Studies on structural, optical and photoelectron transportation in solution grown nanosize CdS thin films for photosensor application

S D Chavhan, S V Bagul, A R Patil & R P Sharma*

Thin Film and Semiconductor Laboratory, Research Centre, Department of Physics, G. T. Patil College,
Nandurbar 425 412, India

CdS Thin films of different thicknesses have been deposited onto glass substrates at 60°C.The source materials for Cd and S have been used as $CdCl_2$ and NH_2-CS-NH_2 in ammonia solution respectively. The reaction mechanism involved the preparation of film onto precleaned glass substrate through Cd^{2+} and S^2 ions in aqueous solution. Deposited thin films were annealed in air from 50 to 450°C. The XRD results are presented only for the films annealed from 300 to 450°C, as below 300°C there is no appreciable change in crystal structure. From the XRD patterns, films are seen to be polycrystalline in nature with the formation hexagonal phase. The crystallinity of the films was improved by annealing in air at 400°C. The optical transmittance, reflectance and absorption of annealed CdS thin films with different value of thicknesses are then studied in the energy range 1.1-4.0 eV. The CdS films showed allowed direct optical band gap E_g = 2.38 eV. Films of different thicknesses have same maximum transmittance intensity at same wavelength, 590 nm but refractive index varies in the range 2.15-2.85. The photoconductivity of different thicknesses CdS films has been measured with varying light intensity level as $L^{0.2}$-L^1 and it has been observed that the photoconductivity is changed. The decay time constants and demarcation time (60-80 s) have been calculated by photoconductivity measurement and have same values for all different thicknesses of CdS films. The above results are useful for low cost photosensor device applications.

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Cadmium sulfide (CdS) thin films received considerable attention due to their application in thin film solar cells[1], electrochemical cells[2], gas sensor[3], semiconductor metal[3], metal and Schottky barrier cells[1]. CdS does not play a direct role in photovoltaic conversion of solar radiation. However, it is adequate as an optical window and preferred over other materials of wide band gap due to its compacts crystallographic cell and electronic affinity with $CuInSe_2$, InP, CdTe, and other *p*-type semiconductors used as absorber. The precise measurement of film thickness gives valuable information about the growth kinetics of very thin films. It also helps in obtaining reproducible thin films characteristics. CdS photosensitivity films have been studied in view of their potential application in various electronic devices. Studies of the CdS films prepared by various methods such as thick film technique[4,5], chemical bath deposition[6-9], spray pyrolysis deposition[10,11], and vacuum deposition[12-15] have been reported in the literature. The deposition of good quality, adherent and nano-crystalline CdS film has been studied by deposition technique, i.e., solution growth technique. Although there are a few reports on the solution growth, the most recent studies demonstrate that the production of thin film is very difficult. In this study, nano-crystalline CdS thin films of different thicknesses have been prepared by using our improved process, which was optimized and the amounts of ammonia playing an important role and the structural, optical, and photoelectron transportation properties of the films have been investigated.

Experimental Procedure

CdS films with different thickness were prepared on precleaned glass substrates by solution grown technique. The $CdCl_2$ is a cadmium source material in ammonia solution, and NH_2-CS-NH_2 is a sulphur source material dissolved in ammonia solution. These two solutions were mixed with each other and *p*H of the solution was maintained as ≥ 9. Initially the solution was stirred thoroughly, so that all the ions should be mixed with each other. The *p*H value played an important role in uniform film deposition. The uniform thin films were deposited onto vertically inserted precleaned glass substrates at 60°C for one to two hours. A set of films of different thicknesses 800,

*For correspondence (E-mail : ramphalsharma@yahoo.com)

1355, 2009, 3016 and 3515 Å were prepared and the deposited films were annealed from 50 to 450°C and then annealed films were characterized. The accuracy ±0.01 of the measurement technique has been considered. The film thickness was measured by transmittance spectra using interference technique reported:

$$t = \frac{M \lambda_1 \lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_2]} \qquad \dots (1)$$

where, M is the number of oscillations between two extremes occurring for λ_1 and λ_2, $n(\lambda_1)$ and $n(\lambda_2)$ being corresponding refractive indices.

$$n = [N + (N^2 - n_s^2)^{1/2}]^{1/2} \qquad \dots (2)$$

where, $N = \dfrac{1 + n_s^2}{2} + \dfrac{2n_s(T_{max} - T_{min})}{T_{max} T_{min}} \qquad \dots (3)$

where, n_s is refractive index of the substrate and T_{max} and T_{min} correspond to maxima and minima in transmission interference curve.

The X-ray diffractogram was taken by X-ray diffractometer (Rigaku Japan) with glancing angle 0.3° using CuK$_\alpha$ target for films annealed at different temperatures. The dependence of photoconductivity at room temperature, current-voltage characteristic and photocurrent-intensity behaviour of the films were studied. Using digital Pico-ammeter (Lab Tech. Equip) dark current, photocurrent, and decay of photocurrent measurements were carried out. The least count of instrument was 1 PA and it can measure current upto 1 mA in five different ranges. To established current-voltage relationships, a d.c. regulated variable voltage power supply (Aplab Model H1003) was used. The samples were photoexcited by using Philips 60 W bulb. "Suryamapi" measured intensity of radiation. The photocurrent was measured for each sample: (i) as a function of intensity of photoexcitation, keeping accelerating voltage constant. (ii) as a function of acceleration voltage, keeping photoexciting intensity constant, that is photo *I-V* characteristic and (iii) further delay of photocurrent was also measured.

The experimental arrangements for both transmittance and reflectance have been performed for different thicknesses CdS films. The constant deviation spectrometer (Andhra Scientific Co.) was first calibrated by a white light source to get continuous spectrum to detect the incident intensity in the wavelength range of 400-700 nm. Then, transmitted and reflected

intensities were measured for all different thicknesses of the samples in the above wavelength zone.

Results and Discussion

The Cd to S ratio of annealed (400°C) film was measured by EDAX technique. There was no appreciable change in from starting composition of film, i.e., annealed film have same Cd to S ratio on glass substrate as elements were taken at starting composition in solution. The XRD was used for conformed the crystal structure. There was no appreciable change in XRD patterns, when films (2500 Å) were annealed in air from 50-300°C. It was interesting to note that CdS films on glass substrates were polycrystalline in nature as presented in Fig. 1. The analysis of different diffraction peaks indicates the formation of CdS hexagonal phase. The diffraction peaks at 2θ values 26.5°, 28.5°, 36.5°, 44.0°, 47.5° and 50.5°; clearly reveal the formation of CdS hexagonal phase[16,25,39]. The most significant feature of spectra of the films annealing in air was an increase in the crystallinity[6,8,30] of the films. However, the relative intensity ratios of these peaks agree with data reported by American
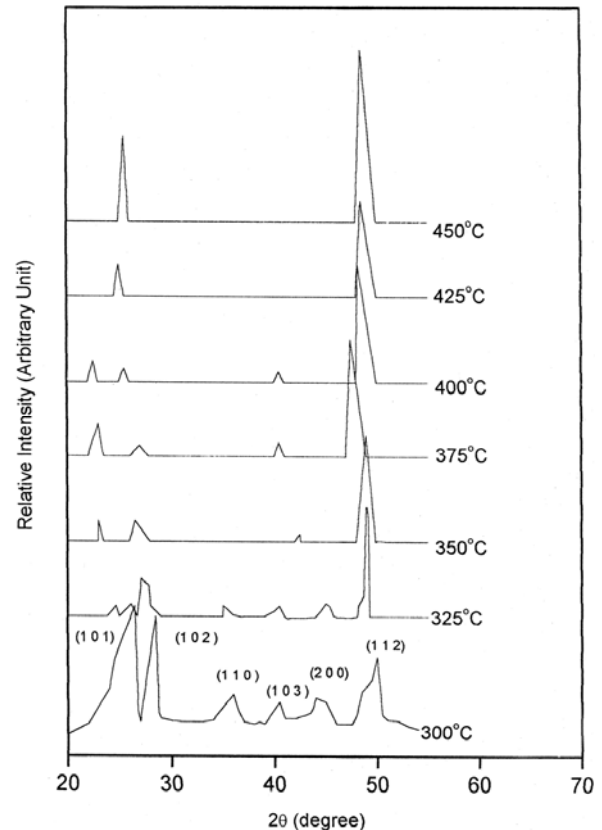
Fig. 1 – X-ray diffraction spectra for annealing temperatures from 300 to 400°C, for films 2500 Å thick.

Society for Testing Materials (ASTM)[6,16,20,30]. In the present case, preferential orientations were along the plane (112) (ref. 16).

Photoconductivity

All samples exhibit photoconductive effect when excited by light source. The variation of photocurrent as a function of acceleration voltage and intensity seems to depends on thickness of the samples having thickness below 1000 and 3500 Å, while it was large for all samples having thickness in the range of 1500-2500 Å, for photoexcitation intensity 24 mW/cm^2 and accelerating voltage of 100 V as shown in Fig. 2. A simple model, based on direct recombination of electron-hole pair annihilation, predicts that at a given accelerating voltage, the photoconductivity varies

with light intensity level L as L$^{0.5}$. It was found that plots of log of photocurrent versus log of intensity give two straight lines with different slopes. At low intensities (below 10 mW/cm^2) the values of slopes were different than those at higher intensities (above 10 mW/cm^2) for all samples of different thicknesses[18-39]. The values of slope (S$_1$) at low intensity and slope (S$_2$) at high intensity are presented in Table 1. For all different thicknesses of the samples, it can be seen from the Table 1 that the values of slopes S$_1$ (low intensity) and S$_2$ (high intensity) represent the higher values at 2009 Å thickness than the other thickness of the films[17]. It may be suggested that such thickness (2009) Å film will be more useful for the device fabrication than the other thickness of the samples.

Table 1– Values of slopes from the photocurrent variation with intensity

	Present study		Reported value
Thick-ness, Å	Slopes S$_1$ (Low power intensity)	Slopes S$_2$ (High power intensity)	
800	0.21	0.24	0.5 to 1.0 or
1355	0.50	0.76	even higher 0.43
2009	2.10	1.00	to 1.33
2500	1.22	0.57	
3016	0.50	0.54	
3515	0.72	0.60	

Table 2– Dark and photocurrent and photosensitivity as a function of thickness

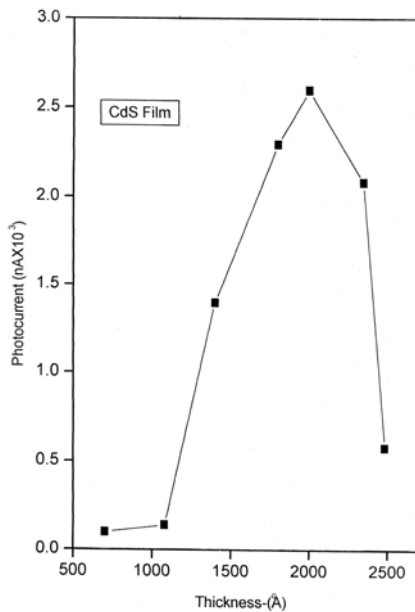| Sample thickness, Å	Dark current I_d, nA	Photocurrent I_p, nA	Ratio I_d/I_d
800	19	35	1.84
1350	30	169	5.63
2009	30	1400	46.66
2500	360	2800	7.77
3016	400	2400	6.00
3515	90	630	7.00

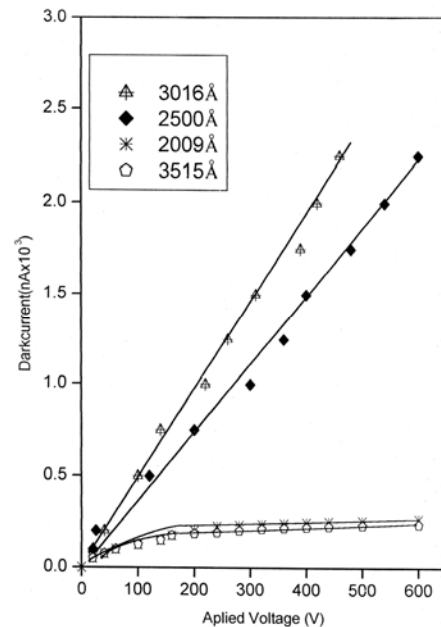Fig. 2 – Photocurrent as function of film thickness

Fig. 3 – Dark current as a function of accelerating voltage

Photosensitivity

The study of variation of dark and photocurrent for the same acceleration voltage depends on thickness. The dark current and photocurrent (100 V at constant accelerating voltage and photoexcitation intensity 24 mW/cm^2) for all samples of different thicknesses are presented in Table 2. From this table it is found that the sample of thickness of 2009 Å was the most photosensitive as the ratio of photocurrent to dark current is between 40 and 50. The dark current-voltage characteristic (*I-V*)[25,39] for the sample having thicknesses 2800, 2009, 3016 and 3515 Å are presented in Fig. 3 and represent the linear and ohmic behaviour, while the characteristic were slightly deviated from linear nature at constant photoexcitation intensity (Figs 4 and 5) applied to the films[18]. It can be seen from these figures that the film 2000 Å thickness at low intensity (8 mW/cm^2) and 3315 Å thickness at higher intensity have the more ohmic nature than the other thicknesses of the films.

Photocurrent decay

From observation of decay time it was noted that plot of log (photocurrent) versus time is not a straight line. This indicates that the decay is not exponential. The plots of log (photocurrent) versus log (time) are straight giving two straight regions I and II. After removing incident radiation, this abrupt change in the slope occurs after a certain time of 60-80 s as presented in Table 3. The change in slope occurs as the photocurrent reduces to 30-45% of I_o. This may be attributed to the recombination mechanism. In the first region, the recombination may be direct while in second region it may through trapping centers.

Absorbance measurements

The absorbance was measured under identical conditions of all samples of different thicknesses. For each sample the following graphs were plotted: (i) absorption coefficient (α) as a function of photon energy (hν) (Fig. 7) and (ii) (αhν)^2 versus (hν) (Fig. 8)

From the graphs of (α) versus (hν) and (αhν)^2 versus (hν), the values of band gap were estimated. In

Table 3– Demarcation time as a function of thickness

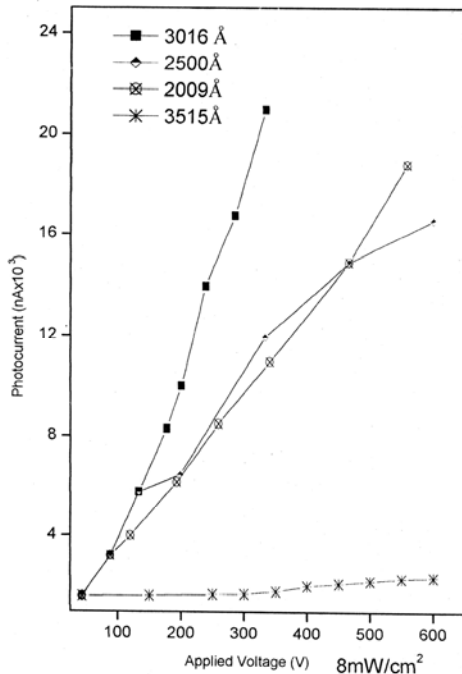| Thickness, Å	Slope S$_1$	Slope S$_2$	Demarcation time, s
800	0.70	0.75	70
1350	1.00	1.42	80
2009	0.56	0.88	62
2500	0.48	0.68	62
3016	0.40	0.50	80
3515	0.60	1.00	80

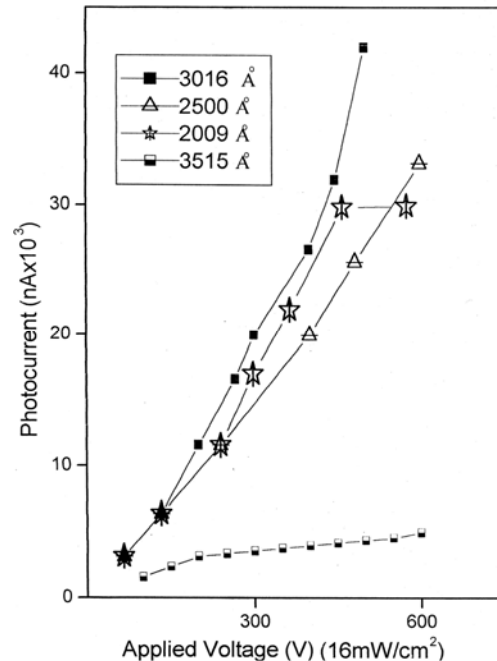Fig. 4 – Photocurrent as a function of accelerating voltage (8 mW/cm^2).

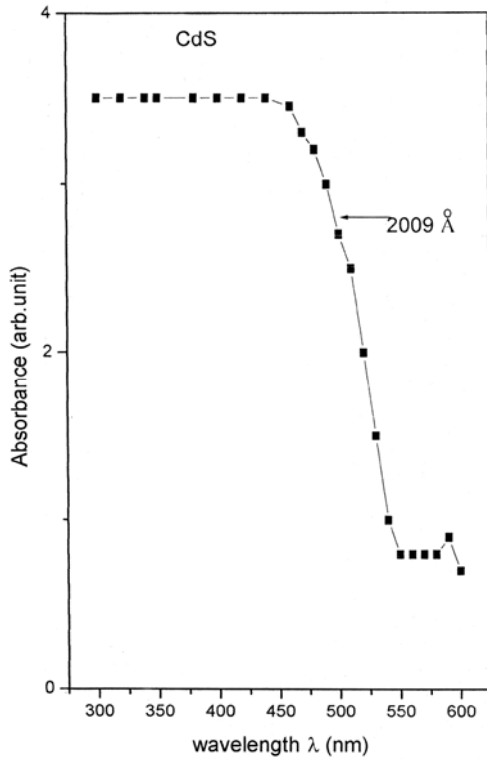Fig. 5 – Photocurrent as a function of accelerating voltage (16 mW/cm^2).

Fig. 6 – Absorbance versus wavelength of films of thicknesses 3016 and 2009 Å

Fig. 7– Absorption coefficient as a function of photon energy

addition to this, for a sample thickness 2009 Å absorbance observations as a function of wavelength were recorded (Fig. 6) on spectrophotometer (Hitachi U-2000, Japan make) from this observation, the wavelength at which 'α' rises suddenly, corresponds to the band gap energy were estimated. The estimated and reported values of band gap energy are presented in Table 4. From this study it also observed that maximum value of absorption coefficient for thicknesses 2009, 2500, 3016, and 3515 Å samples are found. Again from the transmittance study, the extinction coefficient K_1 is determined from the plot of log T versus thickness. Its value was found to be 0.05 at the wavelength of 580 nm. It can be also seen from the Table 4, for various samples the maximum and minimum transmittances were observed at the wavelengths 600 and 490 nm respectively.

Reflectance measurement

From the study of reflectance measurement, it was observed that for all samples, the graph of reflectance against wavelength indicates at least two-three maxima and minima (Figs 9a and 9b). These well defined turning points R_{max} and R_{min} were within theoretically calculated values, which were used for calculating refractive indices. Using the reflectance of
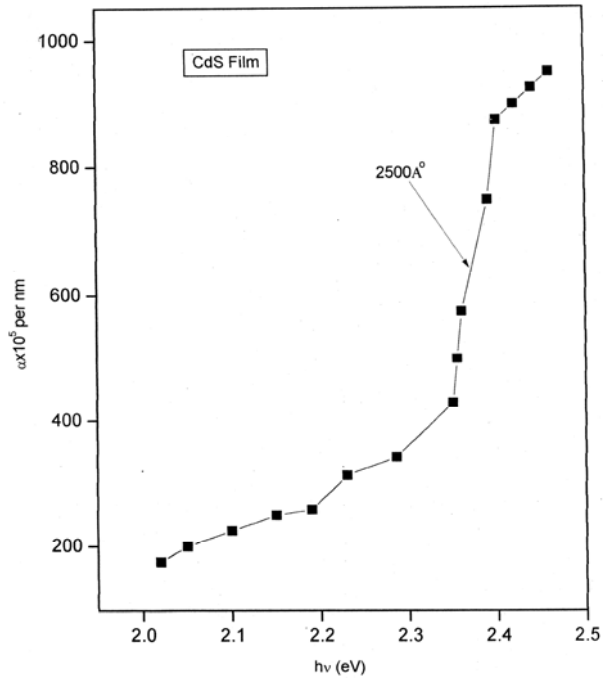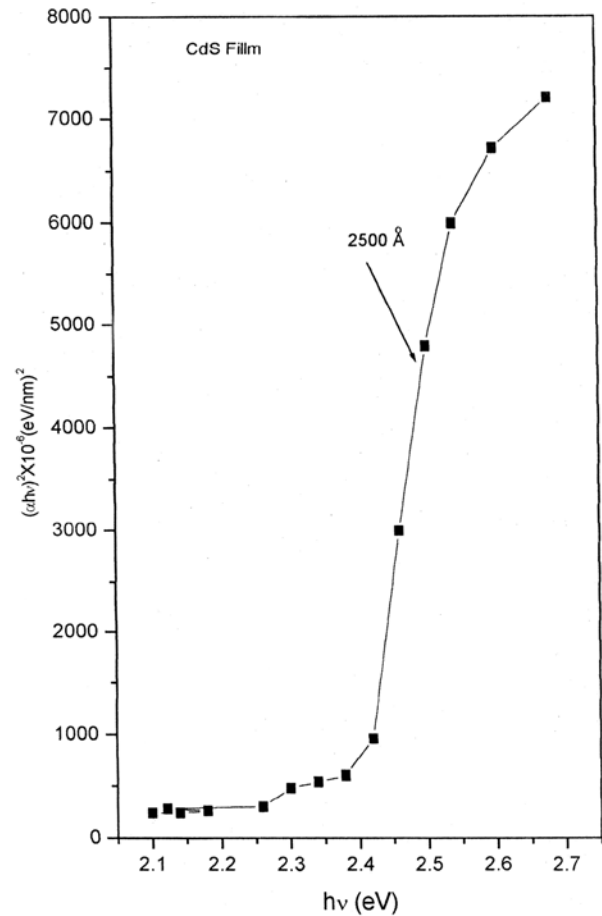

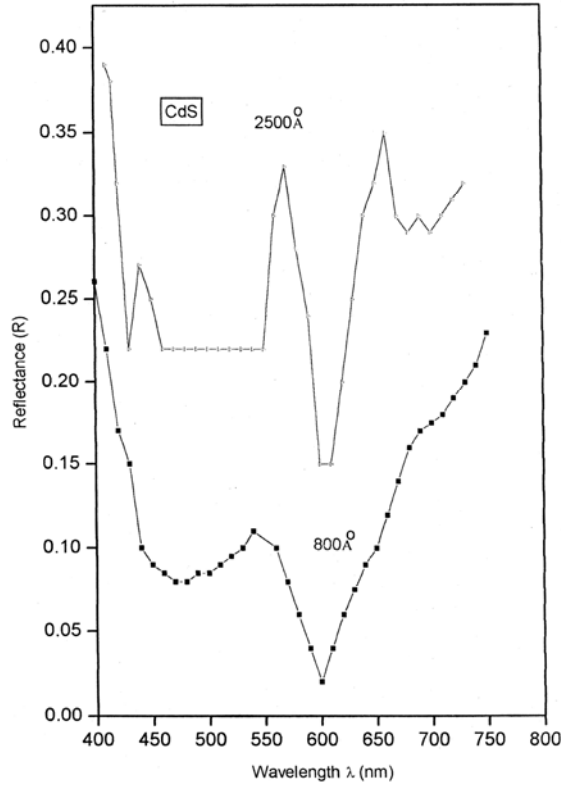Fig. 8 –Plot of $(\alpha h\nu)^2$ versus photon energy

Fig. 9a – Reflectance as a function of wavelength for films of thicknesses 800 and 2500 Å
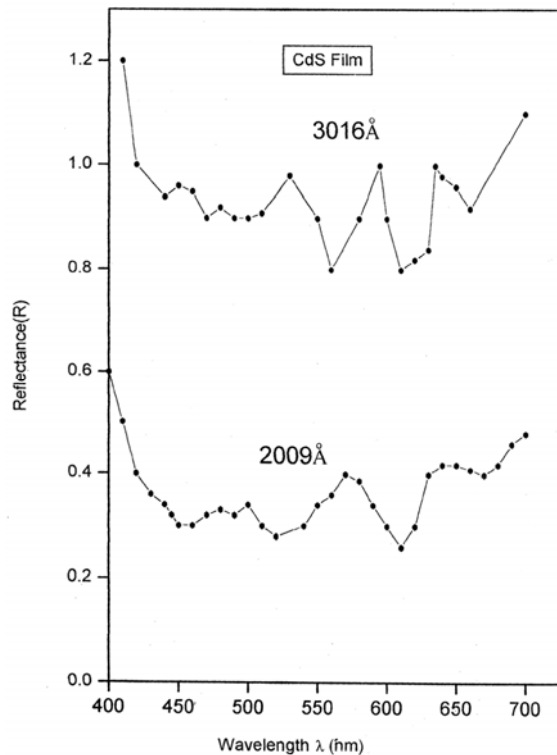

Fig. 9b – Reflectance as a function of wavelength for films of thicknesses 2009 and 3016 Å

Table 4– Estimated values of band gap, maximum and minimum transmittance and maximum transmitted intensity of samples of different thickness

Thickness, Å	E_g from $(\alpha h\nu)^2$ versus $h\nu$ (eV)	E_g from α versus $h\nu$ (eV)	Wavelength (nm) at which	
			T_{max}	T_{min}
2009	2.42	2.43	600	490
2500	2.37	2.43	600	480
3016	2.32	2.40	590	490
3515	2.35	2.41		490

Table 5– Refractive indices as a function of thicknesses

Thickness, Å	n by Eq. (4)	n by Eq. (5)	Wavelength corresponding to R_{max}	Reported values
800	2.56	2.85	520	2.42
2009	2.80	2.58	560	2.52
2500	2.15	2.40	550	1.5 - 2.7
3016	2.61	2.58	570	

580 nm wavelength, refractive indices were calculated[37]. The calculated values were found in good arrangement with reported values and are presented in Table 5. The values were calculated from the following relations.

$$R_{max} = \frac{(n_1 - n_0)^2 + k_1^2}{(n_1 + n_0)^2 + k_1^2} \qquad \ldots (4)$$

$$R_{min} = \frac{(n_1^2 - n_0 n_1)^2}{(n_1 + n_0 n_1)^2} \qquad \ldots (5)$$

where, n_0, n_1 and n_2 refractive indices of air, glass and film material respectively

Conclusions

The CdS thin film deposited by solution growth technique have polycrystalline and hexagonal structure. The annealed films represent the good crystallinity with hexagonal phase. It would be interesting to conclude that photoconductivity and photosensitivity are found to be thickness dependent in solution grown cadmium sulfide films. Band gap energies and other optical constants have the optimum values for photosensor technology developments.

Acknowledgement

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