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Study of Structural, Optical & Solid State Properties of Nanocrystalline Cadmium Sulfide Thin Films

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Abstract: Nanocrystalline cadmium sulfide (CdS) thin films have been prepared on glass substrate using a simple and inexpensive chemical deposition technique by varying the deposition parameters. The structural and morphological properties have been studied by x-ray diffractometer (XRD) and scanning electron microscopy (SEM). The optical and solid state properties such as absorbance/ transmittance/ reflectance, refractive index, extinction coefficient, dielectric constant, optical conductivity have been investigated for the photovoltaic applications. The band gap measured was found to be in the range 2.39 eV to 2.68 eV. The physical conditions were kept identical while growing all the samples. Keywords: Cadmium sulfide, chemical deposition, thin films.

I. INTRODUCTION

Numerous techniques have been reported for the preparation of thin films such as spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition technique. Out of this chemical deposition technique has become more popular in recent decades, especially for thin film deposition, due to its numerous advantages. It is easy, inexpensive and convenient method for large area preparation of thin films, at close to room temperature. Also films can be deposited on different kinds, shapes and sizes of substrates [1-4].

CdS is an important & useful material for optoelectronic applications, because its expected gap emission lies very close to the highest sensitivity of the human eye. Thus one might assume that CdS thin films are an appealing host for photonic devices. For the development of such optoelectronic devices, CdS thin films require comprehensive optical & solid state characterization. The physical properties were studied earlier by our group [10, 11].

In this work, effects of cadmium ion source on the optical & solid state properties of CdS thin films were reported. The objective is to provide the comprehensive study of optical & solid state properties of CdS thin films useful for optoelectronic applications, especially solar cells.

II. EXPERIMENTAL DETAILS

Thin films of CdS were deposited by the controlled chemical deposition technique using various cadmium ion sources as cadmium chloride, cadmium sulfate, cadmium nitrate and cadmium Iodide and thiourea as sulfur ion source. 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±2°C for 40 minutes. The substrate used is glass slide. Cleaning of substrate is important in deposition of thin films. The crystallographic structure of films was analyzed with a diffractometer (EXPERT-PRO) by using Cu-K α 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.

III.RESULTS AND DISCUSSION

A. Effect Of Cadmium Sources On Film Thickness, Structural & Surface Morphology

Fig. 1 shows XRD pattern of CdS films for different cadmium sources. 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 CdI₂ 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]



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

The average size of grain (g) has been obtained from the XRD patterns using Debye-Scherrer's formula, [8] $g = K\lambda / \beta \cos\theta \qquad \dots (1)$

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.

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.

B. Optical Studies

Fig. 2 shows the optical absorbance spectra of cds thin films for all four cadmium sources. All the films shows low absorbance in the visible/near infrared region from ~500nm to 1100nm. However the absorbance is more than 80% in the ultraviolet region. It is observed that with the cadmium source the absorbance edge shifts towards the longer wavelengths. Similar behaviors in the optical spectra of cds films prepared by other technique have been reported elsewhere [5,6]. The sharp fall in absorbance near 500nm is an identification of good crystallinity of films. [8,9]



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



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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 - absorbance, T - optical transmission and d - film thickness.

The absorption co-efficient α was found to follow the relation, [7]

 $\alpha = [A (hv - Eg)^{1/2}] hv$

....(3)

....(2)

The band gap Eg was determined from each film by plotting $(\alpha hv)^2$ versus hv and then extrapolating the straight line portion to the energy axis at $\alpha = 0$. The band gap energy Eg obtained for each Cd source is different. CdCl₂-based film has the least band gap (2.39eV) and CdSO₄-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) [7-9].



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

The variation of refractive index (n) with hv for all CdS thin films is shown in fig 4. The average values of n ranged between 1.997 and 2.112 with maximum values that ranged between 2.196 and 2.474 as the Cd source changes from $CdSO_4$ to CdI_2 .







Fig. 5 Variation of k with hv for all CdS thin films

The variation of extinction coefficient (k) with hv for all CdS thin films is shown in fig 5. The average values of k ranged between 0.0367 and 0.0508 with maximum values that ranged between 0.0722 and 0.1233 as the Cd source changes from $CdSO_4$ to CdI_2 .



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Fig. 6 Variation of $\epsilon_{\rm r}$ with wavelength for all CdS thin films.

The plot of ε_r and ε_i against wavelength are shown in fig. 6 and Fig. 7 respectively. The average values of ε_r ranged between 3.92 and 4.47 with maximum values that ranged between 4.93 and 6.18 as the Cd source changes from CdSO₄ to CdI₂.

On other hand the average values of ε_i that ranged between 0.19 and 0.36 with maximum values that ranged between 0.67 and 1.39 as the Cd source changes from CdSO₄ to CdI₂ for all the samples.



Fig. 7 Variation of ε_i with wavelength for all CdS thin films.

A plot of optical conductivity (σ) against wavelength is shown in Fig. 8. It has the average values that ranged between 3.056x10¹³ S⁻¹ and 4.645 x10¹³ S⁻¹ with maximum values that ranged between 7.108x10¹³ S⁻¹ and 12.143x10¹³ S⁻¹ as the Cd source changes from CdSO₄ to CdI₂.



Fig. 8 Variation of $\boldsymbol{\sigma}$ with wavelength for all CdS thin films.

It is observed that the values of optical constants (n, k, $\varepsilon_{r_1} \varepsilon_{i_1} \sigma$) were very sensitive with the Cd ion source. The value of optical conductivity is high in case of CdI_{2.} Table 1 shows the optical and solid state properties with the Cd ion source and thickness of CdS thin films.



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	Cd source	Grain size (nm)	Max n	Max k	Max ε _r	Max ε _i	Max σ x10 ¹³ S ⁻¹	Energy bandgap (eV)	
	CdSO ₄	3.852	2.20	0.072	4.82	0.32	7.11	2.68	
	$Cd(NO_3)_2$	3.086	2.34	0.084	5.44	0.39	8.03	2.50	
	CdCl ₂	3.090	2.41	0.103	5.77	0.33	8.92	2.52	
	CdI ₂	2.911	2.48	0.123	6.12	0.58	12.14	2.39	

 Table 1.

 Optical & solid state properties with Cd sources for all CdS thin films.

IV.CONCLUSIONS

CdS thin films with various Cd ion sources have been successfully deposited by chemical deposition technique. The effects of Cd source on structural, morphological, optical and solid state properties have been studied. The XRD study reveals that the asdeposited CdS films are cubic structured with the average grain size between 2.9nm and 3.8nm. The UV-VIS spectroscopy showed high (>80%) transmittance, and low absorbance in the visible near infrared region from ~500nm onwards and poor transmittance in UV region. This makes the films suitable for optoelectronic devices, for instance window layers in solar cells also effective as protective coatings.

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