Structural and optical properties of spin coated $Cd_{1-x}Zn_xO$ thin films

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Thin films of CdO have been prepared by spin coating method on the glass substrates taking solution(s) of cadmium acetate dihydrate and /or zinc acetate dehydrate in 2-methoxyethanol and monoethanolamine, and subsequent annealing at 250-450°C for 2h in air. CdO thin films cast are polycrystalline in nature and exhibits f.c.c. (NaCl-type) structure with lattice-parameter decreasing and average grain size increasing with increase in sol molarity and film thickness (number of coatings),. Further, they exhibits (i) optical transmittance of 50-90% in wave length range of 900-600 nm, (ii) broad absorption in the interval 400-550 nm, (iii) decrease of energy band gap (E_g) with increase in the molarity, number of coating.The $Cd_{1-x}Zn_xO$ (x = 0 -1) thin films prepared similarly on the glass substrate with 15 coatings continue to correspond to f.c.c. (NaCl-type) structure with lattice parameter in the range (4.697- 4.703) ± 0.006 Å up to x = 0.4, but exhibits wurtzite-type hexagonal structure of ZnO with lattice parameters a = 3.246± 0.003 Å, c = 5.225± 0.007 Å for x =1, and mixture of the two phases for 0.6 ≤ x <1. They display (i) improved optical transmittance of 60-95% (ii) shift in transition zone towards the higher energy (iii) increase in energy band gap (E_g) with increasing zinc content. The values of E_g lie in the range 2.42 – 3.28eV for x lying in the range 0 – 1.

(Received June 03, 2010; accepted July 14, 2010)

*Keywords:*Cd-Zn-O, Thin film, Spin coated films

1. Introduction

Bulk and thin films of CdO have attracted attention in recent past because of their unique optical, semiconducting, piezoelectric, and mechanical properties. As a consequence, they have found numerous multifunctional applications as transparent electrodes and in photodiodes [1], phototransistors [2], photovoltaic cells [3], liquid crystal displays, IR detectors and antireflection coatings [4]. Cadmium oxide exhibits f.c.c. (NaCl type) structure with lattice parameter a = 4.695Å and the space group Fm3m, excellent n-type electrical conductivity, good chemical stability, high optical transparency in the visible range, direct band gap ranging from 2.2 to 2.7 eV [5], and indirect band gap of 1.98 eV [6]. The deposition techniques employed for the CdO thin films include dc magnetron sputtering [7-8], reactive evaporation [9-10], pulsed laser deposition (PLD) [11], molecular beam epitaxy (MBE) [12], chemical vapour deposition (CVD) [13], chemical bath deposition [14], sol-gel [15-16], spray pyrolysis [17-18], Langmuir-Blodgett deposition [19], and rf sputtering [20]. The band gap engineering in the cadmium oxide is possible by doping with different elements such as zinc [21-22], flourine [23], gallium [24], lanthanum [25], europium [26], magnesium [27] and aluminum [28], etc. However, the behaviour of doped CdO is still not well understood. An attempt has, therefore, been made here to prepare $Cd_{1-x}Zn_xO$ ($0 \leq x \leq 1$) thin films by spin coating and study them with regard to phase (s) and optical behaviour.

2. Experimental details

Cadmium acetate di-hydrate is first dissolved in a mixture of 2-methoxyethanol and monoethanol-amine (MEA) and then heated at 50-60°C for 1h under constant stirring to obtain a solution (sol). Thin films are cast by dropping 2 ml of sol on the cleaned glass substrates in a spin coater revolving at the rate of 3000-6000 rpm for 20-60s at room temperature and annealed at 200°C for 15 min to remove organic species. The process is repeated several times to get a thin film of desired thickness. Finally, thin films are annealed by raising the temperature at the rate of 3°C per minute to 250-450°C and holding there for 2h in air. For the preparation of zinc containing cadmium oxide thin films, a similar procedure is adopted with addition of a solution of appropriate amount of zinc acetate dihydrate in MEA. For characterization, X-ray diffractometer (Thermo Electron ARL X'TRA) and UV-visible double beam spectrophotometer (Hitachi Model U-3310) have been employed.

3. Results and discussion

3.1 Phase evaluation

Fig. 1 shows the X-ray diffraction patterns of cadmium oxide thin films prepared on the glass substrate with 5 coatings of sol of different molarity (0.3 ,0.5 ,0.7 and 1.0 M) at a spinning speed of 4000 rpm for 40 seconds after annealing in air for 2h at 250°C. Perusal of the Fig. 1 shows that a number of distinct peaks are observed in each case suggesting hereby that the films are polycrystalline in nature. It may be noted that the intensity of the peaks improves progressively with increase in the sol-molarity. All XRD patterns correspond to f.c.c. (NaCl-type) structure with lattice parameter decreasing slightly with increase in the sol-molarity; typical values being 4.707 and 4.700 ± 0.006 Å for sol-molarity 0.3M and 1M, respectively.

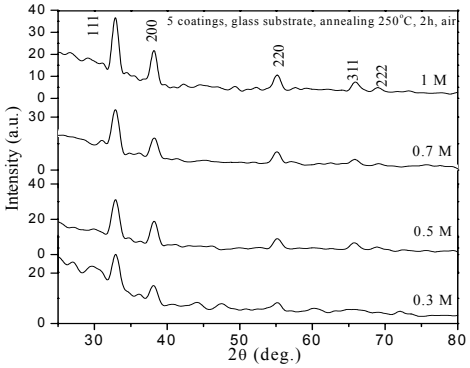

Fig. 1. X-ray diffraction patterns of CdO thin films prepared with sols of molarity 0.3-1M on glass substrate after annealing at 250°C in air for 2h.

The crystal data match well with the standard bulk value of 4.695Å of CdO [29]. The average crystallite size 'D_{gs}' determined from the Scherrer relation [18] is found to increase with the sol-molarity and is observed to lie in the range ~10-14 nm for 0.3- 1M.The values of various XRD parameters are shown in Table 1.

Table 1 Crystallographic data of CdO thin films prepared with five coatings of sol (molarity 0.3, 0.5 .0.7 and 1M) after annealing at 250°C for 2h in air.

S. No.	0.3 M 2θ (deg.)	I/I_0	0.5 M 2θ (deg.)	I/I_0	0.7 M 2θ (deg.)	I/I_0	1M 2θ (deg.)	I/I_0	hkl
1	32.916	100	32.940	100	32.916	100	32.968	100	111
2	38.186	35	38.194	40	38.248	49	38.232	62	200
3	555.199	21	55.211	25	555.234	26	55.248	28	220
4			65.828	13	65.862	12	65.879	16	311
5	a = 4.707 Å D_{gs} = 10 nm		a = 4.704 Å D_{gs} = 11.7 nm		68.856 a = 4.702 Å D_{gs} = 12.6 nm	6	68.890 a = 4.700 Å D_{gs} = 13.9 nm	7	222

a - lattice parameter ± 0.006 D_{gs} – average grain size

Fig. 2 shows XRD patterns of zinc containing cadmium oxide ($Cd_{1-x}Zn_xO$; x=0 ,0.2, 0.4, 0.6, 0.8, 1.0) thin films prepared on the glass substrate with 15 coatings at a spinning speed of 4000 rpm for 40s each after annealing at 450°C for 2h in air. These exhibit polycrystalline nature and continue to have f.c.c. (NaCl-type) structure similar to CdO but, XRD pattern with lattice parameter from 4.703 to 4.697±0.006 Å as zinc content increases from zero to 0.4. This observation means decrease in unit cell volume as well and can be attributed to lower ionic radii of Zn^{2+} ions as compared to Cd^{2+} ions in octahedral configuration (ionic radii of Zn^{2+} and Cd^{2+} ions being 0.74 and 0.97 Å, respectively) [21].

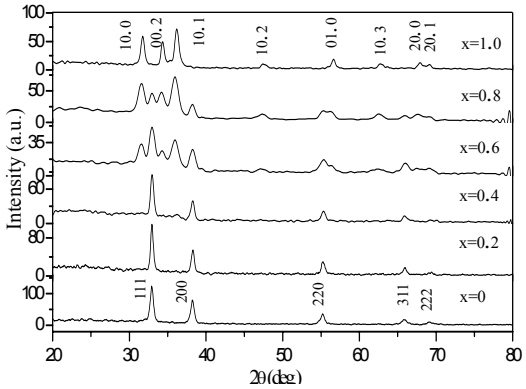

Fig. 2 X-ray diffraction patterns of $Cd_{1-x}Zn_xO$ (x=0-1.0) thin films; the indexing for pure CdO (f.c.c.) and ZnO (wurtzite) phases are marked as hkl and hk.l respectively.

Also, the average grain size is found to decrease with increase of zinc content and lies in the range 10-13 nm. At x=0.6 and 0.8 $Zn_xCd_{1-x}O$ thin films display mixture of both rock salt CdO and wurtzite ZnO phases. For x=1.0, pure ZnO phase having wurtzite hexagonal structure is obtained with lattice parameters a= 3.246 ±0.003Å, c= 5.225 ±0.007 Å, matching well with standard crystal data, i.e., a= 3.249 Å, c=5.205Å respectively [30].

3.2 Optical absorption

The optical transmittance versus wavelength plots of CdO thin films prepared by spin coating with sol of different molarity after subsequent annealing at 250°C for 2h in air are shown in figure 3. The transparency of thin films decreases slowly with decrease in wavelength and remain 90-100% for lower molarity (0.3 and 0.5 M) in the wavelength range 500-900 nm. The inset of figure 3 shows the first derivative of the transmittance spectrum with the peak point corresponding to the energy band gap (E_g= 2.68eV) of CdO thin films (5 coatings with sol of molarity 0.5 M). The energy band gap deduced from the maximum in the derivative plot is found to decrease slightly from 2.76 to 2.62 eV with increase in the molarity from 0.3 to 1M. According to the band structures of CdO, the conduction band minima lies at the centre of Brillouin zone (Γ_1) while the valence band maximum falls at L_3 or $\sum_3$, away from the centre of the zone (Γ_{15}), the value of direct energy band gap of the CdO lies in the range (2.2-2.8 eV) while the two indirect band gaps lie in the ranges

1.09- 1.11 eV and 0.84- 0.95 eV[31]. This band transition is due to the interaction of the orbital sets consisting of the 4d and 5s of cadmium and the 2s and 2p of oxygen.

The absorption coefficient (α) is related to the energy band gap (E_g) [32] as

$$\alpha = [\ (A / h\nu)(h\nu - E_g)^m\ ] \quad (1)$$

where 'A' is a constant dependent on the material, 'h' is the Planck constant and 'ν' is the frequency of the radiation. The nature of the transition is represented by 'm'.

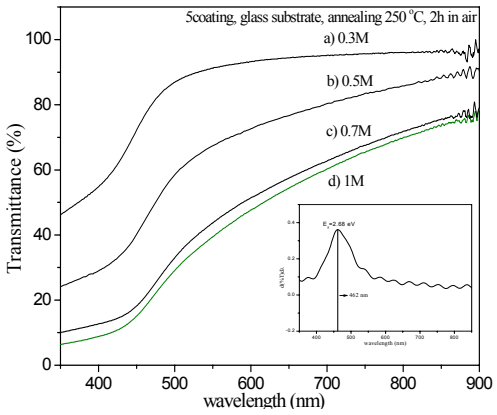

Fig. 3 Optical transmission spectra of CdO thin films prepared by spin coating with sol of different molarity after annealing at 250 °C for 2h in air. The inset depicts the d(T%)/dλ versus λ plot corresponding to spectrum 'b' showing with peak at 462nm (2.68 eV).

For direct and indirect allowed transitions, the values of 'm' are 1/2 and 2, respectively whereas for forbidden transitions, the corresponding values are 3/2 and 3, respectively [30]. The value of 'm' can be determined from the slope of the ln (αhν) verses ln (hν-E_g) plots, taking E_g value as deduced from the first derivative of the transmittance spectrum (Fig. 3.14). Linear fitting of the plot gives the value of 'm' as 0.4, which is close to 0.5 known for the allowed direct transition. The relation (1) in conjunction with $(\alpha h\nu)^2$ versus hν plot can then be employed to determine the energy band gap (E_g) precisely. Fig. 4 shows $(\alpha h\nu)^2$ versus hν plot for a typical CdO thin film prepared on glass substrate with sol of molarity 0.3M after annealing at 250°C for 2h in air. Its linear portion when extrapolated intersects the x-axis giving the value of E_g as 2.81 eV.

Since the grains/ crystallites are invariably very small (size range being 10-14 nm), quantum size effects are expected to influence the energy band diagrams of CdO [33]. The energy band gap (E_g) for a spherical particle of radius R is given [34] by

$$E_g = E_{g1} + (\ h^2\pi^2 / 8\ \mu\ R^2) \quad (2)$$

where E_{g1} is bulk energy band gap, h is the Planck constant and μ is the reduced mass of the carrier (electron or hole). So, decrease in the average particle size and, in turn, increase in the degree of confinement causes rise in the energy band gap (E_g). The reproducibility of the above result has been ensured by repeating the experiments. Figure 5 shows (E_g) verses $(1/R)^2$ plot. In addition, the refractive index (n) of cadmium oxide has been determined using relation [35].

$$[(n^2-1) / (n^2+2)] = 1 - \sqrt{}\ (E_g / 20) \quad (3)$$

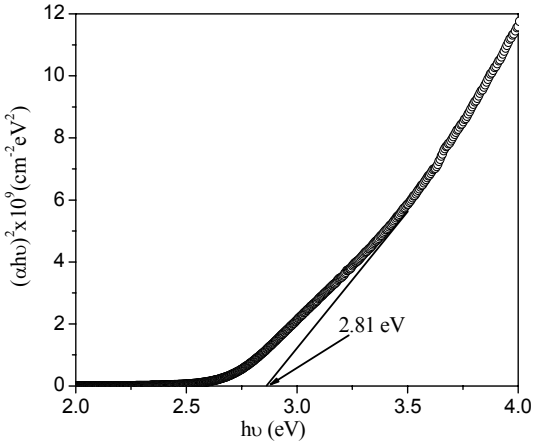

Fig. 4. The plots of $(\alpha h\nu)^2$ versus hν for CdO thin films prepared on glass substrate with a sol of molarity 0.3M and annealed at 250°C for 2h in air.

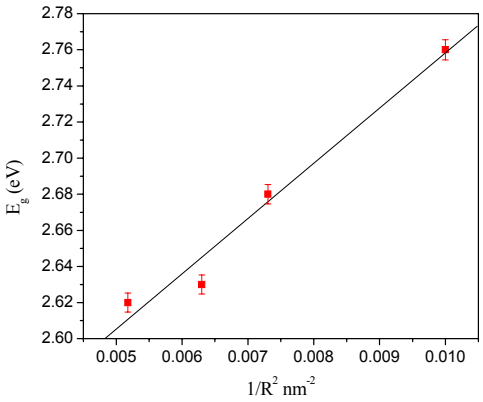

Fig. 5. Energy band gap (E_g) versus $1/R^2$ plot.

The value of (n) was found to be 2.46 for thin films cast with sol molarity 0.3M. This matches well with a recently reported value 2.42 of CdO thin films prepared by DC magnetron reactive sputtering technique.

Fig. 6 shows the optical transmittance of $Cd_{1-x}Zn_xO$ (0<x<1) thin films, prepared with 15 coatings on glass substrate using spinning speed of 3000 rpm for 30s each after annealing at 400°C for 2h in air. Pure CdO thin films are less transparent; the value of average transmittance lies in the range of ~ 30-50 % in the visible range.

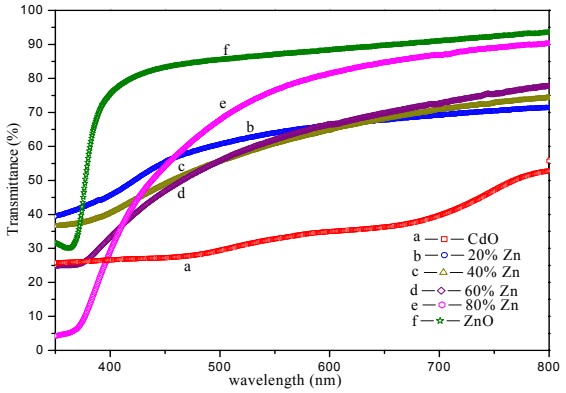

Fig. 6. Optical transmittance spectra of $Cd_{1-x}Zn_xO$ ($0 \leq x \leq 1.0$) thin films, prepared by spin coating on glass substrate, after annealing at 400°C for 2h in air.

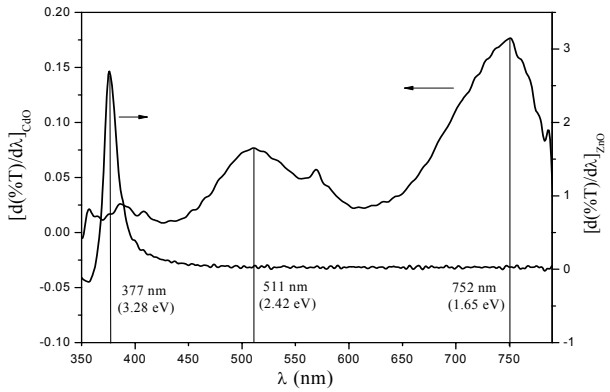

Fig. 7. d(%T)/dλ versus λ plot corresponding to spectrum a) and f) of Fig. 6.

While there are two peaks in the d (%T) /dλ versus λ plot in case of pure cadmium oxide, only one peak is observed for the pure zinc oxide (Fig. 7); the peaks at ~ 2.42 and 1.65 eV correspond to direct (~ 2.20- 2.80 eV) and indirect band gaps of CdO whereas the the peak at 3.28 eV matches well with direct band gap of ZnO (3.33 eV) [36]. With the increase in zinc content transmittance increases in the visible range and the absorption edge shifts toward the higher energy; typical value of the transmittance being ~35 to 90% at the wave length ~700 nm. Also, the films turn from reddish yellow to complete transparent (Fig. 8). These results are consistent with the findings of Tabet-Derraz et al. [37] and Caglar et al. [38]. When the zinc content is increased from 0 to 0.6, a feature of sharp absorption is not observed. Nevertheless, the value of E_g is found to increase from 2.42 to 3.28 eV with increase of zinc content from 0 to 1 (Table 2). This increase of band gap energy may be attributed to quantum size effect since the crystallites are invariably very small. The results clearly demonstrate that band gap engineering is possible in $Cd_{1-x}Zn_xO$ system by varying the zinc content (x).

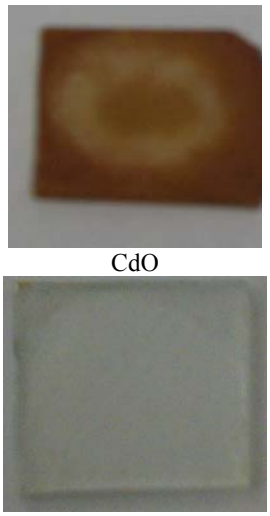

Fig. 8. CdO and ZnO thin films.

Table 2. The values of energy and gap of $Cd_{1-x}Zn_xO$ thin films as a function of x together with E_g of pure CdO and ZnO [(d)-direct and (i)- indirect band gap].

$Cd_{1-x}Zn_xO$	Bulk E_g (eV)	Observed E_g (eV)
x = 0.0	2.2-2.8 (d) 1.6-1.9 (i)	2.42 1.65
x = 0.2	-	2.92
x = 0.4	-	2.98
x = 0.6	-	3.15
x = 0.8	-	3.20
x = 1.0	3.3	3.28

4. Conclusions

$Cd_{1-x}Zn_xO$ ($0 \leq x \leq 1$) thin films can be prepared by spin coating process on the glass substrates using solution of cadmium acetate dihydrate and zinc acetate hydrate in 2-methoxyethanol and mono-ethanolamine and after subsequent annealing at 250-450°C for 2h in air. Thin films of composition $Cd_{1-x}Zn_xO$ ($0 \leq x \leq 0.4$) possess face centered cubic (NaCl-type) structure similar to pure CdO. However the lattice parameter decreases and average grain size increases with increase of sol of molarity and number of coatings. Typical values of lattice parameter and average grain size being in ranges 4.700 - 4.707 ± 0.006 Å and 10 - 14 nm for sol molarity of 0.3 - 1.0 M. $Cd_{1-x}Zn_xO$ (x = 0.6 - 0.8) thin films contains both CdO and ZnO phases. ZnO thin films exhibit wurtzite hexagonal structure with lattice parameters a = 3.246 ± 0.003Å, c = 5.225 ± 0.007 Å. Band gap (E_g) engineering is possible in $Cd_{1-x}Zn_xO$ system as E_g varies from from 2.42 to 3.28 eV when zinc content (x) increases from 0 to 1.

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