopic studies. Gupta et al. [11] reported the effect of oxygen partial pressure on the structural, optical, and electrical properties of titanium-doped CdO thin films. They succeeded in fabricating highly conducting and transparent film with high mobility using this technique. Liu et al. [12] reported the synthesis of CdO nanoneedles by chemical vapor deposition technique and they reported the electronic transport properties of the CdO nanoneedles. Gutierrez et al. [13] reported some physical properties of Sn-doped CdO thin films prepared by chemical bath deposition. They were successful in preparing colloid-free surface thin films using this technique. Dakhel et al. [14] have studied the structural and optoelectronic properties of Zn-incorporated CdO films prepared by sol-gel method and showed that the electrical conductivity of host CdO film increases by 200% and carrier concentration by about 270% with 0.51% Zn^{2+} ions incorporation. In this work, spray pyrolysis technique using perfume atomizer is used to deposit Zn-doped CdO (ZCO) thin films with different Zn concentrations (0, 2, 4, 6, and 8 at%) and the effects on the structural, morphological, optical, and electrical properties of the films due to Zn doping is investigated. To the best of our knowledge, there is no previous

report on Zn-doped CdO films deposited by spray pyrolysis technique using perfume atomizer.

2 Experimental

2.1 Preparation of Zn-Doped CdO Thin Films

CdO and Zn-doped CdO (ZCO) thin films were prepared from aqueous solution containing cadmium acetate, $\text{Cd}(\text{CH}_3\text{COO})_2$ (0.1 mol/L) dissolved in 50 mL of deionized water. Zinc acetate, $\text{Zn}(\text{CH}_3\text{COO})_2$ was added to the starting solution for zinc doping in a concentration of 0, 2, 4, 6, and 8 at% Zn. The precursor salts used were of analytical reagent grade with a purity of 99.8% (supplied by SIGMA-ALDRICH). The solution was stirred thoroughly using a magnetic stirrer for 30 min and then sprayed manually in fine droplets using a perfume atomizer on the pre-heated glass substrates kept at 375 °C. Before the deposition process, the glass substrates were degreased with organic solvent, rinsed with deionized water, and dried in air. The use of perfume atomizer has some specific advantages over the conventional spray technique which uses spray gun assembly: low cost, no need for carrier gas, fine atomization, improved wettability between the sprayed micro particles, and loss of the precursor to the surroundings is almost nil. Recently, we have reported that this simplified spray technique can be a desired alternative for the conventional spray technique by successfully fabricating CdO films [15].

2.2 Characterization of ZCO Thin Films

The as-deposited ZCO films were orange in color, uniform, pin hole free, and strongly adherent to the glass substrates. The thickness was measured by gravimetric weight different method using sensitive microbalance assuming that the samples were uniform and dense as that of bulk having density of 8.150 g/cm³. The thickness of ZCO films was found to vary from 0.995 to 2.171 μm with an accuracy of 5%. The structure, crystallinity, and phase of the undoped and Zn-doped CdO thin films were determined with a diffractometer “XPRT-PRO” model, using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm) with 2θ ranging from 10° to 80°. The surface morphology of the films was characterized by scanning electron microscope HITACHI model S-3000H. In order to determine the band gap energy of CdO and ZCO in thin film form, the optical transmission studies were carried out in the wavelength range of 300–1,100 nm, using PerkinElmer UV-vis-NIR double beam spectrophotometer (LAMBDA-35). Measurements of electrical resistivity were carried out with a four point probe with vander Pauw configuration.

Fig. 1 XRD patterns of Zn-doped CdO thin films fabricated by the simplified spray pyrolysis technique

3 Results and Discussion

3.1 Structural Studies

Figure 1 shows the XRD patterns of ZCO thin films deposited on glass substrates at 375 °C with different Zn-doping concentrations (0, 2, 4, 6, and 8 at%) in the starting solution. All the films show a preferential growth along the (1 1 1) direction and the other peaks observed in the XRD patterns are associated with the (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes corresponding to cubic crystal structure of pure CdO according to JCPDS Card No. 75-0594 [16]. This behavior of preferential growth along the (1 1 1) plane was also observed by Sravani et al. [17] for CdO thin films prepared by activated reactive evaporation. They observed that the CdO films deposited under varied oxygen partial pressure showed (1 1 1) preferential growth. Tanaka et al. [18] also reported a similar preferential orientation for the CdO films deposited by dc magnetron sputtering [18]. Similar results were reported by Seo [19] for the CdO thin films prepared by spray pyrolysis technique. The preferred growth of the (1 1 1) plane observed here for the Zn-doped CdO films remained predominant irrespective of Zn-doping level. This consistency in preferred growth suggests that the precursor solution has uniformity in composition. The variation of preferential orientation factor $f(hkl)$ for (1 1 1) and (2 0 0) planes as a function of zinc concentration in the starting solution shown in Fig. 2, depicts that $f(111)$ increases as zinc concentration attains a maximum of 6 at% and decreases for further doping concentration. This may be due to the fact that up to 6 at% doping, the

Fig. 2 Variations of $f(hkl)$ for (1 1 1) and (2 0 0) planes as a function of zinc concentration

added zinc atoms are probably placed in the interstitial positions of the CdO lattice. Further incorporation of zinc atoms tends to form separate ZnO sites in the CdO lattice and hence $f(111)$ decreases whereas $f(200)$ increases and attains a maximum value which confirms that the preferential orientation starts changing from (1 1 1) to (2 0 0) plane. This is a consequence of reorientation effect in the crystalline structure of CdO with doping level. Similar results are reported by Agashe et al. [20]. The results obtained here infer that the structural properties of the CdO thin films are strongly influenced by the zinc concentration in the precursor solution.

No extra peaks were detected in the XRD patterns, suggesting that the incorporation of Zn^{2+} ions in the CdO lattice does not affect its crystal structure. The reason for that is, Zn in such small quantities got dissolved in the lattice of CdO and accumulated on the crystallite and grain boundaries of the host CdO in the form of amorphous state [14]. Normally Zn doping in CdO thin films involves replacement of host Cd^{2+} ions with that of Zn^{2+} ions in the host CdO lattice. To achieve successful replacement of Cd^{2+} ions with that of Zn^{2+} ions both elements must have the same coordination number, valency, and ionic radius more or less equal. Even though the coordination number of both these elements is equal to six; the valency is equal to 1.7, the ionic radius of Zn^{2+} ions is 0.074 nm which is very small compared to that of the ionic radius of Cd^{2+} ions (0.095 nm), and this strongly supports the unfavorable condition for the substitution of Zn^{2+} ions in the CdO host lattice. But the absence of any secondary phase in the XRD patterns clearly indicates that Zn^{2+} ions are well dissolved in the CdO lattice. Figure 3 shows the shift of (1 1 1) peak toward higher angle with the increase of zinc concentration which strongly favors the fact that Cd^{2+} ions are

Fig. 3 Shift in (1 1 1) peak Bragg angle of Zn-doped CdO films

Table 1 Comparison of observed and standard *d*-spacing values of Zn-doped CdO thin films

<i>(h k l)</i>	<i>d</i> -standard ^a (10 ⁻¹ nm)	<i>d</i> -observed (10 ⁻¹ nm)				
		Zinc concentration (at%)				
		0	2	4	6	8
(1 1 1)	2.7112	2.7116	2.7061	2.7045	2.7044	2.7038
(2 0 0)	2.3480	2.3488	2.3442	2.3421	2.3424	2.3414
(2 2 0)	1.6602	1.6615	1.6580	1.6570	1.6570	1.6565
(3 1 1)	1.4158	1.4163	1.4139	1.4130	1.4131	1.4126
(2 2 2)	1.3556	1.3567	1.3546	1.3534	1.3530	1.3526

^a JCPDS, International Center for diffraction data, Card No. 75-0594

substituted by Zn²⁺ ions in the host lattice. The comparison of observed and standard *d*-spacing values of the ZCO films is presented in Table 1.

The lattice constant '*a*' values of the cubic structure of ZCO thin films calculated using the equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (1)$$

are presented in Table 2. The value of lattice constant is 0.4696 nm for undoped CdO film which exactly matches with the standard value (0.4695 nm–JCPDS Card No. 75-0594). For doped films there is a slight variation in the lattice constant values which supplements the fact that zinc incorporation in the CdO lattice causes strain in the samples and the presence of zinc is confirmed in the elemental analysis (Sect. 3.3). It is seen that the lattice parameter value decreases monotonically from 0.4696 to 0.4683 nm with the increase of Zn concentration. This unit cell volume contraction is due to the ionic radii mismatch between Cd²⁺ and Zn²⁺ ions, and this strongly favors that Cd²⁺

ions are substituted by Zn²⁺ ions in the host lattice. Due to this volume contraction, strain has been introduced in the films and hence their crystalline qualities are deteriorated.

The crystallite size, *D* is calculated using the Scherrer formula:

$$D = \frac{0.94\lambda}{\beta \cos \theta}, \quad (2)$$

where β is the broadening of diffraction line measured at half of its maximum intensity (radian) FWHM and λ is the wavelength of the X-ray used (0.15406 nm). The other microstructural parameters such as lattice strain (ε), dislocation density (δ), and the number of crystallites per unit area (*N*) of the films were calculated using the formulae [21, 22]:

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

$$N = \frac{t}{D^3} \quad (5)$$

The calculated structural parameters are presented in Table 2. The minimum value of strain and dislocation density obtained for ZCO film with 6 at% zinc concentration shows that this film is less strained which might be due to the successful replacement of Cd²⁺ ions with Zn²⁺ ions in the host lattice. This is well acknowledged by the high *f*(1 1 1) value obtained for this film.

3.2 SEM Studies

Figure 4 shows the SEM images of undoped and Zn-doped CdO thin films fabricated by the simplified spray technique with different zinc at% concentrations. Excepting some small voids and pores, the SEM images of all the films show uniform surface with well-defined grain boundaries. In nanoscale dimension, CdO thin films exhibit numerous structures like nanoparticles [23], nanowires [24], nano-needles [25], and nanocrystals [26]. Among these structures of this compound, cauliflower-like structure emerges from the construction of nanorod bundles [27]. Tadjarodi et al. [27] reported that CdO with cauliflower-like structure showed high performance on the removal of Congo red from aqueous solution due to its high adsorption capacity. The SEM images of the ZCO thin films with different Zn at% concentrations (Fig. 4b) showed cauliflower-like structure which might have been formed from interwoven nanorods. This structure is of great importance due to its high specific surface area and potential applications in various fields [28].

Table 2 Structural parameters of undoped and Zn-doped CdO films

Concentration of zinc (at%)	Lattice parameter, a (10^{-1} nm)	Crystallite size, D (nm)	Strain, ε (10^{-3})	Dislocation density, δ (10^{15} lines/m ²)	Number of crystallites, N (10^{16})
0	4.696	36.02	3.387	0.771	2.33
2	4.687	30.69	4.259	1.224	3.44
4	4.684	28.58	3.968	1.062	4.68
6	4.684	36.51	3.330	0.750	4.62
8	4.683	34.53	3.523	0.838	2.79

Fig. 4 SEM images of undoped and Zn-doped CdO films: **a** undoped, **b** 2 at% Zn, **c** 4 at% Zn, **d** 6 at% Zn, **e** 8 at% Zn

3.3 Elemental Analysis

The elemental analysis of undoped and Zn-doped CdO thin films was made by energy dispersive X-ray spectroscopy. The EDAX spectra of ZCO films (Fig. 5b) confirm the presence of Zn in the films. The presence of other elements Ca and Si observed in undoped CdO film (Fig. 5a) might be probably from the glass substrate [29]. The weight and atomic percentage compositions of Cd, Zn, and O in the solid films are presented in Table 3. It is clearly seen from the table that the amount of Cd element decreases with increasing Zn content, which very well supports the

successful substitution of dopants in the Cd sites. The O/(Cd + Zn) ratio of undoped and CdO film doped with 6 at% zinc concentration are exactly equal confirming the fact that zinc atoms added is probably placed in the interstitial position of the CdO lattice, with the replacement of Cd^{2+} ions by Zn^{2+} ions.

3.4 Electrical Studies

The electrical measurements were carried out using a four-point probe setup. The variation of electrical resistivity of ZCO films as a function of Zn-doping concentration is

Fig. 5 EDAX spectra of undoped and Zn-doped CdO films: **a** undoped, **b** 2 at% Zn, **c** 4 at% Zn, **d** 6 at% Zn, **e** 8 at% Zn

Table 3 Results of quantitative elemental analysis of Zn-doped CdO thin films

Material	Element						O/(Cd + Zn) compositional ratio (atomic)
	wt%			at%			
	Cd	Zn	O	Cd	Zn	O	
Undoped CdO	89.40	0	10.60	54.56	0	45.44	0.83
CdO : 2% Zn	85.78	0.92	13.30	51.68	0.87	47.44	0.9
CdO : 4% Zn	87.01	1.96	9.47	50.72	1.96	38.78	0.74
CdO : 6% Zn	86.63	2.89	10.48	52.44	3.01	44.55	0.8
CdO : 8% Zn	87.26	2.51	10.23	53.38	2.64	43.98	0.79

shown in Fig. 6. The resistivity value ($88.9 \Omega \text{ cm}$) obtained for undoped CdO film matches with the value obtained by Carballeda-Galici et al. [30]. They reported that CdO thin film coated by the sol-gel method having a thickness of 160 nm displayed a resistivity of $\sim 200 \Omega \text{ cm}$. They obtained this value only when the films were annealed at 200°C and reported that the resistivity value further decreased when the annealing temperature was increased. The resistivity value obtained in the present work is remarkably lesser than the value obtained by Carballeda-Galici et al. [30] even though the sample is not annealed. This strongly favors the increased surface smoothness of the films fabricated in this work by the simplified spray technique using perfume atomizer. It is observed that the resistivity decreases with increase in zinc concentration up to 6 at% and then for higher doping concentration it slightly increases. These results can be interpreted as follows: Up to 6 at% zinc concentration, zinc atoms added initially is probably placed in the interstitial positions of the CdO lattice. Therefore, they introduce

disorder in the lattice which creates more oxygen vacancies which tends to increase the conductivity of the films. With further incorporation of zinc atoms (above 6 at%), oxygen vacancies decreases as Zn^{2+} ions tends to form separate ZnO sites with O^{2-} and hence the resistivity starts increasing.

From the resistance values recorded at different temperatures ($30\text{--}100^\circ \text{C}$), the temperature coefficient of resistance (TCR) of the CdO films with different zinc doping concentrations are evaluated. The variation in TCR as a function of zinc concentration is given in Fig. 6. The figure reveals that the magnitude of TCR is smaller for the ZCO films than the undoped sample, indicating that the doped films have good heat resistant property (better thermal stability), which is one of the desirable qualities for solar cell TCO layers [31]. Among the Zn-doped CdO films, the magnitude of TCR of the film coated with 6 at% zinc concentration is remarkably lesser than the other doped films confirming that the CdO film coated with this concentration has better thermal stability.

Fig. 6 Variations of electrical resistivity and TCR and ZCO films with different Zn doping concentrations

Fig. 7 Transmittance spectra (inset variation of maximum transmittance) of CdO films doped with different Zn concentrations

3.5 UV-vis-NIR Analysis

The analysis of optical absorption spectra is one of the most productive tools for understanding the energy band gap (E_g) of crystalline materials. Optical properties of the deposited films were studied from the transmittance spectra measured by a UV-Vis-NIR spectrophotometer. The transmittance spectra of CdO thin films deposited on glass substrates with different Zn-doping concentrations are shown in Fig. 7. It can be observed that the maximum transparency of the films lie in the range of 74–82% in the visible and near-IR region. It can be observed that the film coated with 6 at% zinc concentration has a maximum transmittance of 89%. The transmittance decreases with further increase in Zn and attains the value obtained for undoped CdO. These results infer that Zn doping up to

Fig. 8 Sketch of $(\alpha h\nu)^2$ against $h\nu$ (inset variation of E_g with Zn doping concentrations) of Zn-doped CdO films

6 at% introduces oxygen vacancies in the CdO lattice and for further doping; ZnO sites were created in the host CdO lattice which tends to decrease the oxygen vacancies with a reduction of the transparency due to increased resistivity as evident from the electrical studies.

The band gap energy (E_g) values can be calculated using the fundamental absorption, which corresponds to electron excitation from the valence band to conduction band. E_g is usually obtained by extrapolation of the linear portion of the plots of $(\alpha h\nu)^2$ versus $h\nu$ to the $\alpha h\nu$ axis, as shown in Fig. 8, where $h\nu$ is the photon energy and α is the absorption coefficient expressed as

$$\alpha = \frac{\ln(\frac{1}{T})}{t}, \quad (6)$$

where T is the transmittance and t is the film thickness. The value of 2.46 eV obtained for undoped CdO film is in agreement with the band gap energy of CdO [4]. For the ZCO thin films, the absorption edge shifts toward UV range following an increase in Zn-doping concentration and the band gap arrives to a value of 2.65 eV (blue shift) for the film coated with 6 at% Zn concentration (as shown in the inset of Fig. 8) and for further Zn doping, the band gap energy decreases. Zaoui et al. [32] theoretically proposed that if Cd^{2+} ions in the CdO lattice are replaced by Zn^{2+} ions, band gap of CdO increases with zinc incorporation. Similar trend observed in the present work up to 6 at% Zn-doping concentration, confirm the fact that Cd^{2+} ions are successfully replaced by Zn^{2+} ions in the CdO lattice which very well acknowledges the results obtained in XRD and electrical studies. The blue shift of the absorption edge of ZCO thin films can be attributed to an increase in carrier concentration, a phenomenon known as

the Burstein–Moss (BM) effect [33, 34]. The decrease in the band gap value of ZCO film coated with zinc concentration higher than 6 at% might be due to the interposition of impurity energy levels into the band gap of intrinsic host CdO. This is in accordance with Dakhel et al. [14] for Zn-doped CdO thin films prepared by sol–gel method.

Due to its low E_g , CdO is not a popular TCO material compared with other conducting oxide thin films. For solar cell applications, TCOs should have widened E_g . In the present study, widened E_g is obtained for CdO films while doping with zinc. Therefore combining with its obvious improved electrical properties, ZCO films have the potential to be applied for photovoltaic solar cells and other optoelectronic devices.

4 Conclusions

The results of study of structural, morphological, optical, and dc-electrical properties of Zn-doped CdO thin films prepared on glass substrates by a simplified spray pyrolysis technique are reported here. XRD measurements revealed that all the films show cubic crystalline structure with slight variation of lattice parameter values due to the substitution of Cd^{2+} by Zn^{2+} ions. The band gap of CdO (2.46 eV) was tuned to 2.65 eV upon Zn doping up to 6 at%. This band gap tuning was well acknowledged by the shift of (1 1 1) peak in XRD. All ZCO films show a high optical transmission in the visible and near-IR region. For their improved optical and electrical properties, ZCO films could be an excellent candidate for future optoelectronic devices.

Acknowledgments The authors are grateful to the Secretary and Correspondent, AVVM Sri Pushpam College (Autonomous), Poondi for his excellent encouragement and support to carry out this work.

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