



Fabrication and Characterization of Cadmium Sulfide (CdS) Buffer Layer Thin Film by Using Chemical Bath Deposition Method for Solar Cell

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Abstract: Cadmium sulfide (CdS) thin film has been prepared by chemical bath deposition technique as buffer layer for solar cell application with the variation of molar concentration of thiourea and deposition times. From the variation of thiourea concentration CdS-1, CdS-2 and CdS-3 thin films have been deposited with same deposition conditions and CdS-2(a), (b) and (c) thin films have been deposited by varying the deposition time i.e. 20 min, 30 min and 50 min with same molar concentration. The effect of deposition time and molar concentration of CdS thin films has been studied. The surface morphology and chemical composition of CdS thin films is investigated by scanning electron microscope and energy dispersive X-ray spectroscopy. The structure with crystal composition of thin films has been detected by X-ray diffraction method. The crystalline nature of the films has been observed to be dependent on thiourea concentration. The thin films showed preferred (002) plane orientation of the hexagonal phase of CdS. A minute change in band gap i.e. from 2.92 to 3.0 eV is found for different thicknesses and a significant change has been observed to lie in the range of 2.96 to 2.50 eV due to the variation of thiourea concentration.

Keywords: Chemical bath deposition; CdS thin film.

I. Introduction

For the p-n junction operation of solar cell there needs buffer layer as n type material for the absorber layer of p type material to be used as thin film. CdS, ZnS, ZnSe, etc. is used as buffer layer as thin film of solar cell [1]. Among various buffer materials CdS thin film which is II – VI compound semiconductor is extensively investigated because of their suitable band gap alignments [2]. CdS remains the most widely investigated buffer layer, as it has continuously yielded high-efficiency cells [3]. Several non-vacuum and vacuum based techniques have been attempted to fabricate CdS thin films. Among various fabrication techniques the vacuum techniques involve thermal evaporation [4], close spaced sublimation [5], sputtering [6], etc. and the non-vacuum techniques involve spray pyrolysis [7], spin coating [8], Chemical bath deposition [9] etc. In this work CdS thin films have been fabricated by chemical bath deposition (CBD) method for having advantages to obtain uniform films with good adherence and reproducibility. It also offers the advantages of economy, convenience and the capability of large area deposition [10]. This method allows the deposition of very thin films, of the order of a few nanometers. The physical properties of the chemical deposition of CdS films are dependent upon the growth parameters such as the bath temperature, the relative concentrations of the various reactants in the solution, the pH value and the type of substrate [9]. Usually the deposition of the CdS thin films by CBD is carried out using an alkaline aqueous solution (high pH) composed mainly of some sort of Cd compounds (chloride, nitrate, sulfate salts, etc), thiourea as the sulfide source and ammonia as the complexing agent. Ammonia helps to prevent the undesirable homogeneous precipitation by forming complexes with Cd ions. Different cadmium sources such as cadmium sulfate [11], cadmium acetate [12], cadmium chloride and [13] cadmium iodide/nitrate [14] have been used in this process. Several researchers took the attempt to fabricate CdS thin films varying thiourea concentration applying CBD method and found significant changes in their physical properties. The crystalline structure of CdS thin films is found hexagonal or cubic and the surface morphology and band gap changed significantly due to thiourea concentration [8, 15, 16]. In this paper the focus is to study the influence of thiourea concentration by evaluating the surface morphological, chemical compositional, crystalline structural and optical properties of CBD deposited and annealed CdS thin films.

II. Experimental

A. Sample preparation

Cadmium chloride (CdCl_2), thiourea, sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and liquid ammonia (NH_3) were taken for the preparation of CdS thin film. The CdS thin films were grown from decomposition of thiourea ($\text{SC}(\text{NH}_2)_2$) in an alkaline solution containing a cadmium salt i.e. cadmium chloride (CdCl_2), and suitable complexing agent, ammonia (NH_3) and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$). The CdS thin films were deposited by using CBD method onto soda lime glass (SLG) substrates. The substrates were cleaned by ultrasonic bath and degreased in methanol-acetone-methanol-deionized water for 10 minutes successively. Degreased substrates were dried by a hotplate. CdS precursors were prepared with 0.0199 M of Cadmium Chloride, 0.019835 M of Sodium Citrate in DI water for all types of CdS thin film samples. Then the mixture was placed in the Chemical bath. After reaching the temperature of 50°C ammonia was mixed in the solution. Thiourea was taken 0.142319 M, 0.087581 M and 0.065686 M, for CdS-1, CdS-2 and CdS-3 thin films respectively. Thiourea was mixed when the temperature was at around 80°C . The pH of the solution was maintained at 11. The deposition time was varied for CdS-2(a), CdS-2(b) and CdS-2(c) thin films from 20, 30 and 40 mins respectively to get different thicknesses. The deposited thin films were annealed in an annealing chamber (MTI corporation, GSL-1100X) in N_2 environment under dynamic vacuum of around 2 Torr and at 430°C temperature for 1 hour. The thickness of the cadmium sulfide (CdS) thin films were measured by using Surface Profilometer (DAKTAK-150).

B. Characterization

The ultraviolet visible (UV-vis) spectroscopy of annealed CdS thin films were performed 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. To investigate the structural properties the X-ray diffraction spectroscopy was done using a XRD spectrometer (Bruker, D8). The surface morphology and chemical composition were observed using a scanning electron microscope (JEOL JSM-7600F).

III. Results and Discussion

A. Surface Morphology and Compositional Analysis

The micrographs in Figures 1 (a) to (c) shows some spheroid granules due to the creation of nucleation centre on the film surfaces which are uniformly distributed throughout the surface. It is also observed that the density of the spheroid granules decreases when thiourea concentration increases. Similar morphological behavior for the CdS thin films is reported by Ouachtari *et al.* They narrated that when $[\text{S}]/[\text{Cd}]$ ratio is less, the small particles accumulate continuously and cover the entire surface of the substrate leading to an homogeneous layer [17].

Figure 1: (a) SEM image of CdS-1, (b) SEM image of CdS-2 and (c) SEM image of CdS-3

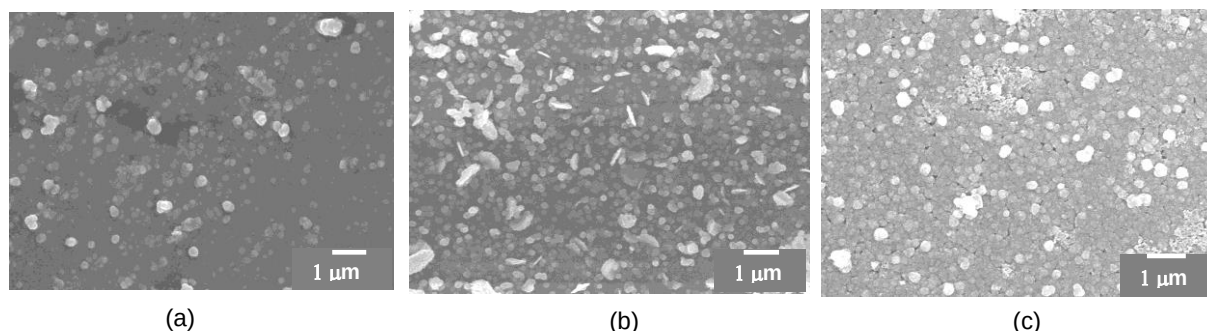


Table 1: Amount of compositions from EDX analysis of CdS thin films.

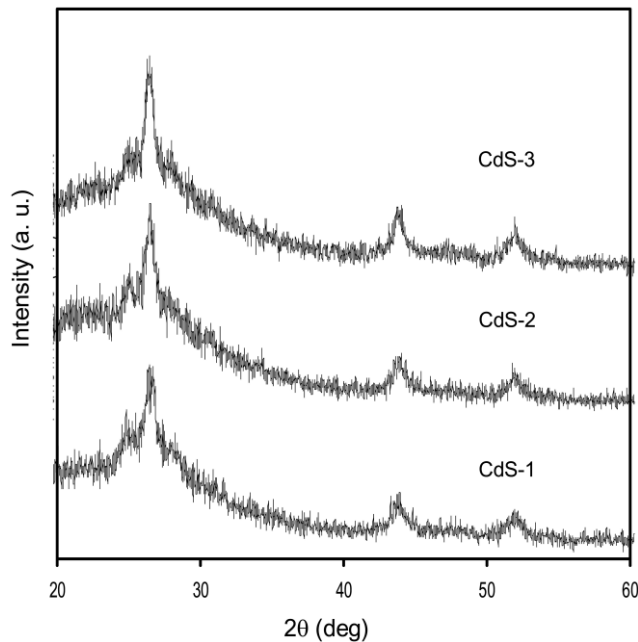
Element	Mass in %			Atom %		
	CdS-1	CdS-2	CdS-3	CdS-1	CdS-2	CdS-3
Sulphur (S k)	9.23	11.82	13.5	9.01	11.89	16.98
Cadmium (Cd L)	51.58	51.84	62.46	14.36	14.87	22.41
Oxygen (O k)	39.19	36.33	24.04	76.63	73.24	60.61
Total	100	100	100	100	100	100

From Table 1 it can be seen that the atomic% of Cd is higher than that of S indicating cadmium rich CdS thin films due to the higher reactivity of Cd compared with S and suggesting the presence of sulphur vacancies (excess of cadmium) in the deposited films, which act as donors, leading to n-type conductivity. [18]. It is also observed that the atomic% of S has decreased with increasing thiourea concentration whereas the O has increased. It is known that S has great affinity towards O, so some portion of S might have converted to SO_2 [7].

B. X-Ray Diffraction

In Figure 2 the CdS-1 thin film shows (100), (002), (101), (110) and (112) plane and shares the five most prominent reflections closes to the values of 24.9°, 26.5°, 28.2°, 43.8°, and 51.9°. The CdS-2 and CdS-3 thin film

Figure 2 Superimposed XRD pattern for CdS thin films for different thiourea concentration.



shows the same planes with same angles as CdS-1. This indicates the respective oriented crystallites with the (002) planes for all CdS thin films. It can be seen that the major peak at around 26.5° is strongly dominating the other peaks indicating a strong preferred orientation along the (002) plane of the hexagonal phase of CdS (JCPDS collection code: 01-074-9663). Additional peak corresponding to unreacted Cd or S has not been observed. The preferred orientation (002) peak indicates that the crystal nature of CdS thin films is Wurzite (Greenockite) with hexagonal structure matched with JCPDS 01-074-9663. The intensity of the (002) plane is found to be slightly increased with increasing thiourea concentration. This suggests that the crystallinity of these films increase. The results of X-ray analysis are agreed with earlier investigators report [8]. The poor increase in crystallinity may be due to the incorporation of O in the thin films which have been detected from EDX. It has been reported that an increase in O concentration can reduce the grain size of the hexagonal structure while the higher O content

can amorphize the film structure [19].

The crystalline size of the deposited film is calculated using FWHM data and Debye-Scherrer formula [20].

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

where d is the calculated grain size of the film, λ is the wavelength of x-ray radiation (1.54059 Å of CuKα radiation). β is full width at half-maximum (FWHM), θ_B is a peak position of diffracted X-ray beam. The grain or particle sizes calculated are 17, 23 and 58 nm for CdS-1, CdS-2 and CdS-3 respectively.

C. Optical properties

C.1 Transmittance

Figure 3.1 shows the variation of transmittance T (%) with wavelength λ (nm) in the wavelength range from 300 to 1100 nm for CdS-2(a), CdS-2(b) and CdS-2(c) thin films of various deposition time. The maximum

Figure 3.1 Transmittance versus wavelength graph for CdS-2 thin films for different deposition time.

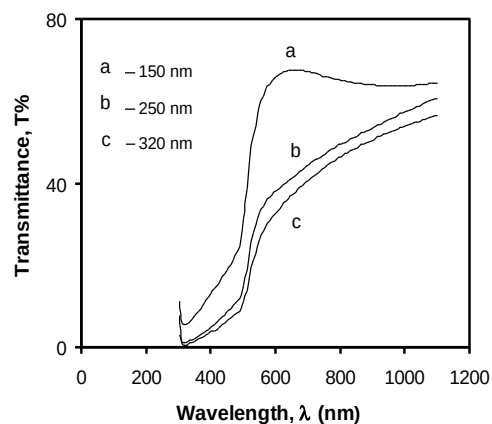
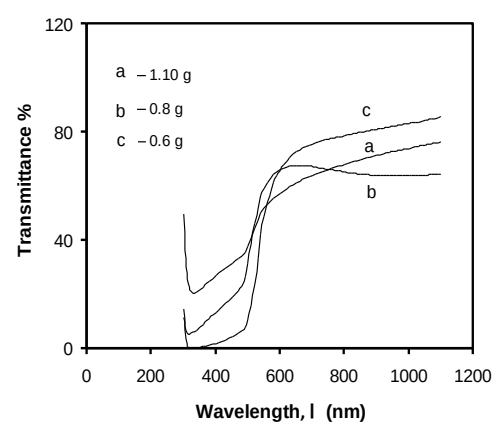


Figure 3.2 Transmittance versus wavelength graph for CdS thin films for different thiourea concentration.



transmittance is observed around 67%, 44% and 40% respectively in the visible region (400 to 700 nm). Figure 3.2 shows the variation of transmittance T (%) with λ (nm) for CdS thin films of three different molar concentration of thiourea. The transmittance decreases with the increase of thiourea concentration. The CdS-1, 2 and 3 deposited films show the maximum transmittance around 64 %, 67 % and 75% respectively in the visible region (400 to 700 nm). It can be seen that the films present high transmission (40% to 75%) in the visible range

and have sharp fall at the band edge which is good for opto-electronic devices, especially for solar cell window layers, which is an indication of the presence of good crystallinity of CdS thin films [16].

C.2 Absorbance

Figure 3.3 shows the variation of absorbance measured in the wavelength ranging from 200 to 800 nm with the variation of thicknesses ranging from 150, 250 and 320 nm for CdS-2 (a) (b) and (c) thin films of three different deposition times. It is observed that the absorbance increases with increasing thickness. Figure 3.4 shows the variation of absorbance for three annealed CdS-1, 2 and 3 thin films deposited with different molar concentrations of thiourea. The thickness of these deposited and annealed films were 200, 250 and 320 nm respectively. It is seen that the absorbance increases with the decrease of thiourea concentration and hence also with the increase of thickness of the CdS thin films. It is also observed that the absorption peak broadens with increasing thickness. An increase in thickness with increase of thiourea concentration should have been observed but this discrepancy might have taken place due to annealing. As sulphur (S) has great affinity towards oxygen, so it might have converted to SO₂ and then evaporated [7] resulting thinner films. The EDX also shows a decrease of S with increasing thiourea concentration.

Figure 3.3 Absorbance versus wavelength plots for CdS-2 thin films for different deposition time.

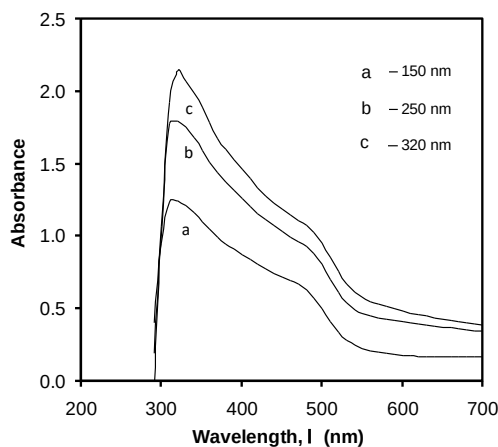
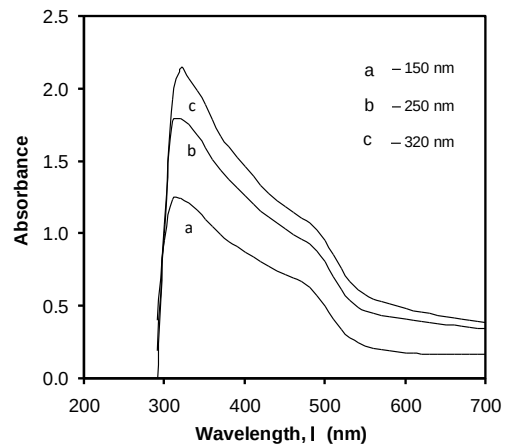


Figure 3.4 Absorbance versus wavelength plots for CdS thin films for different concentration of thiourea.



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.

Figure 3.5 Absorption co-efficient vs wavelength plots for CdS thin Films for different deposition time.

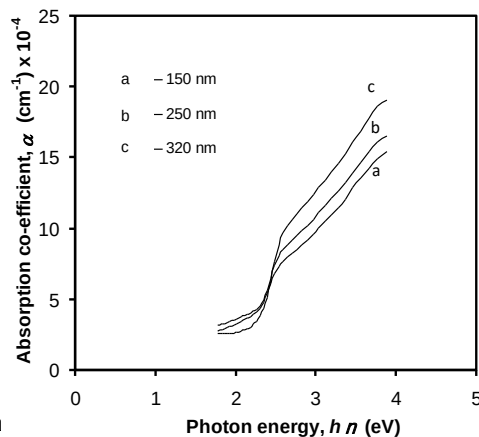
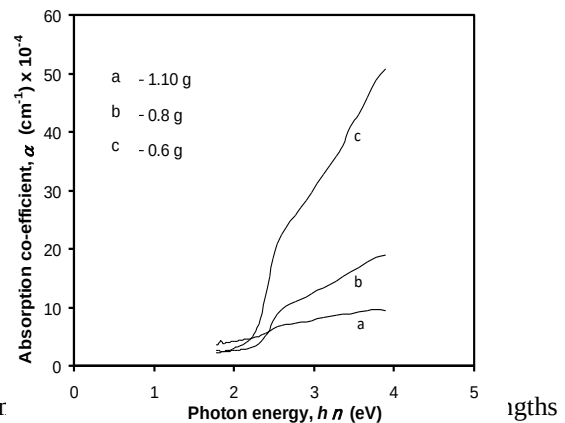


Figure 3.6 Absorption co-efficient vs wavelength plots for CdS thin Films for different concentration of thiourea.



The α corresponding to different photon energies at room temperature using equation (2).

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

where $A = \log_{10} \left(\frac{I_0}{I} \right)$ is the absorbance and d is the thickness of the film.

The spectral dependence of α , on the photon energy, $h\nu$, for CdS thin films deposited by varying deposition time as well as thiourea are presented in Figures 3.5 and Figures 3.6 respectively. The absorption coefficient of all CdS thin films increases with increase in photon energy.

C.3 Transition Energy Gap

The dependence of optical absorption coefficient on the photon energy helps to study the band structure and the type of electron transition involved in absorption process. In crystalline and amorphous materials the photon absorption is observed to obey the Tauc relation [22],

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

where, $h\nu$ is the incident photon energy, h Planck constant, ν 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 photon absorption. The index n equals $\frac{1}{2}$ and 2 for allowed direct and indirect transitions respectively. Therefore, the direct transition energy gap (E_{qd}) can be obtained by plotting $(ah\nu)^2$ versus $h\nu$ curve and then extrapolating the linear portion of the plots to the intercept in the $h\nu$ axis. In Figures 3.7 and 3.8 $(ah\nu)^2$ as a function of $h\nu$ is plotted to obtain the E_{qd} for CdS-2(a), CdS-2(b) and CdS-2(c) thin films having various deposition time and CdS-1, CdS-2 and CdS-3 thin films of different molar concentration of thiourea respectively. The E_{qd} is determined from the intercept of the linear part of the curves extrapolated to zero α in the photon energy axis. From Figure 3.7 it is seen that the band gap energy is changed from 2.92 to 3.00 eV for CdS-2 thin films of different thicknesses. For the variation of thiourea concentration the band gaps are obtained 2.5, 2.79, 2.96 eV for CdS-1, CdS-2 and CdS-3 respectively.

Figure 3.7 $(ah\nu)^2$ vs. $h\nu$ plots for CdS-2 thin films having different deposition time.

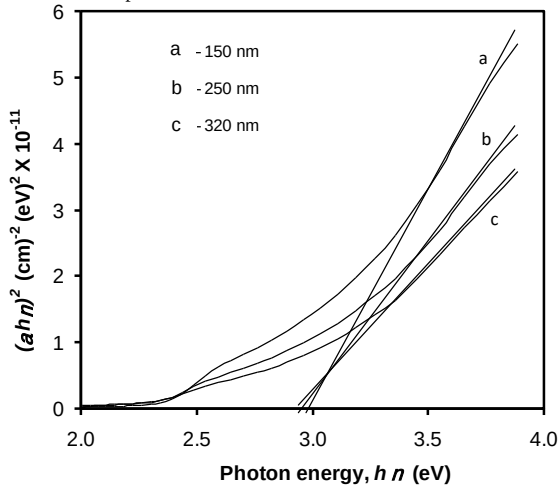
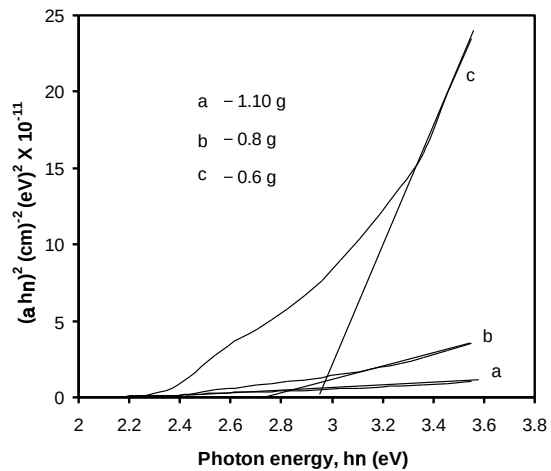


Figure 3.8 $(ah\nu)^2$ vs. $h\nu$ plots for CdS thin films having different molar concentration of thiourea.



The band gaps obtained from Figure 3.7 and Figure 3.8 are listed in Table 2.1 and Table 2.2 respectively. It can be seen that the band gap does not change significantly with the variation of deposition time for CdS-2. There is a little increase of band gap with increasing thickness. On the other hand, it is found that the band gap energy of the CdS thin films decreases significantly with increase of thiourea concentration. Decrease of band gap with increasing thiourea concentration is also reported by Shah [12, 3]. It is observed that with thiourea

Table 2.1: Variation of band gap with deposition time of annealed CdS-2(a), (b) and (c) thin films.

Deposition Time (min)	Film Thickness (nm)	Band Gap (eV)
20	150	2.92
30	250	2.96
50	320	3.00

Table 2.2: Variation of band gap with thiourea concentration.

Thin film	Film Thickness (nm)	Thiourea (M)	Band Gap (eV)
CdS-1	200	0.130	2.50
CdS-2	150	0.087	2.79
CdS-3	120	0.065	2.96

concentration, though the crystallinity increased slightly the band gap increased significantly. This occurrence can be explained based on the O incorporation. Similar explanation on annealed CdS thin film was reported by Islam [23]. Wu *et al.* studied on RF sputtered CdS deposition using an O_2/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 [24].

IV. Conclusion

SEM image confirms the uniform distribution of the granules in the thin films. The desired chemical compositions i.e. Cd, S and O are detected from EDX analysis. The preferred orientation (002) peak indicates that the crystal nature of CdS thin films is Wurtzite (Greenockite) with hexagonal structure. The crystallinity is found to increase with increasing thiourea concentration. O is found to be responsible for small increase in crystallinity compared to the higher increase in the band gap with thiourea concentration. The physical properties of the CdS thin films is possible to vary with thiourea concentration and thus can be a good candidate as the buffer layer of thin film solar cell.

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