Research Paper Engineering

Structural and Optical Properties of Cds Thin Film Before and After Annealing for Different Thickness of Cds Films Grown by Pulsed Laser Ablation

Shatha S. M. Al – azzawi | Baghdad University, Physics Department

ABSTRACT

The thin films of CdS were deposited on glass substrates using pulsed laser deposition (PLD). The search had included studying some of the structure and optical properties of CdS thin film before and after annealing for different thickness of CdS films. The film properties were determined using a X-ray diffraction (XRD). The effect of the annealing treatment on the structural and optical properties on the film quality investigated. The results of X-ray examination showed that there was two phases before annealing but after annealing we got only one type, also the grain size increases that indicated that the films began approaching the crystalline structure. the X-ray diffraction patterns were seen to sharpen by annealing.
The measurement of the transmittance spectra within the range of wavelength of (300-1100) nm. It was found the transmittance increase after annealing and also the energy gap decreases with annealing from (2.49) to (2.175) as an average.
The average roughness of CdS thin films increas with increasing thickness, and mostly the grain size increas with increasing thickness.

KEYWORDS CdS, pulsed laser ablation, effect of thickness and the annealing temperature on structural and optical properties of the films.

1- Introduction

Thin films represent a prominent place in the applied research of solid state physics, where it is possible to know the physical and chemical characteristics that can not be studied in some bulk cases [1].

Cadmium sulfide is the inorganic compound with the formula CdS. Cadmium sulfide is a yellow solid[2][3] It occurs in nature with two different crystal structures as the rare minerals greenockite and hawleyite, but is more prevalent as an impurity substituent in the similarly structured zinc ores sphalerite and wurtzite, which are the major economic sources of cadmium.

Cadmium sulfide has, like zinc sulfide, two crystal forms; the more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blended structure (found in the mineral Hawleyite). In both of these forms the cadmium and sulfur atoms are four coordinate. There is also a high pressure form with the NaCl rock salt structure[4].

Cadmium sulfide is a direct band gap semiconductor (gap 2.42 eV). The magnitude of its band gap means that it appears colored[5].

CdS and cadmium selenide are used in manufacturing of photo resistors (light dependent resistors) sensitive to visible and near infrared light.

In thin-film form, CdS can be combined with other layers for use in certain types of solar cells[6]. CdS was also one of the first semiconductor materials to be used for thin-film transistors (TFTs)[7].

Thin films of Cadmium Sulfide can be piezoelectric and have been used as transducers which can operate at frequencies in the GHz region.

2- Theory:

2-1 Structural Properties

X-ray diffraction and determine the crystalline structure of the prepared thin film using X-ray diffraction instrument with the specifications of source Cu-Kα and wavelength of 1.54050 Ao. The spacing of the planes, dhkl, is the interplanar spacing (in Angstrom) calculated using Bragg's law equation (1) [8].

$$Sin \quad \theta \quad = \quad \lambda \quad / \quad 2 \quad d_{hkl} \qquad (1)$$

The distance between two lattices (d) can be determined from the angle that the reflection occurs is the Bragg's law equation.

The particle diameter was calculated by using Scherrer's equation (2) [9].

$$D \quad = \quad K \quad \lambda \quad / \quad \beta \quad \cos \quad \theta \qquad (2)$$

Where D is the grain (G.S),K constant equal to (0.94), λ is the wavelength of CuKα (the source of radiation was CuKα) equal to (1.5406Ao), Θ is the Bragg's angle, B full width at half maximum (in radian) of the peak.

2-2 Optical properties

Investigation of the optical properties for semiconductor are the most important source of information on the electronic band structure , type of the transition , permittivity , and other properties of semiconductor [10].

The optical properties of a semiconductor are related to intrinsic effect. Based on the intrinsic location of the top of the valence band (V.B) and the bottom of the conduction band (C.B) in the band structure, the electron–hole pair generation occurs directly or indirectly[11].

Optical Absorption and Absorption Edge

The absorption depends on the photon energy (hν); where h is Plank's constant, ν is the incident photon frequency, The maximum wavelength (λ) of the incident photon which creates the electron–hole pair defined as equation (3)[12].

$$\lambda c(\mu m) = \frac{hc}{E_g} = \frac{1.24}{E_g(eV)} \qquad (3)$$

The intensity of the photon flux decreases exponentially with distance through the semiconductor according to the following equation (4)[12].

$$I = I_o \exp(-\alpha t) \quad (4)$$

Where I_o is the incident light intensity, I is the transmitted photon intensity, t is the thickness of the film, α is the absorption coefficient, which is defined as the relative number of the photons absorbed per unit distance of semiconductor.

Direct Transitions

The direct transition in general occurs between top of valence band and bottom of conduction band (vertical transition) at the same wave vector Δk = 0 for conservation of momentum. The allowed direct transition refers to that transition which occurs between top of the valence band and bottom of the conduction band when the wave vector equal to zero (k = 0)

This transition is described by the following relation (5)[11]:

$$\alpha h \nu = B (h \nu - E_g)^{1/2} \quad (5)$$

where B is inversely proportional to amorphousity.

Optical Constants

The optical constants are very important parameters because they describe the optical behavior of the materials. The absorption coefficient of the material is a very strong function of the photon energy and band gap energy. Optical constants included refractive index (n), extinction coefficient (k), and real (εr), and imaginary(εi)parts of dielectric constant.

The refractive index value can be calculated from the formula (6)[13]:

$$n = \left(\frac{4R}{(R-1)^2} - k^2 \right)^{1/2} - \frac{(R+1)}{(R-1)} \quad (6)$$

R is the reflectance, and can be expressed by the relation (7) [14]:

$$R = \frac{(n-1)^2 + k^2}{(n-1)^2 + k^2} \quad (7)$$

The extinction coefficient, which is related to the exponential decay of the wave as it passes through the medium, is defined as relation (8) [15]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (8)$$

λ is the wavelength of the incident radiation and α is given by equation (9)[13]:

$$\alpha = 2.303 \frac{A}{t} \quad (9)$$

A is the absorbance.

The real and imaginary part of dielectric constant can be calculated by using the following equations (10),(11),(12)[16]:

$$(n - ik)^2 = \varepsilon_r - i\varepsilon_i \quad (10)$$

where

$$\varepsilon_r = n^2 - k^2 \quad (11)$$

and

$$\varepsilon_i = 2nk \quad (12)$$

3- Experimental work

High purity (99.99%) cadmium oxide powder was used as a source for deposition of CdS films on soda lime glass substrates (2.5x6) cm2 using pulsed laser ablation. The glass substrate were first treated with detergent and washed in running water and alcohol its concentration is 96% respectively. The substrates then dried with a fine tissue paper and cleaned with isopropyl alcohol (IPA) in an ultrasonic cleaner. All the films were deposited by Nd:YAG pulsed laser of 100J and a pulse duration of 10ns by a coating unit. The source to substrate distance is 1cm.

Film thickness measurements by optical interferometer method have been obtained . This method is based on interference of the light beam reflection from thin film surface and substrate bottom, with error rate at 3% . He-Ne laser (632 nm) was used and the thickness was determined using the formula[17]:

$$d = \Delta x/x \times \lambda/2$$

Where x is the fringe width, Δx is the distance between two fringes and λ wavelength of laser light. Thickness of sample (1) = 128nm, sample (2) = 314nm, sample (3) = 470nm,sample (4) = 815nm.

A vacuum of $4x10^{-1}$ mbar was maintained in the chamber during deposition. The substrate temperature during deposition was at room temperature (273)K. The annealing process done for all samples 493K, time for annealing for all samples 1 hr. The structures of the prepared thin films were obtained using the X-ray diffraction (XRD) techniques. The X-ray diffract meter type (Philips) was used with the following features, Source $Cu_{K\alpha}$, current 20mA, voltage 40kV and wavelength 1.5405 A.

The optical transmission spectra of the deposited thin films were measured by UV-VIS spectrophotometer, the optical properties was calculated as a function of the photon energy at the wave length in the range 190-1100 nm.

Surface topography was studied by using atomic force microscopy (AFM) using (Scanning probe Microscope type AA3000), supplied by Angstrom Advanced Inc. to determine the nano spikes dimensions range of the prepared thin CdS films deposited on glass substrate and their statistical distribution.

2- Results and discussion

Structural properties of CdS films (X-ray diffraction pattern)

The CdS films prepared by pulsed laser method, were uniform, and strongly adherent to the films. Figure (1) shows that the structure of sample (1) CdS thin films are amorphous before and after annealing.

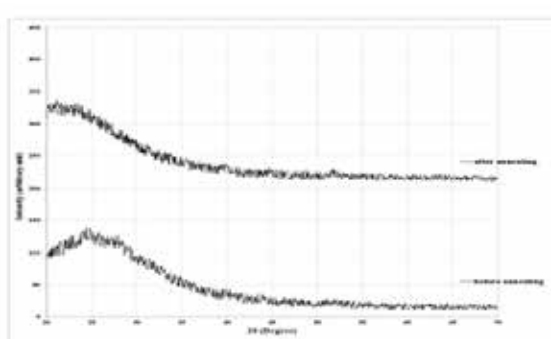

Fig. (1) X-ray diffraction patterns 0f sample (1) CdS thin films deposited on glass substrate before and after annealing temperature.

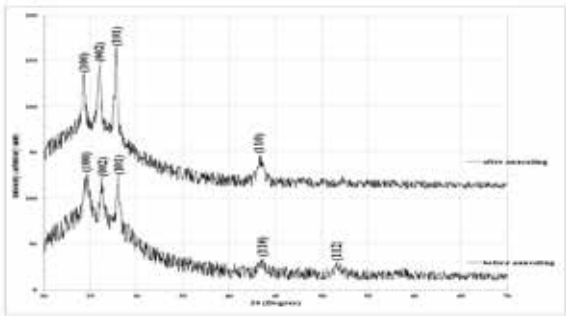

Fig. (2) X-ray diffraction patterns 0f sample (2) CdS thin films deposited on glass substrate before and after annealing temperature.

Table (1) Structural parameters (2Θ, FWHM, dh_{kl}, G.S, hkl) for sample (2) CdS thin before and after annealing temperature.

	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp. (Å)	G.S (nm)	d_{hkl} Std. (Å)	hkl
	24.6451	0.734	3.6094	11.1	3.5940	(100)
Before	26.2725	0.491	3.3894	16.6	3.3685	(002)
annealing	28.0244	0.470	3.1814	17.4	3.1710	(101)
	43.5978	0.724	2.0743	11.8	2.0750	(110)
	51.6208	0.916	1.7692	9.6	1.7667	(112)
	24.2943	0.432	3.6607	18.8	3.5940	(100)
after	26.0027	0.411	3.4240	19.8	3.3685	(002)
annealing	27.7972	0.421	3.2069	19.4	3.1710	(101)
	43.3810	0.731	2.0842	11.7	2.0750	(110)

From figure (2) and Table (2) it can be observed for the films of thickness 128nm that peaks at 2θ = (24.6451, 26.2725, 28.0244, 43.5978,and 51.6208) degree appeared which correspond to diffraction from C(100), C(002), C(101), C(110), C(112) before annealing. And 2θ = (24.2943, 26.0027, 27.7972 and 43.3810) degree appeared which correspond to diffraction from C(100), C(002), C(101), C(110) after annealing.

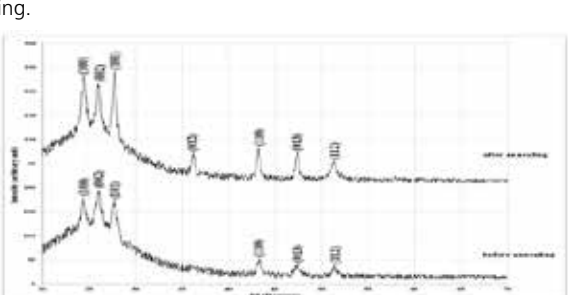

Fig. (3) X-ray diffraction patterns 0f sample (3) CdS thin films deposited on glass substrate before and after annealing temperature.

Table (2) Structural parameters (2Θ, FWHM, d_{hkl}, G.S, hkl) for sample (3) CdS thin before and after annealing temperature.

	2θ (Deg.)	FWHM (Deg.)	dhkl Exp.(Å)	G.S (nm)	dhkl Std.(Å)	hkl
	24.4054	0.544	3.6443	14.9	3.5940	(100)
	26.0408	0.507	3.4190	16.1	3.3685	(002)
Before	27.7610	0.590	3.2110	13.9	3.1710	(101)
annealing	43.3475	0.594	2.0857	14.4	2.0750	(110)
	47.4177	0.731	1.9157	11.9	1.9045	(013)
	51.4113	0.586	1.7759	15.1	1.7667	(112)
	24.433	0.519	3.6402	15.7	3.5940	(100)
after	26.043	0.503	3.4188	16.2	3.3685	(002)
annealing	27.758	0.458	3.2113	17.9	3.1710	(101)
	36.206	0.438	2.4790	19.1	2.4577	(012)
	43.219	0.435	2.0916	19.7	2.0750	(110)
	47.388	0.454	1.9169	19.1	1.9045	(013)
	51.313	0.740	1.7791	11.9	1.7667	(112)

From figure (3) and Table (2) it can be observed for the films of thickness 128nm that peaks at 2θ = (24.4054, 26.0408, 27.7610, 43.3475, 47.4113and 51.4113) degree appeared which correspond to diffraction from C(100), C(002), C(101), C(110), C(013), C(112) before annealing. And 2θ = (24.433, 26.043, 27.758 , 36.206, 43.219, 47.388 and 51.313) degree appeared which correspond to diffraction from C(100), C(002), C(101), C(012), C(110), C(013), C(112) after annealing.

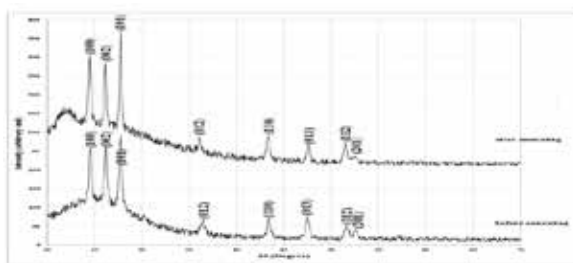

Fig. (4) X-ray diffraction patterns 0f sample (4) CdS thin films deposited on glass substrate before and after annealing temperature.

Table (3) Structural parameters (2Θ, FWHM, d_{hkl}, G.S, hkl) for sample (4) CdS thin before and after annealing temperature.

	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp. (Å)	G.S (nm)	d_{hkl} Std. (Å)	hkl
	24.5480	0.3303	3.6235	24.6	3.5940	(100)
	26.1730	0.3120	3.4021	26.2	3.3685	(002)
Before	27.7386	0.3245	3.2135	25.2	3.1710	(101)
annealing	36.3967	0.5861	2.4665	14.3	2.4577	(012)
	43.4220	0.4216	2.0823	20.3	2.0750	(110)
	47.4913	0.4408	1.9129	19.7	1.9045	(013)
	51.6518	0.4312	1.7682	20.5	1.7667	(112)
	52.6005	0.3003	1.7385	29.5	1.7363	(201)
	24.4725	0.3230	3.6345	25.2	3.5940	(100)
	26.1181	0.2450	3.4091	33.3	3.3685	(002)
after	27.7379	0.2340	3.2136	35.0	3.1710	(101)
annealing	36.0753	0.4418	2.4877	18.9	2.4577	(012)
	43.3529	0.4458	2.0855	19.2	2.0750	(110)
	47.5726	0.3240	1.9099	26.8	1.9045	(013)
	51.5330	0.4540	1.7720	19.4	1.7667	(112)
	52.5095	0.4336	1.7413	20.4	1.7363	(201)

From figure (4) and Table (3) it can be observed for the films of thickness 128nm that peaks at 2θ = (24.5480, 26.1730, 27.7386, 36.3967, 43.4220, 47.4913, 51,6518 and 52.6005) degree appeared which correspond to diffraction from C(100),

C(002), C(101), C(021), C(110), C(013), C(112), C(201), before annealing. And 2θ = (24.4725, 26.1181, 27.7379 , 36.0753, 43.3529, 47.5726, 51.5330 and 52.5095) degree appeared which correspond to diffraction from C(100), C(002), C(101), C(012), C(110), C(013), C(112), C(201) after annealing.

The d values were compared with the standard ASTM data to confirm the structure of CdS, we see that the film has two phases before annealing hexagonal and cubic but after annealing (220°C) we got only one type which is hexagonal. The crystallite size were found to increase, and the X-ray diffraction patterns were seen to sharpen by annealing this is agree with [18].

And also we see that the grain size increases that indicated that the films began approaching the crystalline structure.

Optical Studies

The optical properties for thin CdS films with (128, 314, 470, 815) nm thicknesses on glass substrate for annealing temperature (T_a = 220)°C for 1 hr. have been determined using UV-visible recording spectrometer in the region of (400–1100) nm before and after annealing. Also the energy gap and optical constants have been determined.

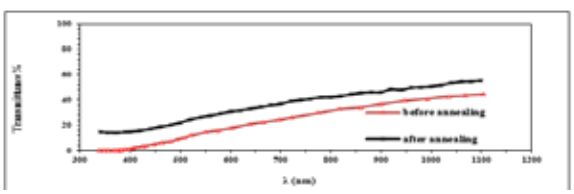

Fig (5) the transmittance spectra of CdS thin films before and after annealing for sample (1) thickness 128nm.

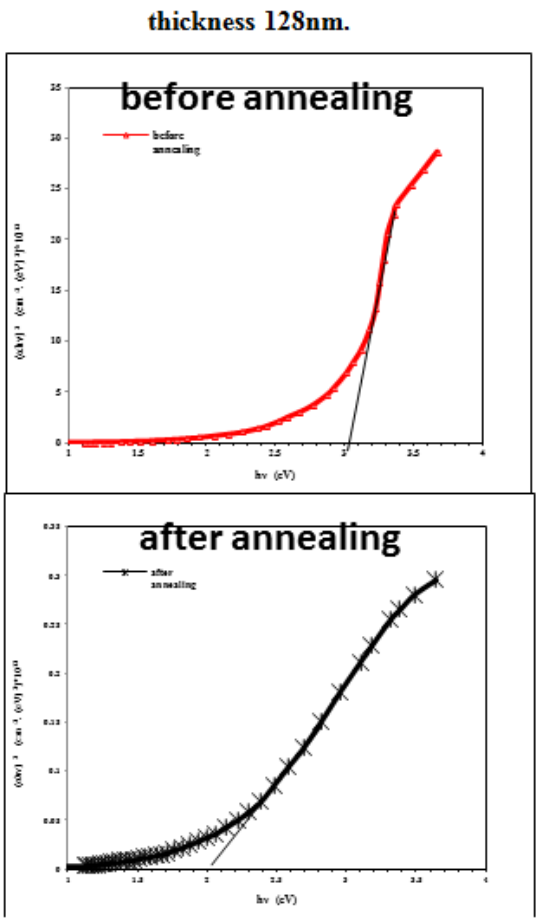

Fig. (6) $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for thin CdS films before and after annealing for for sample (1) thickness 128nm.

Table (4) The values of E_g and optical constants for thin CdS films before and after annealing for sample (1) thickness 128nm.

	Eg (eV)	λ, nm	T%	α (cm^{-1})	k	n	ε_r	ε_i
Before annealing	3.03	409.24	2.459	868580	2.85	2.35	18.45	18.45
After annealing	2.10	590.48	30.911	91740	0.44	14.66	14.66	3.38

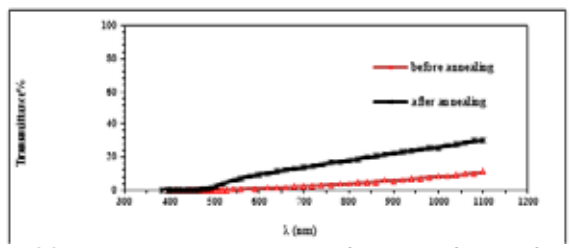

Fig (7) the transmittance spectra of CdS thin films before and after annealing for sample (2) thickness 314nm.

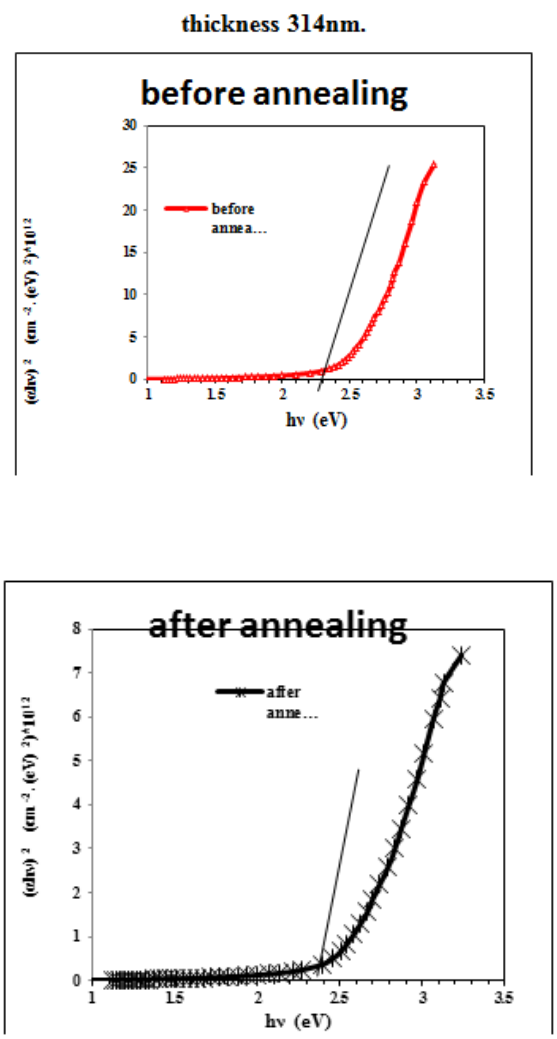

Fig. (8) $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for thin CdS films before and after annealing for sample (2) thickness 314nm.

Table (5) The values of E_g and optical constants for thin CdS films before and after annealing for sample (2) thickness 314nm.

	Eg (eV)	λ_c nm	T%	α (cm^{-1})	k	n	ε_r	ε_i
Before annealing	2.55	486.27	3.975	483845	1.88	2.48	2.62	9.29
After annealing	2.60	476.92	15.839	276456	1.04	2.04	3.06	4.23

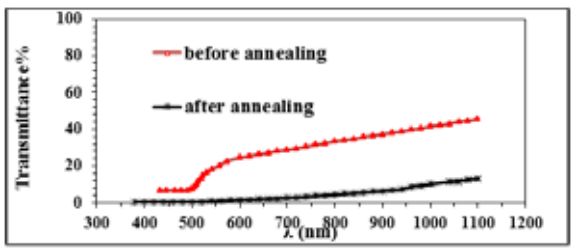

Fig (9) the transmittance spectra of CdS thin films before and after annealing for sample (3) thickness 470nm

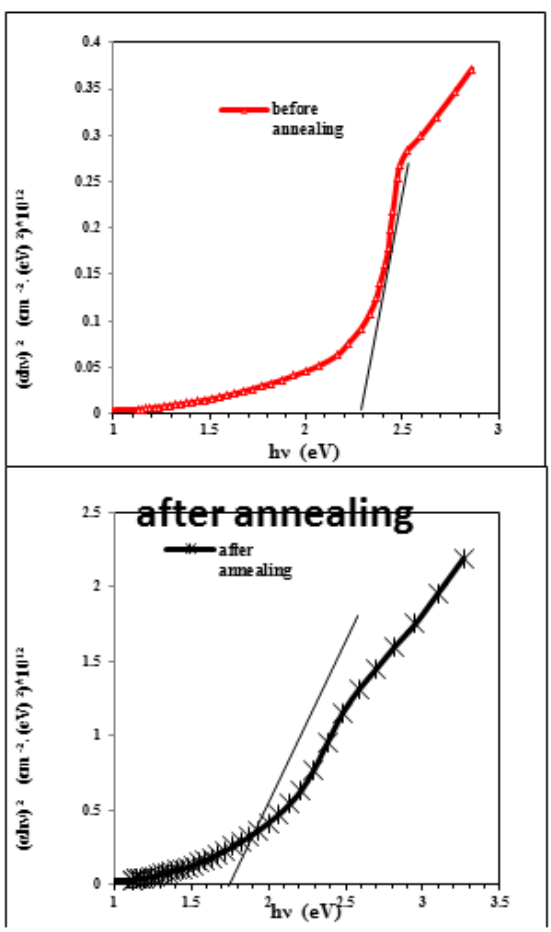

Fig. (10) $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for thin CdS films before and after annealing for sample (3) thickness 470nm.

Table (6) The values of E_g and optical constants for thin CdS films before and after annealing for sample (3) thickness 470nm.

	Eg (eV)	λc nm	T%	α (cm^{-1})	k	n	εr	εi
Before annealing	2.28	543.86	10.388	271787	1.17	2.13	3.17	5.00
After annealing	1.90	652.63	26.456	159593	0.81	1.85	2.78	3.02

Fig (11) the transmittance spectra of CdS thin films before and after annealing for sample (4) thickness 815nm

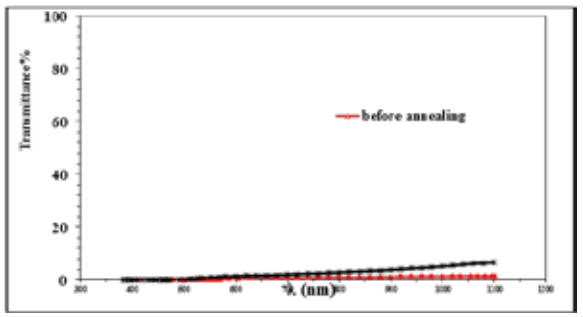

Fig. (12) $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for thin CdS films before and after annealing for sample (4) thickness 815nm.

Table (7) The values of E_g and optical constants for thin CdS films before and after annealing for sample (4) thickness 815nm.

	Eg (eV)	λc nm	T%	α (cm^{-1})	k	n	ε,	ε,
Before annealing	2.10	590.48	15.829	184363	0.86	1.84	2.63	3.17
After annealing	2.10	590.48	31.789	143282	0.66	2.27	4.72	3.01

From the Figures (5-12) and Tables (4-7). Sample (1) thickness 128nm the transmittance increase after annealing and the energy gap decreases to 210 eV, for sample (2) thickness 314nm the transmittance increase after annealing and the energy gap increases letal bil 2.60 eV, for sample (3) thickness 470nm the transmittance increase after annealing and the energy gap decreases to 1.90 eV. For sample (4) thickness 815nm the transmittance increase after annealing and the energy gap remains the same before and after annealing.

The energy gap of the films was found to decrease by annealing. The optical properties of the films were seen to be dependent on the film thicknesses. The band edge sharpness of the optical absorption was seen to oscillate by thermal annealing. and this result agree with [18]

Atomic Force Microscopy Analysis (AFM)

The effect of thickness for CdS thin film on the morphology of CdS thin films before annealing.

AFM for sample (1)

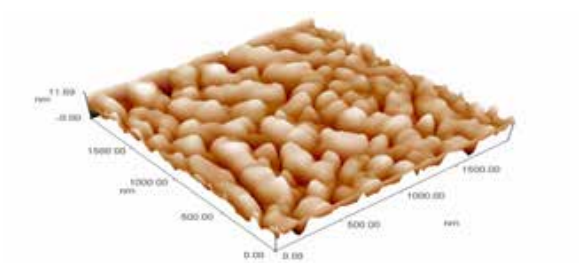

Fig.(13) AFM image for sample (1) thickness 128nm before annealing for CdS thin film.

Table (8)The average crystallite and roughness of CS thin film of thickness 128nm.

Thickness nm	Roughness average nm	Pick to pick nm	Grain size nm
128	1.89	11.7	93.86

AFM for sample (2)

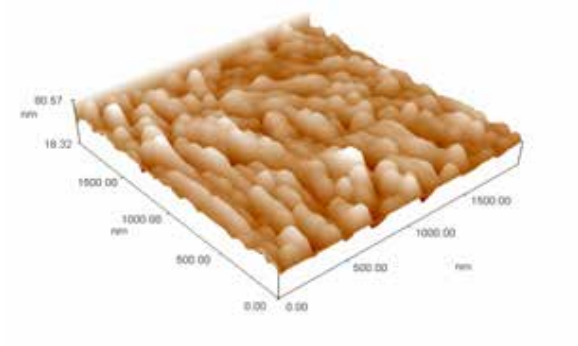

Fig.(14) AFM image for sample (2) thickness 314nm before annealing for CdS thin film.

Table (9)The average crystallite and roughness of CS thin film of thickness 314nm.

Thickness nm	Roughness average nm	Pick to pick nm	Grain size nm
314	4.53	30.2	94.55

AFM for sample (3)

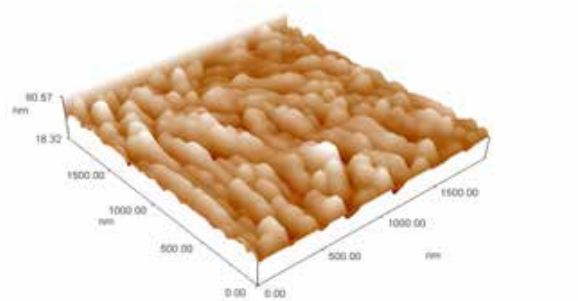

Fig.(15) AFM image for sample (3) thickness 470nm before annealing for CdS thin film.

Table (10)The average crystallite and roughness of CS thin film of thickness 470nm.

Thickness nm	Roughness average nm	Pick to pick nm	Grain size nm
470	6.48	59.2	102.45

AFM for sample (4)

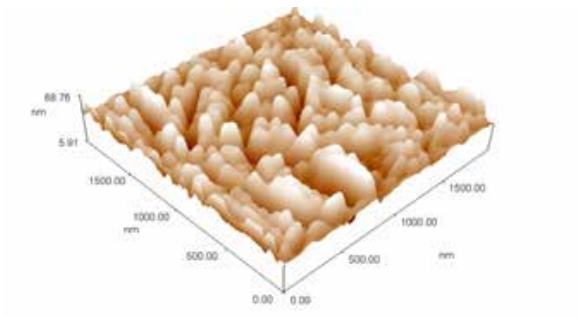

Fig.(16) AFM image for sample (4) thickness 518nm before annealing for CdS thin film.

Table (11)The average crystallite and roughness of CS thin film of thickness 518nm.

Thickness nm	Roughness average nm	Pick to pick nm	Grain size nm
518	9.35	62.8	88.99

The average roughness of CdS thin films increas with increasing thickness and also the pick to pick valuo, and mostly the grain size increas with increasing thickness. The CdS film has good morphology[19] and the roughness and grain size effect by changing the thickness of the film.

REFERENCES

[1]- Chopra, K.L., "Thin film phenomena", MC-Graw Hill Book Company, New York, 1969. | [2]- Lide, David R. (1998). Handbook of Chemistry and Physics (87 ed.). Boca Raton, FL: CRC Press. pp. 4–67; 1363. ISBN 0-8493-0594-2. | [3]- Zumdahl, Steven S. (2009). Chemical Principles 6th Ed. Houghton Mifflin Company. p. A21. ISBN 0-618-94690-X. | [4]- Wells A.F. (1984) Structural Inorganic Chemistry 5th edition Oxford Science Publications ISBN 0-19-855370-6 | [5]- Egon Wiberg, Arnold Frederick Holleman (2001) Inorganic Chemistry, Elsevier ISBN 0-12-352651-5. | [6]- Agarwal, Ritesh; Barrelet, Carl J.; Lieber, Charles M. (2005). "Lasing in Single Cadmium Sulfide Nanowire Optical Cavities". Nano Letters 5 (5): 917. doi:10.1021/nl050440u. PMID 15884894. | [7]- P.K. Weimar, "The TFT a new thin-film transistor", Proc. IRE, Vol. 50, No. 6 (1962) pp. 1462-1469, [2] doi:10.1109/JRPROC.1962.288190 | [8]- H.Yamaguchi, T.Komiyama, M.Yamada, K.Sato, T.Aoyama, Physica. 401-402, (2007). 391. | [9]- John E.Jaffe, James A. Snyder, Zijing Lin, and Anthony C.Hess, Phys. Rev. B62, 3, (2000). 1660. | [10]- H.M.Smith and A.F.Turner, Appl. Opt. 4, (1965). 147. | [11]- J. Pankove, "Optical Processes in Semiconductors", Prentice – Hall, Inc., Englewoodcliffs, 285, 111, 1971. | [12]- M. A. H. Kadhim and K. Patel, "Engineering Materials", University of Technology Baghdad, Part 1, 1978. | [13]- J.Millman "Microelectronics" Murray – Hill, Book Company Kogakusha, 642, 172, 1979. | [14]- S.R.Elliott, "Physics of Amorphous Materials", Longman Inc., New York, 1984. | [15]- G. Burns, "Solid State Physics" Academic Press, Inc., Harcourt Brace Jovanovich, New York, 324, 42, 1985. | [16]- M. Roth,"Nuclear instruments and methods in physics Research",283 291-298 ,1989. | [17]- K.L. Chopar, "Thin Film Phenomena", McGraw- Hill, New York ,1969. | [18]- H.Metin, R Esen, "Annealing studies on CBD grown CdS thin films, Journal of Crystal Growth, Vol. 258(1), 2003. | [19]- Hui Zhang, Xiangyang Ma, Deren Yang, "Effect of complexing agent on CdS thin films prepared by chemical bath deposition", Materials Letters, Vol.58(1), 2004.