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Advances in Applied Science Research, 2012, 3 (1):227-234

Advances in Applied Science Research
Pelagia Research Library
ISSN: 0976-8610
CODEN (USA): AASRFC

Characterization of Thin Films of Cd - doped SnO for Optoelectronic Applications

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ABSTRACT

Cadmium tin oxide Cd_2SnO_4 thin films were prepared by RF magnetron sputtering technique on glass substrates at room temperature. The as-prepared films were amorphous. The optical parameters as transmittance, optical energy gap, refractive index and the width of the band tails of the localized states found to be affected by changing the annealing temperature and thicknesses of the films. The electrical resistivity found to be affected by annealing temperature too.

Keywords: Thin films, transmittance, reflection index, optical gap, resistivity.

INTRODUCTION

Tin oxide SnO_2, Indium oxide InO_3 and Zink oxide ZnO are good examples of degenerate semiconductors which are highly transparent and conducting binary metal oxide transparent conducting oxides (TCOs). These materials have been thoroughly investigated and employed in many applications. However, ternary oxide TCOs such as Zn_2SnO_4 [1], $CdInO_4$ [2], $ZnGa_2O_4$ [3] and Cd_2SnO_4 [4] have eminent properties required for a transparent conducting oxide. It is reported that Cd_2SnO_4 thin films show electrical resistivity (10^{-4} Ω cm), high transmission (> 90%) in the visible region and smoother surface than conventional SnO_2 TCO film [5-6]. This aspect makes Cd_2SnO_4films an important material for the application of electrode material in solar photovoltaics. It is known that transparent conducting oxides are a class of materials which transmit visible radiation and conduct electricity. It was found that it has a wide applications as transparent electrode, flat panel display, heat reflective coatings on energy-efficient windows, and electrochromics such as smart mirrors [7-9] solar cells [10-11], abrasion resistance coatings [12] corrosion resistant coatings [13], gas sensors [14], ohmic contacts to surface-emitting lasers [15-16] ohmic contacts to photodetectors [17-18], Shottky contacts to photodetectors [19-23], and heat mirrors for energy efficient windows and light bulbs [24]. The properties of these films are highly dependent on the method of deposition and the substrate upon which they are deposited. Cadmium oxide is an n-type semiconductor, with direct band gap at approximately (2.4 – 2.7 eV) and has a poor optical transmittance in the visible spectral region [25]. Tin oxide (SnO2) is an *n*-type semiconductor which possesses perfect physical properties,. Additionally, the material shows high variations of the electrical resistance in the presence of oxidizing and reducing gases. Thin tin oxide films exhibit high optical transparency (> 80 %) in the visible region [26]. Cadmium sulfide has been prepared in the form of nanocrystalline thin films, their optical characterization indicates that film deposited by sol gel has larger band gap than those prepared using spray pyrolysis. [27]. The crystallalographic structure and the optical properties of cadmium sulfide has been studied by Dipalee et al. [28], showing that annealing results in decreasing the energy gap. The spectral studies on noanocrystalline $Cd_{1-x}CO_xS$ thin films [29] in the range of wavelength between 500 nm to 1300 nm showed absorption is high (10^4-10^5 $cm^{-1)}$ ^{and} the estimated band gap decreased from 2.42 eV to 1.94 eV as x varies from 0.0 to 0.5. Krishnakant et al [30] found that incorporation of nano particle improves the electrical conductivity.

The present work was carried out with an aim to identify the possibility of preparing cadmium stannate thin films using rf sputtering. Hence an attempt was made to prepare and study cadmium stannate thin films under different condition, specially annealing the films in air which has been paid little attention as far as we know.

MATERIALS AND METHODS

Thin films of Cd_2SnO_4 ($Cd:SnO_2$ ato,ic ratio of 2:1) targets from Cathay Advanced Materials Limited (China) were deposited onto ultrasonically cleaned glass substrates using UNIVE 350 sputtering unit with DC power model Turbo drive TD20 classic (Leybold), rf power model CESAR RF power generator and rate thickness monitor model INFICON SQM-160 . The deposition conditions were: base pressure of about $2x10^{-3}$ Pa, substrate to target distance of 10 Cm, rf power of 150 W, self bias 400V, deposition pressure of 2 Pa, argon flow rate of 10SCCM. The substrate temperature during deposition was maintained at room temperature. As-deposited Cd_2SnO_4 films have been annealed in air at different temperatures in the range from 250 to 550 ^oC.

Investigations of the microstructure were carried out using a Philips-PW1710 X-ray diffractometer with Cu-K_α as a target and Ni as a filter.

The optical transmittance (T) and reflectance (R) of the films under test have been measured by means of a computer programmable Jasco V-570 (Japan) double beam spectrophotometer in the wavelength range from 200 to 2500 nm at normal incidence. In case of reflectivity measurement, an additional attachment model ISN-470 is provided. The absorption coefficient α of the films was determined directly from the spectrophotometer reading using the formula [31]:

$$\alpha = \frac{2.303}{d} Log_{10}\left(\frac{1-R}{T}\right) \qquad (1)$$

Where d is the film thickness.

The optical energy band gap was estimated from the optical measurements by analyzing the optical data with the expression for the optical absorbance, and the photon energy, $h\nu$ using the following equation:

$$(\alpha h\vartheta) = A(h\vartheta - E_g)^n \qquad (2)$$

Since, h is the Planck's constant; A is a constant and E_g is the optical energy gap, which were obtained by Extrapolating the linear portion of the plots of $(\propto h\vartheta)^{1/n}$ versus $(h\nu)$ to $\alpha = 0$
The refractive index n was calculated from the following equation:

$$n = \frac{1+R}{1-R} \pm [\left(\frac{R+1}{R-1}\right)^2 - (1+k^2)]^{1/2} \qquad (3)$$

Where $k = \alpha\lambda/4\pi$ is the extinction coefficient and λ is the incident light wavelength.

To calculate the refractive index of thin films showing some fringes accompanied with the transmission spectra, the following equations will be used:

$$n = \sqrt{N + \sqrt{(N^2 - s^2)}} \qquad (4)$$

Where $N = \frac{1+s^2}{2} + \frac{2s(T_M+T_m)}{T_M T_m}$ (5)

and the refractive index of the substrate s;

$$s = \frac{1}{T_s} + (\frac{1}{T_s} - 1)^{1/2}$$

T_s, T_M, T_m are the transmission of the substrate, maximum and minimum transmittance of the fringes respectively.

The spectral dependence of refractive index, n, optical gap E_{op}, width of the band tails E_e of the localized states and others were estimated.

The resistivity measurements were carried out at room temperature using two-terminal configuration by applying constant voltage to the film and measuring the current through it using Keitheley 614 electrometer. Electrical contacts were made by applying silver paste over the surface of the films with separation of 2 mm.

RESULTS

Figure 1 shows the X-ray diffraction patterns of as –deposited and annealed Cd_2SnO_4 film of 350 nm thick at 550 ^oC for 2 hrs. It is seen that the as-deposited film exhibits the amorphous structure, which agree with others [32].

The effect of annealing temperature 550 ^oC on the structural properties of the films of same thickness 350 nm thick reveals a tendency of beginning crystallization at 2θ = 32 and 56^o which is consistent with Jeyadheepan et al [33]. This behavior agrees also with others [32], but with some difference, where it has been reported that as- prepared films become polycrystalline after annealing at temperature above 525 ^oC and our results have not show clear peaks. This difference may be due to differences in the deposition process. Furthermore, our results agree too with X. Wu et. Al [34] who observed that as deposited films by RF sputtering are amorphous and crystallization of the prepared Cd_2SnO_4 films take place during the annealing temperature.

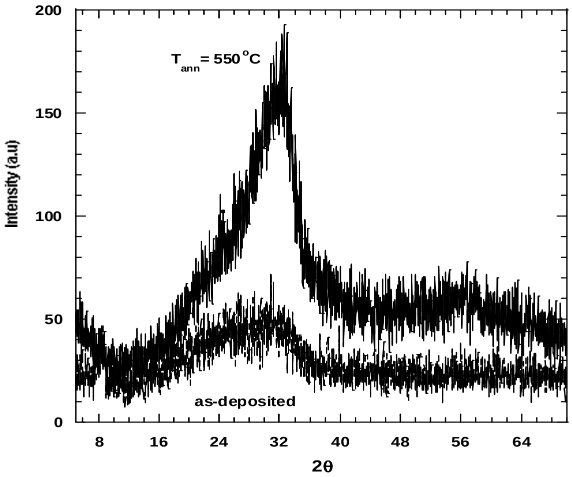
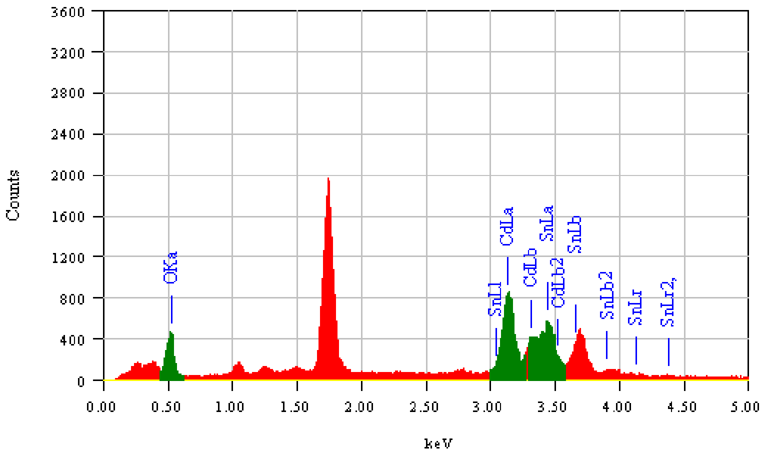


Fig. 1 X-ray diffraction of Cd_2SnO_4 as-deposited and annealed thin films (350 nm thick) at 550 ^{o}c for 2 hrs.

The scan electron microscope analysis asserts the amorphous nature of the as-deposited. The EDAX analysis reveals the stoichiometric composition of the Cd_2SnO_4 compound as shown in figure 2.

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Acquisition Parameter
Instrument    : 6390(LA)
Acc. Voltage  : 20.0 kV
Probe Current: 1.00000 nA
PHA mode      : T3
Real Time     : 55.37 sec
Live Time     : 50.00 sec
Dead Time     : 9 %
Counting Rate: 1972 cps
Energy Range  :  0 - 20 keV
```

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.6238

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
O K	0.525	38.15	1.84	81.59				20.7026
Cd L	3.132	35.45	1.38	10.79				45.3953
Sn L	3.442	26.40	1.55	7.61				33.9022
Total		100.00		100.00				

Fig. 2 SCM for annealed thin film of 270 nm at 600 ^{o}C for 2hr. Also the EDX of the as-deposit film of the same thickness.

Figure 3 shows typical transmission spectra for as-deposited Cd_2SnO_4 films of different thicknesses(150, 250, and 350nm). Interference maxima and minima due to multiple reflection on film surface can be observed indicating that the films have a good plane surface. A very rough surface will destroy the interference due to multiple reflections Hence, reflection may increase and scattering from uneven surface may decrease [35-36]. It is seen in figure 3 that there is a little decrease in the transmittance with increasing the thickness, this might be due to increase of both reflection and absorption [36]. On the other hand, average transmittance of the as-deposited films is excess of 90% in the range of wavelength from 450 to 1000 nm. Transmission loss is in the longer wavelength is seen in figure 4 also which can be interpreted as due photon-electron interaction, which can scatter the photons. Losses occur from both reflection and absorption. Reflection in this region is not strictly a surface phenomenon. Reflection from the bulk of the material can occur, provided that the electron escapes the surface. If the scattered electron does not escape the surface, it can be concluded to have been absorbed [32].

The effect of annealing Cd_2SnO_4 thin films of the same thickness 270 nm at different annealing temperatures (250, 350, 450 and 550 ^oC) for 2 hrs. are shown in figure 4. It is clear that a decrease of transmittance is seen with increasing annealing temperature which agrees with Agbo e al [37] which may be due to improvement of film properties. Interference maxima and minima is shown in figure 4 too.

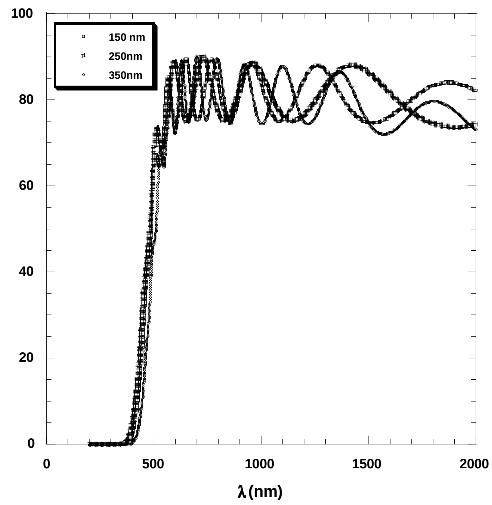

Fig.3 Variation of T% with λ(nm) fot Cd_2SNO_4 thin films of different thicknesses at room temperature.

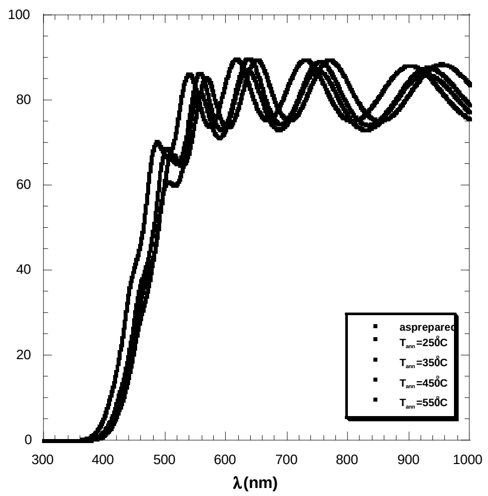

Fig.4 Variations of transmittance T% with wave length λ(nm) for as -prepared and annealed Cd_2Sno_4 thin films at different temperaturs.

The optical energy gap will be estimated from the optical measurements by analyzing the optical data with the expression for the optical absorbance, and the photon energy, $h\vartheta$ using equation 2. The optical band gap can be obtained by extrapolating the linear portion of the plots of $(\alpha h\vartheta)^{1/n}$ versus $h\vartheta$ to α=0. Using the value n=2, the relation found to be straight line as shown in figure 6 representing direct transition. Figure 5 reveals that the optical gap of the Cd_2SnO_4 thin films (300 nm thick) has the values 2.8, 2.86, 2.9, and 2.96 eV for the as-deposited and annealed at 250, 350, and 450 ^oC respectively. It is reported that the optical gap of the Cd_2SnO_4 thin films is 2.7 – 3 eV [32] which is in consistent with the present results. The increase in the band gap energy with increasing the annealing temperature can be attributed to the Burstein-Moss shift in which the absorption edge shifts towards higher energy with an increase of carrier concentration [38-39].The optical band gap E_g increases with increasing annealing temperature, which can be explained as follows; the unsaturated defects are gradually annealed out producing a larger number of saturated bonds leading to a decrease in the density of localized states and consequently the optical gap increase.

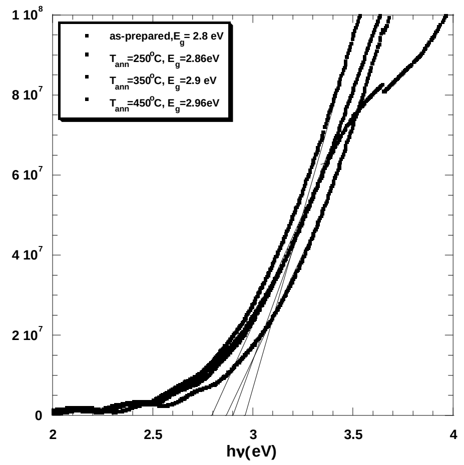

Fig.5 Plots of $(\alpha h\nu)^{1/2}$ vs. hν for Cd_2SnO_4 thin films, as-prepared and annealed at 250, 350, 450 ^oC for 2 hr.

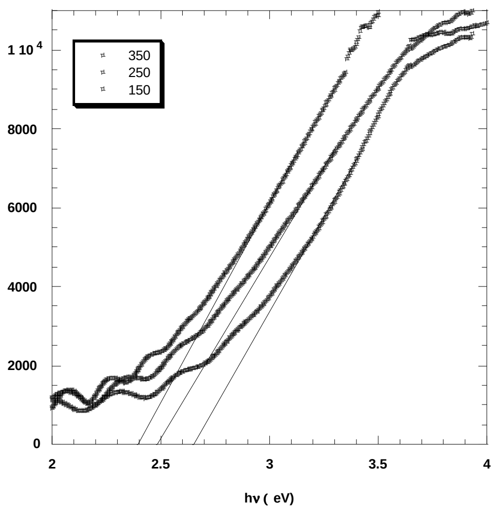

Fig. 6 plot of $(\alpha h\nu)^{1/2}$ vs. (h ν) for as-deposited Cd_2SnO_4 thin films of different thcknesses

Fig. 6 shows the plots of $(\alpha h\vartheta)^{1/2}$ vs. $(h\vartheta)$ for the as-deposited Cd_2SnO_4 thin films of different thicknesses from which the optical gap are determined and found to be 2.4, 2.49, 2.66 eV for the thicknesses 150, 250, and 350 nm respectively i.e. optical gap increases with increasing thickness of the films. Thicker films are characterized by homogeneous network, which minimizes the number of defects and the localized states, thereby increasing the optical gap [40]

To calculate the width of the band tails E_e of the localized states, the following equation [40] will be used:

$$\alpha(\omega) = \alpha_o(\omega)e^{h\vartheta/E_e} \qquad (6)$$

Where $\alpha_o(\omega)$ is constant, h is the Plank's constant. Figure 7 shows the Ln $\alpha(w)$ versus $(h\vartheta)$, the slope of which can be used to calculate E_e of the as-prepared and annealed films of the same thickness 300 nm at different temperatures for 2hr.The calculated values of the band tails of the localized states E_e from figure 8 found to be 0.353, 0.333, 0.329, 0.325 and 0.326 eV, for the as-deposited, annealed films of thickness 300 nm at 150, 250, 350 and 450^{o}C respectively. This behavior of decreasing the values of E_e with increasing annealing temperature agrees well with our results which reveal that E_{op} increases with increasing the annealing temperature. On the other hand, as values of E_e are very much larger than 0.05 eV, Tauc's model based on electronic transitions between localized states in the band edge tails may well be valid in our materials [41].

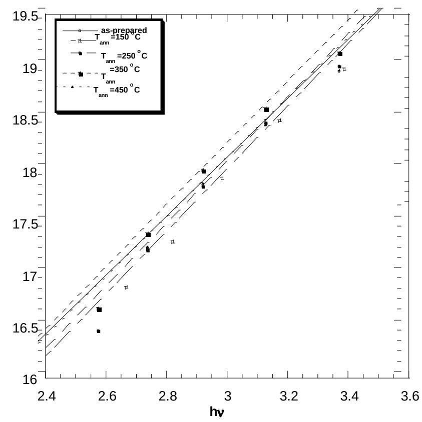

Fig 7 Ln (α) - h ν relations for as-prepares and annealed Cd_2SnO_4 thin films (300 nm thick) at different temperatures

The variation of the refractive index with the wavelength is shown in figure 8, indicating that the refractive index decreases with increasing the wavelength. The effect of annealing is obvious, where the refractive index decreases with increasing the annealing temperature which may be attributed to the decrease in the packing density with increasing annealing temperature [42].

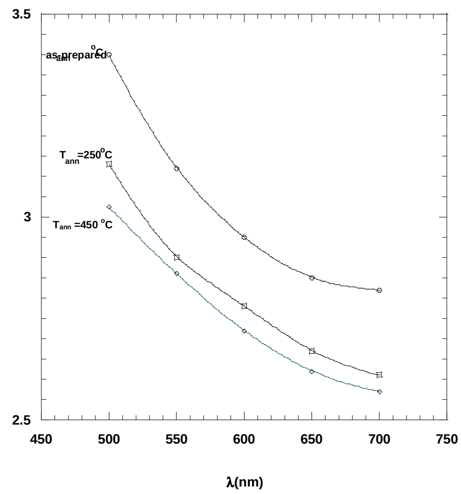

Fig.8 Variations of the refractive index n with the incident wavelength λ for as-deposited and annealed Cd_2SnO_4 thin filmsof thickness 300 nm at different annealing temperatures for 20 mins.

Fig. 9 reveals that the electrical resistivity decreases with increasing the annealing temperature which can be explained as due to grain growth and possibly recrystallization [43].

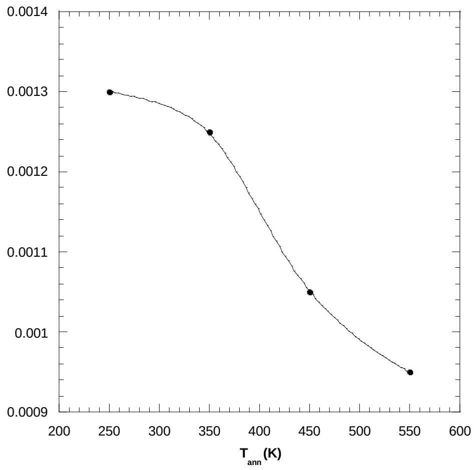

Fig.9 Variations of the resistivity ρ (Ω. cm) with annealing temperature T_{ann}(K) for Cd_2SnO_4 thin film of thickness 300 nm at room temperature.

CONCLUSION

Cadmium tin oxide Cd_2SnO_4 thin films were prepared by RF magnetron sputtering technique on glass substrates at room temperature. The as-deposited films were amorphous whereas a tendency of crystallization appeared with annealing. The optical energy gap was increase with increasing the film thickness and increasing the annealing temperature. The width of the band tails of the localized states found to decrease with increasing annealing temperature. The refractive index was decreases with increasing the incident wave length and with annealing temperature.. The electrical resistivity decreased with increasing the annealing temperature.

Acknowledgment
The authors would like to thank the deanship of the scientific research in Taif University, KSA for supporting this work.

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