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Study of Sol-Gel Derived Spin Coated Cd – Sn Oxide Films on Glass

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Abstract: Cd – Sn oxide films from precursor sol of three different compositions (Cd: Sn = 70 : 30, 50 : 50 and 30 : 70) were deposited on SLS and pure silica glass by sol-gel spinning technique. XRD study revealed presence of desirable spinel Cd₂SnO₄ phase along with some unwanted phases in films derived from Cd : Sn = 50 : 50 and 30 : 70 precursor sol. SEM study showed presence of Sn metallic phase in nano-rod shape in film derived from Cd : Sn = 70 : 30 precursor. Direct band gap of the films varied from 3.27 to 3.56 eV whereas indirect band gap varied from 2.03 to 2.14 eV. Blue shift of band gap with respect to that of bulk was observed. Percentage of transmission at 0.55 μm varied between 60 to 86%. Hall mobility and carrier concentration of the films were in the ranges 0.30 to 3.79 cm² / Vs and 0.41 x 10¹⁹ to 7.05 x 10¹⁹ cc⁻¹ respectively. Sheet resistance varied within the range from 3 kΩ/□ – 13.8 kΩ/□ whereas resistivity varied from 8.49 x 10⁻² to 70.27 x 10⁻² Ω cm. Film derived from Cd : Sn = 50 : 50 precursor sol showed maximum transmission at 0.55 μm and minimum two probe resistivity.

Keywords: Sol-gel, Spin coating, Cd-Sn oxide, thin film

1 Introduction

Transparent conducting oxides (more popularly known as TCOs) have potential applications in various technical areas, such as resistors, gas sensors, transparent heating elements, antistatic coatings, heat reflectors etc. due to their unique opto-electrical property. Indium tin oxide (ITO) is probably the most extensively used material in the field of TCO based devices. But, it is basically composed of indium, which is one of the most expensive and rarest elements. Hence, efforts have already been given to discover and develop new materials with high ionic mobility rather than simply elevated carrier concentration. Thin films of spinel Cd₂SnO₄ combine the characteristics of SnO₂ and CdO and are known to have high electron mobility, high electrical conductivity and low visible absorption [1 - 10]. Despite the encouraging properties of Cd₂SnO₄ films, concerns about the toxicity of Cd in fabrication of targets of physically deposited film often have been raised [11]. In this respect, sol-gel technique emerges as a promising method if a stable solution can be prepared [11, 12]. In this present work, starting with CdCl₂ and SnCl₄ · 5H₂O wettable precursor solutions of Cd – Sn oxide films belonging to M_xM'_yO_z

type, where, M = Cd and M' = Sn, have been prepared. The atomic ratio of Cd : Sn has been varied. Films were deposited on glass by spinning technique which is particularly suitable for coating circular substrates like lens, disks etc. The developed films were characterized to investigate the effect of composition on crystallization behaviour, surface feature and electrical, optical properties. In addition with soda lime silica (SLS) glass substrate the films were also deposited on pure silica glass to calculate the optical band gap of the films as unwanted absorption of soda lime silica glass in the UV region overlaps the fundamental absorption of the films.

2 Experimental

2.1 Preparation of Cd – Sn oxide precursor sol

The starting materials of the precursor sols of Cd – Sn oxide coatings were cadmium chloride (95 %, Qualigens, India) and hydrated stannic chloride (LobaChemie). Sols corresponding to 4 weight % equivalent CdO - SnO₂ maintaining Cd:Sn atomic ratios as 70:30, 50:50 and 30:70 were prepared in the following way. The required amount of cadmium chloride was dissolved in a few ml of ethyl alcohol (dehydrated, Bengal Chemicals and Pharmaceuticals Ltd., India) and 1-propanol (E-merck

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India Ltd., for synthesis) solvent mixture (1:1, by volume) and stirred in a magnetic stirrer for 15 min. Similarly, required amount of stannic chloride was dissolved and

stirred separately for 15 mins in the same solvent mixture. Next, the stannic chloride solution was added to the cadmium chloride solution slowly and the mixture was stirred for 1h and aged for 48h for coating.

2.2 Deposition of Cd – Sn oxide films

Table 1: Sample designation, precursor sol composition, substrate type, physical thickness, refractive index, % transmission and no. of coating operation of various Cd – Sn oxide films.

Sample no.	Cd : Sn	Substrate	Thickness (Å) ± 3 Å	Refractive Index (± 0.003)	% Transmission at 0.55 μm	Number of coating operation
B2S4	70 : 30	SLS glass	6021	1.902	60	4
B3S4	50 : 50	-do-	5476	1.903	86	4
B4S4	30 : 70	-do-	5092	2.103	84	4
B2Si1	70 : 30	Pure silica glass	2238	-	-	1
B3Si1	50 : 50	-do-	2348	-	-	1
B4Si1	30 : 70	-do-	2447	-	-	1

The films were deposited on two types of substrates, (i) pure silica glass and (ii) Soda lime silica (SLS) glass by using spinning technique (Convac 1001) from the precursors of different Cd: Sn ratios. The spinning rpm was 2000. After each deposition the coatings were cured in air at 500°C for 0.5 h and the whole process was repeated four times to increase the physical thickness of the coatings. After the final deposition the coatings were annealed at 500 ± 5⁰ C for 0.5 h in N₂ atmosphere to obtain crystallized Cd – Sn oxide films. Table 1 shows the description of various Cd – Sn oxide films derived from 4.0 wt % equivalent CdO – SnO₂ precursors of different Cd: Sn ratios by the spinning technique (2000 rpm).

3 Characterization

Phase identification of the films was made with a Philips (Expert pro) X-ray diffractometer with Cu K_α radiation. Transmission and absorption spectra of the coatings were recorded by Shimadzu make UV-VIS-NIR spectrophotometer (model, UV3101 PC). Sheet resistance (Ω/□) of the films was measured by two probe system. This was done by connecting the two probes of a multimeter (Philips PM2525) with two silver electrodes placed 1 cm apart on the coated surface. For deposition of silver electrodes condensed silver particles (Eltech Corporation, India) is dispersed into a suitable thinner to form a silver paste, then the paste is coated on the sample by a brush in the form of two narrow lines one cm apart. Next the sample is heated at ~ 150⁰C for ½ h for well adherence of the electrodes. Hall mobility (and free electron carrier concentration (N) of the films were measured in a magnetic field of 0.51T (Tesla) at room temperature by HEM 2000 (EGK Corporation, Korea) using four probe van der Pauw method. Thickness and refractive index of Cd - Sn oxide films was measured ellipsometrically (Gaertner Auto gain 116 B, Gaertner Scientific Corporation, USA) at 632.8 nm (He – Ne laser

source). Microstructure of the films was studied utilizing a Scanning electron microscope (LEO S 430 I).

4 Results and discussion

Identification of Cd – Sn oxide entities were done by X-ray diffraction (XRD) study. Figure 1 shows the diffractograms of the samples of relatively high thickness (5092 – 6021Å). It is interesting to note that the appearance of any specific phase of either Cd – component or Sn – component is dependent on the atomic ratio of Cd: Sn. Surprisingly, the existence of Cd containing phases (namely, spinel Cd₂SnO₄ [13], cubic CdO [14] and orthorhombic CdSnO₃ [15]) are more prominent in case of films containing relatively less amount of Cd (30 atom %). No such phases could be identified in case of films developed from Cd:Sn = 70:30 precursor composition. On the other hand tetragonal Sn metal [16] and tetragonal cassiterite SnO₂ phase [17] were found to be present in all the compositions, but more prominently in Cd:Sn = 70:30 case. Therefore it may be inferred that, existence of either Cd or Sn component in relatively less amount in the precursor sol results more effective crystallization of the corresponding phases in the developed films.

Refractive index of the film deposited on SLS glass was measured and it was in the range from 1.902 to 2.103. Visible transparency is one of the essential criteria of TCO films, hence, percentage of transmission was also measured at 0.55 μm which is the wavelength of maximum luminous efficiency of the eye [18]. Table 1 data shows that more than 80 % transmission is obtained for films derived from Cd:Sn = 50:50 and 30:70 precursor composition. Poor transmission (60%) for the film obtained from Cd : Sn = 70 : 30 precursor composition is possibly due to the dominating presence of metallic Sn (Fig. 1) phase.

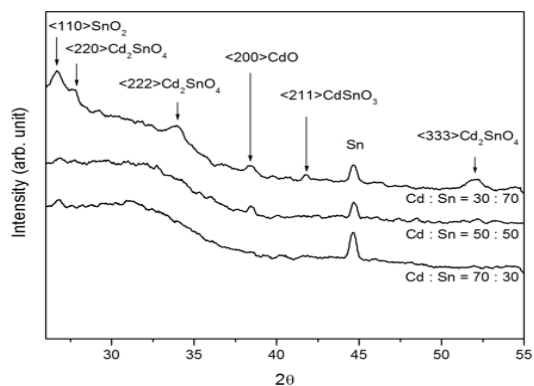


Figure 1: XRD pattern of Cd- Sn oxide films deposited on SLS glass.

Absorption behaviour of the Cd – Sn oxide films of similar physical thickness deposited on pure silica glass (namely, B2Si1, B3Si1 and B4Si1) is shown in Figure 2.

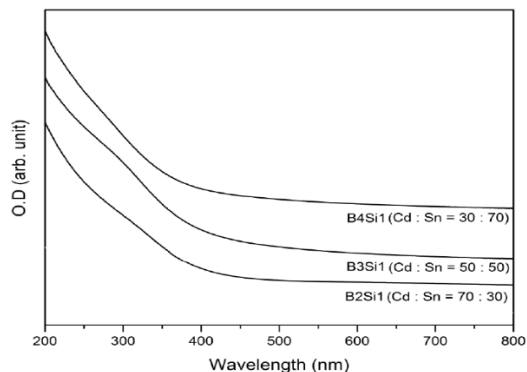


Figure 2: Absorption spectra of Cd-Sn oxide films deposited on silica glass.

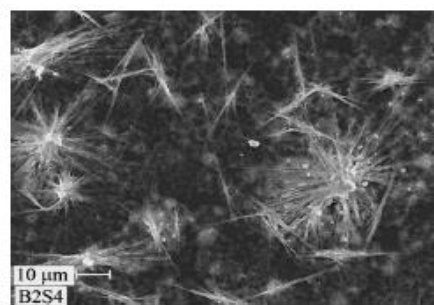
Very weak shoulder was observed at ~300 nm for each composition. This may be due to the presence of defect centres and / or generation of nanoclusters in the film entities as evident from SEM image (Fig. 3).

The tailing effect of the absorption up to 500 nm in the visible decreased its transmission (Fig. 4). The optical density data were utilized for evaluation of absorption coefficient, α , of the films deposited on pure silica glass.

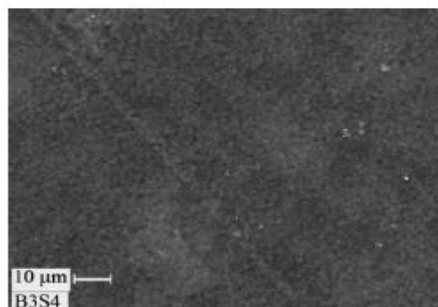
The direct and indirect band gaps (Figs.5 and 6 respectively) of the doped films were evaluated by following the eqn. 1 [19].

$$(\alpha h\nu)^{1/n} = A (h\nu - E_g) \quad (1)$$

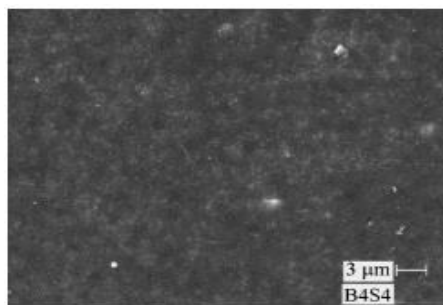
Where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is a constant and E_g is the band gap of the material and the exponent n depends on the type of transition; $n = 1/2, 2, 3/2,$ and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The direct band gap



(a)



(b)



(c)

Figure 3: SEM micrographs of Cd- Sn oxide films derived from (a) Cd: Sn = 70: 30,(b) Cd: Sn = 50: 50 and (c) Cd: Sn = 30: 70 precursor sol.

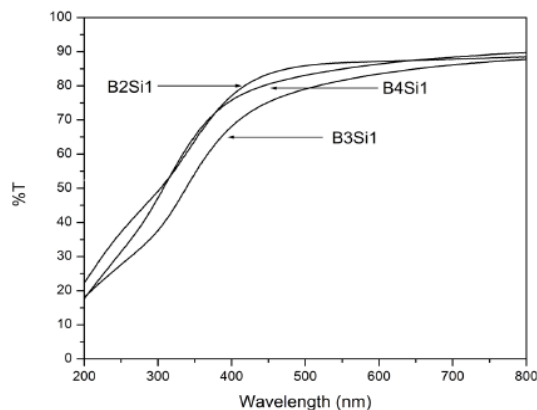


Figure 4: Transmission spectra of Cd-Sn oxide films deposited on silica glass.

Table 2: Direct and indirect band gap of Cd – Sn oxide films deposited on pure silica substrates.

Sample No.	Cd : Sn	Direct Band Gap (eV)		Indirect Band Gap (eV)
		hv range	hv range	
		2.5 - 5.0	4.0 - 7.0	
B2Si1	70 : 30	3.56	4.65	2.14
B3Si1	50 : 50	3.37	4.54	2.03
B4Si1	30 : 70	3.27	4.60	2.10

(Fig.5, Table 2) becomes wider with increase in Cd concentration. In this case, possibly the Moss – Burstein shift [20] is followed. High direct band gap values were observed for Cd - Sn oxide system when evaluated considering hv range, 4.0 – 7.0 eV (Fig. 6 and Table 2). These values were in the range, 4.54 – 4.65 eV which is a blue shift with respect to the band gaps of the possible entities present as CdO, CdSnO₃, Cd₂SnO₄, SnO₂ [4, 21-23]. This blue shift is possibly for the development of nanostructured Cd – Sn oxide films. The nanostructured feature is evident from the film microstructure (Fig. 3).

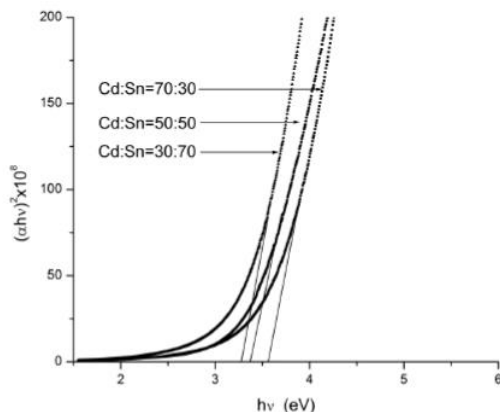


Figure 5: Plot of $(\alpha hv)^2$ versus $h\nu$ to evaluate direct band gap values in the range 2.5 - 5.0 eV.

The indirect band gaps were also evaluated which were in the range 2.03 – 2.33 eV. These values have already been obtained by various workers [11]. They are mainly for inter band transitions.

The SEM image (Fig. 3a) of the film of Cd : Sn = 70 : 30 precursor composition reveals the existence of nano-rods in the matrix of nanoclusters. The nanorod may be of tetragonal Sn as evident from XRD study. On further increasing the Sn content (50 atom %), the rod formation is restricted as the SEM image (Fig. 3b) of the film did not exhibit any rod like feature. On the contrary, the image looks like a homogeneous distribution of nanoclusters as if the rods have been dissolved in a solid solution of the system finally forming the nanoclusters of a mixture of cubic CdO, tetragonal SnO₂ and tetragonal Sn during the treatment of the film. On further increasing

Sn (70 atom%), the nanoclusters become more prominent (Fig. 3c) which are possibly mixtures of SnO₂, Sn, spinel Cd₂SnO₄, cubic CdO and orthorhombic CdSnO₃ as evident from the XRD pattern.

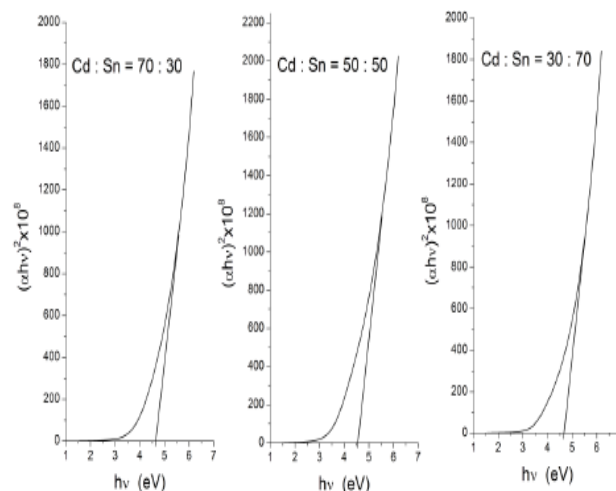


Figure 6: Plot of $(\alpha hv)^2$ versus $h\nu$ to evaluate direct band gap values in the range 4 - 7 eV.

Table 3: Sn content, Sheet resistance, two probe resistivity, Carrier concentration, Hall mobility of Cd – Sn oxide films

Sample no	Sn atom %	Sheet resistance (kΩ / □)	Resistivity $\times 10^{-2}$ (Ω cm)	Hall mobility (μ cm ² / Vs)	Carrier concentration (N X 10 ¹⁹ (cc ⁻¹))
B2S4	30	3	18.06	0.30	7.05
B3S4	50	1.55	8.49	1.71	1.30
B4S4	70	13.8	70.27	3.79	0.41

Sheet resistance and resistivity of the Cd – Sn oxide films were measured by two probe method. Sheet resistance varied within the wide range from 3 kΩ / □ – 13.8 kΩ / □ whereas resistivity varied from 8.49 x 10⁻² to 70.27 x 10⁻² Ω cm (Table 3). The lowest resistivity was obtained for the film derived from Cd: Sn = 50: 50 precursor composition (Sample No. B3S4). The carrier concentration was in the order of 10¹⁹ cc⁻¹. Hall mobility varied from 0.30 to 3.79 cm² / Vs. With increasing Sn content the carrier concentration decreased while Hall mobility increased (Fig. 7).

The opposite trend of carrier concentration and Hall mobility with increasing Sn content results minimum resistivity for the films derived from intermediate composition (i.e. Cd : Sn = 50 : 50). The extremely low value of Hall mobility in the film derived from 30 atom % Sn precursor may be attributed once again to the nano – rod like structure (Fig. 3 a) creating inhomogeneity in the surface feature.

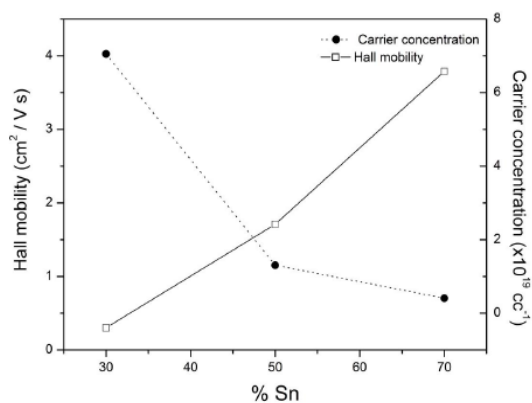


Figure 7: Variation of Hall mobility and carrier concentration with Sn atom % of Cd-Sn oxide films deposited on SLS glass.

5 Conclusion

Cd – Sn oxide films from precursor sol of three different compositions (Cd : Sn = 70 : 30, 50 : 50 and 30 : 70) were deposited on glass (SLS and pure silica) by sol-gel spinning technique and characterized by XRD, SEM, Hall mobility, carrier concentration, transmission in the visible, optical band gap studies. The expected TCO phases like spinel Cd_2SnO_4 orthorhombic CdSnO_3 were identified for films derived from 50 and 70 atom % of Sn precursor composition. Sn metallic phase was formed in the case of all compositions but considerable amount was developed in case of 30 at% Sn. Existence of rod like tetragonal Sn was visualized from SEM micrograph of 30 at% Sn content films. Blue shift of band gap with respect to that of bulk was observed. As far as visible transparency and electrical conductivity are concerned, films derived from Cd : Sn = 50 : 50 precursor sol proved to be most effective because of maximum transmission at $0.55 \mu\text{m}$ (86%) and minimum two probe resistivity ($8.49 \times 10^{-2} \text{ Ohm. cm}$).

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