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Study of optical and structural properties of chemical bath deposited CDS thin films

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ABSTRACT

Cadmium Sulphide (CdS) thin films of different thickness are prepared by the chemical bath deposition technique on well cleaned glass substrates at various temperatures. The thicknesses of the deposited films have been determined by gravimetry. The structural characterization is carried out by X-ray diffraction. The study confirms the polycrystalline nature of films with hexagonal structure. The structural parameters such as grain size, dislocation density, strain and lattice parameters have been evaluated. The composition of various constituents in CdS films have been determined by energy dispersive X-ray analysis. The optical properties like optical transmittance, band gap and refractive index has been studied in detail for the CdS films of various thicknesses which would be a promising material for the photo-voltaic applications. This paper deals with structural and optical properties of chemically deposited CdS films at the temperatures 600 C and 700 C with the composition of CdCl2 in aqueous solution 0.2 gm and 0.3 gm.

1. Introduction

In order to exhibit thin-film optics, the thickness of the layers of material must be on the order of the wavelengths of visible light (about 500 nm). Layers at this scale can have remarkable reflective properties due to light wave interference and the difference in refractive index between the layers, the air, and the substrate. These effects alter the way the optic reflects and transmits light. So, nowadays many researchers have focused their attention towards the different deposition techniques of thin films for photo voltaic applications. Of the various methods, the Chemical Bath Deposition (CBD) technique has many advantages such as simplicity, no requirements for sophisticated instruments, minimum wastage, economical way of large area deposition, no need of handling poisonous gases and possibility of room temperature depositions. With these advantages in mind an attempt has been made to deposit device quality CdS thin films at various temperatures by CBD technique. In earlier days the CBD technique was mainly used for preparing nano crystalline semi conducting thin films and widely used for depositing metal selenides [1]. In CBD the film formation occurs when the ionic product exceeds the solubility product as reported in the preliminary studies [1-4]. So a systematic study has been carried out for CdS films prepared at various temperatures.

2. Experimental

2.1 Material and Instrumentation

The structural characteristics of CdS thin films have been studied using X-ray diffractometer (Model – SHIMADZU XRD – 6000) with nickel filtered CuKa radiation (ג = 0.15418 nm) at 40 kV and 20 mA in the 2θ range 10º to 70º for the films with thickness 1920Aº, 1450Aº and 1740Aº.

The optical transmittance spectra of CdS films have been recorded from 190 nm to 2500 nm wavelength using Jasco UV-VIS-NIR spectrometer (Model – V-570) at room temperature using unpolarized lights from deuterium and tungsten lamps which are used at near normal incidence. The spectrometer is a double beam system with single monochromator having wavelength accuracy ±1.5 nm.

2.2 Preparation of CdS film

CdS thin films are prepared from a deposition mixture of cadmium chloride, thiourea, liquid ammonia and triethanolamine. The mixture containing totally 29 ml i.e., 0.2 gm of $CdCl_2$ dissolved in 10 ml distilled water, 0.7612 gm of Cs $(NH_2)_2$ dissolved in 10 ml distilled water and these two are dissolved in 5 ml liquid ammonia and 4 ml triethanol amine. The solution is mixed thoroughly and carefully. The common complexing agent ammonia is used as mediator and triethanol ammine is used to ensure slow release of Cd^{2+} ions in the deposition mixture. The reduction or oxidation reaction is shown in equation 1,

$$CdCl_{2\,(aq)} + CS(NH_2)_{2\,(aq)} + 2OH^-_{(aq)} \longrightarrow CdS_{(solid)} + CNNH_{2\,(aq)} + 2HCl_{(liquid)} \quad (1)$$

Optical glass slide with thickness of 1.25 mm are used as substrates. Prior to deposition the substrates have been cleaned with detergent solution, distilled water and acetone for about 30 minutes each in an ultrasonic bath to increase the rate of contamination removal and to achieve completeness. Finally the wet, cleaned substrates are dried in a clean oven maintained at about 90 ºC. Five substrates are suspended vertically in the solution maintained at 60 ^{0}C temperature using hot plate and stirred gently with a magnetic stirrer.

The deposition takes place by homogeneous reaction in the solution and by heterogeneous at the substrate leading to the formation of the film [5].

The deposition is allowed to continue for one hour. The thickness of the films for a single dip will be of the order 1000 Aº. A maximum bath temperature is fixed at 70º in order to suppress the rate of homogeneous reaction and minimize the evaporation of ammonia from the chemical bath. The thicknesses of the deposited films have been determined by gravimetric method.

3. Results and Discussion

3.1 Structural properties

The thicknesses of the deposited films have been determined by using Gravimetric technique. The figure (1) to (3) shows X – raydiffractogram of CdS thin films of different thicknesses grown at two different temperatures. The presences of peaks in the diffractogram reveled that the CdS thin films are polycrystalline in nature exhibiting hexagonal structure. G. Shimaoka, et al., reported [6] the existence of the cubic structure in vacuum deposited CdS films. CdS of 100-500 A^0 in thickness evaporated into four different single crystal substrates, (001) MoS_2, (001) Muscovite mica, (111) CaF_2, and (001) NaCl, held at 23°-500°C at various deposition rate (2-10 A^0/sec) have been investigated by reflection electron diffraction and transmission electron microscopy. Films deposited on all substrates consisted of hexagonal (wurtzite) phase at 23°C and a mixture of hexagonal and cubic (sphalerite) phases at 100°-500°C. A mixture of cubic and hexagonal structure is observed in the case of polycrystalline CdS deposited by R.F. Sputtering technique as reported [7] earlier. The presence of well formed hexagonal crystallites in these films are further confirmed using the x-ray diffraction patterns of sputtered films stripped from their substrates and reduced to a fine powder.

Figure 1

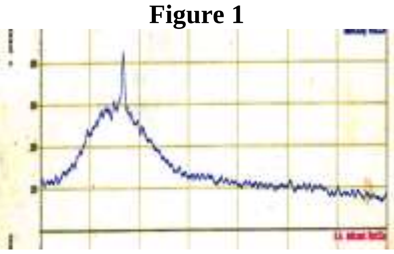
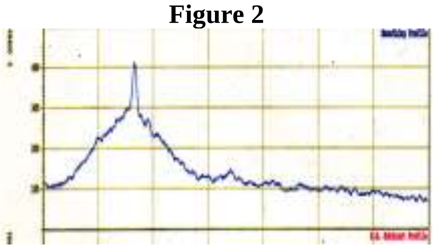


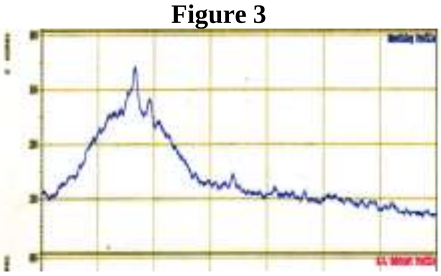
Figure 2



From the diffracting profiles the diffraction angle (2θ) and intensity lines are measured with high accuracy. Possible directions in which the films diffracted the beam of monochromatic X-rays are determined by Bragg's law

$$2d \sin\theta = n\lambda \text{ ---------------------(2)}$$

Figure 3



Where, d is Lattice spacing, θ is Glancing angle of X-rays, n is Order of diffraction and λ - Wavelength of X-rays.

The lattice spacing (d) has been determined from the formula 2, and it has been found that it is in good agreement with that of ASTM data. The thin crystallization are found to have a preferred orientation along the (002) direction. This is in accordance of the report of earlier workers.

The lattice parameters values 'a' and 'b' are found and shown in table I. From the (hkl) planes the lattice parameters such as 'a' and 'c' are calculated by the equation (3)

$$1/d^2 = a^2 [(h^2+k^2)] + c^2 / l^2 \text{ -----(3)}$$

These lattice parameters are found to be in good agreement with earlier workers (T.Nakanishi et al) and also of ASTM data. The crystallite sizes (D) are calculated using the Scherer's formula from the full width half maxima (β) from the equation 4.

$$D = (0.94\lambda) \text{ -----------(4)}$$

The strain (£) is calculated from the slope of β cosθ versus sinθ plot using the equation 5,

$$B = (\lambda / D \cos\theta) - \varepsilon \tan\theta \text{ ---------- (5)}$$

Where, β-Full width half maxima,

D- Crystallite size, λ-Wavelength of X-ray

The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal can be evaluated from the formula 6,

$$\delta = 1/ D^2 \text{ ---------------------------- (6)}$$

Table 1

hkl	Coating Temp	Composition of $CdCl_2$ in aqueous solution	Film Thickness	ASTM		Observed		d A°		D x 10^{-10} m	δ x 10^{15} line /m^2	Strain x 10^{-3}	F.W.H.M
				a	c	a	c	ASTM	Observed				
002	70	0.2	1920	4.1409	6.7198	4.09499	6.68711	3.3599	3.3393	130.396	5.88	5.1087	0.01093
002	60	0.2	1450	4.1409	6.7198	4.10304	6.70026	3.3599	3.5026	102.005	9.611	5.8744	0.01413
002	70	0.3	1740	4.1409	6.7198	4.10380	6.70155	3.3599	3.3508	102.054	9.601	6.5863	0.01395

3.2 Optical properties

3.2.1 Absorption

In the optical studies the absorption (abs) Vs wavelength (λ) spectra have sharp absorption spectra at lower wavelength region. The absorption is high at lower wavelength due to poor crystalline of the film. The wavelength increases more than 500 nm the absorption is completely reduced as shown in figure (4-6).

Figure 4

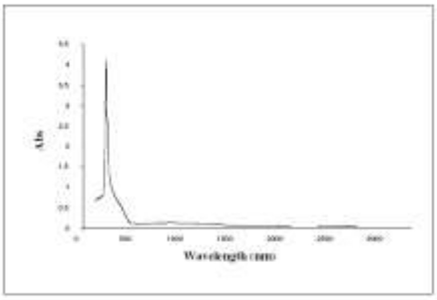


Figure 5

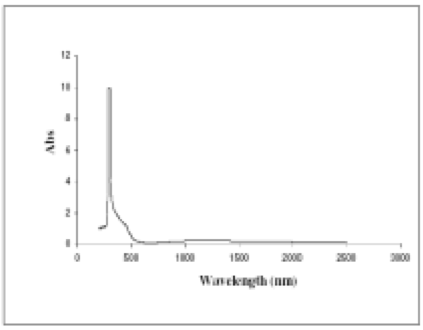
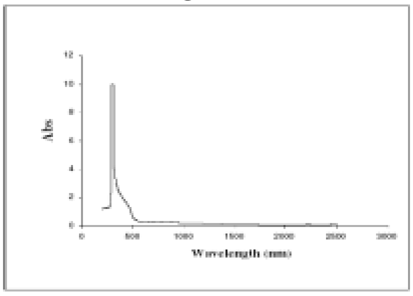


Figure 6



3.2.2 Transmittance

The optical characterization has been studied and the optical transition of the CdS thin film was found to be increase with the increase of the wavelength of the incident light as reported earlier [8]. At 0.5 µm (band gap of CdS), the transmission is 75%. In the wavelength range of 0.5 µm to 1.0 µm, the transmission value increases from 75% to 98%. The transmittance (T) Vs wavelength (λ) spectra have been taken for all the samples. The graph (7-9) shows the typical optical transmittance spectra of chemically deposited CdS thin films. It is observed that the optical transmittance is maximum of 85% in IR region.

Figure 7

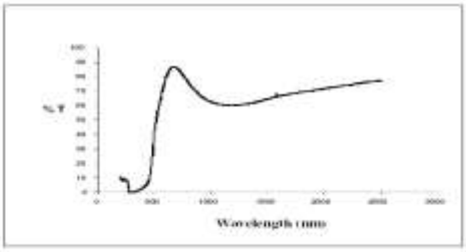


Figure 8

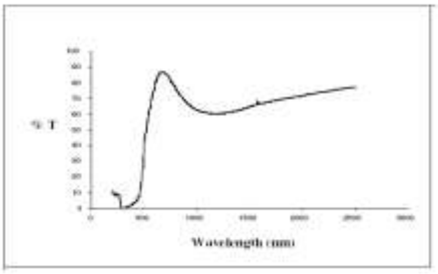
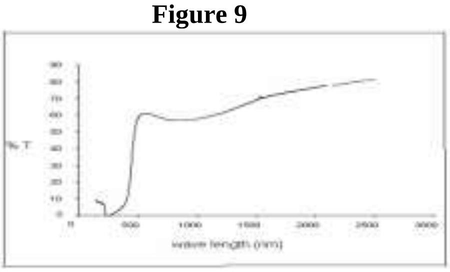


Figure 9



3.2.3 Refractive Index

The refractive indices of the films were calculated from the transmittance spectra. It is clear that the value of the refractive index varies from 2.3 to 2.49 as shown in table II. The random variation of the refractive index may be due to the presence of impurities and strain in this films [9 – 14], the refractive index of the films were calculated using the relations by Manifacier et al..

$$n^2 = N + (N^2 – n_o^2 n_1^2)^{1/2}$$

$$N = (n_o^2 + n_1^2)/2 + 2 n_o n_1$$

$$(T_{max} - T_{min}) / (T_{max}\ T_{min})$$

Where n_o and n_1 are the refractive indices of air and glass respectively.

Table 2

S.No	Composition of $CdCl_2$ in aqueous solution gms	Coating Temperature °C	Thickness A°	Band gap eV
1	0.2	60	1417	2.54
		70	1450	2.51
2	0.3	60	1710	2.5
		70	1740	2.48
3	0.4	60	1940	2.45
		70	1960	2.44

3.2.4 Optical band gap

The optical band gap E_g values of the chemically deposited CdS thin films can be determined from the plot of $(\alpha h\nu)^2$ Vs (hν) as shown in figure (10 and 11) as the representative case. The extension of the straight line portion of the graph $(\alpha h\nu)^2$ Vs (hν) gives the optical band gap. The presence of a single slope in the curves suggests that all the films are single phase in nature and the type of transition is direct and allowed. This type of transition has been reported already by several workers [15-20]. The extension of straight line from the curve gives the optical band gap of chemically bath deposited thin films as shown in figure (10 and 11). It is clear that in this CdS film, the band gap increases with decreasing thickness. These values are found to be good agreement with the reported values of earlier workers [7, 21-23]. By optimizing the thickness parameters the band gap can be reduced which enhances the usage of the prepared thin film in the photovoltaic applications.

Figure 10

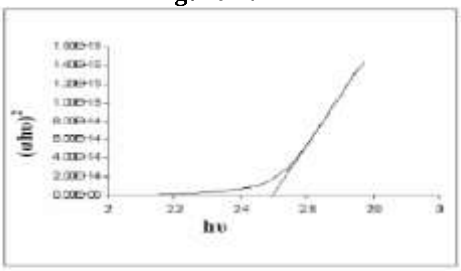
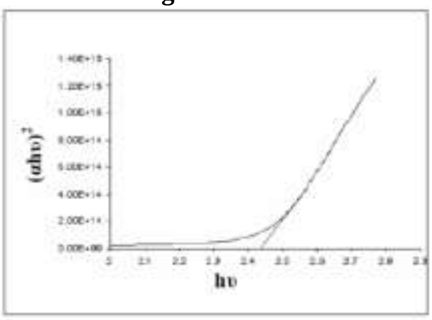


Figure 11



3.2.5 Absorption co-efficient

The plots are drawn that the variation of absorption co–efficient (α) with wave length (λ) of the CdS thin films. From the plots it is revealed that the absorption decreases with increasing wavelength.

The extrinsic co-efficient K_f also decreases as wavelength increases. The absorption of radiation gives rise to transition of electrons from valence band to conduction band. The absorption co-efficient was calculated using the transmittance (T) value measured for a particular wavelength and the film thickness (t) using the relation 7,

$$\alpha = (2.303\ A) / t \quad \text{-------------} \quad (7)$$

Where A is absorbance value and t is thickness of the semiconductor film.

Similarly the absorption co-efficient α can be estimated by the Urbach relation 8

$$\alpha = A (h\nu - E_g)^{p} / h\nu \quad \text{----------------} \quad (8)$$

Where A is constant, E_g is the energy gap, ν is the frequency of the incident radiation, h is the Planck's constant and the exponent p = 0.5 for direct allowed transition, 2.0 for indirect allowed transition.

Table 3

S.No	Film thickness A°	Refractive index
1	1920	2.34
2	1710	2.49
3	1417	2.30

3.3 Conclusions

By using chemical bath deposition technique the CdS films of different thickness have been prepared. X-ray diffraction reveals that the films are polycrystalline in nature with hexagonal structure. The variations in the particle size, strain dislocation density with temperature for different composition have been studied. Using Transmittance spectra the optical band gap and the various optical parameters like absorption co-efficient, extinction co-efficient and refractive index are determined and the results are discussed.

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Legends

Figures

1. X – ray diffractogram of CdS thin film with thickness 1417 Å
2. X – ray diffractogram of CdS thin film with thickness 1710 Å
3. X – ray diffractogram of CdS thin film with thickness 1920 Å
4. Absorption spectra of CdS thin film with thickness 1417 A^0
5. Absorption spectra of CdS thin film with thickness1710 A^0
6. Absorption spectra of CdS thin film with thickness1920 A^0
7. Transmittance spectra of CdS thin film with thickness 1417 A°
8. Transmittance spectra of CdS thin film with thickness 1710 A°
9. Transmittance spectra of CdS thin film with thickness 1920 A°
10. Band gap of Chemical bath deposited CdS thin film coated at 343K with thickness 1710 A°
11. Band gap of Chemical bath deposited CdS thin film coated at 343K with thickness 1920 A°

Tables

1. Structural parameters of CdS thin films
2. Variation of band gap with film thickness
3. Variation of refractive index with film thickness