

Determination of the Optical Constants of Cadmium Stannate (Cd_2SnO_4) Films

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Abstract

Thin films of cadmium stannate were prepared using thermal chemical spray pyrolysis technique. Cadmium stannate solution (0.2M) was prepared by dissolution of $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ in $\text{C}_2\text{H}_5 \cdot \text{OH}$ and dissolution of $\text{SnCl}_2 \cdot 3\text{H}_2\text{O}$ in CH_3COOH at molar 2:1, respectively. The Cd_2SnO_4 solution was sprayed on glass substrate that was kept at 300K. The studies of structure showed that the prepared thin films were amorphous. After annealing, no changes were observed in the structure. The type of electronic transition was determined by studying the Ultra Violet/Visible (UV/V) spectrum. Energy gap, tail width of localized states, refractive index, reflectance, and extinction coefficient were calculated before and after annealing. The optical constants were found to increase by increasing annealing temperature and thickness of the prepared films.

Introduction

Thin films technique is one of the most recent fully-fledged technologies that greatly contribute to developing the study of semiconductors by giving a clear indication of their chemical and physical properties. Thin films are also particularly important for their use in a great number of optical fields such as the manufacturing of ordinary and thermal mirrors, of highly specialized filters and solar cells. The study of optical properties of semiconductors of both crystalline and amorphous structures is extremely essential for an understanding of the mechanism by means of which optically-induced transitions and the structure of bands are carried out.

Optical transitions [1, 2] start in semiconductors when energy of photons is absorbed at a quantity higher than the forbidden energy gap or equal to it. When the required energy is almost equal to the difference between the lowest level of conduction band and the highest level of covalent band, electrons will transfer from

covalent band to conduction. Mott, Davis, and Tauc [3, 4] have proposed a mathematical equation to represent the relationship between optical energy gap and the energy of the incident photon:

$$(\alpha h \gamma) = B (h \gamma - E_{opt})^r \quad (1)$$

where α is the optical absorption coefficient, B is a constant, $h\nu$ is the energy of the incident photon, E_{opt} is the optical energy gap, and r is an index which could take different values according to the electronic transition.

As for amorphous semiconductors, the basic absorption edge slightly differs from crystalline structure. In this case, the value of the optical absorption coefficient could be expressed by the following mathematical relation [5-7]:

$$\alpha = \alpha_o \exp\left(\frac{h\gamma}{\Delta E}\right) \quad (2)$$

where α_o is the correlation constant, and ΔE represents the tail width of localized states within the optical energy gap. Moreover, the optical properties of semiconductors can also be expressed by using the concepts of refractive index (n_o) and extinction coefficient (k) through the following relations:

$$n_o = \left(\left[\frac{4R}{(R-1)^2} \right] - k^2 \right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad (3)$$

$$k = \frac{\alpha \lambda}{4 \pi} \quad (4)$$

where λ is the wavelength of incident photon, and R the reflectance, which could be calculated from the relation: $R + A + T = 1$, where A represents absorption and T represents transmittance.

Studies of the optical properties of cadmium stannate started in the early 1970s. Al-Ani [8,9] dealt with the optical properties of a variety of semi-conductors including cadmium stannate, obtaining under preparation circumstances the energy gap values and the optical absorption of the variety of phases for the material. Mohammed [10] also studied thin films of cadmium stannate prepared by thermal spraying and pointed out that one of the drawbacks of this approach was the difficulty of obtaining the homogeneity of thin films.

Procedure

Thin films of cadmium stannate were prepared by using a solution of cadmium stannate of (0.2M) concentration. The solution results from dissolving $CdCl_2 \cdot 5H_2O$ in $C_2H_5 \cdot OH$ and $SnCl_4 \cdot 3H_2O$ in CH_3COOH at molar 2:1, respectively. Mixing them

by leaving the solution of cadmium stannate for 72 hours to make sure that no residues were left and to ensure the homogeneity of the resultant solution followed this dissolution process. Glass substrates were thoroughly cleaned and placed on a hot plate at 300K. The hot plate was rotating to ascertain that the spraying process was properly done. Following the same procedure, several thin films of cadmium stannate with varying thickness 3000Å – 6000Å were prepared. The mass method was used to calculate the thickness of prepared thin films. Annealing of the prepared samples were carried out at different temperatures 300K – 600K for 90 minutes.

Results and Discussion

Using X-ray diffraction technique, the structural properties of thin films of cadmium stannate prepared by thermal-chemical spraying were studied before and after annealing. It was found that the structure of the prepared thin films were amorphous. The UV/ Visible technique was used to study the structure of transmission and absorption of the prepared samples before and after annealing. The observation of the spectrum of transmission and absorption of the prepared samples showed no major changes occurred before and after annealing. This is in agreement with the aforementioned result, i.e. the structure of the prepared thin films stayed almost the same.

Using equation (1), the type of electronic transition and the calculation of optical energy gap were specified. It was clearly observed that the direct allowed transition was dominant and this is in line with previous studies [8-12]. Therefore, we conclude from this study the following:

- [1] In general, the value of optical energy gap E_{opt} decreases as thin films thickness increases, since the increase in the thickness leads to filling structural gap and hence increasing localized states within the gap, as shown in Fig.(1-a) and Table-1.

Table 1: The value of optical energy gap (E_{opt}) for all films at different annealing temperatures.

Temperature (K)	Thickness (Å)	E_{opt} (eV)
300	3000	2.95
	4000	2.892
	5000	2.851
	6000	2.8
*****	*****	*****
400	3000	3.197
	4000	3.075
	5000	3.05
	6000	3.023
*****	*****	*****
500	3000	3.21
	4000	3.17
	5000	3.15
	6000	3.125
*****	*****	*****
600	3000	3.251
	4000	3.238
	5000	3.231
	6000	3.225

[2] With annealing thin films, it was noticed that the value of the optical energy gap increases. This can be attributed to the fact that an increase in the annealing temperature leads to minimizing structural imperfections in the prepared thin films. This in turn leads to maximizing the value of optical energy gap, Table (1) and Fig.(1-b).

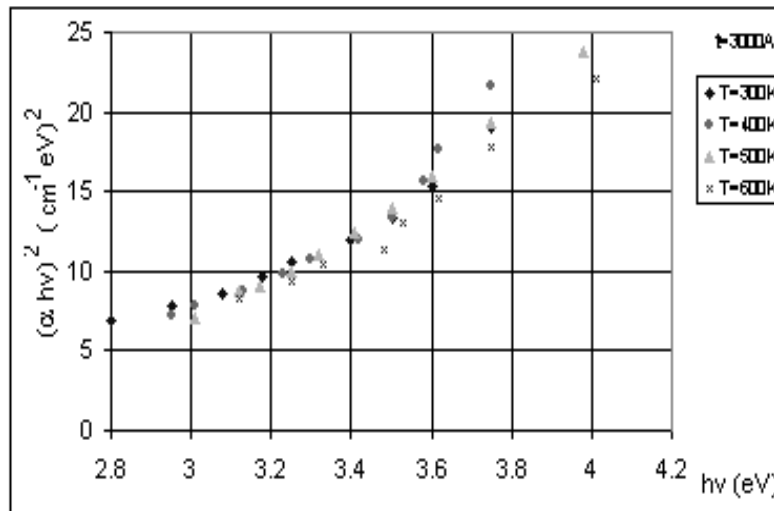


Figure (1-a): $(\alpha h\nu)^2$ versus photon energy with thickness of 3000 Å at different temperatures.

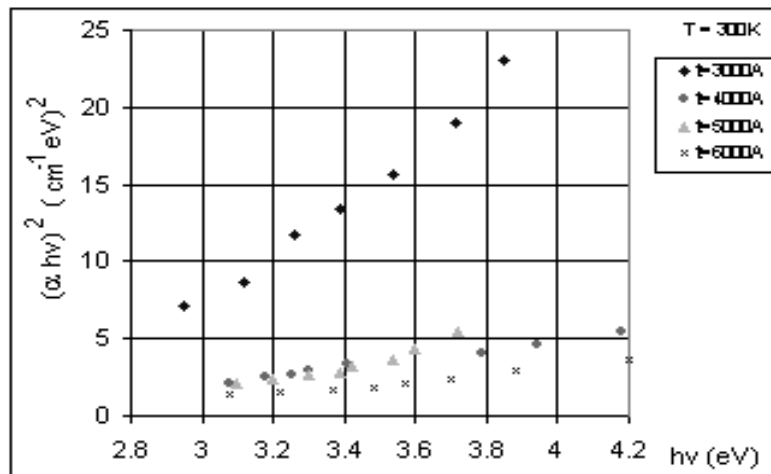


Figure (1-b): $(\alpha h\nu)^2$ versus photon energy at a temperature of 300K for different thicknesses.

- [3] Using equation (2), the tail width of localized states were calculated, Figs. (2-a,b). It was noticed that the value of the tail width of localized states (ΔE) within optical energy gap increases with the increasing the film thickness, Table (2). This can be explained in the light of the fact that the increase in film's thickness could lead to an increase in the structural imperfections of the films. This directly affects the decrease in the optical energy gap.

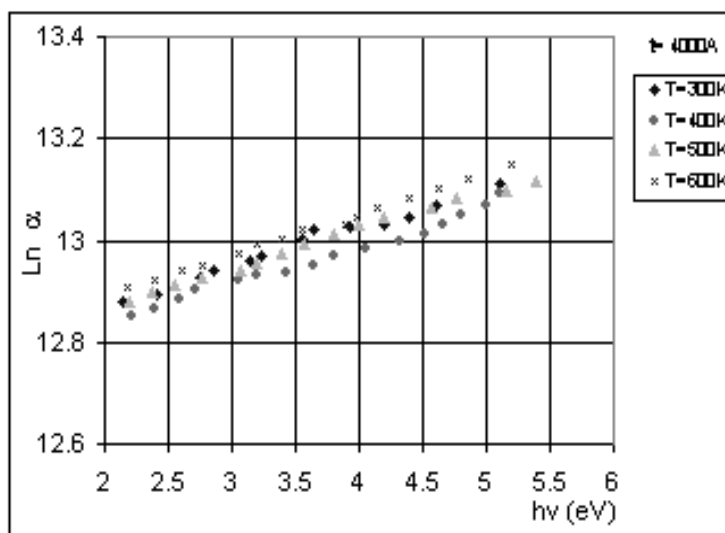


Figure (2-a): $\text{Ln}(\alpha)$ versus photon energy with thickness of 4000 Å at different temperatures.

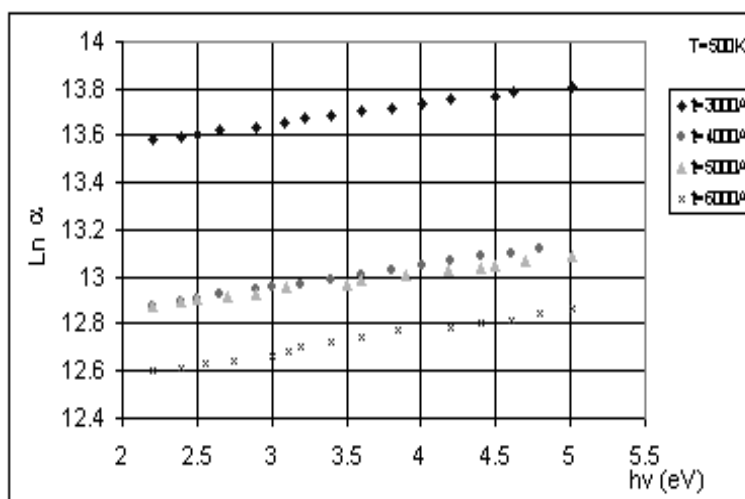


Figure (2-b): $\text{Ln}(\alpha)$ versus photon energy at a temperature of 500K for different thicknesses.

Table 2: The value of tail width of the localized states (ΔE) for all films before and after annealing.

Temperature (K)	Thickness (Å)	ΔE (eV)
300	3000	3.303
	4000	3.516
	5000	4.037
	6000	4.291
*****	*****	*****
400	3000	3.287
	4000	3.323
	5000	3.381
	6000	3.401
*****	*****	*****
500	3000	3.205
	4000	3.303
	5000	3.333
	6000	3.4
*****	*****	*****
600	3000	3.103
	4000	3.213
	5000	3.316
	6000	3.333

- [4] From Table (2), it could be noticed that the value of the tail width of localized states within the energy gap decreases with the increase in the annealing temperature. An increase in the annealing temperature leads to improving the order of the atoms constituting the prepared thin films, which will result in a decrease in the number of localized states within the energy gap, thus, amounting to an increase in the value of the energy gap.
- [5] Fig.(3) represents a variation in the extinction coefficient (k) as a function of photon energy for different thicknesses and at different annealing temperatures. It was observed that the value of the extinction coefficient (k) gradually decreases with the increase in thickness, whereas it increases with the increase in the annealing temperature. This can be interpreted by saying that an increase in temperature leads to an increase in the value of the absorption coefficient (α). The increase in the value of the absorption coefficient directly affects the value of the reflectance. Also, the refractive index was calculated by using an equation relying on the principle of energy conservation. Finally, it was noticed that the highest value for the refractive index is at energy of 2.4 eV where the highest reflectance value is at energy of 1.9 eV to 2.6 eV. The peak value of refractive index and reflectance move towards the lowest energy values as the film thickness increases. However, the

peaks slightly move towards the highest energy values as the annealing temperature increases.

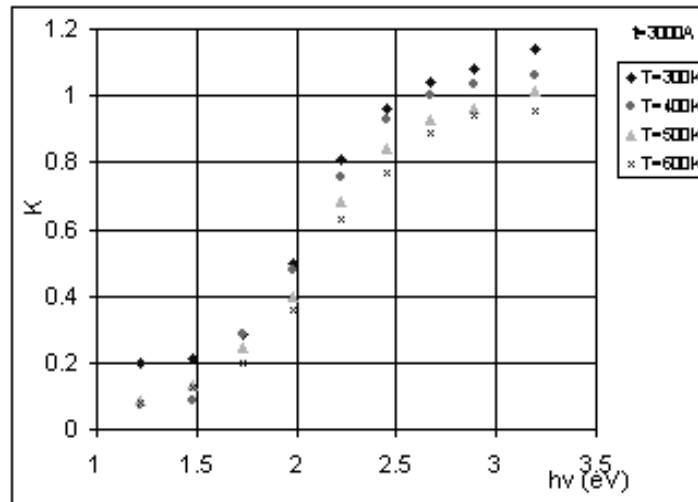


Figure (3-a): Extinction coefficient versus photon energy for thickness of 3000Å at different temperatures.

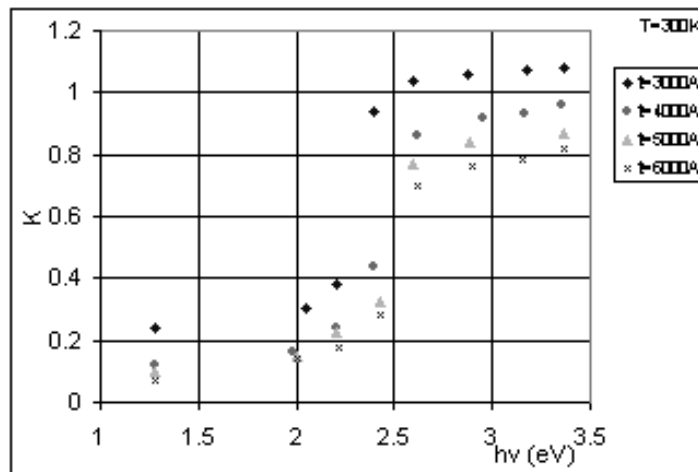


Figure (3b): Extinction coefficient versus photon energy at a temperature of 300K for different thicknesses.

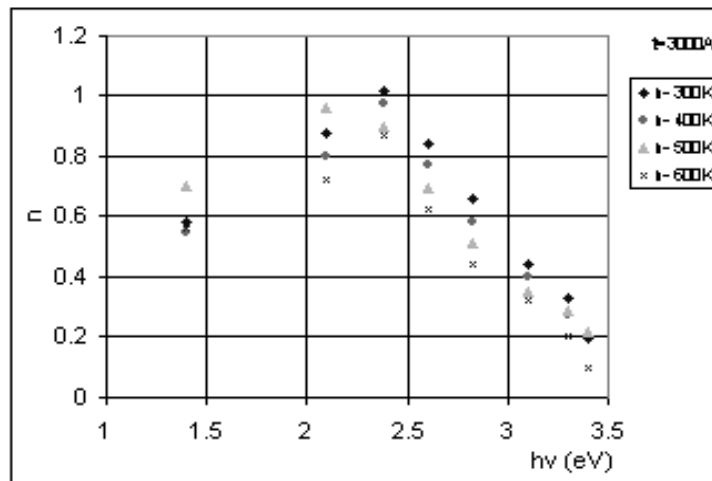


Figure (4-a): Refractive index versus photon energy for thickness of 3000 Å at different temperatures.

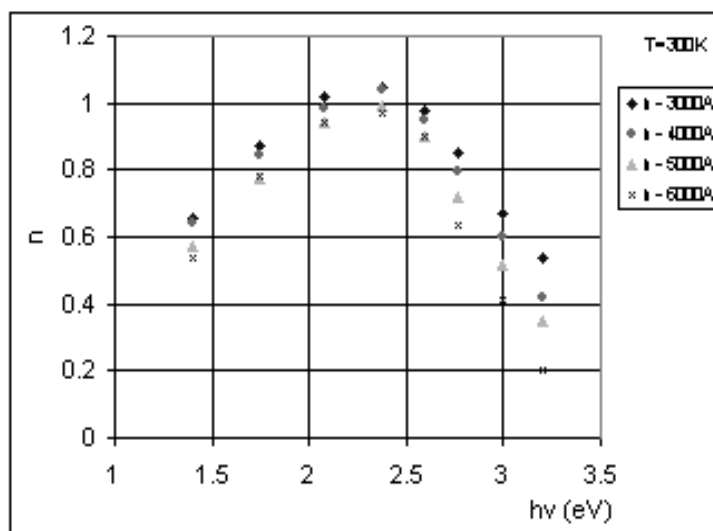


Figure (4-b): Refractive index versus photon energy at a temperature of 300K for different thicknesses.

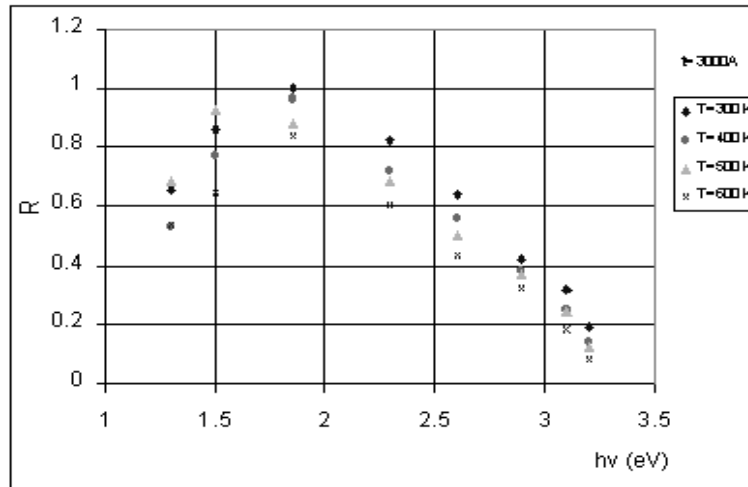


Figure (5-b): Reflectance versus photon energy for thickness of 3000Å at different temperatures.

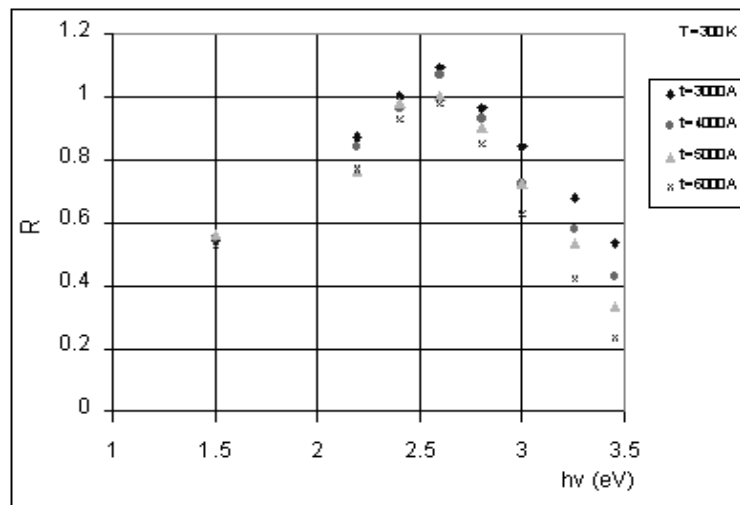


Figure (5-a): Reflectance versus photon energy at a temperature of 300K for different thicknesses.

Conclusions

- [1] Structural examinations of thin films of cadmium stannate prepared by thermal chemical spraying technique have shown that the structure is amorphous before and after annealing.
- [2] UV/ Visible spectrum test has shown that the direct allowed transition is the dominant electronic transition.

- [3] Calculations of optical energy gap have shown that its value decreases as thickness of thin films increases, and increases as the annealing temperature increases.
- [4] Calculations of the tail width of the localized states have shown that its value increases as thickness of thin films increases, and decreases as the annealing temperature increases.
- [5] Calculations of the extinction coefficient have shown that its value decreases as the thickness of thin films increases, and increases as the annealing temperature increases.
- [6] The refractive index has peak values at energy of about 2.4 eV whereas the reflectance has peak value at energy of 1.9 eV to 2.6 eV. The peaks move towards the lowest energy value as the thickness of thin films increases. The peaks move slightly towards the highest energy value as the annealing temperature increases.

References

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