The Effect of Annealing on the Physical Properties of Thermally Evaporated Cadmium Sulphide Thin Films

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ABSTRACT

Pure CdS thin films with different condition have been successfully deposited by thermal evaporation in vacuum on glass slide substrates. The substrates temperature of about $100^{o}C$ and the vacuum of about 10^{-6} torr. The film was annealing with different temperature (300 to $500^{o}C$) and different time of annealing (10 to 85min). The film structure properties were characterized by x-ray diffraction (XRD). XRD patterns indicated the presence of single –phase hexagonal CdS with good crystalline, some of the structural characterization such as lattice constant, average grain size and micro strain are calculated from the X-rays pattern. The average roughness was obtained by using AFM scanning microscope, which shows that the average roughness decreased with increase the annealing temperature. Direct band gap values of (2.35 to 2.15eV) for different annealing temperature (300-$500^{o}C$) and (2.34 to 2.33eV) for (10min to 85min) annealing time at $200^{o}C$ annealing temperature respectively, the transmission value of prepared samples are between (50-80%).

Keywords: CdS thin film , The physical properties of CdS thin film

تاثير التلدين على الخصائص الفيزيائية للاغشية الرقيقة لكبريتيد الكادميوم المحضرة بواسطة التبخير الحراري

الخلاصة

حضرت اغشية رقيقة نقية من كبريتيد الكادميوم وبظروف مختلفة على قواعد زجاجية في الفراغ باستخدام تقنية التبخير الحراري في درجة حرارة للقاعدة مساوية الى 100 درجة مئوية وتحت ضغط فراغ =10^{-6} تور وبدرجات حرارة تلدين مابين (300-$500^{o}C$) وزمن تلدين ما بين(85min - 10) . درست الخصائص التركيبية للاغشية من خلال حيود الاشعة السينية. وقد اظهرت النتائج لحيود الاشعة السينية ان الاغشية ذات نظام سداسي منفرد وان المادة عالية التبلور وقد تم حساب بعض المتغيرات التركيبية من طيف الاشعة السينية مثل ثابت الشبيكة ومعدل الحجم الحبيبي والاجهاد المايكروي. كذلك تم استخدام تقنية مجهر القوى الذرية (AFM) للتعرف على طبوغرافية الاغشية وقد تبين ان الغشاء تقل خشونته مع ازدياد درجة حرارة التلدين. وان فجوة الطاقة هي مباشرة تتراوح ما بين (2.15–2.35eV) للنماذج المحضرة في درجات حرارة تلدين ($500^{o}C$ - 300) وفجوه طاقة (2.34 eV - 2.33) للنماذج التي زمن التلدين لها ما بين(10min to 85min) وعند درجة حرارة $200^{o}C$. ومن طيف النفاذية للنماذج المحضرة تبين ان قيمة النفاذية للنماذج المحضرة تتراوح ما بين50-80%.

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INTRODUCTION

Materials in thin film form such as opto –electronic device , electrochromic devise, narrow band coating, temperature controls in satellites, sensors etc, have attracted the attention due to their wide rang of applications both in industry and research *[1]*. Metal chalcogenides (sulfide, tellurides and selenides) are of great important for researches because they are potential candidates for these applications. CdS thin films are regarded as one of the most promising materials for hetrojunction thin film solar cells . Wide band CdS (Eg = 2.4 eV)) has been used as the window material together with several semiconductors such as CdTe , CuS,InP and CuInSe with 14-16% efficiency. Beside that the metal sulfide components have excellent optical properties in the visible and IR region of the spectrum *[2-4]*. For the development of such optoelectronic devices, CdS thin films require comprehensive optical characterization. There are a number of physical and chemical routes for preparing CdS thin films. These include , sol-gel spin coating method, evaporation method, spray pyrolysis, chemical bath deposition, etc. *[5-11]* .

In the present work , thermal evaporation techniques has been chosen for the deposition of CdS thin films as it is simple compared with other new and sophisticated techniques. Here, we report a detailed study on the structural and optical properties of CdS thin films as the knowledge of the structural and optical properties of these films is very important in many scientific, technological and industrial applications in the field of optoelectronic device, particularly solar cells *[12]*

EXPERIMENTAL DETAILS

Film Preparation

High purity (99.99%) cadmium sulphide from Johnson Matthey (U.K) was used in the thin films preparation. The CdS powder was housed in a vacuum deposition chamber for the preparation of thin film. The evaporation was carried out in a conventional vacuum coating unit (INFICON V90) under a vacuum of order of $6X10^{-6}$ torr. A molybdenum boat was used as the evaporation source and the substrates were cleaned glass plates held at 100^{o}C, which were placed directly above the source at a distance of nearly 18cm . The glass substrates were cleaned with freshly prepared chromic acid, detergent solution and distilled water. Films of different thickness deposition were prepared through different individual evaporations. The dimensions of the substrate were 3.8cm x 1.5cm x 0.2cm.

A summary of the deposition conditions is shown in table (1). Film thickness was measured after evaporation by optical interferometer method, using He-Ne Laser λ =0.632 μm and the thickness were determined using the formula:

$$d = \frac{\Delta x}{x} . \frac{l}{2} .... \quad .....(1)$$

Where :d is the thickness of sample, x is fringe width, Δx is the distance between two fringes and λ is the wavelength of He-Ne laser light. The X-ray diffraction (XRD) patterns of the deposited CdS thin film were recorded using diffractrometer kind "Shimadzu XRD 6000", with source radiation of CuKα with $1.54\ 1^{o}$ wavelength. The AFM (Atomic force micrograph) model (AA3000) scanning prop microscope are used to obtained the average surface roughness. Optical transmitting are obtained by using PU 8720 uv-visible scanning spectrophotometer.

RESULTS AND DISCUSSION

Structural analysis

The structural elucidation of CdS film for the preparation condition of the films are presented in Fig (1) with the diffraction 2θ from 20 to 60^o. The observed d spacing and the respective prominent peaks correspond to reflections from (002) planes at 2θ=26.54^o which coincide well with JCPDS data *[13]*. Therefore it has been concluded that the deposition CdS thin films are polycrystalline in nature with hexagonal structure. It was observed that the increase of annealing temperature increased the diffraction peak intensity which means that the crystallinity as well as the grain size of the films is enhanced. The lattice parameter (a) for the hexagonal structure is determined using the relation*[14]:*

$$\frac{1}{d^{*2}} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \text{..........} .(2)$$

Where, d* is the spacing between the planes in the atomic, hkl are the Miller indices.

The grain size (D) for CdS thin films are calculated using Scherrer's formula*[5]*,

$$D = \frac{(k\,l\,)}{b_{2\Theta} \cos \Theta} \text{..........} \text{....}(3)$$

The constant k is the shape factor , taken as 0.94 , λ is wavelength of x-ray (1.5406A^o for CuKα), θ is the Bragg's angle and β is the full width at half maximum.

The dislocation density (δ) has been evaluated from Williamson and Smallmans formula *[15]*.

$$d = \frac{1}{D^2} lines \ / m^2 \text{..........} \text{....}(4)$$

The micro strain (ε) is obtained using the relation :

$$e = b \cos J \ / 4 \text{..........} \text{....}(5)$$

All these parameters are calculated and presented in table (2), it is observed that the structural properties are improved with increased annealing temperature and that are shown as in figure (2:a,b,c).

Surface Morphology

AFM is a convenient and versatile method to study the microstructure of thin film. The surface morphology of CdS thin film is shown in Fig.(3:a,b,c). These films have very smooth surfaces, with an average surface roughness of 3.53nm, 2.43nm, 1.85nm, for different annealing temperature (300,400 and 500^{o}C) respectively. From this result we conclude that the roughness decrease with increasing annealing temperature as it shown in table (3).

Optical Propertie

The optical transmission for CdS/glass thin films before and after annealing for the range (375nm to 900 nm) was studied. The data from transmission spectrum can be used in the calculation of the absorption coefficient (α) for CdS films, according to the following equation *[16]:*

$$a = \frac{1}{d} \ln \frac{1}{T} \text{ ....(6)}$$

where d is the thickness of thin film, and T is the transmission.

In the direct band gap structure or direct transition semiconductors, the absorption coefficient and optical band gap (Eg) are related by *[17]*.

$$a = (hu - Eg)^{1/2} \text{ .....(7)}$$

where *h* is Plank′s constant and ν is the frequency of the incident photon.

We have found that the films have high transmission at long wave lengths approximately (70 – 80 %), and decreasing transmission to (10%) at short wavelengths.

For different annealing temperature and different annealing time of the as-deposited films decreases the optical transmittance and the absorption edge shifts towards lower energy region and becomes much sharper. Figure (4:a,b,c) shows the transmission spectra for different condition of CdS films. Figure (5:a,b) exhibits the variation of the absorption coefficient as a function of wave length for CdS films annealing in different temperature and time. Figure (6:a,b) 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 $(a\,hu)^2$ versus photon energy. The annealed samples show a relative decrease in band gap with both annealing temperature and time, Figure (7: a, b). These results are consistent with other published results *[17]*, which attribute this decrease in the band gap in the annealed samples to the grain size growth.

CONCLUSIONS

CdS thin films prepared by thermal evaporation technique have been characterization using XRD diffraction and optical measurements and deduction to obtain such optical and solid state properties as the T-A spectra, optical band gap energy, the variation of these with incident photon energy/wavelength has been studied. All the films exhibit high transmittance (~80 %), low absorbance and low reflection is the visible/near infrared region from ~500nm to 900nm, thus the films suitable for optoelectronic devices, for instance as window layers in solar cells. The films show a direct transition and the energy gap decreased for both increasing of annealing temperature and annealing time.

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Table (1) summary of deposition conditions

Coating Unit	**INFICON V90**
Materials	**cadmium sulphide powder 99.99%**
Substrates	**glass slides**
Vacuum	**$6x10^{-6}$ torr**
Substrate to film gap	**15 cm**

Table (2): The structural parameters of CdS thin film

CdS Annealing temp. (°C)	2θ (degree)	d(spacing) A°	(B) FWHM	(hkl)	Lattice (a) A°	Grain size(D) nm	Density (δ)x10^{14} lines/m^2	Microstrain(ε) x10^{-3}
300	26.5427	3.35550	0.1961	002	4.13544	41.4537	5.583	3.396
400	26.5477	3.35488	0.1899	002	4.14092	44.9153	4.966	3.290
500	26.5489	3.35470	0.1877	002	4.14439	45.4418	4.842	3.252

Table (3) Values of roughness average with different annealing temp. of CdS thin films

Annealing temp. (°C)	Roughness Average (nm)
300	3.53
400	2.43
500	1.85

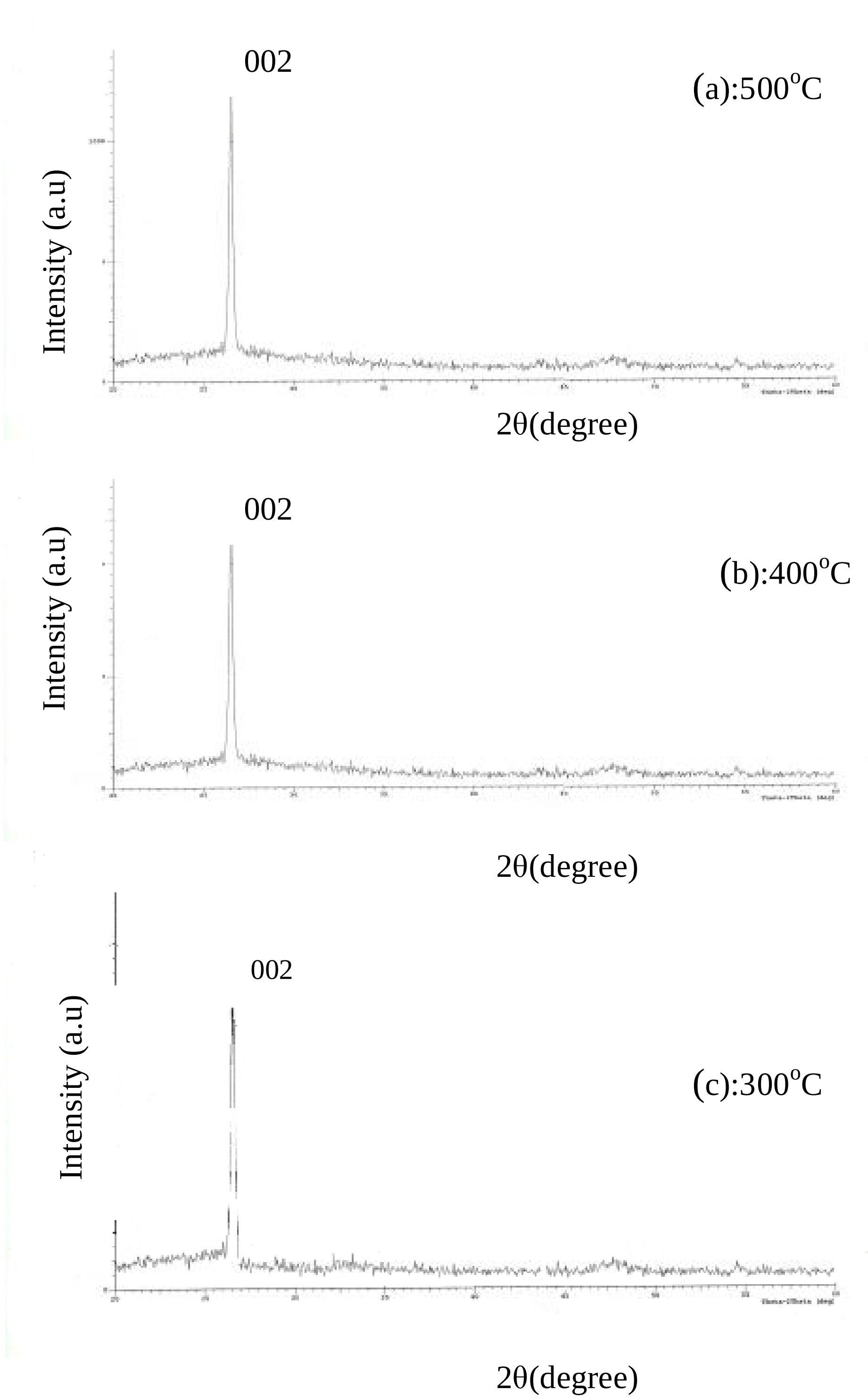

Figure (1:a,b,c) X-Ray diffraction pattern and miller indices of CdS films prepared with different annealing temp.

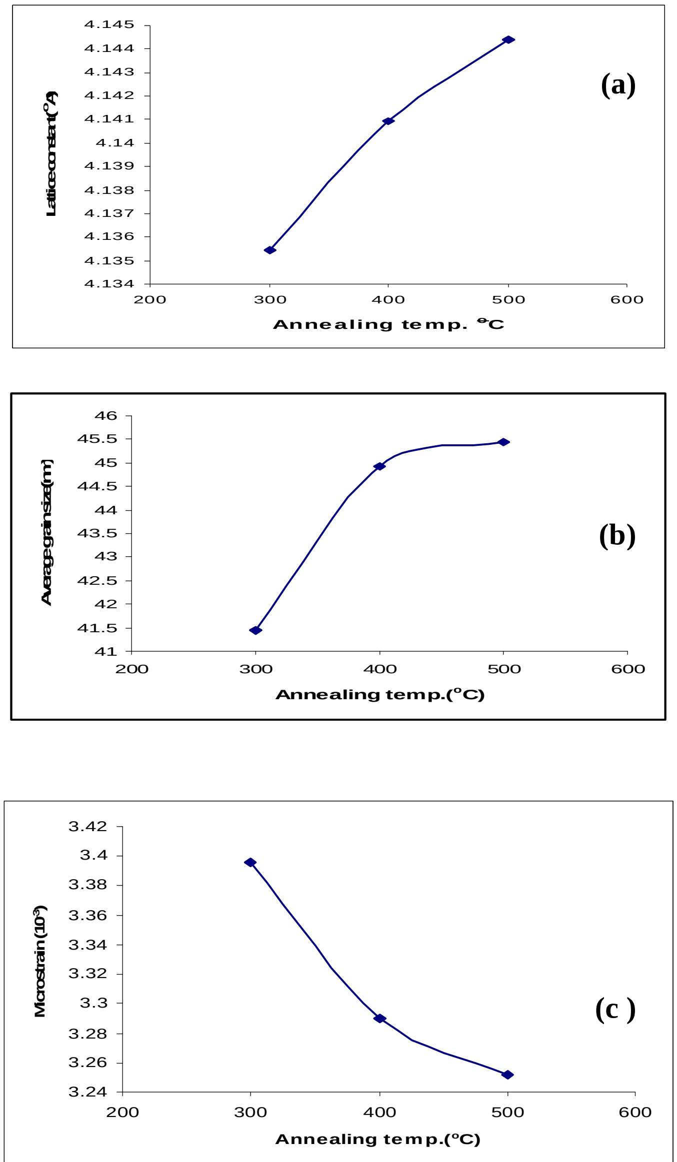

Figure (2). The variation of annealing temp. with (a) Lattice constant . (b) average grain size . (c) Microstarin for CdS films

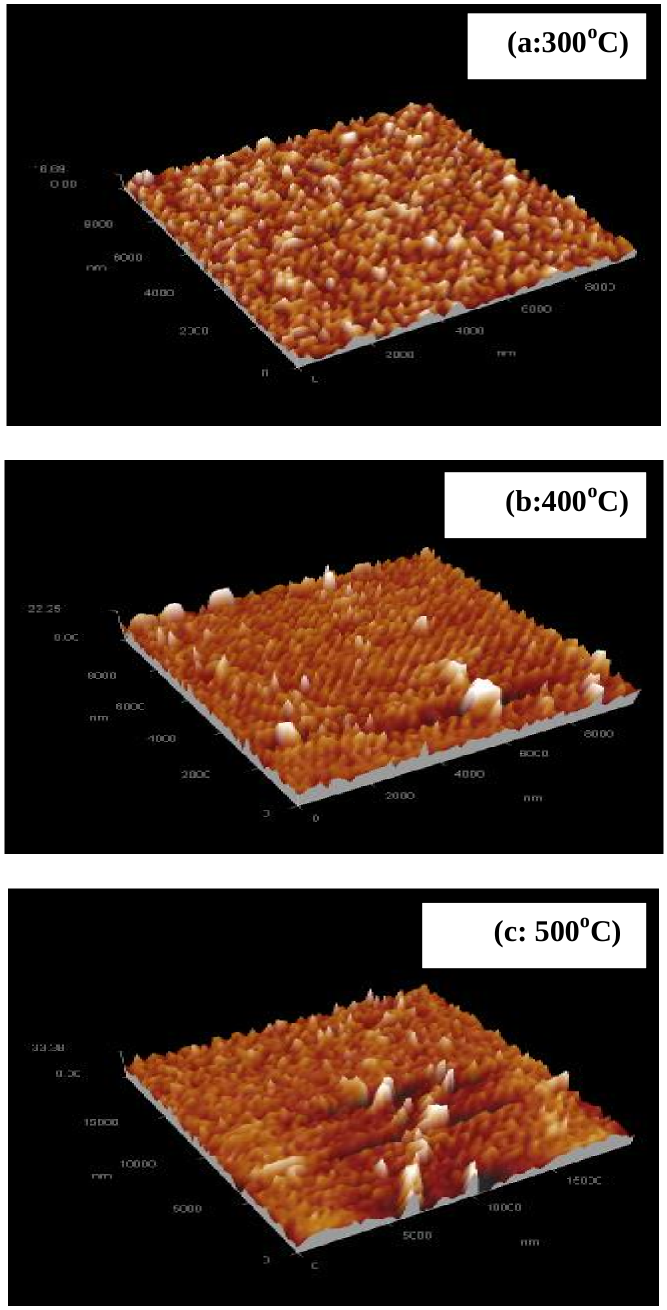

Figure (3) An atomic force micrograph of the surface of CdS films for different annealing temp : (a: 500°C), (b: 400°C), (c: 300°C)

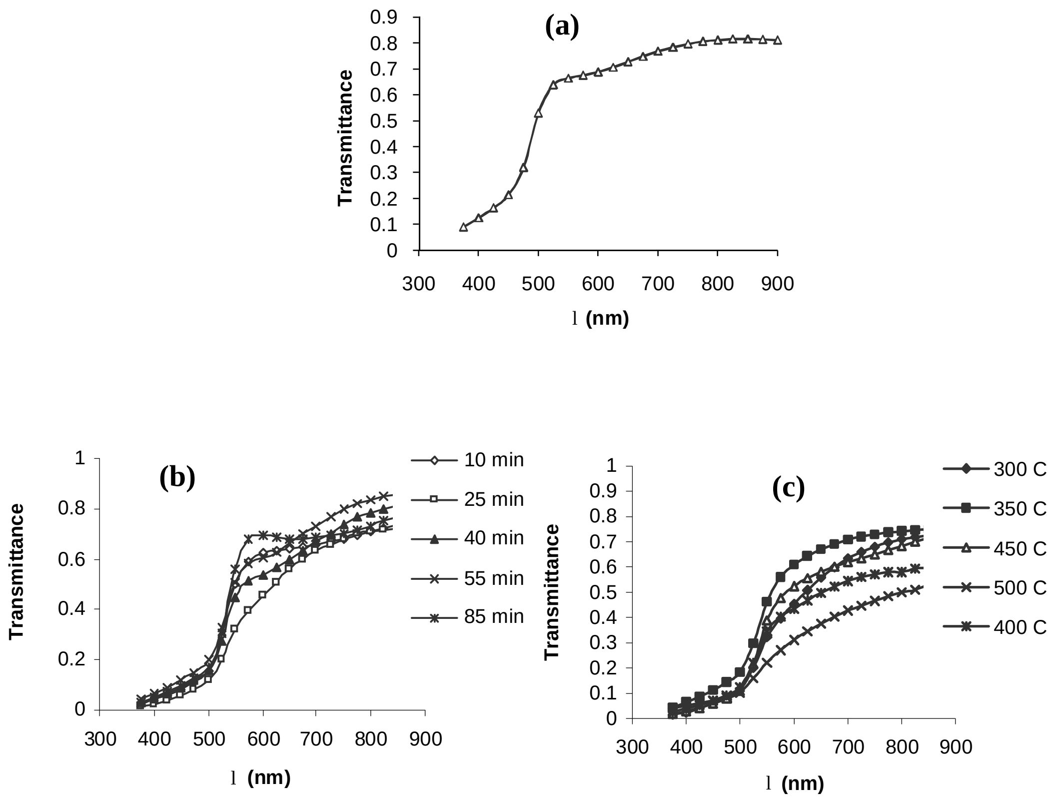

Figure (4) (a, b, c) The optical transmission spectra of CdS films at different conditions. (a) For an annealed films. (b) For different annealing time. (c) Different annealing temperatures.

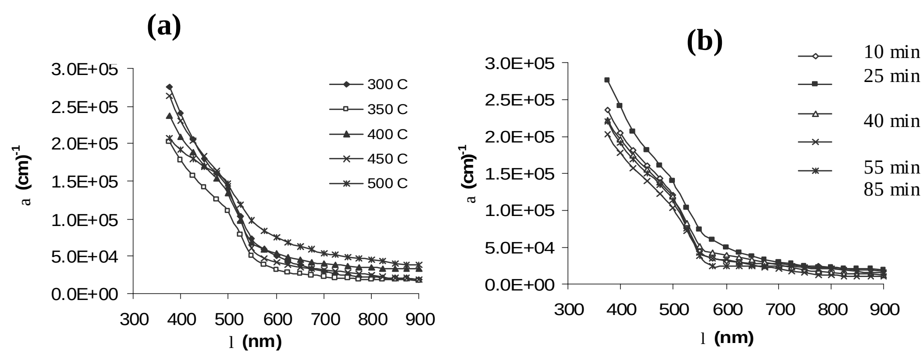

Figure (5) the absorption coefficient as a function of wave length for CdS films for. (a) Different annealing temperatures. (b) Different annealing time

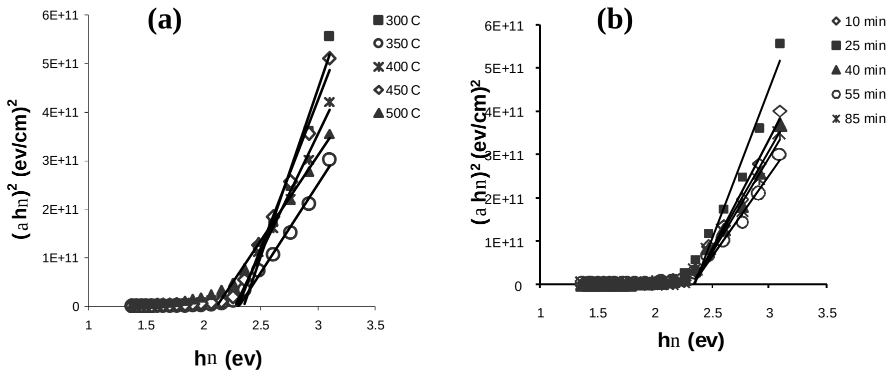

Figure (6) Plot of $(a\,hu)^2$ versus (hu)

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

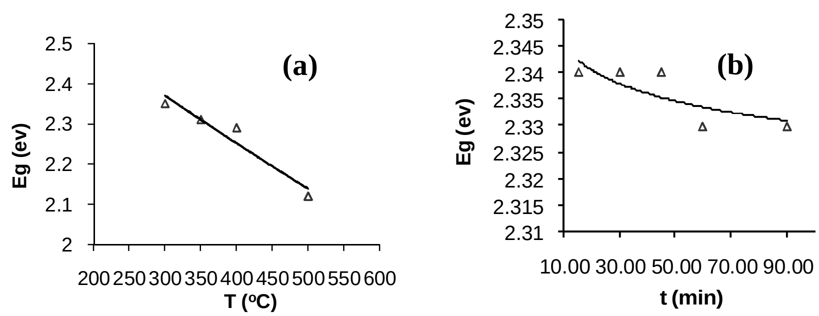

Figure (7) Optical band gap of CdS films at different. (a) Annealing temperatures. (b) Annealing times.