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OPTICAL STUDY OF EFFECT OF CADMIUM SOURCES ON NANOCRYSTALLINE CdS THIN FILMS

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Thin films of cadmium sulfide (CdS) have been prepared on glass substrates by chemical bath deposition (CBD) technique using various cadmium (Cd) sources. Cadmium iodide, cadmium chloride, cadmium nitrate and cadmium sulfate have been used as a cadmium source. The effect of cadmium source on film thickness, grain size, crystal structure, surface morphology, optical properties has been studied. The as–deposited CdS films were characterized by XRD, SEM and spectrophotometer. All the CdS films have cubic structure. The grain size of CdS films has been found to be minimum for CdI2 and maximum for CdSO4. The films have 70-80% transmittance, 10-16% absorbance and ~4% reflectance towards the VIS-Near IR region. The band gap found to be sensitive to cadmium source used.

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1. Introduction

Metal chalcogenides like Sulfides, tellurides and selenides are of great importance for researchers because they are potential candidates for optoelectronic applications. CdS thin films are one of the most promising materials due to its photoconducting nature and suitable band gap (2.42 eV). It has been used as a partner of several types of thin film solar cells. Specially, CdTe/CdS heterojunction solar cells with efficiency of about 16 % have been reported [1, 2]. For the development of such optoelectronic devices, CdS thin films require comprehensive optical characterization.

Spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition and chemical bath deposition (CBD) are widely used techniques for deposition of thin films. Particularly the CBD technique is easy, inexpensive and convenient method for large area preparation of thin films, at close to room temperature. Also it is a controllable chemical reaction. Another advantage of the CBD method with respect to the other techniques is that films can be deposited on different kinds, shapes and sizes of substrates [2-4].

Here, we were prepared the thin films for various cadmium ion sources and their effects on the properties of CdS thin films were reported. The objective is to provide the comprehensive study of physical properties of CdS thin films.

2. Experimental details

The CdS film were fabricated by the controlled CBD technique using thiourea as sulfur precursor and cadmium chloride, cadmium sulfate, cadmium nitrate and cadmium Iodide were

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used as cadmium precursors, which slowly releases the Cd^{++} ions. Thiourea releases s^{--} ions by means of an alkaline hydrolysis process.

2.1 The films were synthesized as:

0.1 M cadmium ion source solution and an equal volume of 0.2 M thiourea solution was added in 100-120 ml of de-ionized water. Ammonia was added slowly to adjust the pH. The solution was stirred and transferred to another container containing substrate. The resulting solution was kept at 70±2ºC for 40 minutes. The substrate used is glass slide. Cleaning of substrate is important in deposition of thin films, cleaning steps and growth procedure is reported elsewhere [5-7]. The crystallographic structure of films was analyzed with a diffractometer (EXPERT-PRO) by using Cu-Kα lines (λ= 1.542Å). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). Optical properties were measured at room temperature by using Perklin-Elmer UV-VIS lambda-35 spectrometer in the wavelength range 100-1000nm.

3. Results and discussion

3.1 Effect of cadmium sources on film thickness

Table 1. shows the film thickness dependence on the cadmium source used in the deposition process. The thickness is maximum for $CdSO_4$ and it is minimum in case of CdI_2. This observation was in agreement with the report by Kitaev et al. [6]. It is observed that the film thickness was dependant on the release of Cd ions. It should be noted that, CdS thin film was much thinner when CdI_2 was used as Cd source, due to slow release of Cd ions and it was highest thick when $CdSO_4$ was used as Cd source, due to fast release of Cd ions. This shows the role of Cd complexes in the growth process of thin films.

Table 1. A summary of film thickness, grain size from XRD, optical band gap for different Cd sources.

Cd source	Film thickness t nm	Grain size (XRD) g nm	Band gap Eg (eV)	Lattice constant a nm
$CdSO_4$	148	3.852	2.68	0.5748
$Cd(NO_3)_2$	137	3.086	2.50	0.5826
$CdCl_2$	121	3.09	2.52	0.5809
CdI_2	92	2.911	2.40	0.5785

3.2 Structural and surface morphology

The XRD pattern of CdS films for different cadmium sources are shown in fig. 1. A comparison of the peak position (2θ values) of the JCPDS XRD spectra data for CdS suggests that the as-deposited CdS films have the cubic structure with the X-ray diffraction peaks corresponding to (111), (200) and (311) peaks. It was also observed that the diffraction angle (2θ) is different for different cadmium source used. The fourth peak (220) was detected in case of CdI_2 based films, which is also cubic in nature. The lattice parameter (a) have been calculated which is in agreement with the standard data (0.582nm). [Table 1]

The average size of grain (g) has been obtained from the XRD patterns using Debye-Scherrer's formula, [8]

$$g = K\lambda / \beta \cos\theta$$

Where,

K = constant taken to be 0.94,

λ = wavelength of X-ray used (1.542Å),

β = FWHM of the peak and

θ = Bragg's angle.

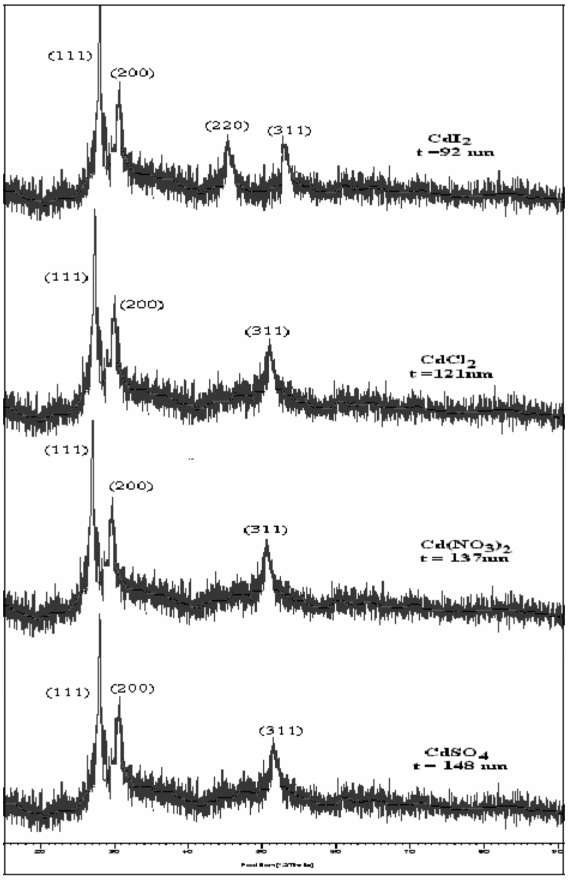

Fig. 1. XRD pattern of CdS films for different cadmium sources

Table 1 shows the grain size for different cadmium sources used. Highest grain size of $CdSO_4$-based films shows a much faster growth rate than other three films; this may due to cluster by cluster deposition process whereas in other cases smaller grain size may due to ion by ion deposition process.

The SEM micrographs shows much smoother and more uniform films in case of $CdCl_2$ based films. The grain size obtained from SEM matches with the grain size obtained by XRD.

3.3 Optical studies

Fig. 2 shows the optical transmission spectra of CdS thin films for all four cadmium sources. All the films shows more than 70% transmission for wavelengths longer than 500nm. It is observed that the transmission in case of $CdCl_2$ based films is better than other three. The sharp rise in transmission near 500nm is an identification of good crystallinity of films. It is observed that a shift towards longer wavelengths in case of $CdCl_2$-based films. Similar behavior in the transmission spectra of CdS films prepared by other technique have been reported elsewhere [9, 12]

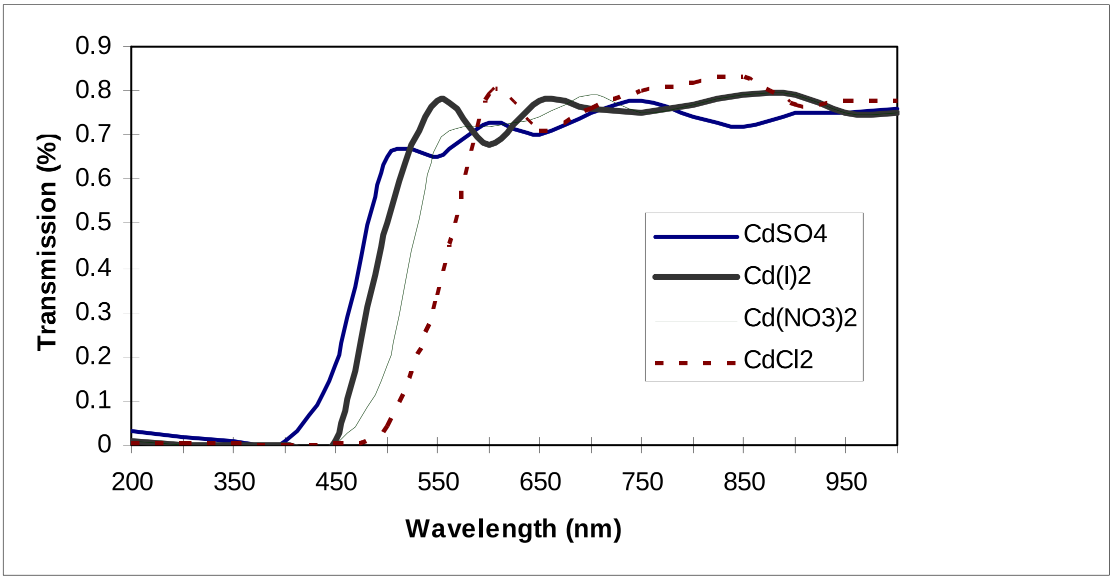

Fig. 2. Optical transmission spectra of CdS thin films for all four cadmium sources

The absorbance spectra indicates the low absorbance from ~500nm onwards, however absorbance is high in the UV region. From the absorbance data, the absorption co-efficient α was calculated using Lambert's law [10],

$$\ln (I_0/I_t) = 2.303\ A = 2.303 \log 1/T = \alpha\ d$$

where, I_0 and I_t are the intensity of incident and transmitted light respectively. A the absorbance, T the optical transmission and d the film thickness.

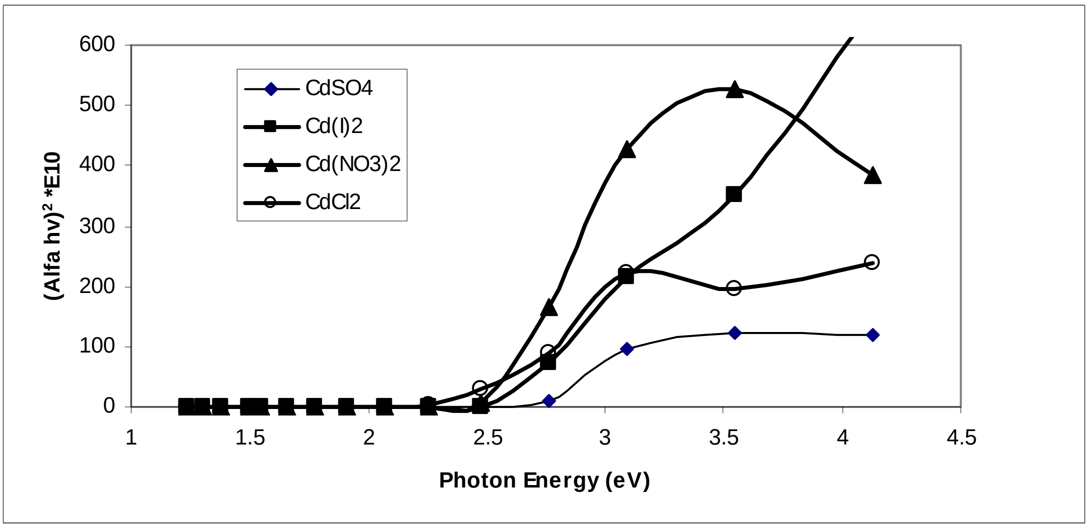

Fig. 3. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for all CdS films

The absorption co-efficient α was found to follow the relation, [11]

$$\alpha h\nu = A\ (h\nu - Eg)^{1/2}$$

The band gap Eg was determined from each film by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight line portion to the energy axis at α =0. The band gap energy Eg obtained for each Cd source is different. $CdCl_2$-based film has the least band gap (2.4eV) and $CdSO_4$-based film has highest band gap (2.68eV). The band gap of other two films is intermediate. Fig. 3 shows all band gap values observed are closest to the band gap of single crystal CdS (2.42eV).[9,11]

4. Conclusions

CdS thin films prepared by CBD technique for various Cd sources have been characterized using optical measurements as T-R-A spectra, optical band gap energy as well as thickness, structure, surface morphology. $CdCl_2$-based films have better transmission and much uniform, smooth surface than other films. The optical band gap was found to increase in the order $CdCl_2$, $Cd(NO_3)_2$, CdI_2 and $CdSO_4$, whereas the thickness increases in the order CdI_2, $CdCl_2$, $Cd(NO_3)_2$, $CdSO_4$. For all Cd sources the films were found to be cubic in structure. All the films exhibit high transmittance ~75%, low absorbance and low reflectance in the region from ~500 nm onwards. This makes the films suitable for optoelectronic devices, for instance window layers in solar cells.

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