Effect of Annealing Temperature on the Optical Properties of Spin Coated CdS/PVA Thin Films

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Abstract— CdS thin films have been prepared using cadmium nitrate (mw=308.47and 0.6 M) as cadmium source and thiourea (mw=76.12 and 1 M) as sulfur source. Polyvinyl alcohol (PVA) as a matrix. Thin films are deposition on glass substrate using spin coating technique. The sample thickness measured is 67.7 µm. The effect of annealing temperatures (100, 150, 200^{o}C)on the structural and optical properties of CdS thin films is investigated. The surface morphology is tested by AFM, also X-ray study is represented. The results show that the Grain size of the sample increased with increasing of annealing temperatures. The Absorption coefficient, Refractive Index, Extinction coefficient and dielectric constant increased with increasing of annealing temperature. while the transmission and energy gap decreased with increasing of annealing temperature.

Index Terms— additive, annealing, optical properties, thin film, CdS.

1 Introduction

The discovery of semiconductor is one of the great scientific and technological breakthrough of the 20th century [1]. Combinations of the characteristics of different material are required [2], thus, the technique of thin films is considered as an important technique, which contributes to the development of study of semiconductor for a long time. The thin film has great importance in many fields, like glass industry ceramic industry, in solar cells, capacitor, transistor, electric switches and detectors [3].Cadmium sulfide is an II-VI compound semiconductor. Bonding in these compounds is a mixture of covalent and ionic type's .Group VI atoms are considerably more electronegative than
group II atoms and this introduces iconicity. This character has the effect of binding the valence electrons rather tightly to the lattice atoms. Thus, each of these compounds has higher melting point and larger band gaps than those of the covalent semiconductors of comparable atomics weights [4, 5]. In recent year CdS thin films has attracted wide attention as window layers [6,7] in low-cost , high efficiency thin film solar cells, because of its suitable band gap , high optical transparent and absorption coefficient in the visible range of solar spectrum [8,9]. CdS is a direct band gap (2.42 eV) [10,11] .Its density is approximately 4.84 g/cm^3 . CdS does not show intrinsic behavior at room temperature, i.e. deposited CdS thin films doesn't need doping to become n-type. Formation of p-type CdS is very difficult, because of the strong self-compensation effect caused by sulfur vacancies.[12,13]

Pure CdS crystals have a high resistivity about 10^{12} Ω-cm. polycrystalline CdS thin film's resistivity can be reduce by In ,Sn ,Al ,Cr or Br doping or by some growth techniques. The grain sizes of CdS films differ according to synthesis technique. As the film thickness is increased, large crystallites are formed in the film. Annealing at high temperatures enhance the grain size and re-crystallization of CdS. [14].
In this work we represent (CdS-PVA) thin films fabricated by spin coating technique. The preparing of the as-deposited films structure and optical properties at room temperature is done, detailed studying and analysis of structure, optical properties and optical constants is also presented . The effect of annealing at (100 , 150 and 200 C^o for 20 minute) is examined and reported.
Experiment

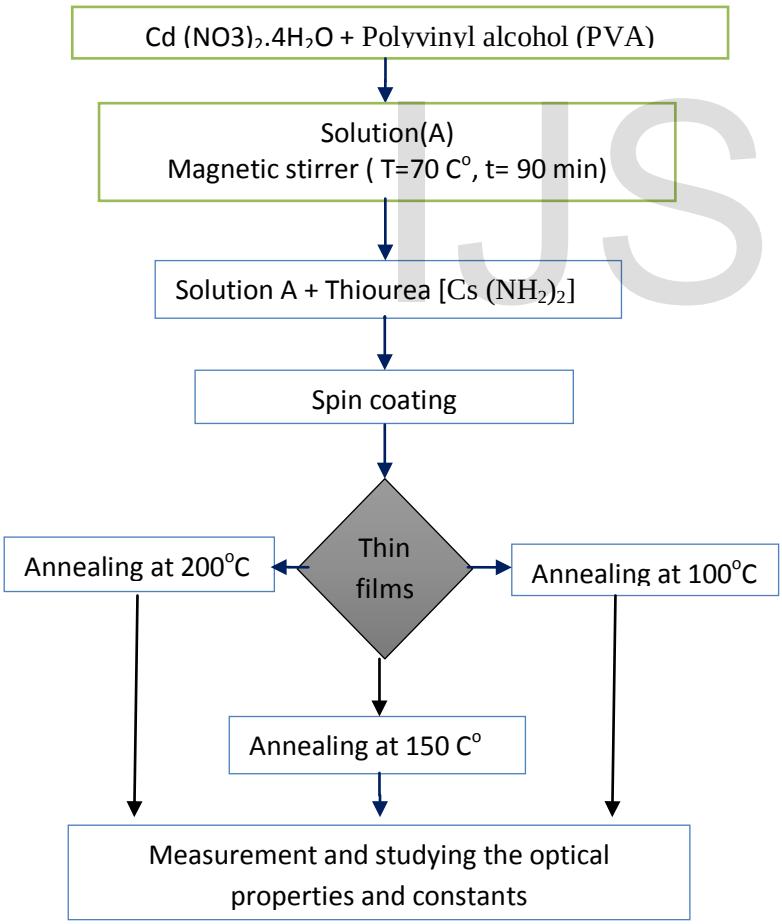
The technique employed in this work is the spin coating, which involves adding drops of the material on the cleaned glass slide and then rotating it to deposit the solution on the substrate. Annealing at different temperatures (100, 150, 200 ^{o}C for 20 minute) is applied in order to study the effects on the samples optical parameters.

Devices used in this work: Spin coating device, magnetic-stirrer, balance, oven. sample thickness are measure using coating thickness gauge (CONACOAT III), and they are equal to 67.66 µm. the specifications of the chemicals used are shown in table (1):

Table (1): the chemical parameters of the substances

Material	atomic weight	Purity	Chemical Composition	Concentration	Company
Cadmium Nitrite	308.47	99%	$Cd(NO3)_2.4H_2O$	0.6M	BDH
Thiourea	76.12	99%	$Cs(NH_2)_2$	1M	BDH
Polyvinyl alcohol (PVA)	1400	99%			BDH

For sample preparation we followed the chart shown below:



R.T, then annealed at (100,150,200)C°, then examined by X-ray diffractions using a Philips X-ray diffractometer.
The average size of CdS grains has been obtain from x-ray diffraction pattern use the Scherer's formula

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

where, D is the grain size, K is a constant taken to be 0.94, β is the full width at half maximum (FWHM) and λ is the wave length of the x-ray.
Optical Interference Fringes method is used to obtain the thin film thickness where Fizeau fringes of equal thickness are obtained in an optical apparatus. the film thickness (t) is given by:

$$t = \frac{\lambda}{2}\frac{\Delta X}{X} \qquad (2)$$

where ΔX is the shift between interference fringes, X is the distance between interference fringes and λ is the device source wavelength.

2 Results and discussion

2.1 X-ray Diffraction

The structure properties of the spin coating CdS films have been investigated by x-ray diffraction technique.Figures1,2, and 3 show the x-ray diffraction patterns at annealing temp.:100C°, 150C° and 200C° respectively for 20 minutes each. The patterns exhibit peaks at 24.16o, 20.94° and 22.000 respectively, these results are comparable to the values obtained by (R. Meshram, 2012) [15] . The presence of small peaks in x-ray diffraction reveals the formation of nano-crystalline CdS films (also proved by AFM study). The peaks are not sharp indicating that the average crystalline size is small. Due to size effect the peaks in the diffraction broaden and their widths became large as the particles became smaller. The average size of CdS grains has been obtain from x-ray diffraction pattern using equation 1.The values corresponding to each annealing temp. are given in Table 2. It is obvious that the grain size of CdS increases from 29.97 nm to 32.897 nm as the annealing temperature increase from 100C to 200C.

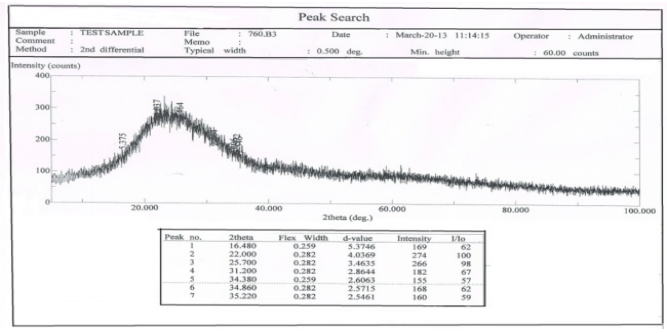


Fig. 1. X-ray diffraction pattern for CdS at 100C°, 67.66 µm thickness

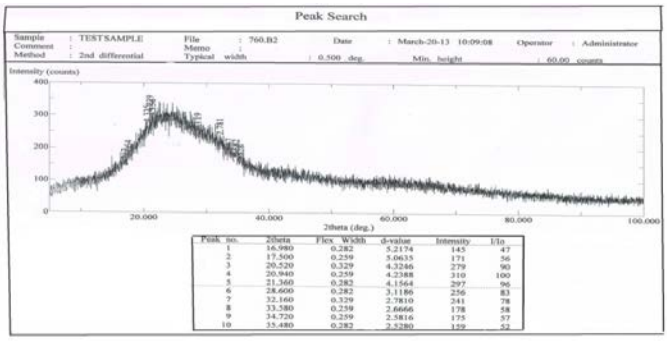


Fig. 2. X-ray diffraction pattern for CdS at 150C°, 67.66 µm thickness

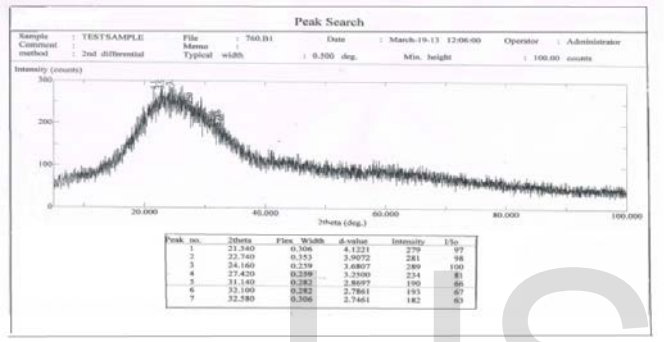


Fig. 3. X-ray diffraction pattern for CdS at 200C°,67.66 µm thickness

2.2 Atomic Force Microscopic analysis

Figures (4, 5 & 6) show the atomic force microscopic picture for the three samples at different annealing temperature (Ta=100, 150 and 200℃) respectively.

Figures 4(a, b, c,) show the AFM analysis of the surface of sample annealed at 100 °C ; figure (a) shows a 3D magnified picture of the sample surface ,where we can see the nano-structure of the rough surface. Figure (b) is a panel diagram presents the height profiles measured along the sample surface, it is clear that most particles of (CdS- PVA) are around 250-300 nm with an average diameter of 224.45 nm. As indicaed in figure (c) the average roughness is 0.722nm, this roughness average will be directly changed with increasing the annealing temperature.

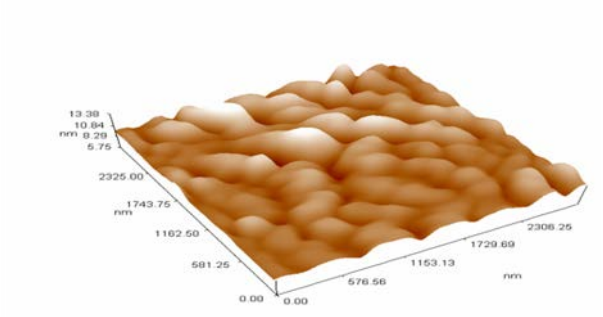


fig. 4 (a)

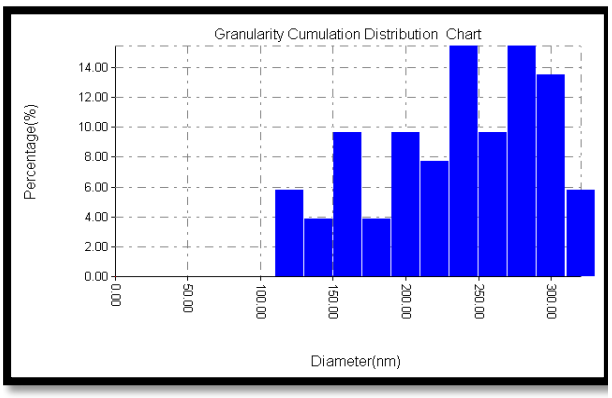


fig. 4 (b)

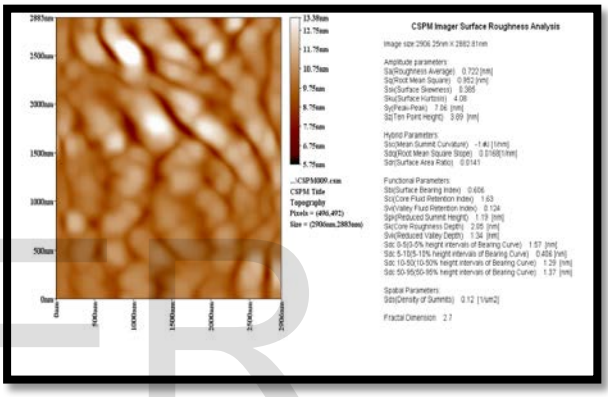


fig. 4 (c)

Fig. 4. (a) 3D magnified picture of the sample surface ,where we can see the nano-structure of the rough surface.(b) a panel diagram of the height profiles measured along the sample surface, it is clear that most particles are around 250-300 nm . (c) surface roughness analysis.

Annealing the sample under 150 °C, the surface shows more obvious structure ,the average particle diameter (CdS- PVA) becomes (212.96 nm) , the crystalline structure of the film is disturbed, resulted in randomly distributed particles we believe that this is due to the melting of sulfur (melting temperature is 131°, rather than the cadmium which has a melting temperature 321°C), also the effect of overcoming the voids and surface defects and rearrangements of the particles. This result is obviously shown in figure (5-a). In figure (5-b) we can see that most of the particles have diameters in the range of (130 -300) nm. Figure (5c) indicates the surface roughness to be 1.21 nm with longer range order.

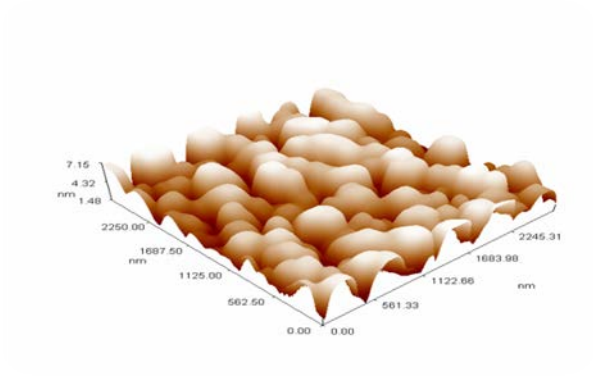


fig. 5 (a)

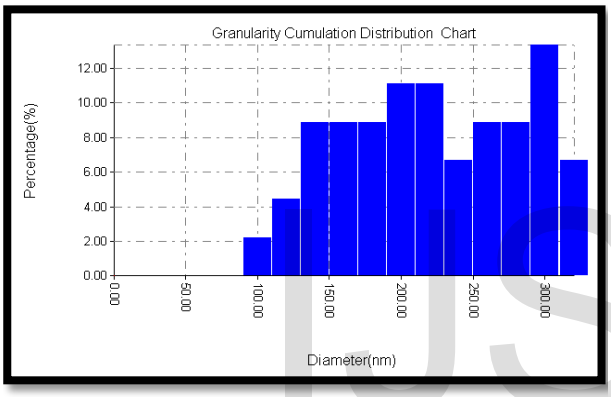


fig. 5 (b)

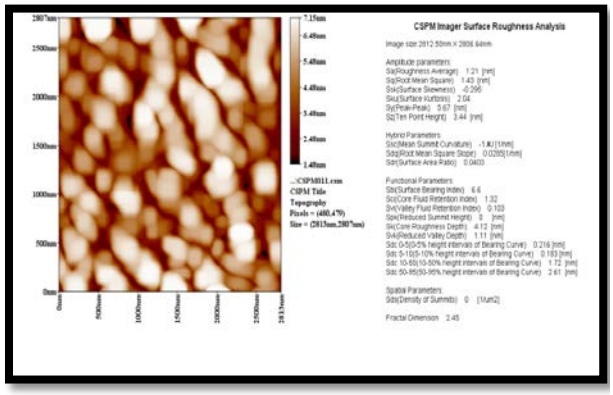


fig. 5 (c)

Fig. 5. (a) 3D magnified picture of the sample surface ,where we can see the nano-structure of the rough surface. (b) a panel diagram of the granularity cumulating distribution measured along the sample surface, it is clear that most particles are around 125-270 nm . (c) surface roughness analysis.

Figure 6(a) shows the annealing under 200 ^{o}C which leads to a change in the surface particle distribution giving an average diameter of 156.23 nm., figure 6(b) shows a dramatic change in granularity cumulating distribution, this could be attributed to the particles creep caused by the full melting of PVA and sulfur particles (melting temperature is 131^{o}) and sweeping the Cd particles with them. Figure 6(c) indicates the surface roughness to be 3.5 nm with longer range order.

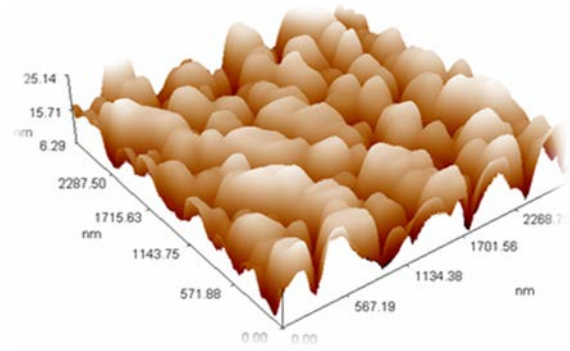


fig. 6 (a)

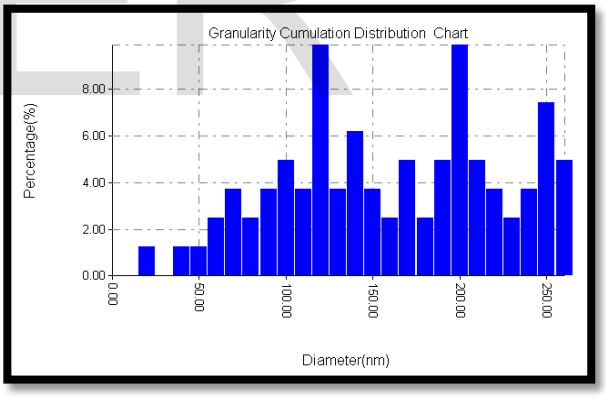


fig. 6 (b)

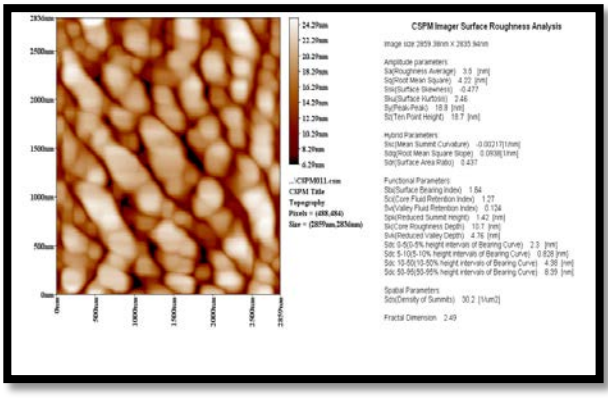


fig. 6 (c)

Fig. 6 (a) 3D magnified picture of the sample surface ,where we can see the nano structure of the rough surface. (b) a panel diagram of the granularity cumulating distribution of sample surface.. (c) surface roughness analysis.

It is concluded that there is a direct correlation between surface roughness average and annealing temperature. There is also an indirect correlation between the particle size of (CdS- PVA) and annealing temperature.

Optical Properties of CdS Films

The absorbance and transmittance spectrum of the samples have been determined by UV- VIS-IR spectrophotometer in the region 300–1100nm. Also the energy gap and optical constants (n, K, α, ε_1, ε_2) have been determined. Which shows agreement with our result of XRD.

Absorption spectra:

The absorption of CdS thin films are shown in figure 7. we can notice that the values of absorption increase with increasing the annealing temperature. from the spectra it is evident that the absorption edges are blue shifted with respect to the bulk (520 nm), this result agrees those reported by J.Osuwain, 2009 [16].

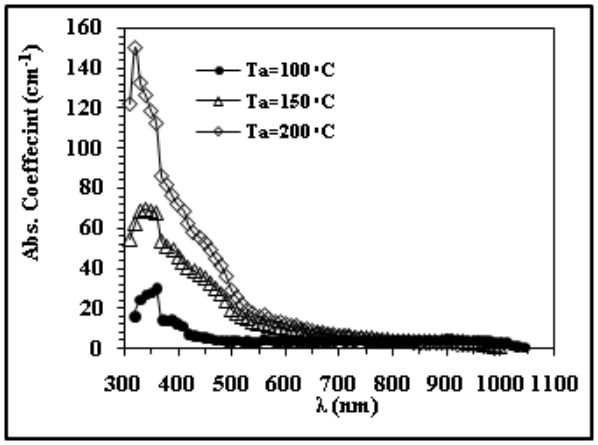


Fig. 7. Absorption spectra of CdS/PVA samples, 67.66 μm thickness

The Absorption Coefficient:

The dependence of the absorption coefficient on the wavelength for different annealing temperatures (T_a) of the deposited CdS films is shown in figure 8; One can see from these figures that the absorption coefficient of the CdS films is characterized by a strong absorption at the shorter wavelength region between 300–460 nm and without sharp edge on the long wavelength side from 470–530nm.

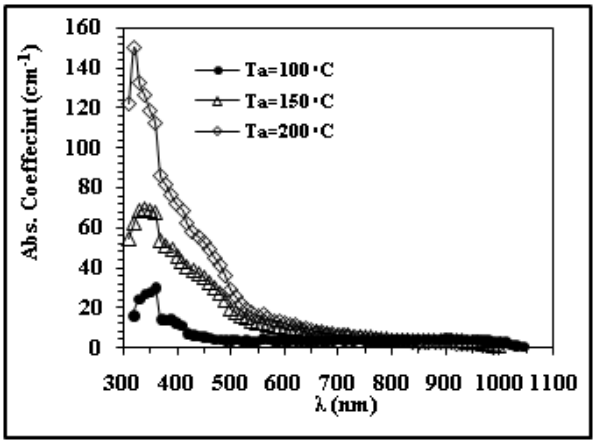


Fig. 8 Absorption Coefficient versus wavelength

Transmission spectrum

The transmission spectrum for CdS/ PVA thin films show good transparency (T > 85%). Studying the silicon response curve, figure 9, we can notice that the response extends from about 400-1000nm, in this region the studied films show an excellent transparency. Also it is clear that transmission decrease with increase the annealing temperature as show in Table (3), this could be due to PVA deformation at higher temperature.

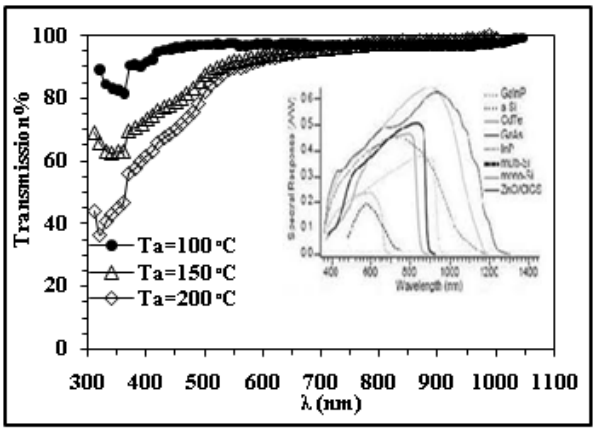


Fig. 9 Transmission spectra for CdS/PVA films at different T_a

The Optical Energy Gap

The optical energy gap values (E_g) for CdS films have been determined by using Tauc equation which is used to find the type of the optical transition by plotting the relations of $(\alpha h\nu)^2$ versus photon energy (hv) and selecting the optimum linear part. The optical energy

gap decreases with increasing annealing temperature as show in the figures (10). The values are given in Table (2).we find the results are comparable to those obtained by M. S. Tyagi in1991 which is (2.42 eV) [17].

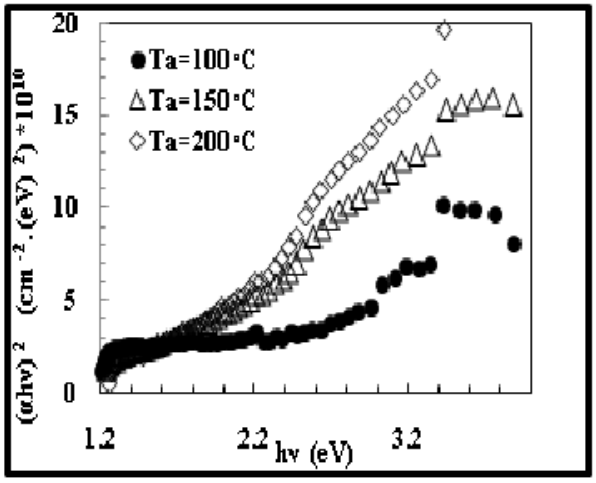


Fig. 10 Energy Gap for CdS/PVA films with different T_a

Table 2: values of (CdS) grain size at different annealing temp.(obtained from Scherrer's formula) and Energy gap values.

Annealing temperature	(CdS) Grain size from XRD	Energy gap
100	29.97	2.25
150	32.58	1.65
200	32.89	1.60

Refractive Index

The variation of the refractive index versus wavelength in the range (300–1100) nm, at different annealing temperature (100,150, and 200) ^{0}C is shown in Figure 11. We can notice from these figures and the Table (3) that the refractive index, in general decreases slightly with increasing of T_a.

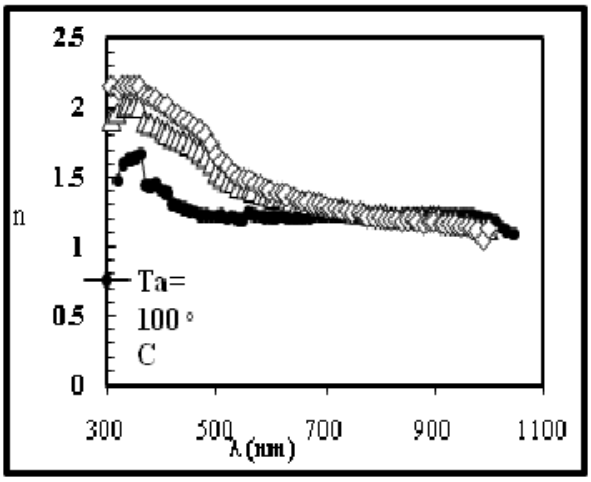


Fig. 11 Refractive index versus wavelength

Extinction Coefficient

The variation of extinction coefficient with wave length, shown in figure (12). from this figure can note that the extinction coefficient decreased with increasing the wave length due to high value of absorption coefficient. And increase with annealing.

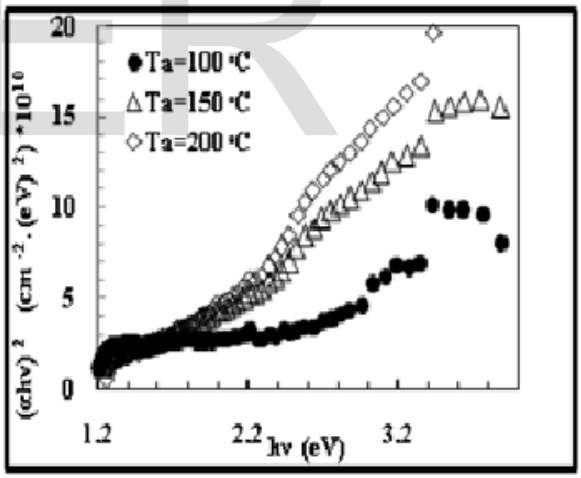
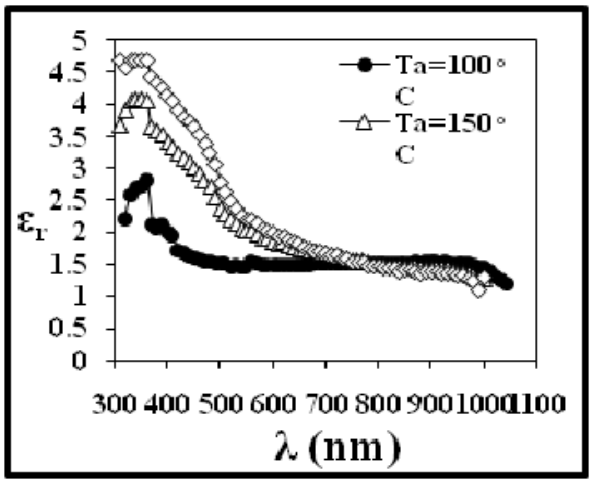


Fig. 12 The Extinction coefficient versus wavelength

The Dielectric Constants

The variation of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant values versus wavelength in the range 300-1100 nm at R.T then annealing the films for (100, 150 and 200) ^{o}C are shown in Figures (13 and 14). The behavior of ε_1 is similar to that of the refractive index, while ε_2 is mainly depends on the k values, which are related to the variation of absorption coefficient**.** It is found that ε_1 increase with increase the

annealing temperatures and ε_2 decrease with decrease of annealing temperatures.



Ta (°C)	A	T%	α (cm^{-1})	Eg (eV)	K $*10^{-5}$	n	ε_r	ε_i $*10^{-5}$
100	0.011	97.427	3.854	2.25	1.84	1.217	1.482	4.48
150	0.028	93.691	9.634	1.65	4.60	1.359	1.848	12.51
200	0.035	92.235	11.949	1.60	5.71	1.405	1.974	16.04

Fig. 13 The Dielectric Constants (Real part)

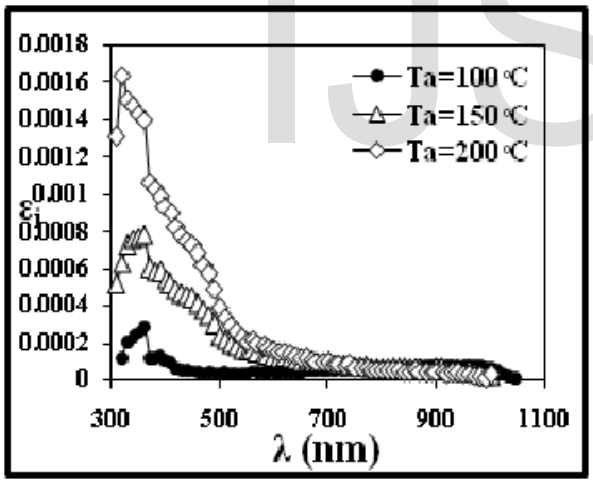


Fig. 14 The Dielectric Loss (imaginary part)

Table 3:optical constants at λ =600 nm

	T=100 C^0	T=150 C^0	T=200 C^0
Grain size	29.9nm	32.58nm	32.9nm
Absorption of films	0.011	0.028	0.035
Transmission spectra	97.427 %	93.691%	92.235 %
Optical Energy Gap	2.25	1.65	1.60
Absorption Coefficient	3.854	9.634	11.949
Refractive Index	1.217	1.359	1.405
Extinction Coefficient	$1.84*10^{-5}$	$4.60*10^{-5}$	$5.71*10^{-5}$
Dielectric Constants	ε_r	1.482	1.848	1.974
	ε_i $*10^{-5}$	4.48	12.51	16.04

conclusion

In summery the CdS embedded in PVA matrix in thin films was prepare using spin coating technique. The effect of annealing on prepare films at thickness about 67.66 μm were. From the x-ray diffraction the crystal grain size increase with increase the annealing temperature .The absorption of the films and the absorption coefficient increase with increases the annealing temperature. While the transmission of the films are decrease directed with the simple annealing temperature.

The energy gap for CdS thin films decrease due to increase annealing temperature.

The refractive index and extinction coefficient increase slightly by increasing of annealing temperatures for all samples. The variation of the real and imaginary parts of the dielectric constant have similar trend as for n and k respectively. All results are summarized the table below:

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