Influence of Substrate Temperature on the Structural and the Electrical Properties of $CdIn_2Se_4$ Fhin Films

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$CdIn_2Se_4$ thin films of different thicknesses were prepared on pre-cleaned glass substrates by the thermal evaporation technique under vacuum 10^{-5} Torr. The influence of substrate temperature on the structural and the electrical properties has been studied. The crystal structure and orientation of the prepared films were investigated by x-ray diffraction. The x-ray analysis confirmed that thin films of $CdIn_2Se_4$ thermally evaporated at room temperature are polycrystalline with cubic crystal structure. The films were preferred orientation along plane (202). The crystallite size (ranged between 17.8 nm and 24.7 nm) increases with increasing substrate temperature. The room temperature resistivity for the films deposited at room temperature was in the order of 10^7 Ωcm, which decreased to 10^2 Ωcm for substrate temperature at 523 K. The activation energy varied from 0.32 eV to 0.22 eV with increasing substrate temperature from 298 K to 523 K. The thermoelectric power measurements of $CdIn_2Se_4$ thin films revealed that all deposited films at different substrate temperature were n-type semiconductors. The density of charge carriers of films grown at 298 and 498 K were $7.01x10^{18}$ and $1.45x10^{19}$ cm^{-3} respectively.

1. Introduction

$CdIn_2Se_4$ is a promising material in optoelectronic applications and solar cells [1,2] due to its high absorption coefficient in the visible region. $CdIn_2Se_4$ thin films were prepared by different techniques [3,4]. The characterizations of $CdIn_2Se_4$ films were extensively studied [5-10]. The structural properties were investigated by means of *x-ray* diffraction. It has been revealed that $CdIn_2Se_4$ *has a* cubic structure with lattice parameter, a =5.815 Å [11,12].

No work was reported about the effect of substrate temperature on the structural and the conduction mechanisms of $CdIn_2Se_4$ thin films. The aim of the present work is to study the effect of substrate temperature on the structural, transport properties and conduction mechanisms of $CdIn_2Se_4$ thin films.

2. Experimental Techniques

Powder of $CdIn_2Se_4$ was used to deposit the thin films of different thickness (160 nm – 700 nm) were deposited on a pre-cleaned glass substrates using a high vacuum-coating unit (Edwards type E 306 A) under vacuum 10^{-5} Torr. The deposition rate of the films was about 7nms^{-1}. The substrate temperatures were set at 298 K, 330 K, 380 K, 395 K, 460 K and 523K. Thin tantalum boat was used as source heater. The film thickness was measured by Tolansky's method [13]. The rate of deposition and the film thickness were controlled using a quartz crystal thickness monitor (Model FTM4, Edwards co, England). An X-ray diffractometer (Philips PW 3710BASED), using CuK_α radiation operating at 40 kV and 30 mA, was used to investigate the structure.
Electrical resistivity measurements at various substrate temperatures were performed in the temperature range of 300 K to 550 K by the two probe technique using an electrometer (Keithly617). The ohmic contacts were made by evaporating high purity aluminum electrodes through a suitable mask onto the films. The ohmic nature of the contacts was confirmed by the linear J-V characteristics throughout the above mentioned temperature range. Thermoelectric power was measured using the differential technique [14].

3. Results and Discussions

3.1. Structural Properties of $CdIn_2Se_4$ thin films

Fig.(1) shows the XRD pattern of $CdIn_2Se_4$ thin films on glass substrates at different substrate temperatures. It can be seen that, over the studied range of substrate temperature, the films are polycrystalline and the most intense peak corresponds to plane (202). Other planes are also observed in all patterns. The intensity of diffraction peaks for the thin films has been found to increase and slightly shifts towards higher values of 2θ as the substrate temperature increased from 298 to 523K. Analysis of Fig.(1) indicates that $CdIn_2Se_4$ thin films have cubic structure. For the cubic lattice parameters evaluation, we have used the quadratic relation:

$$d_{hkl} = a/[h^2+k^2+l^2]^{1/2} \qquad (1)$$

where (h, k, l) are the Miller indices of reflecting planes appearing in the diffraction spectrum and $d_{h,k,l}$ is the interplaner spacing. It was observed that both the calculated lattice parameter (a) and the unit cell volume ($V = a^3$) were decreased as the substrate temperature was increased. The lattice constant values, 5.83Å at 298K, 5.81Å at 460K and 5.80Å at 523K are in agreement with the standard values of *JCPDS* data card [11,15,17].

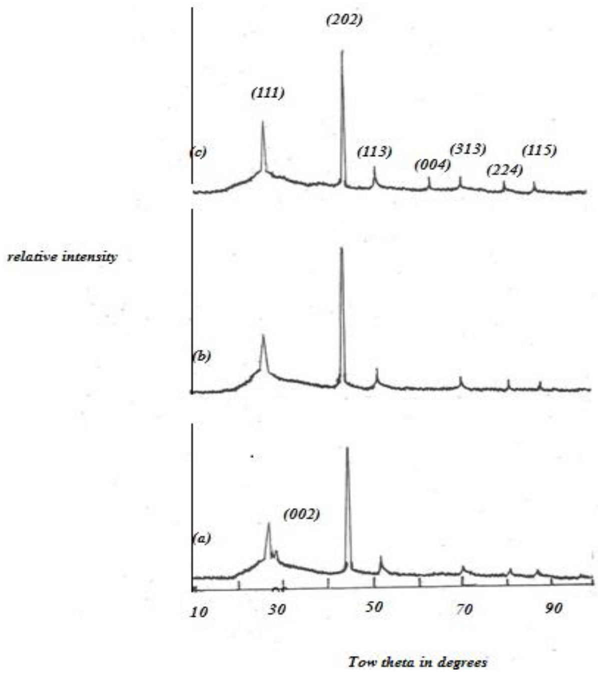

Fig.(1): XRD patterns of $CdIn_2Se_4$ films with thickness 450 nm at: a) 298K, b)460 and c) 523 K.

The crystallite size of the samples is determined from x-ray data using Scherer's formula:

$$D = k\lambda (\beta_{2\theta} \cos \theta)^{-1} \tag{2}$$

where k = 0. 9 is the shape factor, λ is the wavelength of the x-rays, $\beta_{2\theta}$ is the full width half maximum (FWHM) and θ is the Bragg's angle. The x-ray analysis and calculated crystallite size are shown in Table (1). It is found that the crystallite size increases and full width half maximum (FWHM) decreases with substrate temperature. It is found that the crystallite size is ranged between 17.8 nm and 24.7 nm and increases with the substrate temperature. This is due to the sufficient supply of thermal energy for growth of the crystallites [11,12,16].

Table (1): The crystallite size(D) and the observed and standard d values for the *$CdIn_2Se_4$* thin films deposited at various substrate temperature

Standard d-values d (Å)	(*h k l*) planes	Substrate temperature (K)					
		298		460		523	
		d (Å)	D(nm)	d (Å)	D(nm)	d (Å)	D(nm)
3.370	(1 1 1)	3.371	17.8	3.362	21.3	3.361	24.7
2.060	(2 0 2)	2.061		2.059		2.058	
1.750	(1 1 3)	1.779		1.775		1.770	
1.330	(3 1 3)	1.341		1.341		1.340	
1.190	(2 2 4)	1.182		1.181		1.180	

3.2. Electrical resistivity of $CdIn_2Se_4$ thin films

The dark electrical resistivity, r, of *$CdIn_2Se_4$* films of different thicknesses grown at 298K was measured as a function of the sample temperature. The temperature dependence of r, in the range of 300-450K, is shown in Fig.(2) for different film thickness. It indicates a decrease of r against T. A linear relationship for each sample with distinct slope is obtained. The corresponding thermal activation energies, ΔE, were estimated utilizing the following equation:

$$r = r_o \exp (DE/kT) \qquad (3)$$

where, r_o is the resistivity of *$CdIn_2Se_4$* film of thick thickness, and the other symbols have their usual meanings.

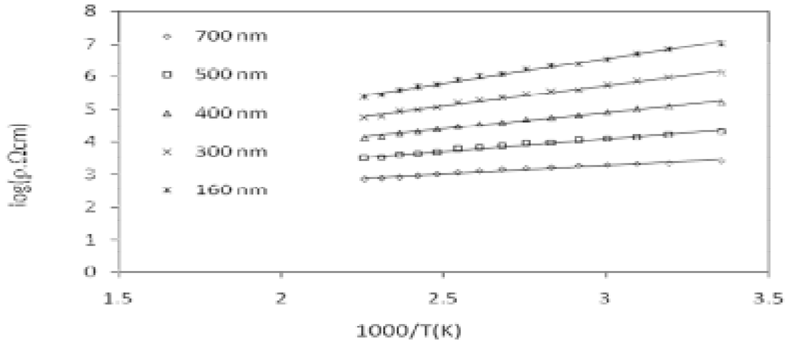

Fig.(2): Log r versus 1000/T for *$CdIn_2Se_4$* thin films for different film thickness, deposited at 298K.

The calculated ΔE for *$CdIn_2Se_4$* of different thicknesses are given in Table(2). The low value of ΔE indicates *that $CdIn_2Se_4$* thin film behaves as an extrinsic semiconductor. Such behaviour can be attributed to lattice defects such as vacancies, interstitials and dislocations which might be developed throughout the first stages of the film growth. From Fig.(2), the dark electrical resistivity of

$CdIn_2Se_4$ thin films, at given constant temperature, tends to decrease with increasing film thickness. The reduction of the dark electrical resistivity with increasing the film thickness may also be attributed to the increase in the size of the individual crystallites as obtained from the structural analysis.

Table(2): The thermal activation energy, *DE*(eV) at various film thickness, deposited at room temperature (298K).

d(nm)	160	300	400	500	700
DE(eV)	0.32	0.27	0.22	0.16	0.11

3.4. Effect of substrate temperature on electrical resistivity of $CdIn_2Se_4$ thin films

Fig.(3) illustrates the relation between the dark electrical resistivity and reciprocal of temperature for *$CdIn_2Se_4$* thin films of various substrate temperatures for a constant film thickness(450nm).

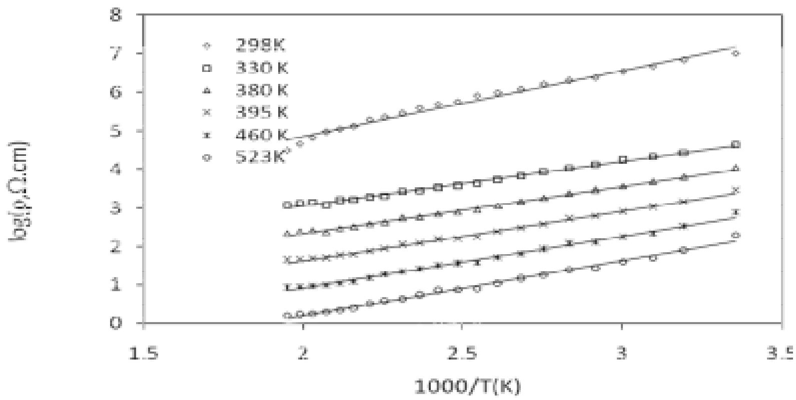

Fig.(3): Log ρ versus 1000/T for *$CdIn_2Se_4$* thin films deposited at various substrate temperatures.

It reveals that the resistivity obeys the relation:

$$\rho = \rho_o \exp(E_a/k_BT) \quad (4)$$

where E_a is the activation energy at different substrate temperature and k_B is the Boltzmann constant. It is clear from Fig.(3) that the resistivity decreases with the increase of temperature [12,18].The estimated values of activation energies for different substrate temperatures and are tabulated in Table(3). For the film deposited at room temperature (298K) shows room temperature resistivity in order of 10^7 Ωcm, while it decreases to 10^2 Ωcm for that deposited at 523K.A corresponding decrease in the activation energy from 0.32 eV to 0.22 eV was observed. Such changes in both activation energy and resistivity as a result of increase substrate temperature can be ascribed to the increase in crystallite size.

Table(3): The thermal activation energy, ΔE(eV) at various substrate temperatures

$T_s(K)$	298	330	380	395	460	523
ΔE (eV)	0.32	0.217	0.230	0.244	0.257	0.271

3.5. Effect of substrate temperature on thermoelectric power of $CdIn_2Se_4$ films

Fig.(4) represents the variation of thermoelectric power, S for $CdIn_2Se_4$ films deposited at various substrate temperatures, against temperature. In general, all samples have negative Seebeck coefficient indicating that $CdIn_2Se_4$ films behave as n-type semiconductors. High thermoelectric power is observed for the film grown at 460 K. This is due to high crystallinity which confirms the optimized substrate temperature of 460 K [12, 18].

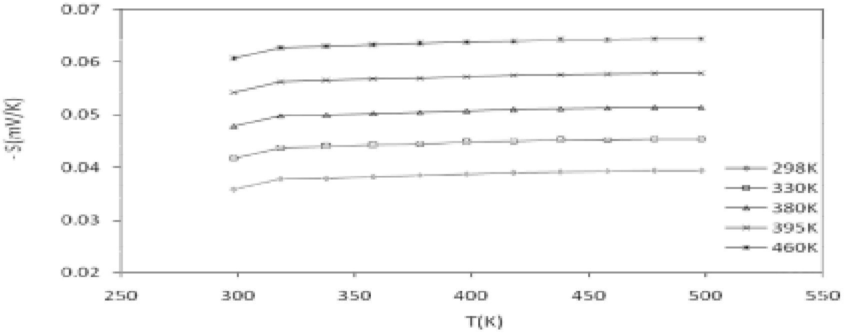

Fig.(4): Variation of thermoelectric power, *S* with temperature, *T* for $CdIn_2Se_4$ thin films deposited at various substrate temperatures.

The thermoelectric power was described by the following equation [19]:

$$S = (k_B / e)[A + \ln (N_n / N)] \qquad (5)$$

where N_n is given by [19]:

$$N_n = 2M^{3/2} = 2.5x10^{19}(T/300)^{3/2}(m^*/m_o)^{3/2} \qquad (6)$$

where $M = 2\pi m^* k_B T/h^2$, m* is the effective mass of the electron ($m^* = 0.15 m_o$ [19]) and the symbols have their usual meanings. The measured thermoelectric power of $CdIn_2Se_4$ is used to estimate the concentration of the free charge carrier, N, for $CdIn_2Se_4$ thin films as following:

$$N = 2.5x10^{19}(T/300)^{3/2}(m^*/m_o)^{3/2}exp(2-1.16x10^4 S) \qquad (7)$$

The free charge carrier concentration for $CdIn_2Se_4$ thin films calculated from thermoelectric power measurements are given in Table(4). It is clear that the carrier concentration were decreased as results of substrate temperature, since the values of thermoelectric power were increased as results of substrate temperature.

Table(4): The free charge carrier concentration, $N(10^{18}cm^{-3})$ of $CdIn_2Se_4$ thin films calculated from thermoelectric power measurements with different substrate temperature.

T(K)	Substrate temperatures,K				
	298	330	380	395	460
298	7.014	6.542	6.102	5.659	5.2482
318	7.554	7.046	6.573	6.095	5.653
338	8.259	7.704	7.186	6.664	6.180
358	8.971	8.368	7.806	7.239	6.713
378	9.711	9.058	8.449	7.835	7.266
398	10.46	9.752	9.097	8.436	7.823
418	11.23	10.47	9.768	9.059	8.401
438	12.01	11.21	10.45	9.694	8.990
458	12.83	11.97	11.16	10.35	9.602
478	13.67	12.75	11.89	11.03	10.23
498	14.53	13.55	12.64	11.72	10.872

3.6. Effect of substrate temperature on grain boundary potential barrier

Using the concentration of free charge carrier obtained from thermoelectric power measurements with the resistively data for the same samples, the mobility, μ $(=1/e\rho N)$, at any given temperature for different substrate temperature was calculated. Fig.(5) shows the variation of Log(μ) versus $\frac{1000}{T}$. It is clearly noticed that the mobility, μ, for each film obeys a relation described by [20]:

$$\mu = \mu_o \, exp(-q\phi_b/k_B T) \qquad (8)$$

where ϕ_b is the barrier potential of the grain boundary and μ_o is the grain boundary limited mobility and q is the electronic charge. Regarding the slope of each curve the mobility activation energy, $q\phi_b$, for each substrate temperature can be evaluated. The obtained mobility activation energy $(q\phi_b)$ is given in

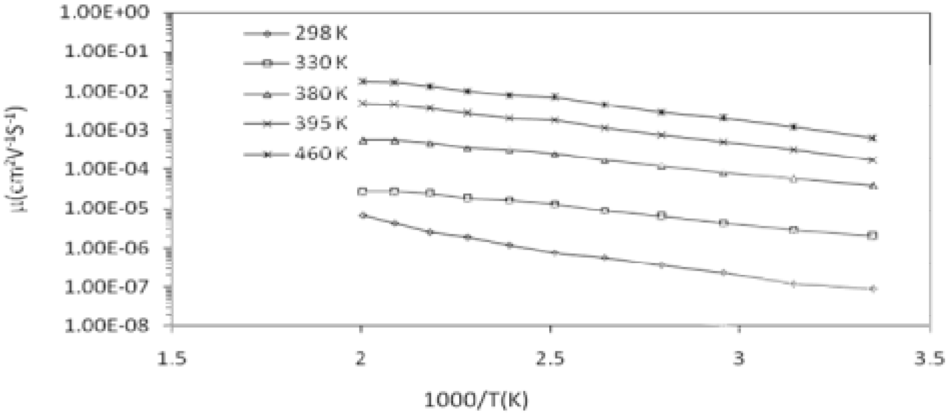

Fig.(5): *Log(μ)* versus $(\frac{1000}{T})$ for $CdIn_2Se_4$ thin films at various substrate temperatures.

Table (5) in comparison with the thermal activation energy (ΔE) for substrate temperature. It can be observed from the table that the substrate temperature governs the potential barriers at grain boundaries. The higher the substrate temperature the lower the potential barrier at grain boundaries and hence the lower is the mobility activation energy. In addition the values of mobility activation energy $(q\phi_b)$ are likely smaller than the thermal activation energy (ΔE).

Table(5): The mobility activation energy in comparison with thermal activation energy at various substrate temperature.

T_S (K)	ΔE (eV)	qf_b(eV)
298	0.32	0.275
330	0.217	0.182
380	0.230	0.182
395	0.244	0.214
460	0.257	0.215

3. Conclusions

Analysis of the X-ray diffraction data showed that $CdIn_2Se_4$ films are highly oriented along (202) planes. The deposited films are of polycrystalline nature with cubic structure. Nano crystallite size of 17.8 - 24.7nm has been recognized. The increase in crystallite size as results of substrate temperature indicates the structure improvement of $CdIn_2Se_4$. Room temperature resistivity for the film deposited at 298K is found to be of order of 10^7 Ωcm, while it decreases to 10^2 Ωcm for the sample deposited at 523K. Correspondingly, the activation energy decreased from 0.32 eV to 0.22 eV. The reduction of the dark electrical resistivity as function of film thickness may be due to the increase in crystallite size. Also, the electrical resistivity of $CdIn_2Se_4$ decreases with increasing the film thickness can be attributed to lattice defects such as vacancies, interstitials and dislocations which might be augmented throughout the first stages of the film growth. These defects add an extra percentage of resistivity. These defects diffuse and accordingly the corresponding resistivity decreases as the film thickness increases. Thermoelectric power measurements showed that $CdIn_2Se_4$ thin films are n-type semiconductor with carriers concentration in the order of 7.01×10^{18} cm^{-3}, at 298 K. The behavior of resistivity with temperature and the low value of ΔE indicate *that* $CdIn_2Se_4$ thin film behaves as an extrinsic semiconductor.

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