Annealing Effect on Structural, Electrical and Optical Properties of CdS Films Prepared by CBD Method

Adawiya J. Haider, Ali M. Mousa, and Selma M.H. Al-Jawad

***Abstract*—In this work CdS films were prepared by using chemical bath deposition, which is simple and inexpensive technique suitable for large deposition area. Annealing in air at different temperatures (300, 350, 400, 450 and 500 °C) at constant time of 30 min, also for different times (15, 30, 45, 60 and 90 min) at constant temperature (300 °C) is achieved. X-Ray analysis has confirmed the formation of cadmium oxide (CdO) with slight increase in grain size, shift towards lower scattering angle due to relaxation in the tensile strain for deposition films, and structure change from cubic and hexagonal to the hexagonal. From electrical properties, significant increase in electrical conductivity appeared in samples annealed at 300 °C for 60 min, and at 350 °C for 30 min.**

***Index Terms*—Cadmium sulfide, chemical bath deposition, CdS films, thermal annealing**

I. Introduction

The chemical deposition technique which also is referred to as the electrodless or solution technique for the preparation of CdS thin films is based on the slow release of Cd^{2+} ions and S^{2-} ions in solution. The slow release of the Cd^{2+} ions is achieved by the dissociation of a complex species of cadmium $[Cd(NH_3)_4]^{2+}$, which is formed from react ion of cadmium salt ($CdSO_4$, $CdNO_3$,$CdCl_2$, and $CdCH_3COO$) with ammonium hydroxide (NH_4OH). The S^{2-} ions are supplied by the decomposition of thiourea $SC(NH_2)_2$ in alkaline solution (pH>9), and react with Cd^{2+} ions to give cadmium sulfide CdS. Deposition occurs by an ion–by–ion process, or by colloidal particles of CdS adsorbing onto the substrate [1,2].

Cadmium sulfide has crystal cubic structure (zinc-blende) or hexagonal structure (wurtzite), or mixture from them according to growth deposition [3]. The films have a strong preferential orientation of either hexagonal H[002] or cubic *C*[111] planes parallel to the substrate surface [4]. The material properties that are of interest for these films are the optical properties within the range of UV, visible, and near infrared (NIR) which strongly depend on the dielectric constants, refractive index, and the band-gap of the thin film and depends very much on the nature of the film material properties [5].

When cadmium salt ($CdSO_4$) is used in deposition solution, the films have mixture of hexagonal and cubic structure [6-8], and heat treatment of CdS films in air at 450 °C for 2 hours does not modify the CdS crystalline structure [6]. Kalhe et al. [9] found that the as prepared film is of cubic phase and the air annealed film is at 300 °C for 30 min, cubic CdS films are converted into the hexagonal phase with the formation of cadmium oxide (CdO). Call et al. [10] use $CdNO_3$ as a source for cadmium ions with KOH as a complex agent, from XRD patterns, the films have hexagonal CdS structure, and interplanar spacing (*d*) slightly smaller than in ASTM. Annealing the films in forming gas (90% N_2-10% H_2) at 350 °C for 15 min, increases the interplanar spacing of films. The peak shift was attributed to relief of thermal stresses induced during deposition of the films.

When annealing CdS films, the dark resistivity decreases, which is dependent on the annealing condition and deposited film quality. Hydrogen annealing of CdS films at temperatures between 150 °C and 300 °C decreases the resistivity as a result of increased electron density by

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reducing the sulfide [11] whereas, Danaher et al. [12] found that the vacuum annealing at 300-330 °C for 2 hours reduces the resistivity. The lowering of the resistivity was attributed to O_2 desorption. For annealing CdS films in H_2 containing indium or cadmium vapour, lower resistivities are obtained, where indium acts as a donor in CdS. Heating of CdS films at 250-300 °C for 1 hour causes changes in dark conductivity. This arises from the cumulative effect of grain size enhancement and oxygen incorporation at grain boundaries, significant decrease in the electrical resistivity is observed in samples heated at temperatures of 350 °C and 450 °C. This is due to the partial conversion of CdS to CdO [12].

The main goal of this work is concentrated on enhancing the properties of the annealed CdS structures. The most important properties are the electrical conductivity, absorption coefficient and the grain size of the annealed structures.

II. EXPERIMENTAL WORK

CdS films grown using CBD technology on glass slides. This technology offers the deposition of a thin uniform film on the substrate surface. Substrate used for deposition CdS is borosilicate glass slides, which were first cleaned in distilled water in order to remove the impurities and residuals from their surfaces. Followed it rinsing in chromic acid (for one day), to introducing functional groups called nucleation and/or epitaxial centers, which formed the basis for the thin films growth. Then, repeated washing in deionized water, and finally put in ultrasonic wave with distilled water for 15 min then dried.

The reaction cell was a 100 ml beaker containing 0.1 M $CdSO_4$ aqueous solution, 0.2 M thiourea aqueous solution and 5.6 M NH_4OH in the volume ratio 1:1:1. the substrate were then suspended in the reaction cell. Reasonably good films of CdS were obtained in 20 min at a constant temperature. The freshly grown films were thoroughly washed by water jet, dried and kept in a vacuum.

III. MEASUREMENTS

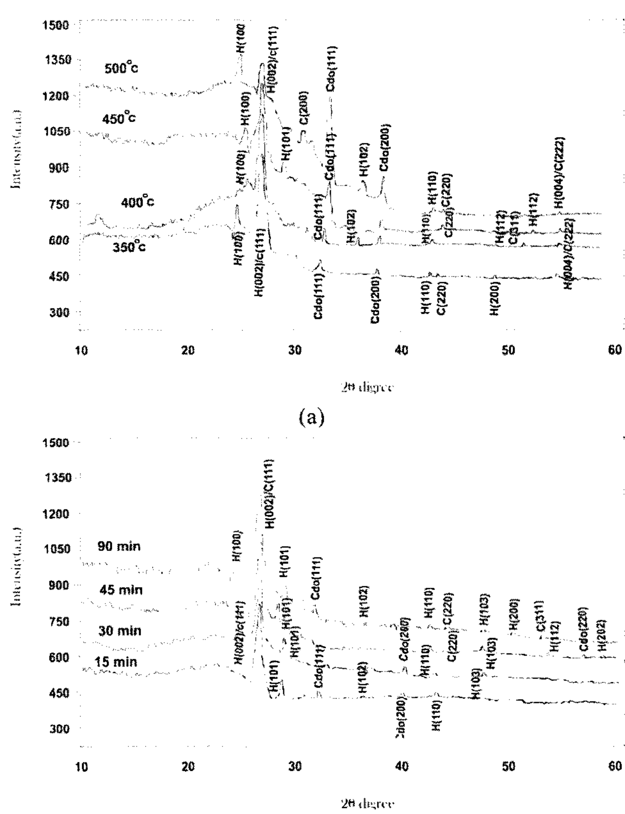
The crystal structure of the films was determined by XRD (using Cu Kα radiations, λ=1.54 Å). The film thickness was measured by optical interferometer method. Optical transmission spectra were taken by A *Cecile CE 7200* Spectrophotometer supplied by Aquarius company for CdS/glass thin films.

In order to measure the electrical properties, ohmic contacts are needed. It was obtained by under vacuum of indium wire of high purity (99.999). The evaporation process was started at a pressure of 10^{-5} torr. The best condition for good ohmic contact was satisfied by a layer of 200 nm.

IV. RESULTS AND DISCUSSION

1. Structure Properties

To demonstrate the effect of annealing, this already presented film is deposited under optimum conditions where temperature is 80 °C, pH 11.5 and a deposition time of 20 min. Annealing is performed in air and temperature of 300 °C for different times and at 30min for different temperatures. Fig. 1 illustrates an XRD pattern of an air-annealed film. It is evident that the as-prepared film is of both hexagonal and cubic phase and the air annealed film



(b)

Fig. 1. X-ray diffraction of CdS films for different annealing conditions. (a) For different annealing temperatures and for 30 min. (b) for different annealing time at 300 °C.

is converted cubic CdS films into the hexagonal phase with a slight shift towards lower scattering angle. The shift towards lower scattering angle is the consequence of an increase in the lattice parameter due to the relaxation of the tensile strain induced by grain boundaries along the film plane, probably due to a slight grain growth, and lets the interplanar distance increase towards its stress free value [4,11]. Fig. 2 shows the variation in lattice constant (c) at different annealing temperature and time.

XRD analysis confirms the formation of cadmium oxide (CdO), as illustrated by the additional reflection lines at *d*=0.2712 nm, 0.2349 nm and 0.1661 nm (Fig. 1) and a slight increase in grain size has been observed as shown in Fig. 3 which illustrates the variation in average grain size at different annealing temperatures and times, the average grain size is determined by using the breadths of the peaks *H*[002]/*C*[111] and Scherrer formula. The cubic phase of CdS indicates smaller lattice parameter according to the diffraction angle (θ) compared to the hexagonal phase, which indicates much stress among the grains.

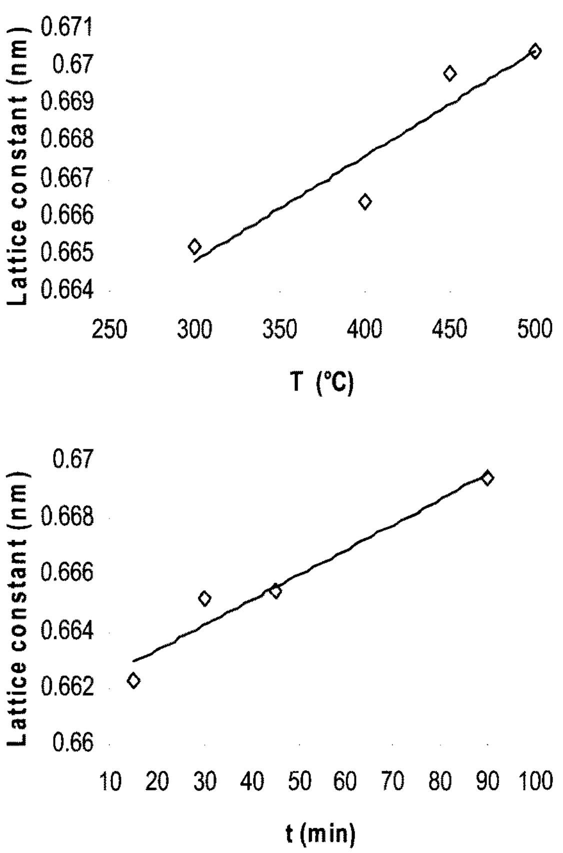


Fig. 2. Variation in lattice constant with annealing temperature and time.

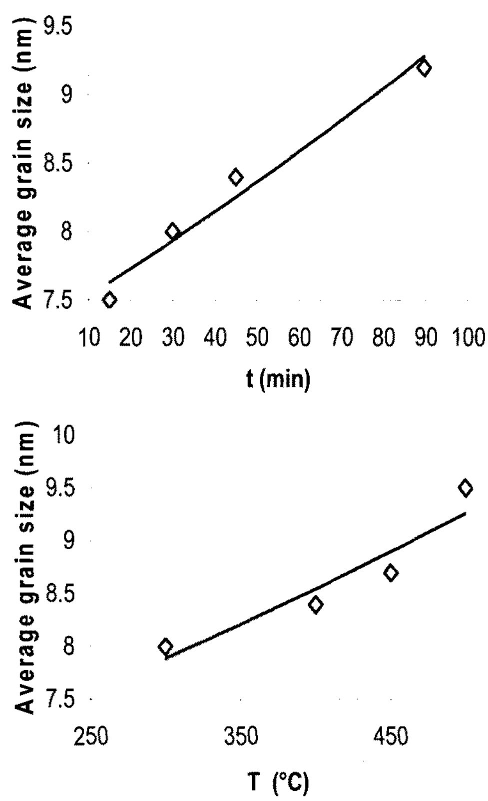


Fig. 3. Variation average grain size with annealing temperature and time.

2. Electrical Properties

Fig. 4 shows the variation of resistivity as a function of annealing temperature and time for CdS films. The as-prepared CdS films show near intrinsic conductivity. Heating of the CdS films at 300-500 °C for 30 min causes changes in the dark resistivity to various extents. This arises from cumulative effect of grain size enhancement and oxygen incorporation at grain boundaries. Significant decrease in the electrical resistivity is observed in samples heated at 300 °C for 60 min (8×10^4 Ωcm) and for 350 °C for 30 min (4×10^4 Ωcm). This is due to the partial conversion of CdS to CdO as seen from Fig. (1) [13]. These results are consistent with other published results such as results of Danaher et al. [2] who attribute this decrease to O_2 desorption, while Ramaiah et al. [14] attribute similar results to the creation of number of sulfur vacancies in the films.

Fig. 5 indicates the variation in the measured electrical resistivity ρ of CdS films with temperature. The resistivity decreases as the temperature is increased, this agrees with semiconductor behavior.

Fig. 6 shows the relationship between ln ρ and 1000/T

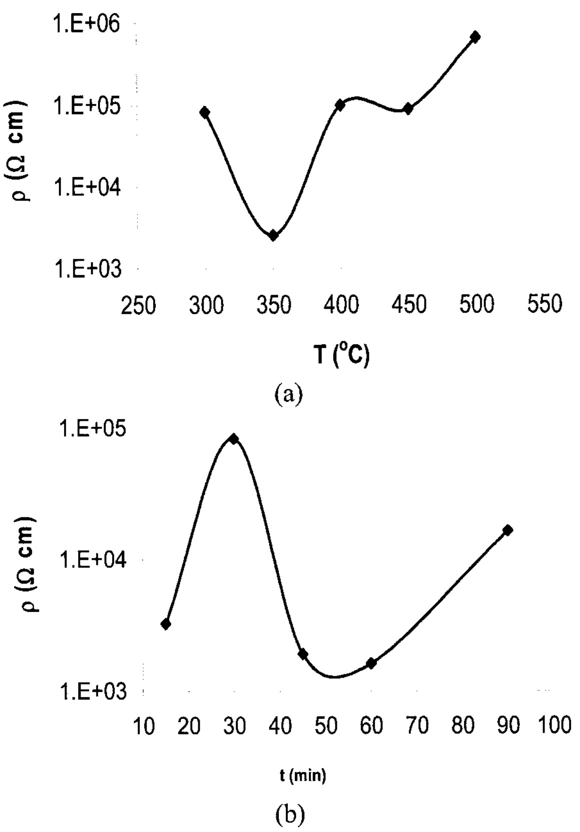


Fig. 4. The variation in resistivity as a function of annealing temperature and time for CdS films. (a) At different annealing temperatures for 30 min. (b) For different annealing times at 300 °C.

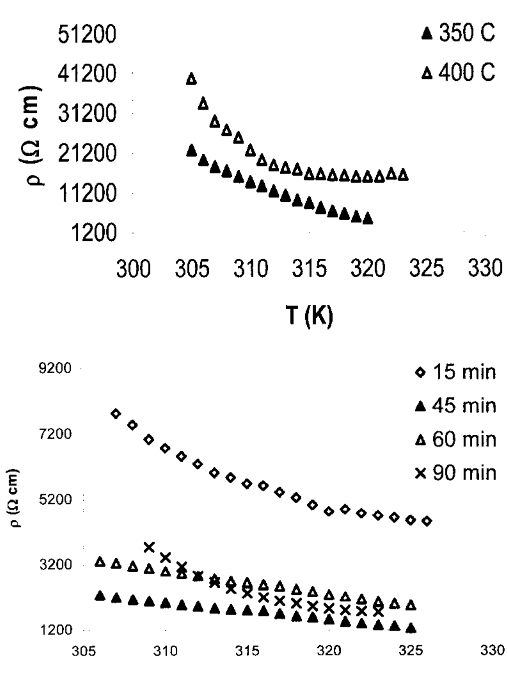


Fig. 5. The relationship between resistivity and temperature for annealed CdS films.

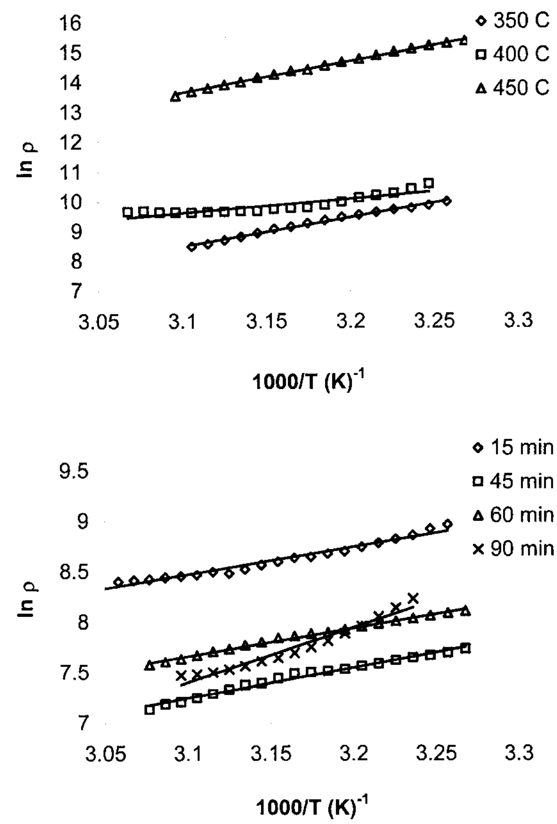


Fig. 6. The relationship between ln ρ and 1000/T for annealed CdS films.

Table 1. Experimental results.

Annealing conditions	Annealing temperature effect			Annealing time effect			
	350°C	400°C	450°C	15min	45min	60min	90min
E_a (eV)	0.84	0.8	0.9	0.23	0.25	0.23	0.46

for annealed CdS films, which shows a level with an activation energy of 0.23 eV found for the films annealed at 300 °C for 15, 45, 60 min. This level appears due to sulfur vacancies in CdS accompanying annealing in air. All vacancies may not be occupied by oxygen, thereby producing a mixture of cadmium oxide and cadmium sulfide with an excess of cadmium. It is known that excess cadmium forms a level within CdS band gap, and also found a level with high activation energy for films annealed at high temperature and time as the same reason for as-prepared films are found. The results of activation energy are tabulated in Table (1).

3. Optical Properties

Annealing of the as-deposited films decreases the optical transmittance and the absorption edge shifts towards lower energy region and becomes much sharper as shown in Fig. 7. Fig. 8 exhibits the variation of the absorption coefficient as a function of wave length for CdS films annealing in different temperature and time.

Fig. 9 shows the effect of annealing conditions on band gap, where the band gap value is estimated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy. The annealed samples show a relative decrease in band gap with both annealing temperature and time. These results are consistent with other published results such as results of George et al. [13] who attribute this decrease in the band gap in the annealed samples to the grain size growth and composition changes taking place in the samples by CdO identified by XRD.

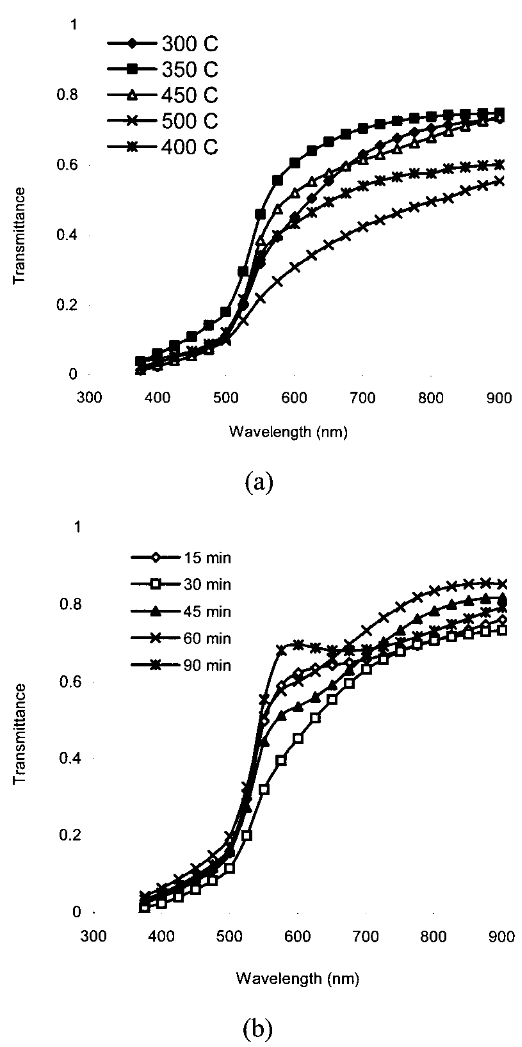


Fig. 7. The optical transmission spectra of CdS films at different annealing temperatures and times. (a) For different annealing temperatures. (b) For different annealing time.

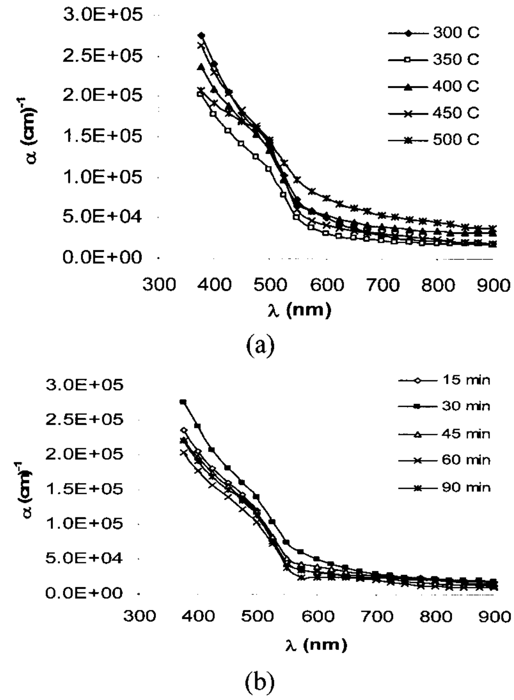


Fig. 8. The absorption coefficient as a function of wave length for CdS films for different annealing temperatures and times. (a) For different annealing temperatures. (b) For different annealing times.

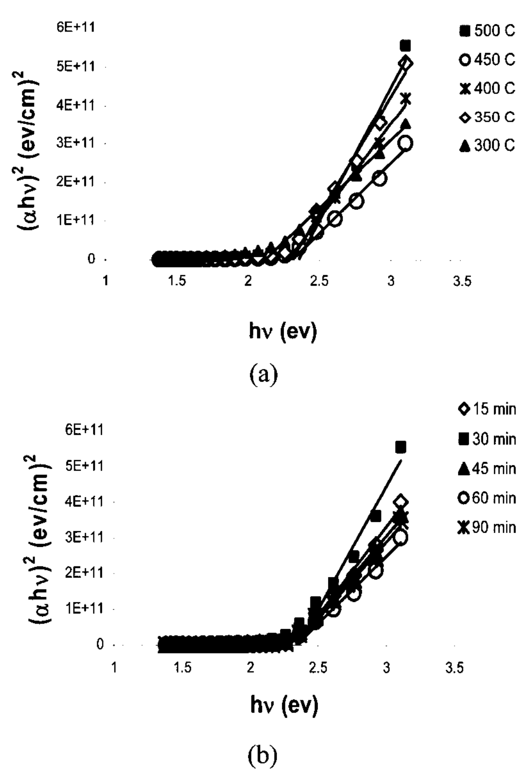


Fig. 9. Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for different annealing temperatures and times.

(a) For different annealing temperatures. (b) For different annealing times.

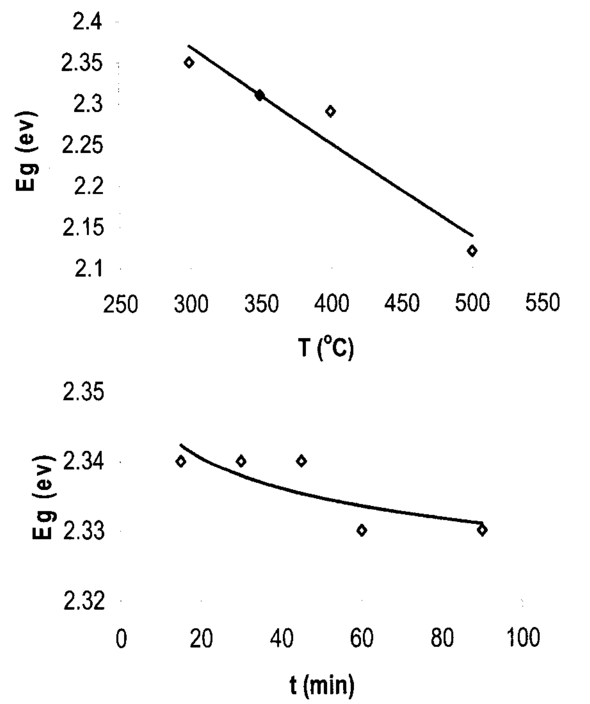


Fig. 10. Optical band gap of CdS films at different annealing temperatures and times.

Conversely, Archbold [15] attributes similar results to the either phase transition from the cubic to hexagonal phase, or a reduction in strain within the film. The energy gap values for different annealing temperatures and times are shown in Fig. 10.

V. CONCLUSIONS

From the obtained results, we can conclude the following. Annealing increases the conductivity of the deposited film with optimum annealing conditions of 300 °C for 60 min and 350 °C for 30 min. The grain size of the CdS structure was increased by annealing which in turn causes to decrease the energy band gap to be used in IR optoelectronic devices. Annealing caused to increase the crystallinity of the resulted structures.

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