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## **Annealing Effects on the Structural, Optical and Electrical Properties of Chemically Deposited CdS Thin Films using NH<sub>4</sub>Cl Complexing Agent**

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### **Abstract**

CdS thin films of different thicknesses were deposited by chemical bath deposition technique by varying deposition time. For the deposition, an aqueous solution of cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea were used. Effect of annealing on structural, optical and electrical properties of the CdS thin films was observed. X-ray diffraction confirmed the cubic CdS phase formation, with a preferred orientation along (111). It is found that the crystallite size is larger in films deposited with low deposition rate. The crystallite size increased with increasing thickness and decreased after annealing. The mobility and carrier concentration of the CdS thin films of different thicknesses increased (and accordingly the resistivity decreases) after annealing. The crystal structure, band gap, Urbach energy and electrical properties of CdS thin films changed after annealing.

**Key words:** CdS thin film, Chemical bath deposition, Annealing effect, XRD, Band gap.

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### 1. Introduction

As a buffer layer in a solar cell heterostructure cadmium sulfide (CdS) plays a significant role as it has the vital properties of direct n-type semiconductor with a band gap of about 2.4 eV and large absorption coefficient of  $4 \times 10^4 \text{ cm}^{-1}$  [1]. Among various other promising cadmium-free buffer layer such as indium (III) sulfide ( $\text{In}_2\text{S}_3$ ), Zinc sulfide (ZnS), tin sulfide (SnS), tin oxide (SnO), etc. the solar cells using buffer layer of CdS is still showing the highest efficiency [2]. Among other nonvacuum or sol-gel techniques such as spray pyrolysis, spin coating, and dip coating the chemical bath deposition (CBD) is came out to be the most simple and low-cost method and produces uniform, adherent and reproducible films. Moreover, CBD is a low temperature technique and can be used for CdS deposition onto a wide range of substrates.

Generally, the formation of CdS thin films by CBD is governed by two mechanisms, heterogeneous growth, i.e. ion by ion condensation of  $\text{Cd}^{+2}$  and  $\text{S}^{-2}$  ions on the substrate and homogeneous growth i.e. adsorption of colloidal particles on the substrate. At the earlier stage of deposition, the  $\text{Cd}^{+2}$  ions in the solution form complexes with a complexing agent and  $\text{NH}_3$ . At this stage, more free  $\text{Cd}^{+2}$  ions are available in the solution and these ions react with  $\text{S}^{-2}$  ions and produce a cluster type of CdS particles. Thereafter when the concentration of  $\text{Cd}^{+2}$  ions gradually decreases then at higher  $\text{NH}_3$  concentration,  $\text{Cd}^{+2}$  ions are strongly complexed by  $\text{NH}_3$  ions and no free  $\text{Cd}^{+2}$  ions are formed in the solution so that further formation of CdS particles is not possible. At this stage heterogeneous mechanism governs the deposition of a uniform thin layer of CdS [3, 4].

A number of studies have been carried out to obtain high quality CdS thin films by optimizing the parameters of CBD method, such as deposition time, temperature, pH value and also by varying the concentrations of various reagents as well as complexing agents [4–9]. The homogeneity and growth rate of CdS thin films depends on the complexing agent used during chemical bath

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deposition. It is reported that good quality CdS thin films can be grown by using ammonia and ammonium chloride as the complexing agent [5]. The anions from the cadmium and ammonium salts are believed to play a role in the growth of CdS films. This role is suspected to be that of a complementary complexing agent [10, 11].

Several post deposition treatment such as annealing in N<sub>2</sub>/Air/H<sub>2</sub> atmosphere at different temperatures have been carried out to see their effect on structural and optical properties of CdS thin film. Maticiuc et al. [12] found different properties of CdS film depending on the neutral, reducing or oxidizing annealing gas. Oxygen containing phases CdSO<sub>3</sub> and CdO are shown by XRD patterns for air- and N<sub>2</sub>- annealed CdS films at 400°C. Longest N<sub>2</sub> annealing generated pure CdS layers, similarly with the H<sub>2</sub>- annealed ones. Lichimura et al. [13] annealed CdS thin films at temperatures up to 500 °C. The cubic phase of the as-deposited film remains dominant until the annealing temperature becomes higher than 400 °C. By the annealing at 450 °C, the XRD pattern turns to that of hexagonal phase. The band gap is decreased by annealing below 400 °C and then abruptly increased by the annealing at 450 °C. Islam et al. [5] annealed the CBD processed CdS thin films for 30 min. at 400°C and 500°C, respectively in a vacuum furnace with pressure 500 mTorr. The cryatallinity of the films increased with increasing annealing temperature.

In this study, the low cost CBD technique is used for the deposition of CdS thin films. Ammonia and ammonium chloride are used as the complexing agent. The CdS thin films are grown at different deposition time to analyze the film growth. The as-deposited films were annealed in N<sub>2</sub> environment at 430 °C to see the annealing effect. The results found from the above analysis are compared for as-prepared and annealed CdS thin films of different thicknesses with respect to the preparation processes.

## 2. Experimental Details

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CBD processed CdS thin films were grown onto sodalime glass substrates from the decomposition of thiourea in an alkaline solution containing a cadmium salt and suitable complexing agent ammonia ( $\text{NH}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ). As we employed  $\text{CdCl}_2$  as Cd source, therefore,  $\text{NH}_4\text{Cl}$  was used as a buffer to control the release of ions during the deposition process, therefore, results in a stable complex.

The substrates were cleaned using ultrasonic bath and degreased in methanol-acetone-methanol-deionized (DI) water for 10 minutes successively. Degreased substrates were dried on a hotplate. CdS precursors were prepared with 0.0199 M of  $\text{CdCl}_2$ , 0.019835 M of  $\text{NH}_4\text{Cl}$  and 0.1423 M of Thiourea in DI water for all types of CdS thin films. First, a beaker containing DI water was immersed in the Chemical bath.  $\text{CdCl}_2$  were added to DI water and after that  $\text{NH}_4\text{Cl}$  was added drop by drop under continuous stirring. The cleaned substrates were immersed in the beakers vertically; the beakers were then covered and heated. At 50 °C ammonia was mixed with the solution. Thiourea was mixed with the solution at around 80 °C. The bath temperature was fixed at 80 °C during deposition because, it has been deduced that, at low solution temperature conditions ( $T_s < 60$  °C), the deposition mechanism was achieved by the lower activation temperature process i.e. the ion by ion one. Whereas at higher temperatures ( $T_s > 60$  °C), where the deposition rate has a larger activation energy, the cluster by cluster process is the dominant growth mechanism. An increase in the solution temperature induces higher hydroxide cluster  $\text{Cd}(\text{OH})_2$  and sulfide ion concentrations [6]. Ammonia solution (28% of  $\text{NH}_3$  solution) was then added to maintain a pH of 10. After the deposition process was done, samples were washed and ultrasonicated with DI water for 1 min to remove the surface impurities, and then dried on a hot plate. The deposition time was varied as 20, 30 and 40 minutes to get different thicknesses. The deposited thin films were annealed in an annealing chamber (MTI corporation, GSL– 1100X) in  $\text{N}_2$  environment under a dynamic vacuum of around 2 Torr and at 430 °C temperature for 1 hour.

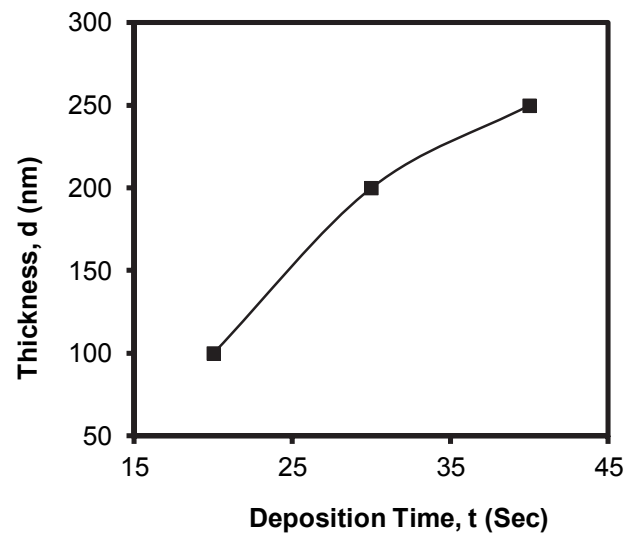
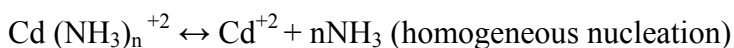
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The thickness of the cadmium sulfide (CdS) thin films were measured by using Surface Profilometer (DAKTAK-150). The X-ray diffraction analysis (XRD) was performed, by a Bruker D8 XRD with copper  $\alpha$  radiation to investigate the crystalline structure of the materials. The absorbance and transmittance were recorded using a dual beam UV-vis spectrophotometer (Shimadzu, UV-1601V). This spectrometer was used to measure the relative transmittance and absorbance of CdS thin films. The sheet resistance was measured by a four point probe measurement set-up and the mobility and carrier concentration was measured by a Hall effect measurement setup (ECOPIA, HMS-3000, SK).

### 3. Results and discussions

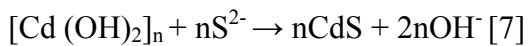
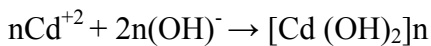
#### 3.1. Deposition Rate

Fig. 1 shows the change in thickness of CdS thin films with increasing deposition time. It is observed that the thickness increases faster following slower increase with increasing deposition time. It has been reported that heterogeneous process is highly desirable rather than homogeneous deposition for uniform thin films. It is also reported that homogeneous process forms precipitation of CdS in the solution resulting non-adherent powdery films. The reactions for both the processes are given as follows:



**Fig. 1** Variation of thickness at different deposition time.

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In our case the precipitation of CdS is observed after 30 mins of deposition i.e. at the earlier stage of deposition the resulting CdS films are dominantly governed by the heterogeneous mechanism and shows a uniform thin layer and gradually ends up with homogeneous growth. Ouachtari et al. reported that increasing the concentration of the cadmium ions in the CBD process produces a higher final film thickness; also longer deposition time is needed to attain the final film thickness. In addition, after a certain deposition time, the absorption and/or dissolution process predominates over the heterogeneous and homogenous precipitation [11].

### 3.2. Crystal structure

It is reported that cadmium sulphide can exist in both sphalerite cubic and hexagonal forms. Cubic CdS grows in the zincblende structure, considered a metastable phase [14]. The XRD patterns of

CdS thin films are shown in Fig. 2.

Three diffraction peaks matched with JCPDS 01-074-9663 correspond to (111), (220) and (311) reflections at  $2\theta$  of  $26.5^\circ$ ,  $44^\circ$ , and  $52^\circ$ , respectively indicating that the obtained CdS films have a cubic structure with the preferential orientation normal to the (111) direction. The similar film structure has also been reported by other

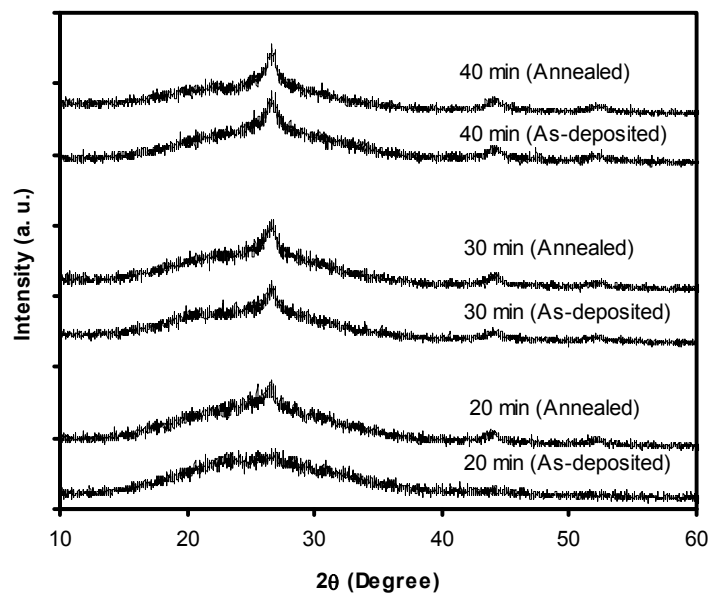


Fig. 2 Superimposed XRD pattern of as-deposited and annealed CdS thin films deposited for 20, 30 and 40 minutes.

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researchers [15, 16]. All the XRD patterns exhibit a broad hump near the (002) peak at  $2\theta = 26.7^\circ$ , which is due to the glass substrate. A comparison between the spectra of the films shows that the peak intensity increases with increasing deposition time i.e. with increasing thickness the thicker film has more crystallinity than the thinner films. The degree of preferred orientation along (111) increased with the increase of thickness. The peak intensity of each of the three films increased after annealing indicating an increase in crystallinity [16]. Annealing helps the atoms to rearrange themselves and eliminate defect density in the film resulting in good crystallinity. Tomas et al. [17] reported that the  $N_2$  or Ar annealing brings reorientation of as deposited CdS films with a significantly improved crystalline quality by increasing the grain size and decreasing the number of grain boundaries in CdS films. Also, such an annealing leads to phase transition from the metastable cubic phase to a stable hexagonal phase of CdS [18], which is undesirable when stacking CdS film with a cubic CdTe absorber [12]. In our case CdS thin films are not gone through any phase transition but improved in structural orientation due to annealing at  $430^\circ\text{C}$  in  $N_2$  environment.

The crystalline size of the CdS thin films film is calculated using FWHM data and Debye-Scherrer formula [13].

$$d = \frac{\lambda}{\beta \cos \theta_B} \dots \dots \dots (1)$$

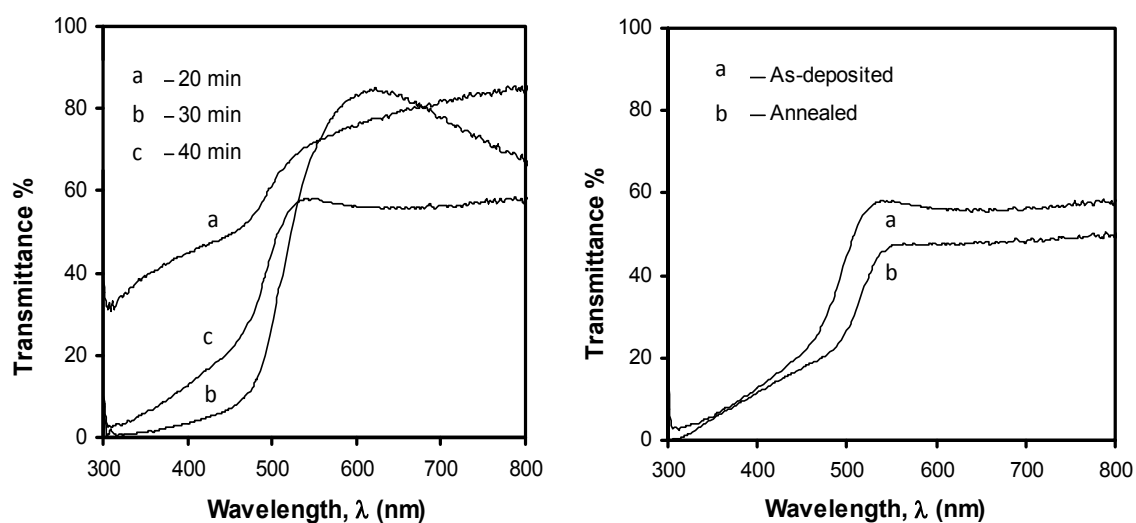
where  $d$  is the calculated grain size of the film,  $\lambda$  is the wavelength of x-ray radiation ( $1.54059\text{\AA}$  of  $\text{CuK}\alpha$  radiation).  $\beta$  is full width at half-maximum (FWHM),  $\theta_B$  is a peak position of the diffracted X-ray beam. The particle sizes calculated are 5.62, 2.38 and 1.53 nm for as-deposited and 4.7, 1.53 and 1.38 nm for annealed CdS thin films deposited for 20, 30 and 40 mins respectively. Thus it is deduced that the particle size increased with increasing thickness and decreased after annealing.

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Moulikia et al. (2009) [6] explained the reduction of the grain size by the variation of the growth rate. At high deposition rates (thicker films), the nucleation step is fast; the nucleation sites concentration is then large. Thereafter, the nuclei size enlargement is limited and blocked by the surrounding nuclei. However, at low deposition rates (thinner films), the low concentration of the nuclei sites enables the nuclei to grow and attain a larger size. Consequently, the grain size is larger in films deposited with low deposition rate.

### 3.3. Optical properties

UV-Vis spectrometry is used to see the optical properties such as transmission, absorption and optical band gap of the thin films. A blank sodalime glass slide was placed in the beam direction during the scanning process. Fig. 3(a) and 3(b) shows the variation of transmittance  $T$  (%) with wavelength  $\lambda$  (nm) in the wavelength range from 300 to 800 nm for as-deposited CdS thin films of various deposition time and 20 min deposited annealed CdS thin film. The maximum transmittance is observed around 82%, 58%, and 84% respectively in the visible region (400 to 700 nm). Fig. 3(b) shows



**Fig. 3** Transmittance vs. wavelength plots for (a) Different deposition time (b) As-deposited and Annealed CdS thin films.

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that transmittance  $T$  (%) decreased after annealing may be due to the denser CdS formation during the process [5]. It is found that the annealed CdS thin films exhibit the maximum transmittance (40% to 75%) in the visible range and have sharp fall at the band edge which is good for optoelectronic devices, especially for solar cell window layers, confirming the presence of crystallinity of CdS thin films [5, 21].

Fig. 4(a) shows the variation of absorbance measured in the wavelength ranging from 300 to 800 nm with the variation of deposition time i.e. 20, 30 and 40 min. Due to the variation of deposition time the thickness were found about 100, 200 and 250 nm for 20, 30 and 40 min respectively. Fig. 4(a) shows that the absorbance increases with the increase of CdS film thickness. Fig. 4(b) shows that the absorbance increases after annealing indicating the formation of denser CdS thin films due to annealing. Similar explanation is given by Islam et al. [5]. From the absorbance spectra, it is also observed that for all types of CdS thin films the maximum absorbance of CdS thin films is observed at around 300 nm. In the visible region the absorbance rises very rapidly before 300 nm, attains its maximum value and then decreases rapidly up to 600 nm i.e. the absorbance decreases rapidly from ultraviolet to visible region.

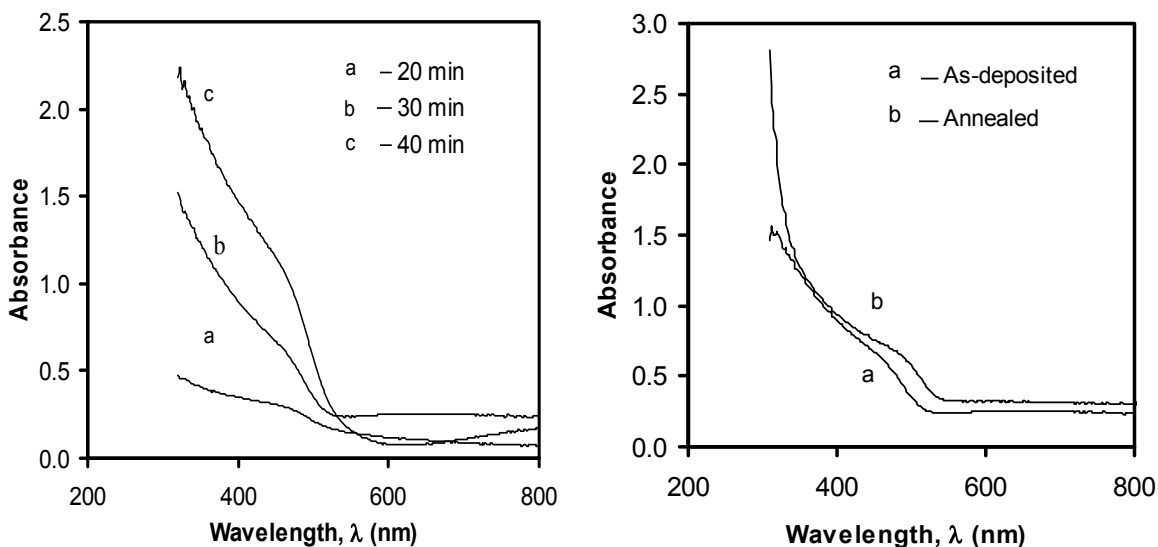


Fig. 4 Absorbance vs. wavelength plots for (a) Different deposition time (b) As-deposited and annealed CdS thin films.

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The absorption coefficient,  $\alpha$ , [22] was calculated from the measured absorbance data for different wavelengths corresponding to different photon energies at room temperature using equation (2).

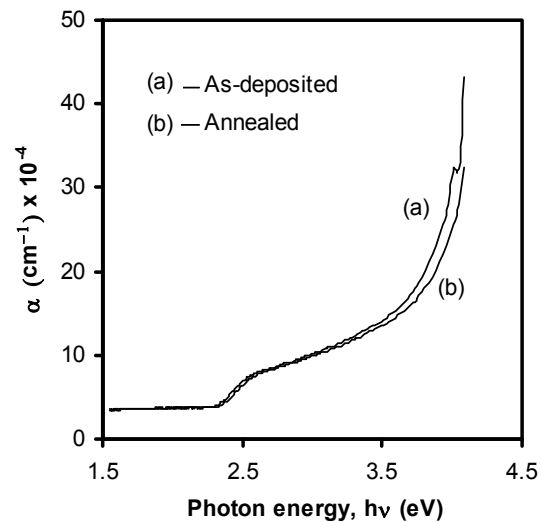
$$\alpha = 2.303 \frac{A}{d} \dots \dots \dots (2)$$

where  $A = \log_{10}(\frac{I_0}{I})$  is the absorbance and  $d$  is the thickness of the film. An idea of the band structure and electronic transition involved in absorption process can be obtained by studying the dependence of optical absorption coefficient on the photon energy.

The spectral dependence of  $\alpha$ , on the photon energy,  $h\nu$ , for as-deposited and annealed CdS thin films is shown in Fig. 5. The absorption coefficient of all CdS thin films increases with increase in photon energy. The absorption co-efficient increased annealing indicating denser films.

In crystalline and amorphous materials photon absorption is observed to obey relation [23],

$$\alpha h\nu = B (h\nu - E_{opt})^n \dots \dots \dots (5.2)$$

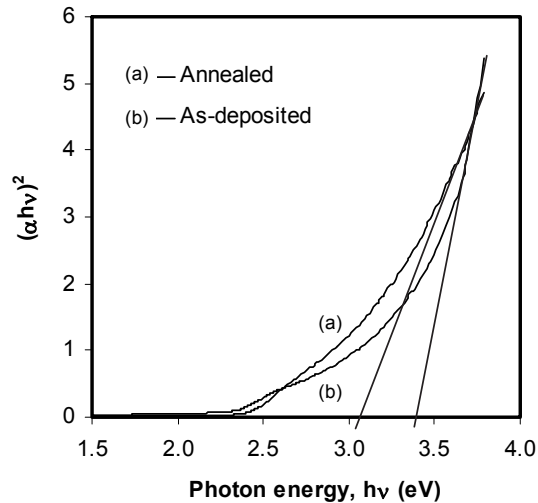


**Fig. 5** Absorption co-efficient vs. photon energy plots for as-deposited and annealed CdS thin films.

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where,  $h\nu$  is the incident photon energy,  $h$  Planck constant,  $\nu$  the frequency of incident radiation,  $B$  an energy independent constant,  $E_{opt}$  the optical band gap and  $n$  is an index depending on the type of optical transition caused by absorption. The index  $n$  equals  $\frac{1}{2}$  and  $2$  allowed direct and indirect transitions respectively. Therefore, the direct energy gap ( $E_{qd}$ ) can be obtained by  $(\alpha h\nu)^2$  versus  $h\nu$  curve and then extrapolating the linear portion of the the intercept in the  $h\nu$  axis. Fig.6 change in bandgap due to annealing. increase in band gap of CdS thin films



**Fig. 6**  $(\alpha h\nu)^2$  vs.  $h\nu$  plots for as-deposited and annealed CdS thin films.

observed after annealing. The band gaps obtained for as-deposited and annealed CdS thin films of different thicknesses are listed in Table 1. From Table 1 it can be depicted that the band gap energy is changed from 2.66 to 2.82 eV for as-deposited CdS thin films of different thicknesses and that for annealed are ranged from 3.60 to 3.87 eV for CdS thin films of different thicknesses. The increase of band gap after annealing can be attributed due to the formation of CdO during annealing. It is observed that the band gap changes slightly with the variation of deposition time i.e. there is a little increase of band gap with increasing thickness may be due to some structural changes as also depicted from XRD. But after annealing the band gap decreased with increasing thickness. This may be due to the fact that, as the thickness increases the relative amount of formation of CdO decreases. This happens because the CdO forms onto the surface of the CdS. When the thickness increases the  $O_2$  cannot penetrate the thicker films. On the other hand, it is found that the band gap energy of the CdS thin films increased significantly after annealing. This

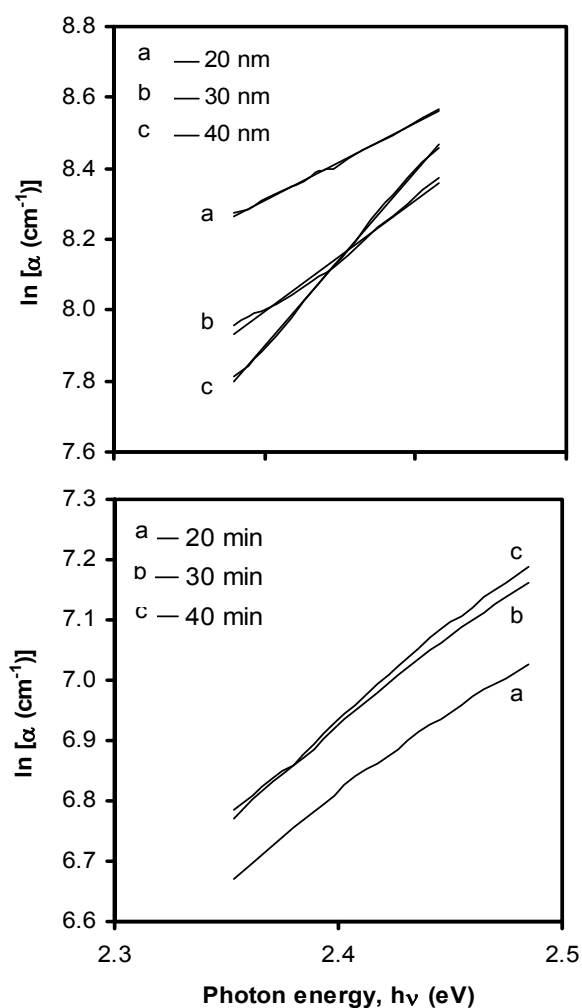
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occurrence can be explained based on the O<sub>2</sub> incorporation. Similar explanation on annealed CdS thin film was reported by Islam (2013) [5]. Wu et al. (2004) studied on RF sputtered CdS deposition using an O<sub>2</sub>/Ar atmosphere and showed that the CdS:O films become transparent in the wavelength range above the band gap of CdS and suggested that CdS films grown with inclusion of oxygen during deposition can be a better choice for thin film solar cells as oxygenation will further increase their band gap [21]. The band gap changes with increasing annealing temperature are thought to be caused by changes in the defects, the composition and the crystalline properties of the CdS thin films. The spectral dependence of  $\alpha$  was studied at photon energies less than the band gap of the films.

The Urbach energy was calculated from the slope of the plots of  $\ln\alpha$  vs  $h\nu$ . This gives the width of the localized states associated with amorphous states in gap at photon energies less than the band gap. The absorption coefficient near fundamental absorption edge is exponentially dependent on the photon energy [24].

$$\alpha = \alpha_0 \exp(h\nu/E_u) \quad (4)$$

where  $\alpha_0$  is a constant and  $E_u$  is the energy. Thus, the plots of  $\ln\alpha$  should be linear whose slope gives Urbach energy. The  $\ln\alpha$  vs  $h\nu$  plots for as-deposited CdS thin



from the slope of the band gap. The  $\ln\alpha$  vs  $h\nu$  plots for the incident light should be linear. The Urbach energy of the films of

**Fig. 7** Urbach plots ( $\ln\alpha$  vs  $h\nu$  curves) for:

(a) as-deposited CdS thin films with different thicknesses and (b) annealed CdS thin films with different thicknesses.

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different thicknesses are shown in Fig. 7(a) and that of annealed CdS thin films are shown in Fig. 7(b). The Urbach energies are calculated from the slopes of the Urbach plots and are listed in Table 1. The Urbach energies are ranging from 2.61 to 5.1 eV for as-deposited and 2.34 to 3.4 eV for annealed CdS thin films of different thicknesses. It is found from Table 1 that as the thickness increased the band gap and tail width of CdS films increased due to the increase in disorder/impurity and film stoichiometry with thickness or deposition time. Dingyu et al. [20] reported that the band gap and tail width change are related to film stoichiometry which changes with deposition parameter. It can be noticed that the Urbach energy decreases after annealing for all the thicknesses. This behavior may be due to decrease in the degree of disorder and decrease in density of defect states (which results in the

**Table 1:** Variation of band gap with deposition time of as-deposited and annealed CdS thin films.

CdS thin film	Deposition Time (min)	Film Thickness (nm)	Band Gap (eV)	Urbach energy (eV)
As-deposited	20	100	2.66	2.61
	30	200	2.75	3.60
	40	250	2.82	5.10
Annealed	20	100	3.87	2.34
	30	200	3.70	3.12
	40	250	3.60	3.40

reduction of tailing of bands) as a consequence, increase in crystallinity. It is also found that the Urbach energy increases with increasing thickness indicating increase in disorder or defects with thickness or deposition time.

### 3.4. Electrical Properties

To characterize the electrical properties of the thin films, Four Point probe and Hall effect measurements is performed in air at room temperature. The as-deposited films exhibit

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semiconducting behaviors with resistivity in the range of  $10^{-2}$   $\Omega$ .cm for as-deposited CdS thin films and  $10^{-3}$   $\Omega$ .cm for annealed CdS thin films. The resistivity decreased one order of magnitude after annealing. This decrease is attributed to the improved crystallinity, growth in grain size and the improvement in film stoichiometry, as is indicated by the XRD patterns. n-type conductivity is observed by the Hall measurements for both types of the CdS thin films. The mobility and carrier concentration of as-deposited and annealed CdS thin films are given in Table 2. It is

**Table 2:** Electrical parameters for as-deposited and annealed CdS thin films.

CdS thin film	Film Thickness (nm)	Resistivity (Ohm.cm)	Mobility ( $\text{cm}^2/\text{Vs}$ )	Carrier concentration ( $\text{cm}^{-3}$ )
As-deposited	100	$4.08 \times 10^{-2}$	$9.62 \times 10^1$	$5.45 \times 10^{11}$
	200	$5.00 \times 10^{-2}$	$1.46 \times 10^0$	$2.80 \times 10^{11}$
	250	$6.43 \times 10^{-2}$	$5.40 \times 10^1$	$9.62 \times 10^{11}$
Annealed	100	$3.32 \times 10^{-3}$	$2.96 \times 10^1$	$1.60 \times 10^{12}$
	200	$2.21 \times 10^{-3}$	$1.41 \times 10^2$	$3.05 \times 10^{12}$
	250	$1.81 \times 10^{-3}$	$1.68 \times 10^2$	$6.12 \times 10^{12}$

observed that both of the mobility and carrier concentration of the CdS thin films of different thicknesses increases (and accordingly the resistivity decreases) after annealing. Generally, the carrier concentration and mobility increases due to the interstitial  $\text{Cd}^{+2}$  ions or sulfur vacancies exist in the film. These carriers act as donors and results in an increase in the carrier concentration as well as a consequent decrease in the resistivity [10]. Any significant change in carrier concentration and mobility is not observed due to thickness variation.

#### 4. Conclusion

The structural, optical and electrical properties of CBD deposited films were investigated. It is found that at the earlier stage of deposition the resulting CdS films are dominantly governed by

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the heterogeneous mechanism and shows a uniform thin layer and gradually ends up with homogeneous growth. The XRD pattern shows that the peak intensity increases with increasing deposition time. Also, the peak intensity of each of the three films increased after annealing indicating increase in crystallinity. The optical band gap lies in the range of 2.66 to 2.82 eV for as-deposited and 3.6 to 3.87 eV for annealed CdS thin films of different thicknesses. The Urbach energies are ranging from 2.34 to 5.1 eV for as-deposited and 2.61 to 3.4 eV for annealed CdS thin films of different thicknesses. Both of the mobility and carrier concentration of the CdS thin films of different thicknesses increase (and accordingly the resistivity decrease) after annealing. The structural, optical and electrical properties of CdS thin films are improved after annealing. These CdS thin films deposited by CBD technique, with the added advantages of cost effective, large area deposition and easy thickness control, can be very important for solar cell application.

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