Study of Annealing- induced changes in Structural and Electrical Properties of CdS and CdS:Al Thin Films

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ABSTRACT *Cadmium sulfide and Aluminum doped CdS thin films have been deposited by thermal evaporation in vacuum on glass slide at substrate temperature (Ts) equals to373 K. Films were annealed in air at different temperatures to estimate the effect of the annealing on the structural and electrical properties of the films. XRD investigations revealed that the CdS alloy and their films are polycrystalline nature and have the hexagonal structures with preferred orientation along (002) plane, and appeared one peak belong to cubic structure for thin films. The increase in annealing temperature led to an increases in the intensity of (002) peak.*
The result of the electrical properties showed that these films were n-type. The conductivity and the carrier concentration of the undoped and Al doped films were increased when the films annealed at different temperature.

Introduction:
Chalcogenide semiconductor thin films are being intensively investigated for low-cost photovoltaic and optoelectronic applications[1].

Cadmium sulfide (CdS) is an important direct band gap II-VI semiconductor and low cost, large area thin film formulation of CdS is necessary for technological application as window material for CdS/CdTe solar cells, light emitting diodes for flat panel displays and transistors for electronic switches, optical filters, photodetectors, gas sensors and piezoelectric transducers, laser materials, optical wave guides, and non-linear integrated optical devices [2-7].

CdS thin films are deposited using various techniques such as vacuum evaporation, chemical bath deposition, spray pyrolysis deposition, close spaced sublimation techniques, chemical vapor deposition, successive ionic layer adsorption and reaction, pulsed laser deposition, and electron beam evaporation [8-15]. Among these vacuum evaporation technique is a well established technique.

Addition of trace amount of dopants into CdS host so as to improve the structure, optical and electrical transport properties, received intensive attention in recent years [16]. CdS can be doped with B, Al, Ga, and In to get n-type conductivity or with Cu, Ag, and Au to obtain p-type conductivity. But it is difficult to form p-type due to its shallow level. In addition CdS is of n-type semiconductor with intrinsically- disturbed stochiometry [17].

Thermal annealing leads to improvement in the crystalline quality of the films by the removal of random strain, which can lead to changes in resistivity [18].

In this present study annealing effect and the influence of Aluminum on the electrical properties of CdS thin films by using vacuum thermal evaporation technique were studied and reported in this paper.

Experimental Procedure:
Cadmium Sulfide with 5N purity and a mixture made from CdS powder and 1% Aluminum was evaporated by using thermal evaporation technique in a 10^{-6} mbar vacuum, from resistive molybdenum crucible on to heated glass substrates (T_s = 373 K), where a radiant heater was used to heat the substrate .The distance crucible- substrate was maintained at 15 cm, and the rate of deposition fixed at 3.33 A/sec. The films thickness was 200 nm .A post deposition annealing was performed in air at (323, 373, 423 K) for an hour.

The crystallographic structures of CdS powder and their thin films were analyzed with diffractometer using Cu-Kα radiations operated at (40)KV and (30)mA , with scanning angle 20°-50° .

In order to measure the electrical properties, ohmic contacts are needed. It was obtained by evaporated under vacuum of Al wire of high purity. The best condition for good ohmic contact was satisfied by a layer of 200 nm.

The electrical properties measurements include; d.c conductivity and Hall effect measurements for CdS and CdS:Al films treated at different annealing temperature. The d.c conductivity as function of the temperature are studied in the range of temperature (300-503) K. From the plot of (lnσ) versus (10^3/T) the activation energies can be deduced. The Hall coefficient(R_H), concentration (n) and mobility (μ) of the carrier have been determined from Hall effect measurement by using the following equations respectively.

$$R_H = \frac{V_H t}{I.B}$$ …………..(1)

$$n = \frac{1}{e.R_H}$$ ………(2)

$$\mu_H = \frac{\sigma}{e.n}$$ ………...(3)

Where I represent the current through the sample, B magnetic induction and t thickness of the samples, which carried out by using Hall effect measurement system (3000 HMS) at room temperature.

Results and discussion:
I-Structural Properties:
x-ray diffraction spectrum of CdS alloy showed the polycrystalline structure and exhibited sharp peaks at 2θ equal to 24.88, 26.50, 28.23, 36.68, 43.80, and 47.88° which correspond to reflection from (100), (002), (101), (012), (110), and (103) planes respectively of hexagonal phase with preferen-
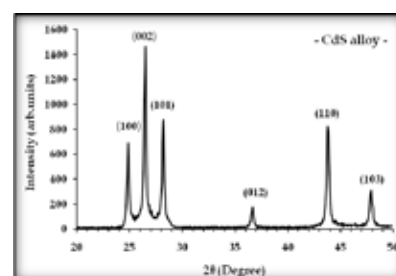

Fig.(1) X-ray diffraction pattern of CdS alloy.

tial orientation along (002) as shown in figure (1).Peaks corresponding to free cadmium or sulfur are not observed, the same observed has been reported by Murali et al [19].

The peak positions are in good agreement with ASTM (American standards for Testing Materials) cards of CdS which given in table (1).

The films which prepared by thermal evaporation technique on glass substrates were mirror-like and showed good adhesion to the substrate. The color of the films was yellow.

From fig.(2) , it can be observed that the dominant structure was hexagonal with preferential orientation along (002)plane which has the lowest surface energy in wurtizite structure, and there are two peaks along (200) and (220) which belong to the cubic structure, as illustrate in table (2).

This is attributed to the nature of chalcogenides of cadmium which normally show the duality in their crystal structure which means that they can be formed with either cubic structure or hexagonal structure [20] or mixed structure [21], the hexagonal phase is believed to be the stable modification between 25 and 900oC [22].
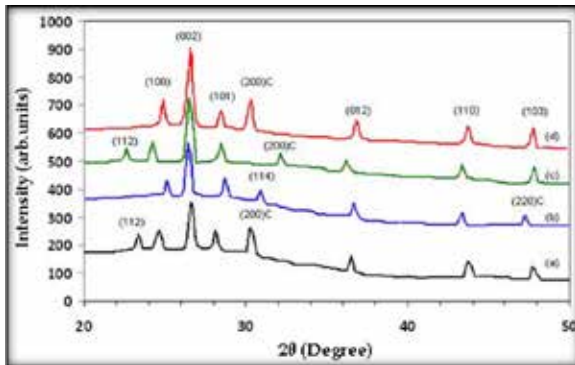

Fig.(2) X-ray diffraction pattern of CdS and CdS:Al thin films.(a) as deposited CdS film (b) annealed at 423 K (c) as deposited CdS:Al film (d) annealed doping film at 423 K.

It is clear from the same figure that the annealing temperature leads to an increase in the peaks height for undoped and doped films. This indicate the increasing of annealing temperature improves the crystallinity of these films and also to the propensity of the films atoms toward their preferential orientation along (002) plane with their stable structure (hexagonal).

The same peaks also appeared in all doped films, which indicates that aluminum doping did not change the structure of these films, as shown in table (2). The similar results were found by Khallaf et al.[23]. The aluminum ions substitute sulfide in lattice positions in good order instead of filling the free spaces, therefore, very low concentration of Al dopants did not change the crystal structure of CdS films.

Table (1): The structural parameters of CdS alloy.

Peak no.	$2\theta_{Exp.}$ (deg)	$2\theta_{Stan.}$ (deg)	$d_{Exp.}$ (A°)	$d_{Stan.}$ (A°)	I/I_o	hkl
1	24.88	24.87	3.575	3.580	46	100
2	26.50	26.50	3.360	3.359	100	002
3	28.23	28.23	3.157	3.160	63	101
4	36.68	36.69	2.447	2.449	12	012
5	43.80	43.79	2.065	2.067	65	110
6	47.88	47.88	1.898	1.898	23	103

Table (2): The structural parameters of as deposited and annealed CdS and CdS:Al films.

T_a (CdS)	Peak no.	$2\theta_{Exp.}$ (deg)	$2\theta_{Stan.}$ (deg)	$d_{Exp.}$ (A°)	$d_{Stan.}$ (A°)	I/I_o	hkl
300K	1	23.229	23.24	3.826	3.824	40	112
	2	24.63	24.80	3.610	3.587	48	100
	3	26.58	26.50	3.350	3.359	100	002
	4	28.177	28.18	3.164	3.164	36	101
	5	30.79	30.80	2.901	2.900	52	200 cubic
	6	36.58	36.64	2.454	2.450	28	012
	7	43.87	43.91	2.062	2.060	20	110
	8	47.88	47.88	1.898	1.898	20	103
423K	1	25.02	25.06	3.556	3.550	29	100
	2	26.56	26.50	3.353	3.359	100	002
	3	28.99	28.39	3.077	3.141	43	101
	4	31.29	31.15	2.856	2.868	19	114
	5	36.73	36.64	2.444	2.450	14	012
	6	43.28	43.73	2.088	2.068	10	110
	7	47.12	47.04	1.927	1.930	5	220 cubic

T_a (CdS:Al)	Peak no.	$2\theta_{Exp.}$ (deg)	$2\theta_{Stan.}$ (deg)	$d_{Exp.}$ (A°)	$d_{Stan.}$ (A°)	I/I_o	hkl
300K	1	23.129	23.24	3.842	3.824	27	112
	2	24.55	24.80	3.623	3.587	30	100
	3	26.57	26.50	3.360	3.359	100	002
	4	28.79	28.39	3.341	3.141	22	101
	5	32.25	32.77	2.773	2.730	16	200 cubic
	6	36.02	36.64	2.491	2.450	8	012
	7	43.35	43.73	2.085	2.068	11	110
	8	47.80	47.83	1.901	1.900	14	103
423K	1	24.72	24.80	3.598	3.587	52	100
	2	26.58	26.50	3.350	3.359	100	002
	3	28.44	28.39	3.135	3.141	19	101
	4	30.80	30.80	2.900	2.900	57	200 cubic
	5	36.63	36.64	2.451	2.450	14	012
	6	43.83	43.73	2.063	2.068	14	110
	7	47.81	47.83	1.900	1.900	38	103

II- Electrical properties:
The measurement of electrical conductivity of the samples were employed in the temperature range 300-503 K.

Firstly, the electrical conductivity increases with increasing the temperature, thus the samples show typical semiconductor behaviors .

The value of conductivity for as deposited films increases from 1.6x10-6 to 2.4x10-5(Ω.cm)-1 when film annealed at 423K, as illustrate in table (3).

This increasing in the conductivity with annealing temperature can be explained by the increase in grain size and the enforcement of crystal growth, or perhaps the resistivity decreases as a result of increased electron density by reducing the sulfide.

The increasing in the conductivity with increase thermal annealing temperature is not unfamiliar and coincides with the results of Haider et al [24],Dipalee et al [25], metin et al [26],and Shadia et al [27].

The same thing notes for aluminum doped films, where the conductivity increases from 1.6x10-6 for as deposited CdS film to 6.1x10-5(Ω.cm)-1 for Al doped film, and increase to 4.4x10-4(Ω.cm)-1 when film annealed at 423K.

The decrease in resistivity with Al doped may be due to an increase in the carrier concentration as a result of doping .

Some researchers found similar behavior such as Jae et al [22] for boron doped CdS films and Khallaf et al [23] for aluminum and indium CdS films.

The variation of lnσ with 1000/T for undoped and Al doped films are shown in fig.(3a&b) respectively. It can be observed there are two separated regions throughout the heating temperature range the first region is at low temperature and

the second region is higher temperature indicating different conduction mechanisms dominating at specific temperature intervals ,this means there are two activation energies.

The first activation energy (Ea1) occurs at low temperatures in which the conduction mechanism is due to charge carriers transport (hopping) to localized states near the conduction band.
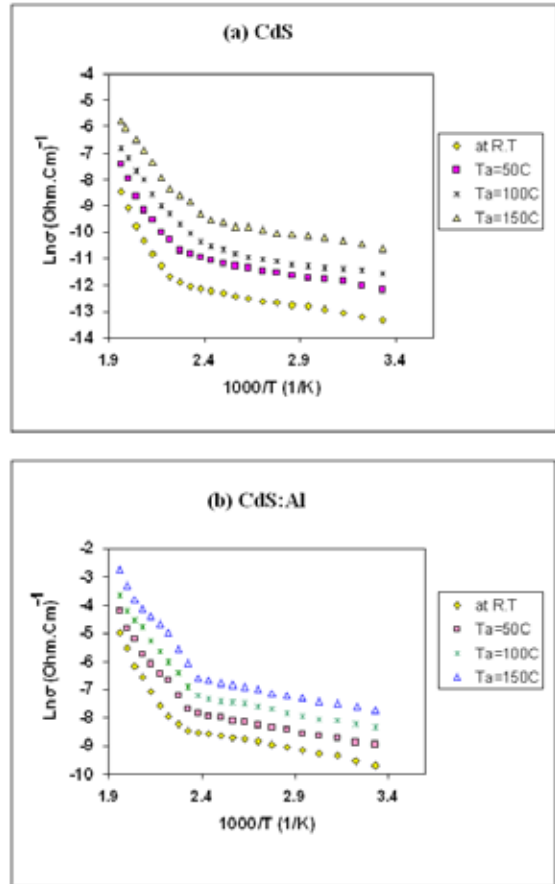

Fig.(3) The plot of lnσ vs. 1000/T for (a) CdS films (b) CdS:Al films at different annealing temperature.

The second activation energy (E_{a2}) occurs at high temperature, in which the conduction mechanism is attributed to the thermal excitation of charge carriers from grain boundaries to neutral region of the grains [28]. It is specifically due to carriers excited in to the extended states beyond the mobility edge.

It is obvious that the activation energy in the high and low temperature regions decreases with increasing thermal annealing temperature and when doped CdS films with Al dopant as illustrated in table (3).

It is notable that the decrease in the activation energies suggests that the grain boundary scattering reduces significantly as the annealing temperature increases.

It is shown that the values of the activation energy obtained from the resistance measurements for the CdS thin films are quite low compared to the values of optical energy gaps(Eg). Similar results were obtained by Metain et al [26].

The low activation energy values obtained from the resistance measurements gives indication of doped levels (trapped levels or additional energy levels) due to the presence of

Table (3): The electrical parameters of CdS and CdS:Al films.

Sample	T_a(K)	$\sigma_{R.T}$ x10^{-5} (Ω.cm)$^{-1}$	E_{a2}(eV) 430-510) K)	E_{a1}(eV) 300-420) K)	n_H x10^{13} (cm^{-3})	μ_H x10^2 cm^2/V. s.
CdS	300	0.160	0.860	0.104	0.337	0.02
	323	0.503	0.810	0.103	0.427	0.06
	373	0.935	0.773	0.103	0.548	0.08
	423	2.400	0.770	0.102	0.598	0.21
CdS doped with Aluminum	300	6.180	0.835	0.103	0.993	0.32
	323	12.71	0.779	0.100	1.031	0.64
	373	24.35	0.731	0.100	1.253	1.02
	423	44.83	0.720	0.100	1.169	2.01

Conclusion:
Effect of annealing temperature on structural and electrical properties of CdS and Aluminum doped CdS thin films deposited by thermal evaporation techniques were investigated. The films have hexagonal wurtzite structure with a preferential orientation of (002) plane, and appear one peak belong to cubic structure. The conductivity increases with increasing impurity atoms in the forbidden gap of the semiconducting thin films. Impurities and imperfections drastically affect the electrical properties of a semiconductor.

Hall effect measurement reveals that the sign of the Hall coefficient for CdS and Al doped CdS films is negative. This confirms that these films have n-type charge carriers.

The charge carriers concentration increase while charge mobility decrease with the increasing annealing temperature and when the films doped with Al dopant, as shown in table (3) which summaries the values of electrical parameters of CdS and CdS:Al. Same results were found by Khallaf et al [23].

The decrease in mobility with doped may be to contribution of scattering mechanisms such as ionized impurity scattering. annealing temperature and when the films doped with 1% aluminum, this improvement in the conductivity is due to the enhancement of the crystal growth as seen in the XRD spectra.

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