ISO 9001 - 2015

ISSN 2349 - 4891

Monthly

IJRRAS

IF 4.665

Volume 4,Issue 9, September 2017

International Journal of Recent Research and Applied Studies

SURRAGH PUBLICATIONS

SURRAGH PUBLICATIONS

Original Article

ISSN: 2349 - 4891

International
Journal of Recent Research and Applied Studies
(Multidisciplinary Open Access Refereed e-Journal)

Studying of deposit time for CdS thin films prepared by chemical bath deposition (CBD) with two different annealing temperature

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Received 1st August 2017, Accepted 8th September 2017

Abstract

In this papers we worked to find the comparing of deposit time of thin films and find that the films deposited at 60 minutes and 90 minutes it's the best films as compared with 30 minutes and 120 minutes in a structure and the optical properties exception of optical properties transmittance and absorbance. Films transmittance values decreased with increasing of the deposition time, but that's lead to increase in absorbance values. Energy gap depends on thickness and grain size. Films that deposit at 120 min has more thickness than the one at 90 min., 60 min. and 30 min. films. All that after annealing temperature at 400 Cº and 500 Cº . Grain size of films that treated at 500 Cº is greater than the films that treated at 400 Cº. Grain size appears, affected by the increasing of annealing temperature and deposition time.

Keywords: Chemical Bath Deposition, CBD, CdS thin films, cadmium sulfide, band gap, annealing.

Introduction

One of the ideas that studying the material as films (thin films) and that was the first step on the way of semiconductors development studies that contributed after that in many branches. At firstly of 19^{th} century shows the interest of semiconductors [2,3,6]. Studying of this material started to produce many information for us, so that all development in world is a result for semiconductors researching [1] . many researchers studying CdS thin films the main studies of thin films defined it as one or more layers of material atoms, ions or particles product by deposition [4,2], Evaporation or Intensification method on substrate glass made of quartz or silicon or aluminum.etc. According to usage and studies nature . Thickness of filmsdose not overtake one micron or more higher, because of this thickness for those films it's easy to split it,by using a substrate of glass [2,3] . The most important subject today is thin films because it simulate the developments at these days, all of our phones , computers and other devicesare the most development pictures on thin films or in another expression it's the development step of thin films , all of that's devices was born from thin films and the experiments of thin films and in another side it considered an applications of thin films [8]. There are many different methods to prepare thin films as many as applications of thin films. In here thin films preparing methods will be classified according to using temperature [5]. The first methods that need a high temperature for preparing thin films and seconds methodsis films that doesn't require a high temperature. Methods that require high temperature to prepare thin films are (Spry pyrolysis, Chemical vapor deposition (CVD) and Vacuum evaporation reaction), Methods that required low temperature to prepare thin films are (Chemical Bath Deposition (CBD), Hydrothermal and Solvothermal) [5]. CBD became the most famous method because of the ability to deposit films on large substrate and large scale deposition, because of low requirements for low temperature methods, for what mentioned above the ability to deposited films on polymer substrates so CBD doesn't required a sophisticated instrumentation[6]. The chemical bath deposition (CBD) method appears to be a relatively simple method to prepare homogenous films with controlled composition [11]. The most element used in chemical bath deposition to prepare films is cadmium , lead and zinc [6]. And that back to low cost of group II-VI semiconductors [9]. CdS has a wide direct band gap (2.42 eV) and so it has been used as a window material together with several semiconductors such as CdTe,Cu_2S and CuInSe [10].

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Experimental

CBD needs a low temperature degree to prepare and deposit thin films with all materials, the most elements that prepared by chemical bath deposition is cadmium and zinc including all dioxides of them and salts. CdS thin films prepared in lab at (**0.2 M**) all of cadmium chloride (**$CdCl_2$**) as a source of cadmium and thiourea (**$CS(NH_4)$**), with (**1.5 M**) ammonium nitrate (**NH_4NO_3**) and potassium hydroxide (**KOH**) at a concentration (**0.5 M**) as a complexing agents[7], all of them in 400 ml of deionized water in a beaker and heated of 80 C°. Glass substrate cleaned with alcohol and deionized water also with ultra-sonic wave, the substrate immerse in solution with 80 C°. Duration of deposition is 30 minutes for the first samples, second samples will be deposited at 60 minutes until arrived to 120 minutes. Chemically the best deposition happen when **pH = 10 – 11** at this work pH was**10.5**, pH meter measure the reaction pH. Mixing procedure has the main role in forming final solution grain size and that means controlling the films grain size. Ammonium nitrate in solution to control pH and save it on the required level. The concentration of potassium hydroxide is so important in deposition procedure that saved the best environment for metal ions in the solution, the complexing agents saved pH in solution on 10.5 to guarantee best deposit films. Mixing process in this methods that according to compounds in reaction specially when any ammonium in reaction as a complexing , some of ways that mixing compounds give us a large grain size as a resulting of deposit films , mixing thiourea directly to cadmium chloride given that results . Separation process of metals and chalcogenides is best way for homogenous solution with small grain size and that we know it a according to experimental . Before films draying on a heat air or leaved dray alone, applying an annealing temperature 400 C° and 500 C° .

Result and discussion

Tests shows the influence of time deposition of samples thickness and effected of time deposition on structural of CdS thin films and grain size of films.

1. Structural properties

X-Ray diffraction test show a lot of phases appear in samples that deposit at 60 and 90 minutes while it decreased at samples deposit at 30 and 120 minutes . The dominate phases at samples is Wurtzite (hexagonal) , (orthorhombic) then zinc-blend (cubic) , and show the prefer growth directions (100 , 011 , 110 , 101) . The ICDD's numbers that has been adopted (42-1411, 21-0829, 43-0985, 41-1049) [12,13,14,15] . D-value calculation for all samples and compare it with standard values by using equation (2) . Crystalline size D (nm) also determined by using Scherer formula equation (1) :

$$D = \frac{0.9\ \lambda}{\beta\ \cos\theta} \quad \dots\dots\dots\dots\dots (1)$$

$$d = \frac{\lambda}{2\sin\theta} \dots\dots\dots\dots\dots (2)$$

All structural results (XRD) are arrange in a table (1) & (2) that illustrate all d-spacing and D Crystalline size for all samples , in X-Ray diffraction use λ = 1.5406 Å CuKa radiation source .

as seen in figures and structural calculations of XRD , can say when annealing temperature increase , the crystalline size increasing too , time deposition influenced at films and controlled in phases appearing , when time deposition increased phases be less in films structure , the best deposit time is 90 min. because it have the best Nanocrystalline (crystalline size) also its the best homogenously films at that time.

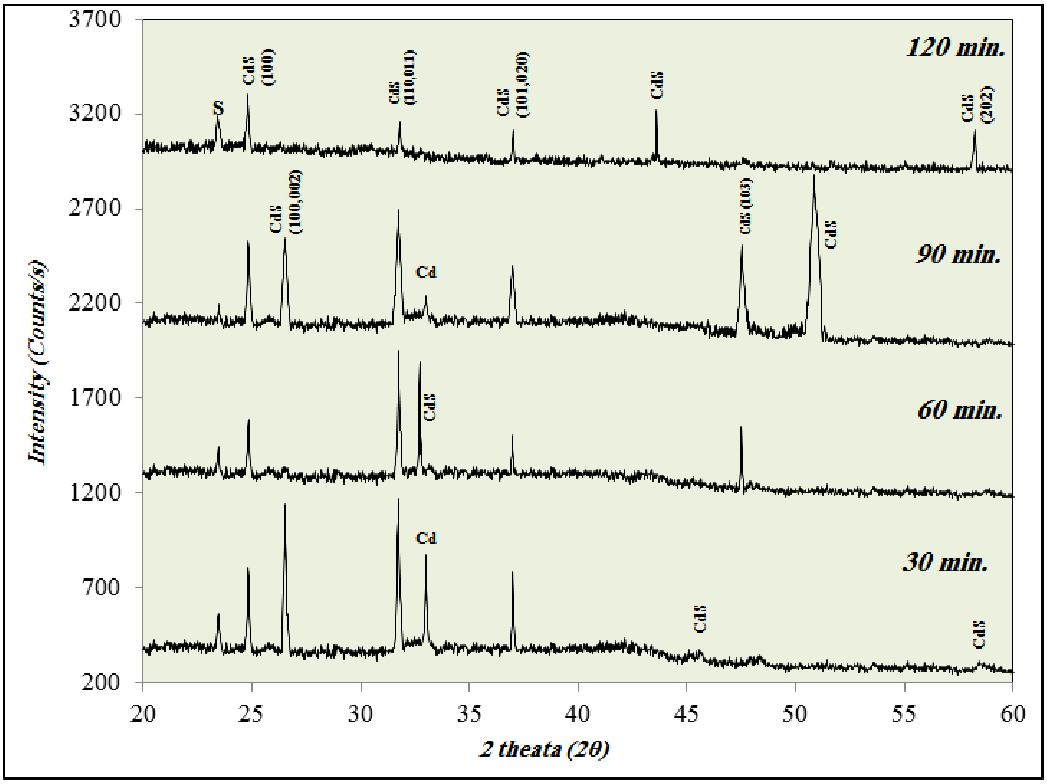

Figure I
XRD form of CdS thin films for samples annealed at 400 C°

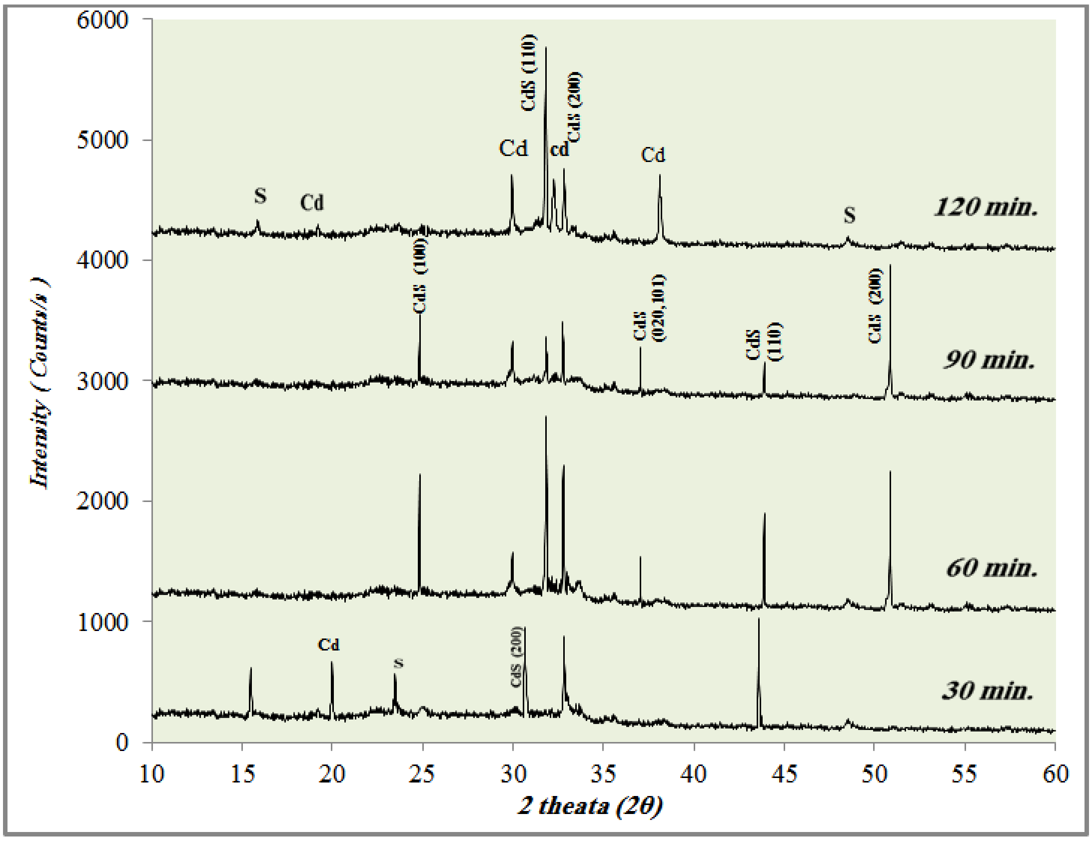

Figure II
XRD form of CdS thin films for samples annealed at 500 C°

Table 1
XRD calculation of CdS thin films samples annealed at 400 C° .

Time Deposition	**2(theta) deg.**	**dhkl Exp. (Å)**	**D (C.S. (nm))**	**phase**
30 minutes	24.8	3.590093955	56.84288425	hexagonal
	26.5	3.363519569	48.36998786	hexagonal , cubic
	31.7	2.822643748	40.53322588	orthorhombic
	37	2.429589306	47.82056712	orthorhombic
	45.7	1.985270309	21.50857204	orthohombic
	58.2	1.585161251	16.12787746	hexagonal
60 minutes	24.8	3.590093955	28.36822402	hexagonal
	31.7	2.822643748	20.61011485	orthohombic
	32.7	2.738573802	31.4000389	cubic
	37	2.429589306	47.82056712	orthohombic
	47.8	1.902840945	43.43463652	hexagonal
90 minutes	24.8	3.590093955	49.90323197	hexagonal
	26.5	3.363519569	46.56434309	hexagonal
	31.7	2.813995469	43.64553187	orthohombic
	37	2.429589306	33.87612065	orthohombic

	47.8	1.902840945	47.74949339	hexagonal
	50.8	1.797288075	23.91363412	hexagonal
120 minutes	24.8	3.590093955	142.8862652	hexagonal
	31.7	2.822643748	91.87531198	orthohombic
	37	2.429589306	91.46921999	orthohombic
	43.6	2.075893296	174.1208574	hexagonal
	58.2	1.585161251	108.752378	hexagonal

Table 2

Structural calculation of CdS thin films sample annealed at 500 Cº

Time Deposition	*2(theta) deg.*	*dhkl Exp.(Å)*	*D (C.S. (nm))*	*Phase*
30 minutes	24.8	3.590093955	53.14839039	hexagonal
	30.66	2.915975762	53.73216475	cubic
	32.7	2.730452724	30.72933499	cubic
	43.6	2.076346324	57.81083224	hexagonal
60 minutes	24.8	3.590093955	54.29678077	Hexagonal
	31.8	2.813995469	51.69267681	Orthohombic
	32.7	2.738573802	50.24006225	Cubic
	37.02	2.428322672	83.88216941	Orthohombic
	43.9	2.062401032	57.55534107	Cubic
	50.8	1.797288075	51.79411813	Hexagonal
90 minutes	24.8	3.590093955	48.20844305	Hexagonal
	31.8	2.813995469	39.99688375	orthorhombic
	32.7	2.738573802	41.04722948	cubic
	37	2.429589306	44.59848596	orthorhombic
	43.6	2.075893296	53.0402858	Hexagonal
	50.8	1.797288075	63.54278097	Hexagonal
120 minutes	31.85	2.809691972	143.93213446	orthorhombic
	32.7	2.738573802	105.14168843	cubic

AFM (Atomic Forces Microscopy) using (AA-3000 Scanning Probe Microscope). shows samples that deposit at 90 min. it's the best deposit time and samples annealed at 400 Cº is best annealing temperature , because it show low Grain size and suitable roughness for all samples annealed at 400 Cº . Table (3) will illustrate average grain size values , roughness average and root mean square . and figure (3) (a),(b),(c) and (d) show samples atomic structure for 400 Cº.

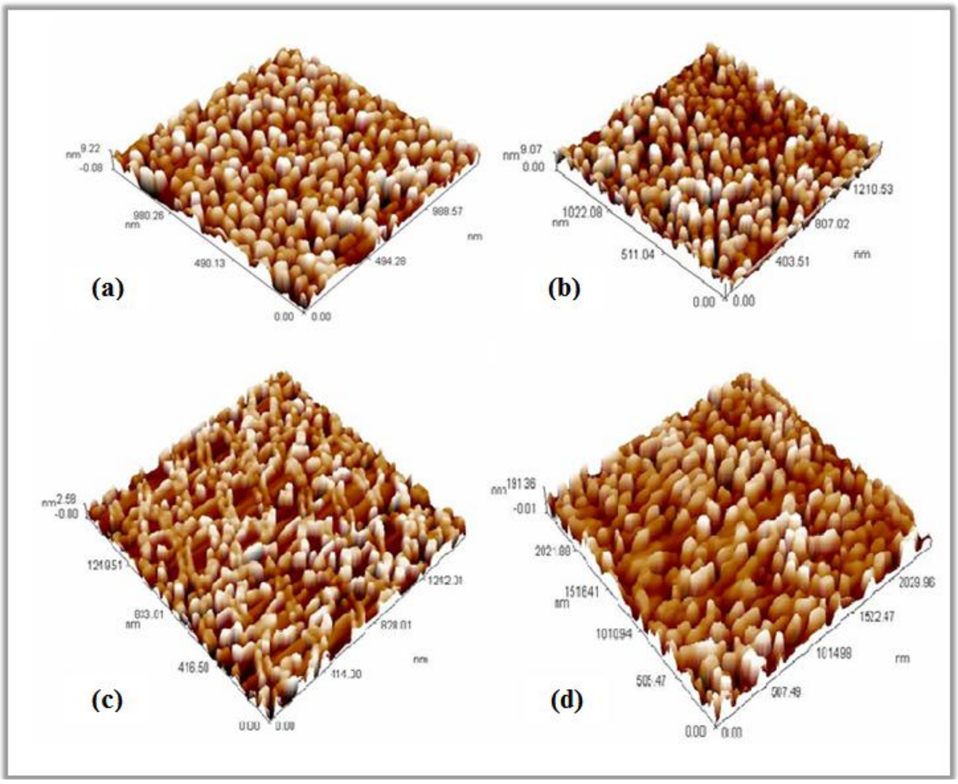

Figure III
AFM tests for 400 Cº annealing temperature for CdS thin films for all deposit times. (a) 30 min. , (b) 60 min. , (c) 90 min. and (d) 120 min. .

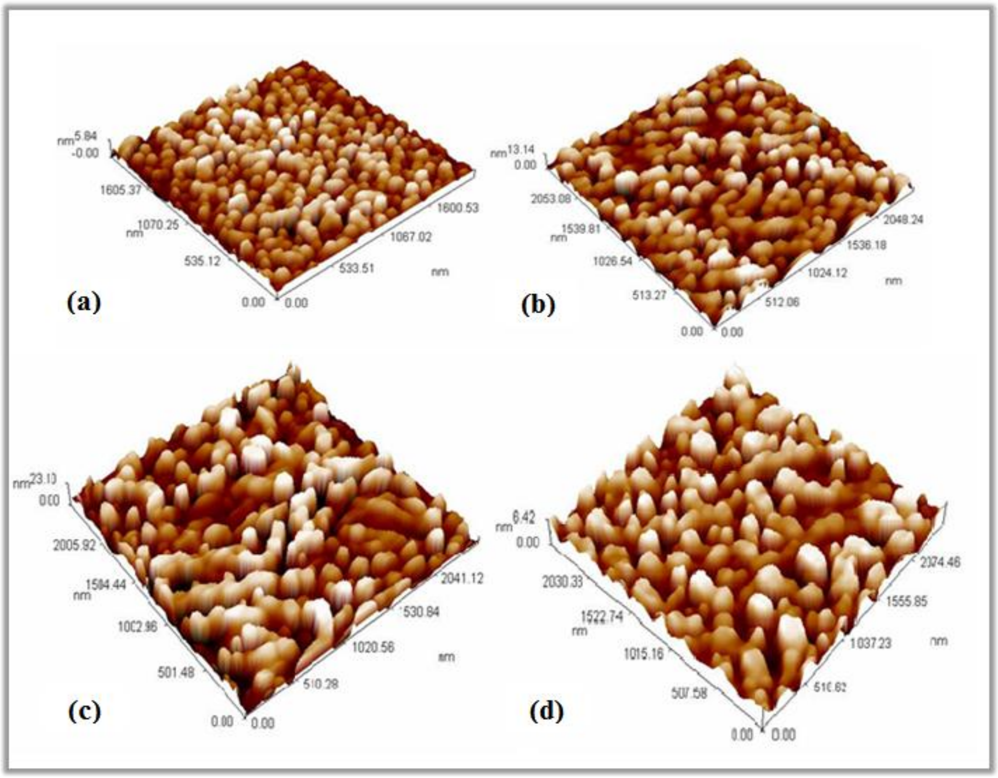

Figure IV
AFM tests for 500 Cº annealing temperature for CdS thin films for all deposit times . (a) 30 min. , (b) 60 min. , (c) 90 min. and (d) 120 min..

From above figures explained average dimeter size and grain size before see table (3) that illustrate average dimeter size (nm) , roughness average (nm) and root mean square , in time deposit 30 minutes grain size seen a small size comparing with 120 minutes in annealing at 500 C° , and all samples it's like a sequence , while in 400 C° it's difficult to explain without return to all values in table (3) . According to the table show down samples annealed at 400 C° begin with average dimeter size about (57.25 nm) until 120 minute average dimeter size (77.53 nm) , while at degree of 500 C° , average dimeter size of 30 minutes (90.9 nm) and for 120 minutes (126.86 nm) . As shown at all AFM tests that the trend of growth is towards the top , and that let a groove also it in regular growth and that useful of photoconductivity and detectors and sensors and solar cells that made of CdS thin films. for compared samples with regard to time deposit can take one annealing temperature degree and compare them with each other , find that differences between them and show clear that increasing of time deposit followed by increasing in grain size.

Table 3

AFM Values of CdS thin films according annealing temperature and times deposition

Annealing Temperature	*Time Deposition*	*Average dimeter size (nm)*	*RoughnessAverage (nm)*	*Root Mean Square (nm)*	*size (nm)*
400 C°	30 minutes	57.25	2.21	2.56	1470-1483
	60 minutes	67.85	2.28	2.63	1533-1614
	90 minutes	68.79	0.829	0.975	1624-1660
	120 minutes	77.53	37.8	45.3	2527-2537
500 C°	30 minutes	90.9	1.17	1.39	2134-2140
	60 minutes	98.05	2.76	3.27	2560-2566
	90 minutes	102.69	5.78	6.67	2507-2551
	120 minutes	126.86	1.41	1.65	2538-2593

2. Optical properties :

All optical tests done by (UV-3000 Nano) . Observed all optical calculations that transmittance and absorbance of films As expected sequent ratio , figures down shows results of both transmittance and absorbance films that annealing at 400 C° and 500 C° . Transmittance and absorbance shows similarity almost of both temperature annealing degree . So that showing them for one degree and there isn't higher difference between 400 C° and 500 C°.

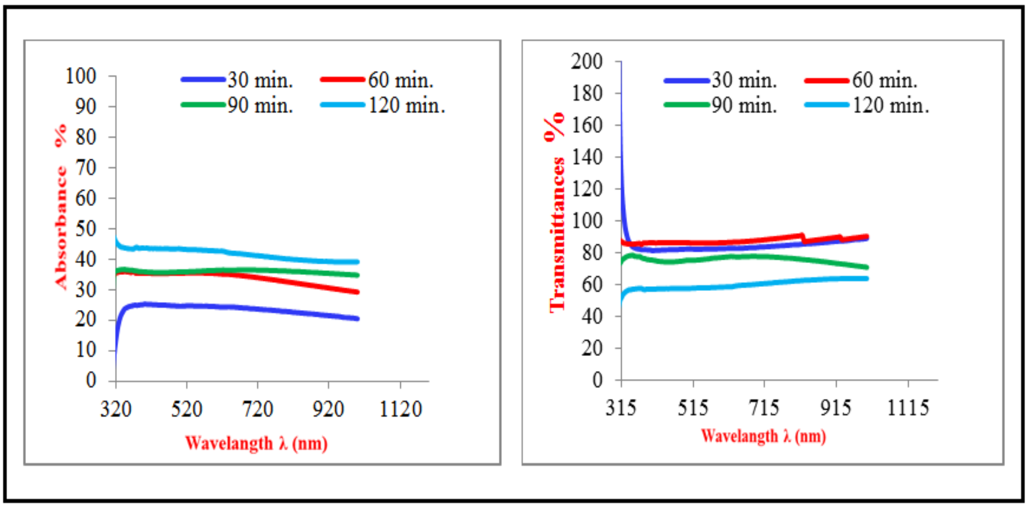

Figure V

Transmittance ratio of CdS thin films annealing at 400 C°

Results of absorption coefficient (α) was Slightly higher for samples that annealing at 500 C° then samples at 400 C° , when measured thickness of samples all calculation be clear thickness approximate similarity values . Figure (6) will illustrate the little difference values of absorption coefficient , in it (a) indicate samples annealing at 400 C° , while (b) show films annealing at 500 C° , and because the similarity of thickness for all films (approximately) that prepared through same solution and the same condition cannot see clear difference right know and that slightly difference is a precision difference as long as there isn't found high value thickness , so here that is as explanation because influence of annealing . Extinction coefficient (K) in figure (7) (b) show relatively higher at 500 C° that is annealing temperature decreasing extinction coefficient increasing , and also it dependent on thickness films because of (K) dependent on (α) .

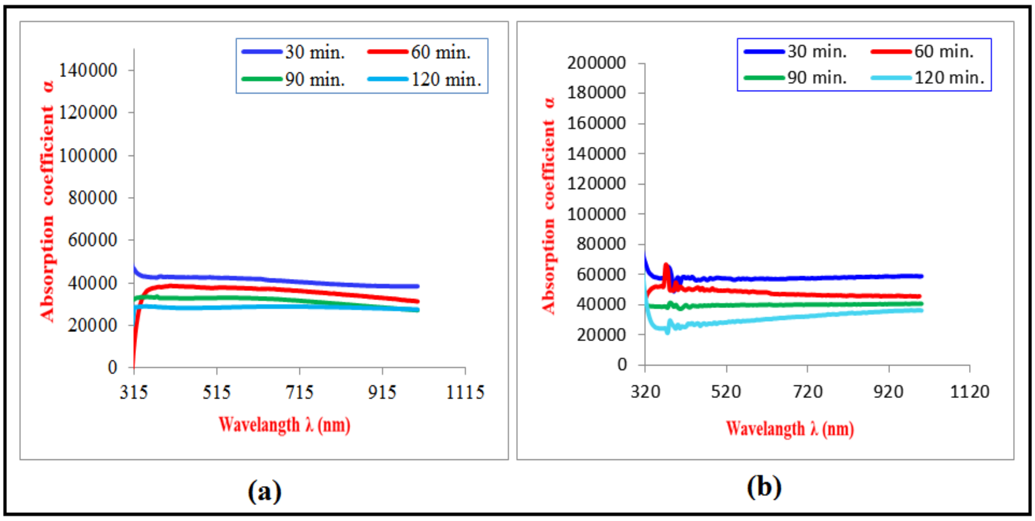

Figure VI
Absorption coefficient (α) of CdS thin films
(a) annealing at 400 C°. (b) annealing at 500 C°.

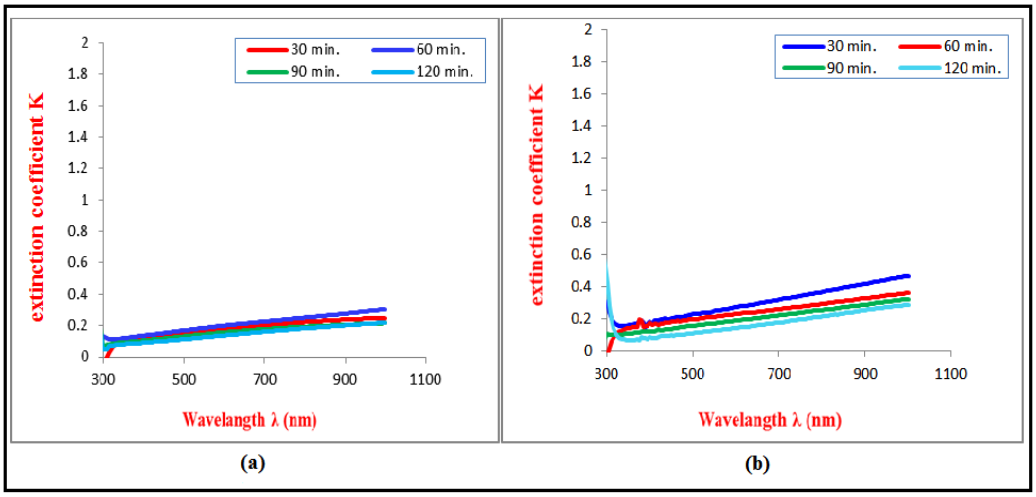

Figure VII
Extinction coefficient (K) of CdS thin films
(a) annealing at 400 C°. (b) annealing at 500 C°.

Energy gap or band gap (Eg) of CdS thin films shows clear difference of both annealing temperature degree, the eighth figure its improved figure for easy to discover values of Eg and that mean is not modified figure , had to edit it to show the real and accurate values to be clear for other , time deposition shows an a large grain size a sequent of thickness and sequent of grain size as coming in structural properties. Generally samples that annealed at 400 C° higher then samples annealed at 500 C° and that because higher annealing temperature lead to increasing in grain size and that causes low energy gap (Eg). the next table show the values of band gap.

Table 4

Values of energy gap of two annealing temperature and times deposition of CdS thin films .

	30 min.	***60 min.***	***90 min.***	***120 min.***
400 Cº	2.47 eV	2.34 eV	2.42 eV	1.92 eV
500 Cº	2.30 eV	2.22 eV	2.15 eV	1.78 eV

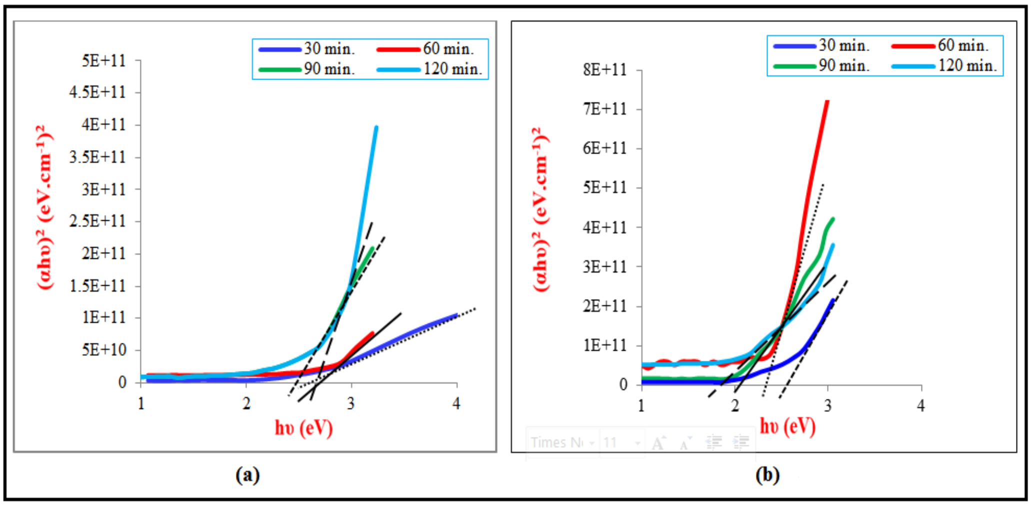

Figure VIII

Energy gap of CdS thin films four times deposition and (a) annealed at 400 Cº . (b) annealed at 500 Cº .

Conclusions

From all above find; increasing at deposition time lead to increasing in films thickness and that lead to decreasing at absorption coefficient, increasing in time deposition lead to low energy gap or band gap , also increasing at time deposition mean less transmittance and high absorbance. When thickness of CdS thin films increased that mean increasing in refractive index. Time deposition decreasing meaning small grain size. increasing at time deposition causes increasing at roughness surface of the films.

Annealing temperature makes films less thick and that what observed when we measured tow films before annealing them at two different degree and that mean corresponds increasing at annealing temperature decreasing at thickness films. Also when annealing temperature increasing the grain size increasing too, also seen decreasing at band gap as a resulting of high annealing temperature.

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