Correlation between Optical and Structural Properties of Chemically deposited CdS Thin Films

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ABSTRACT

Polycrystalline Cadmium sulfide (CdS) films were deposited onto Corning glass substrates from alkaline solutions containing $CdCl_2$, KOH, $Na_3C_6H_5O_7$ and $CS(NH_2)_2$ at different deposition times (10, 20, 30, 40 and 50 min), different bath temperatures and different concentration of the reactants. A comparative study was performed out on thin film via optical transmission and X-ray diffraction (XRD) measurements which reveal that the deposition time has a profound influence on the growth rate and band gap of the deposited layers. Diffraction data are used to evaluate the lattice parameter, grain size, average strain, number of crystallites per unit area and dislocation density in the film are calculated.

*Keywords***:** Cadmium sulfide; chemical bath deposition; CdS films; XRD

1. INTRODUCTION

Cadmium sulfide (CdS) has been emerged as an important transparent conducting semiconductor for thin film CdTe and $CuInSe_2$ heterojunction solar cells (1-4). Of all the thin film deposition methods, chemical bath deposition (CBD) is the simplest one that offers great scope for large area fabrication. Solar cell efficiency as high as 16.5 % has been reported for CdS/CdTe thin film solar cells by using CBD CdS films (5). Most films deposited by CBD adopting the continuous dipping approach where the substrate remains in the reaction bath (6), although a the multiple dip approach have been reported (7).

Although there are a growing number of reports on using the deposition of CdS films from an aqueous solution using $CdCl_2$ salt, very little is known about the influence of different thiourea/$CdCl_2$ concentration ratio, deposition time and path temperature. Therefore, the study of CdS with respect to different growing conditions is a matter of high importance. This is an aspect of great importance because it is well known that structural properties affect the optical and electrical properties of deposited layer and hence device efficiency and its

lifetime. In this work, CdS thin films were prepared by the CBD technique under different growing conditions. The band gap energy, optical and crystalline structure of the CdS films were analyzed as a function of the growing conditions

2. EXPERIMENTAL

2. 1. Substrate cleaning

The substrate used is glass slides with size of $(75 \times 25 \times 1 \text{ mm}^3)$. which were first cleaned in distilled water, followed it rinsing in chromic acid (for one day), to introducing nucleation centers.

2. 2. Solution preparation

Films were deposited on glass slides using 12 ml of 0.05 M $(CdCl_2)$ mixed slowly with 20 ml $Na_3C_6H_5O_7$ at room temperature with continuous stirring. Then 5 ml of 0.5 KOH is added. Substrates immersed in a beaker containing the reaction mixture placed in a water bath at temperature 80 ±2 °C with continuous stirring, 10 ml of 0.5 M thiourea was then added. Substrates were taken out after a suitable time; they were washed with distilled water and ultrasonic agitation to remove the porous cadmium sulfide over layer, then dried in hot air. All the samples were prepared at pH = 11. The same deposition process is repeated by varying the concentration of $CdCl_2$ used.

2. 3. Thickness measurement

Film thickness is measured by optical interferometer method using He – Ne Laser (0.632 μm), the thickness is determined using the formula:

$$d = \frac{\Delta x}{x} \frac{\lambda}{2} \tag{1}$$

where X is fringe width, Δx is the distance between two fringes and λ is the wavelength of laser light.

2. 4. Structure Measurements

X-ray diffraction taken by (Philips 1140) diffractometer of $\lambda = 1.54$ Å from Cu-Kα operating at 36 kV-18 mA and compared with the ASTM cards number 83.The lattice parameters, a and c of the unit cell were evaluated from the relation [8,9],

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \tag{2}$$

where d is the inter planar spacing. The grain size (D) values are calculated using the Scherrer Formula [7]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{3}$$

where β is the full-width at half-maximum (FWHM) of the peak and θ is the Bragg angle. The dislocation density (δ) estimated using the equation [8]:

$$\delta = \frac{1}{D^2} \tag{4}$$

The number of crystallites per unit area (N) and the strain ($\in$) of the films were determined with the use of the following formulae [10]:

$$N = \frac{t}{D^3} \tag{5}$$

$$\in = \frac{\beta \cos \theta}{4} \tag{6}$$

2. 5. Optical Properties

Optical properties for CdS films depend on the dielectric constants, refractive index, the band-gap of the thin film and depends nature of the film material [11]. A (CE595 Double Beam Digital U.V spectrophotometer, CECIL instrument) was used to record the optical transmission for CdS films. from which the absorption coefficient (α) calculated [12]:

$$\alpha = -\ln \frac{(T)}{d} \tag{7}$$

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

3. RESULTS AND DISCUSSION

3. 1. Structure Properties: Crystal structure and phase

The crystal structure of the films was determined by XRD (using Cu Kα radiations, $\lambda = 1.54$ Å). XRD analysis confirms that the deposited films are polycrystalline with less no preferred planes at low deposition time as shown in Fig. 1. The main peak correspond to the plane (111) appears at angle $2\theta = 26.6°$, become predominated with increasing deposition time. Although increasing deposition time should increase film thickness but this thickness increasing have no influence on the peak intensity. At higher diffraction angle (200) plane belong to CdO.

The origin of the impurity could be deriving from oxidation processes (i.e. traces of water present in the film or air) or from reaction of any preformed cadmium hydroxide. Further, the type of substrate or growth condition determines the number of XRD reflection peaks. It is also noticeable that the width of the main peak in film deposited at longer deposition time is smaller than for other samples, this could be due to reduced strain within the film, or an increase in grain size.
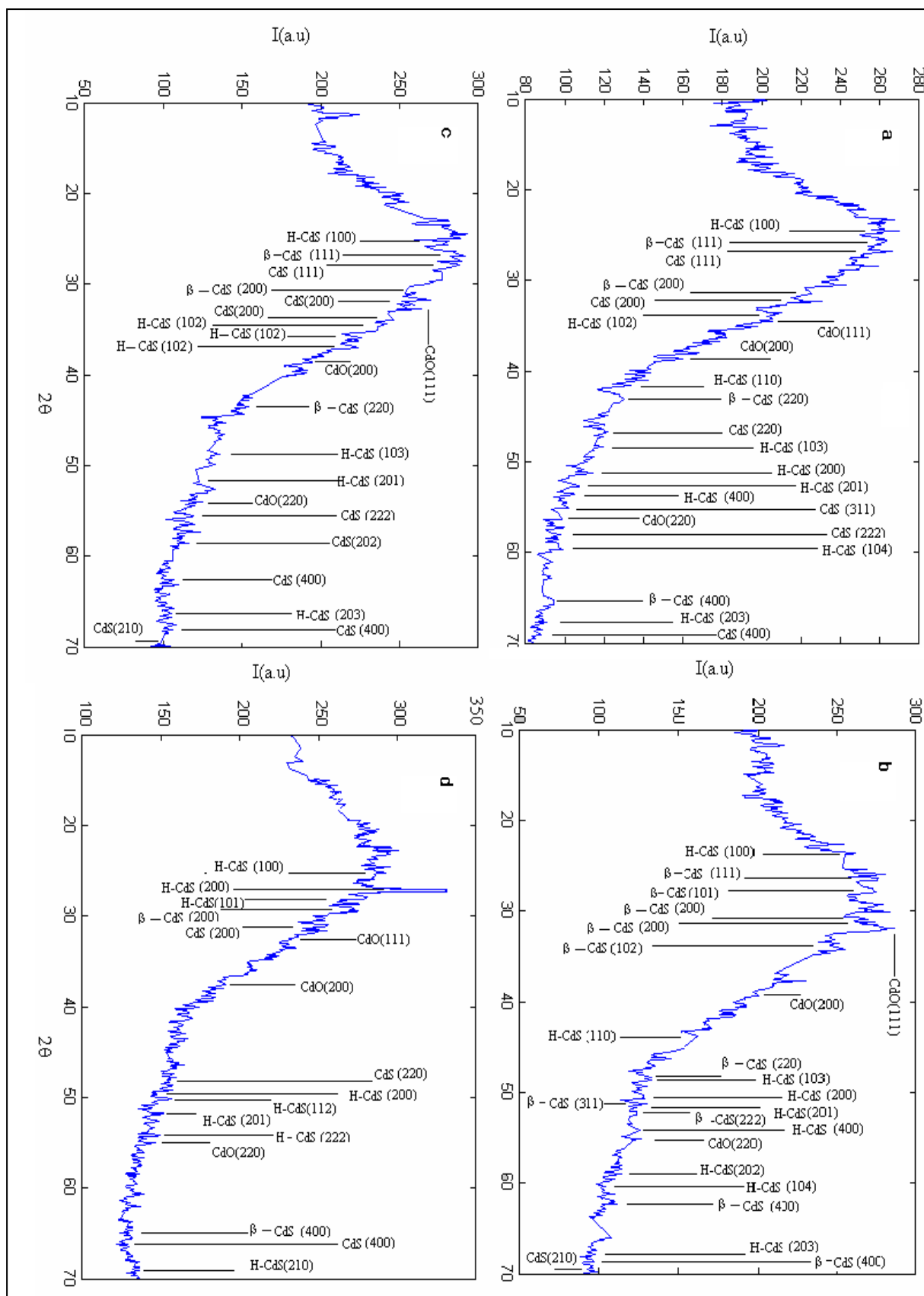
Figure 1. Typical XRD pattern of CBD-CdS thin film using CdCl$_2$ source, at temperature 50 °C, pH = 11 and deposition time at (a) 5 min. (b) 10 min. (c) 15 min. and (d) 20 min.

3. 2. X-ray diffraction analysis

Using the equations (2-6), the results of X-ray diffractgrams can be tabulated. Tables 1 shows the influence of deposition time on the microstructure of deposited CdS .

Table 1. X-ray analysis of samples deposited at 50 °C using $CdCl_2$.

t (min.)	d (nm)	2θ (degree)	β (rad) $\times 10^{-3}$	D (nm)	δ (lines/m^2) $\times 10^{14}$	N $\times 10^{12}$	$\in$ $\times 10^{-3}$
5	46	26.6	1.745	106.957	0.874	37.595	0.324
10	53	26.6	1.396	133.69	0.559	22.180	0.259
15	60	26.8	1.047	196.974	0.257	7.850	0.1759
20	68	26.8	1.0122	203.78	0.240	8.035	0.1700

The variation in grain size with deposition time is shown in Fig. 2. The grain size exhibit saturation at long deposition time. The increase in grain size means a decrease in grain boundaries (lesser scattering area) and pores in the thicker films as compared to the thin films.

Large scattering centers in the lattice due to mismatch at film/ substrate interface gave rise to defects in thin films. The results could be explained by adopting the survivor of the fastest model [14]. According to this model nucleation with various orientations can be formed at the initial stage of the deposition and each nucleus competes to grow but only nuclei having the fastest growth rate survive [15]. Such results have been already seen by others [8,15], More probably this is due to the variation in the surface of the substrate, in short time the film deposited on the glass substrate where the nucleation centers density is high. While in longer time the layers deposited on the already deposited CdS layer.
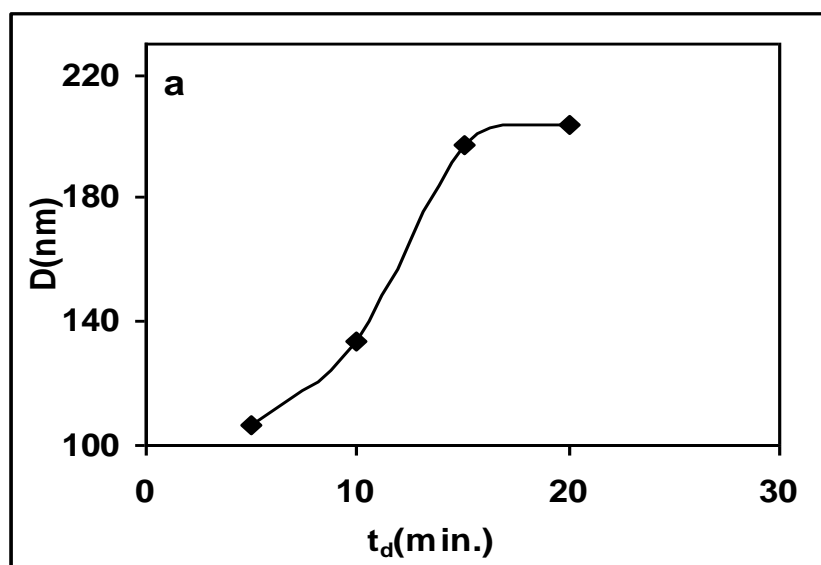

Fig. 2. Grain size as a function of density as deposition time.
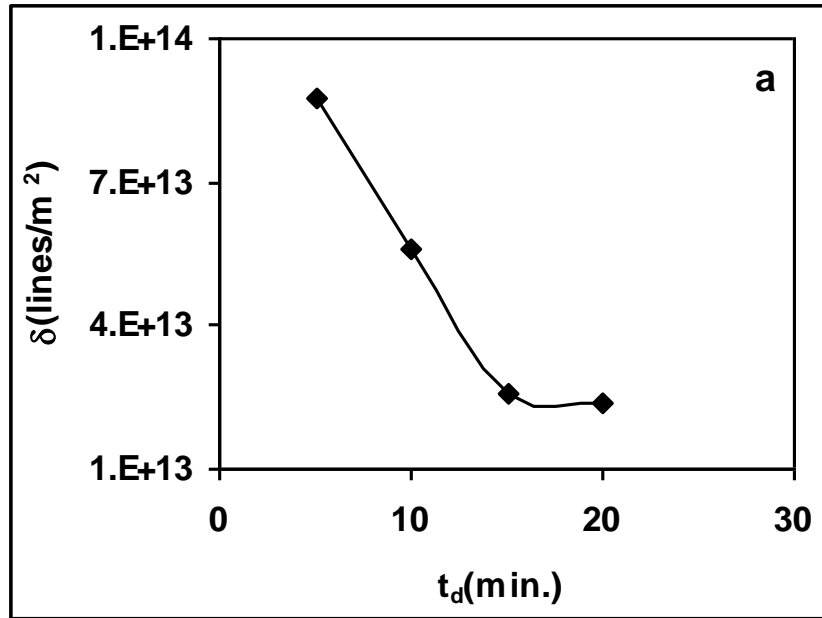
Fig. 3. Dislocation a function of deposition time.

The dislocation density decreases with deposition time as shown in Figure 3. The decreasing is sharp with short deposition time while in longer time the inverse change takes place. Such behavior could be due to the change in grain size accompanied short and longer time deposition. Figures 4 shows the variation in the films strain as a function of deposition time, the decreasing in the strain with time is probably due to the enhancement in the degree of crystallite of deposited film due to the increasing in grain size.
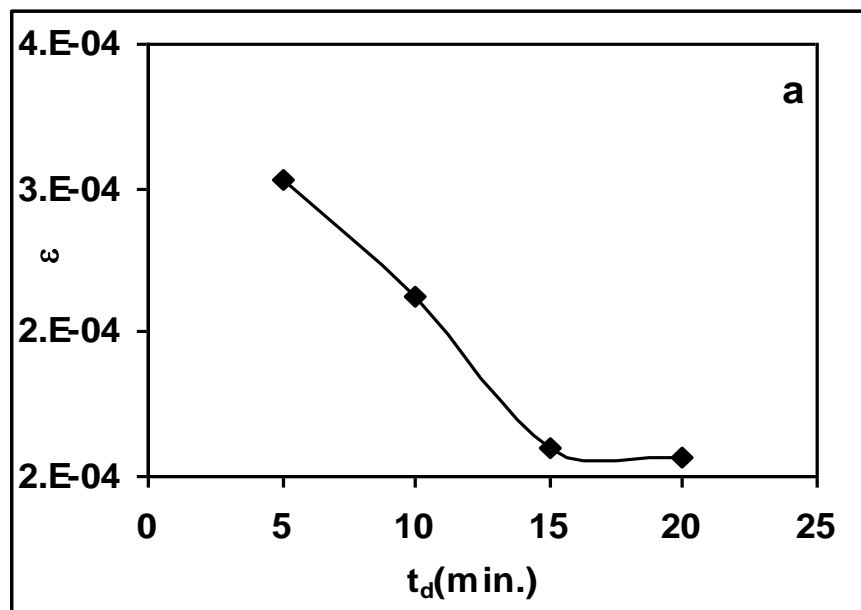

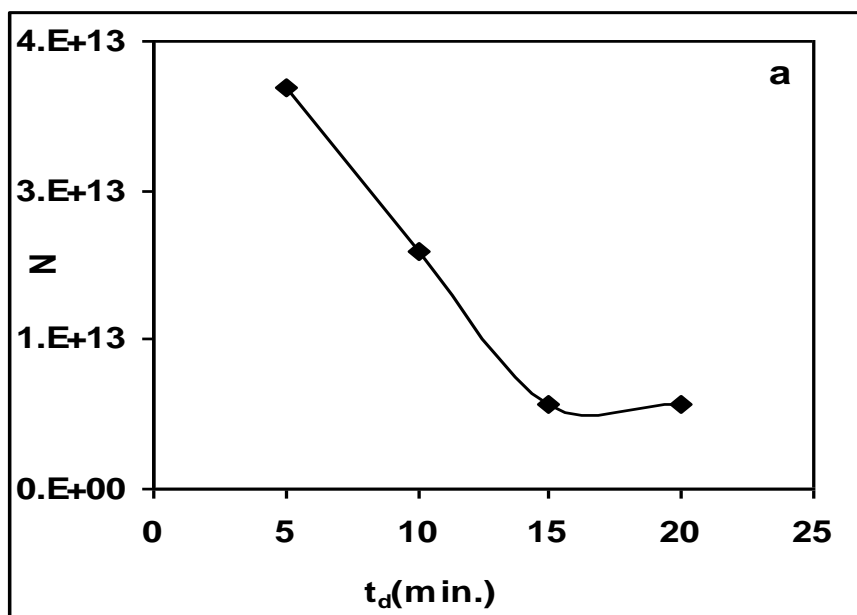**Fig. 4.** CdS films strain as a function of deposition time.

Fig. 5. Number of crystallites as a function of deposition time.

The decreasing in number of crystallites with deposition time is shown in Figure 5. The decreasing accompanied is that the nucleation with various orientations can be formed at the initial stage of the deposition and each nucleus competes to grow but only nuclei having the fastest growth rate survive.

3. 3. Optical Properties: Absorption coefficient

3. 3. 1. The effect of film thickness and growth temperature

The optical transmition and absorption spectra of various deposited films were obtained and analyzed over wavelength range from 450-560 nm at room temperature as shown in Fig. 6(a-c). The samples show high coefficient of absorption ($\alpha > 10^5$ cm^{-1} for $\lambda < 500$ nm), and then decrease at different rates dependence on the films structure to reach constant values at long wave lengths which it above from the (520 nm), where the films become transparence at this wave lengths. It is obvious that the absorption coefficient in the 5 min. deposition is better than that of the longer deposition time. This was actually expected, since the CdCl$_2$-based film is much smoother and more uniform.

3. 3. 2. Effect of changing bath concentrations

The variation in the absorption coefficient with bath volumes is shown in Fig. 7(a-c) at deposition temperature 60 °C, deposition time 10 min. and pH = 11. It is clear that the value of α increases with increasing photon energy. After a certain deposition time, the absorption and/or dissolution process predominates over the heterogeneous and homogenous precipitation, resulting in the decrease of film thickness and hence the absorption coefficient increased as the concentration of cadmium salt increased. The variation in absorption coefficient with KoH concentration is mainly due to the dramatically decreasing of the film thickness beyond 3.5 ml. The film thickness increases with the [NTA]/[Cd] ratio until it reaches its maximum at a ratio of 4, hence the absorption coefficient decreased as the ratio increased Fig. 7(c).
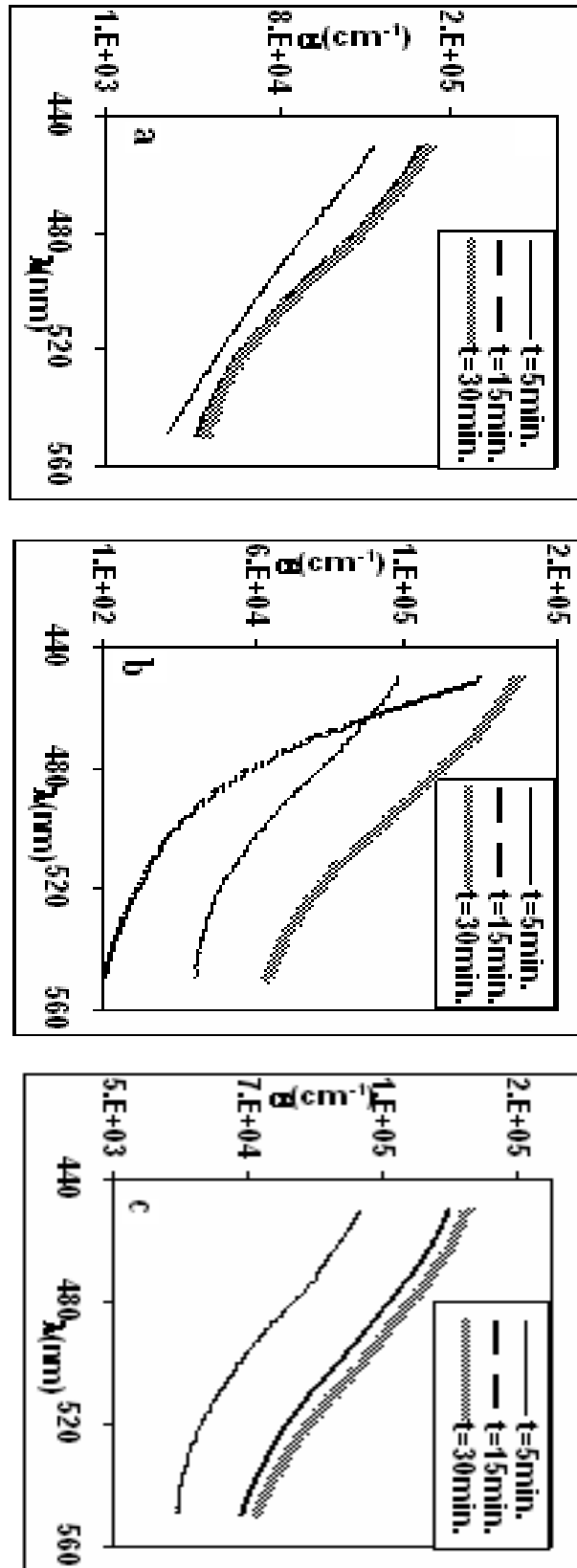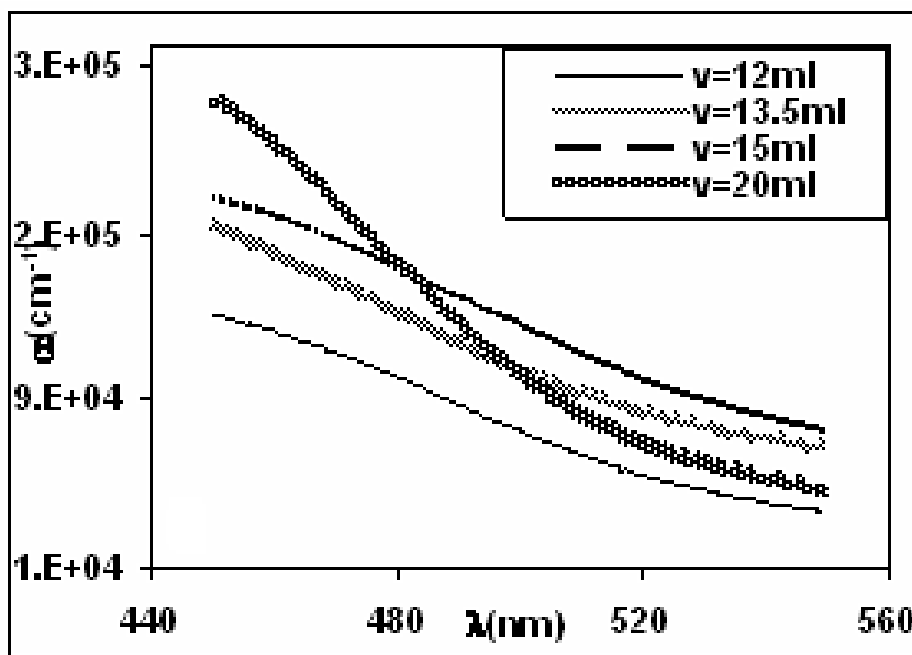
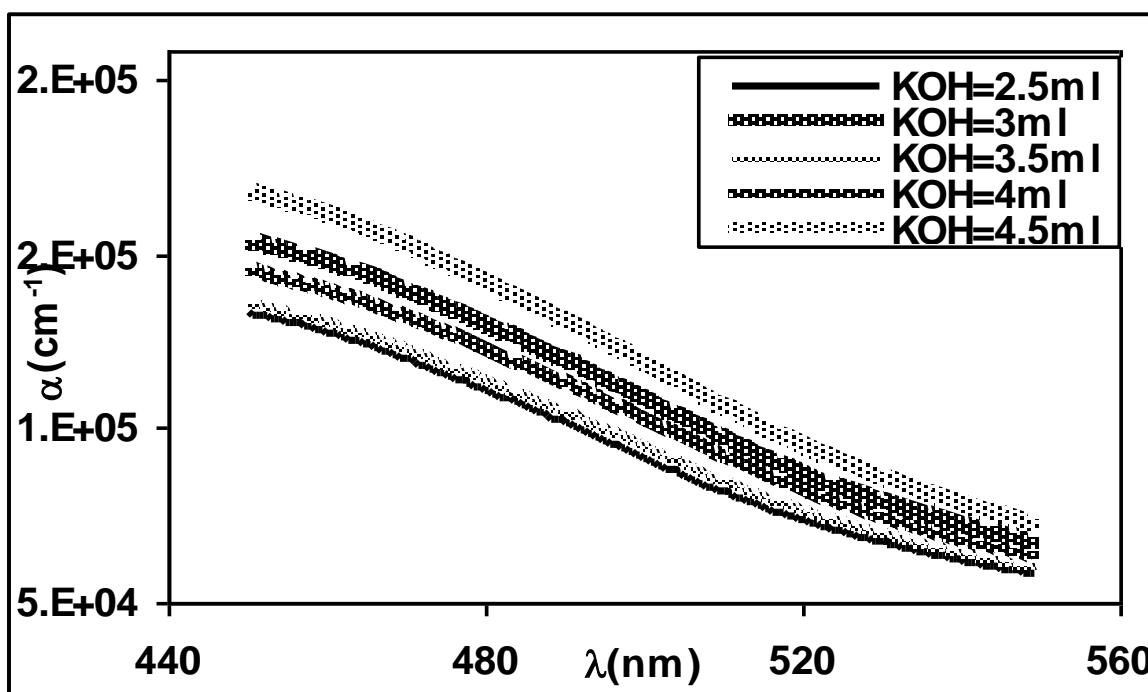**Figure 6.** absorption coefficient of CdS films using CdCl$_2$ source and pH = 11 at deposition time (a) 5 min., (b) 10 min., (c) 15 min.
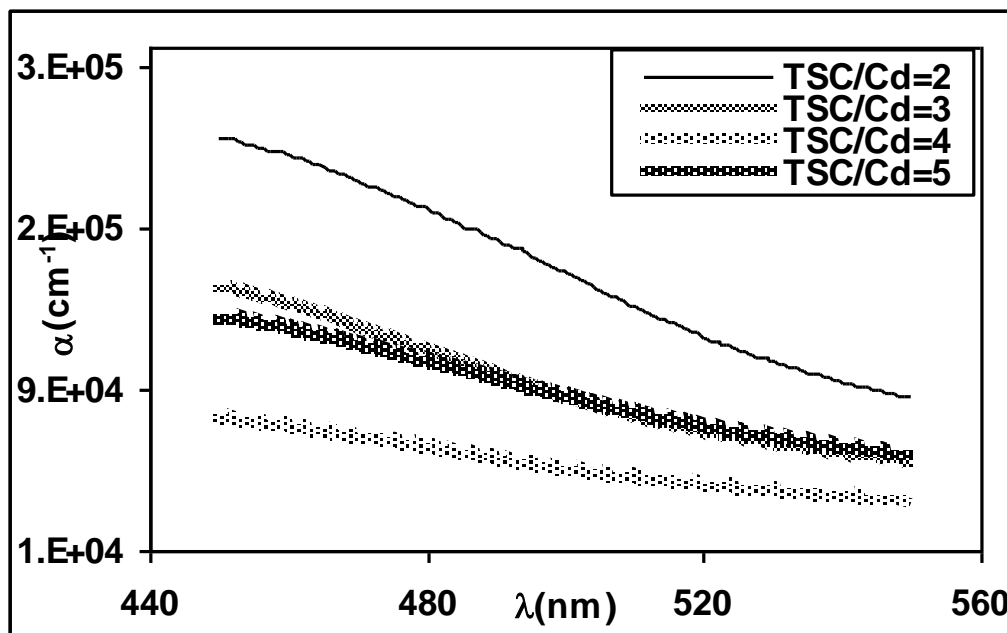
(**a**)

(**b**)

Figure 7. Absorption coefficient vs; (a) CdCl$_2$ volume; (b) KOH concentrations; (c) TSC/Cd ratio.

(c)

Figure 7(continue). Absorption coefficient vs; (a) $CdCl_2$ volume; (b) KOH concentrations; (c) TSC/Cd ratio.

3. 4. Energy gap calculations

3. 4. 1. The effect of film thickness and growth temperature

It is clear that the value of α increases with increasing photon energy. Absorption coefficient is related to photon energy by the following equation

$$\alpha h\nu = A\,(h\nu - Eg)^n$$

where A is constant depending on transition probability, Eg is the band gap of the material and n has different values depending on the absorption process. It was found that n = 1/2 is the best fit for our result.

The energy gap values depend in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice; also it is affected by crystal regularity. The energy gap (Eg) value is calculated by extrapolation of the straight line of the plot of $(\alpha h\upsilon)^2$ versus photon energy.

The values are closed to those already obtained with $CdSO_4$ (16). Table (2) shows the effect of CdS thickness and temperature on the energy gap. It is obvious from the tables that the energy gap decreases as the temperature increased because there is more chance for the polycrystalline film to have greater crystallite size.

The energy gap of CdS films decreased as the film thickness increased (with deposition time) for the same reason.

Table 2. Effect of temperature and deposition time on energy gap using $CdCl_2$ source and pH = 11.

Deposition condition		Eg(eV)				
Time effect		5min.	10 min.	15 min.	20 min.	30 min.
Temperature effect	50°C	2.43	2.39	2.38	2.37	2.37
	60°C	2.42	2.38	2.6	2.34	2.34
	70°C	2.41	2.37	2.32	2.31	2.31

3. 4. 2. Effect of changing bath concentrations

Table (3) shows the influence of the bath constituent concentrations on the band gap values. Increasing the volume of $CdCl_2$ beyond 13.5 ml having the greatest influence in decreasing the band gap value. Increasing in the KOH concentrations having no influence, and the NTA]/[Cd] shows a noticeable change.

Table 3. Effect of $CdCl_2$ volume, KOH concentration and the [NTA]/[Cd] ratio on energy gap at deposition temperature 60 °C, deposition time 10 min. and pH = 11.

$CdCl_2$ volume (ml)	Eg (eV)
10	2.39
12	2.38
13.5	2.38
15	2.33
20	2.31

KOH concentration	Eg (eV)
2.5	2.32
3	2.315
3.5	2.34
4	2.31
4.5	2.31

[NTA]/[Cd] ratio	Eg (eV)
2	2.32
3	2.35
4	2.37
5	2.34

4. CONCLUSION

In this work, we have showed that deposition time and path temperature play a dominant role in controlling the film thickness, growth rate of chemically deposited PbS polycrystalline. On the other hand, XRD investigations show that the grain size increases with deposition time while the dislocation density decreases with deposition time. Also the strain decrease in with time due to the enhancement in the degree of crystallinty of deposited film. The energy gap decreases as the bath temperature increased. The Optical absorption study reveals that PbS thin films have allowed direct transitions, with band gap energy varies from 2.31 to 2.43 eV depending on deposition conditions.

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