Effects of Cations (Cd^{2+}) on Cadmium Sulfide Thin Films

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Abstract **- Cadmium sulfide (CdS) thin films were deposited on glass substrates at three different concentrations of cadmium positive ions by Chemical Bath Deposition (CBD). The effects of cation (Cd^{2+} ions) on structural and optical properties were studied. Structural analysis is done using X-ray Diffraction (XRD) and Scanning Electronic Microscope (SEM) revealed that the films are polycrystalline in nature. The crystalline size lies from 8.9nm to 185nm. Also the dislocation density (d) and strain (ξ) were calculated. All the films have high optical transmittance (>70%) in the visible region. The optical band gap values are decreased in the range of 2.55eV to 2.12eV with increase in cation (Cd^{2+} ions) density in the solution.**

Keywords- Cations, structural analysis, optical properties, Band gap.

I. INTRODUCTION

N-type semiconducting materials are widely used as a window layer in heterojunction realization of p-type CdTe and CuInSe optical conversional devise. Hence, ample of studies have been carried out in order to produce CdS thin films for this suitable material with optoelectronic properties for photovoltaic application. It is also used in light emitting diodes, photo detectors, sensors, address decoders and electrically driven lasers [1]. The crystallites can change entire properties of the films. Crystalline growth was restricted by annealing effects of the films or cation (Cd^{2+}) and anions (S^{2-}) concentration in the bath solution. An increase in cation (Cd^{2+} ions) concentration, the rate of deposition also increases resulting in the decrease of porosity with better structural, optical and adhesive properties.

Among possible deposition techniques, Chemical Bath Deposition (CBD) is one of the most suitable methods to deposit CdS film due to its inexpensive, controlled precipitation, handling at low temperature and possibility to form large area films. And most importantly, the deposited films are found to be of comparable better quality to those obtained by more sophisticated and expensive physical deposition process [2]. This paper deals with the structural and optical analysis of CdS thin films prepared by various cation (Cd^{2+} ions) concentrations in the bath solution.

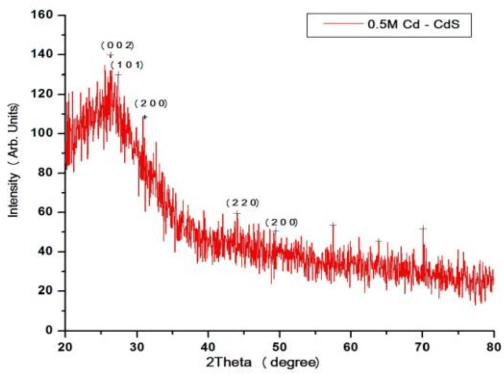
II. EXPERIMENTAL PART

Cadmium sulfide thin films were deposited by using extra pure cadmium sulphate and thiocarbamide (or) thiourea which are used as a cation (Cd^{2+}) and anion (S^{2-}) precursor; ammonium hydroxides are used as a buffer solution to control pH values of the chemical bath [3]. The structural and surface morphology properties have been examined by the X-ray diffraction method (XRD) and Scanning Electron Microscopy (SEM). The optical properties were measured by the UV-Vis and photoluminescence (PL) spectroscopy in the wavelength range of 250nm -1000nm at ambient temperature.

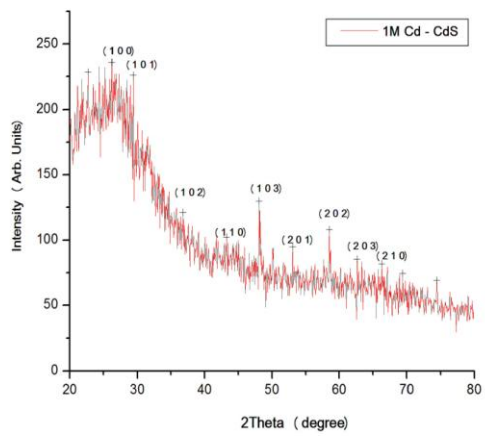
III. RESULTS AND DISCUSSION

A. Structure Analysis

Fig. 1 demonstrate the XRD spectrum of CdS thin films grown with different cation (Cd2+ ions) concentrations such as 0.5M, 1M and 2M deposited on substrates. The presence of a broad XRD peaks is an indication of nanocrystalline nature of the CdS thin films. The diffraction prominent peaks exist at an angle of $2\theta = 26.62^o, 28.2^o, 30.74^o, 44.04^o$ and 51.87^o corresponding to the planes of $(002)^H$, $(101)^H$, $(200)^C$, $(220)^C$ and $(200)^H$ for 0.5M of cadmium molar concentration CdS films.



(a)



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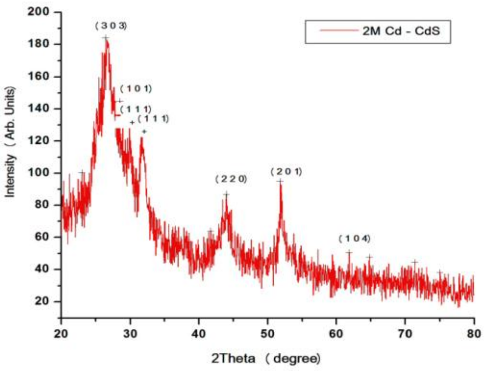


(c)

Fig. 1 XRD patterns of the thin films (a) 0.5M of Cd - CdS (b) 1M of Cd – CdS (c) 2M of Cd - CdS.

The diffraction prominent peaks exist at an angle of 2θ = 26.23°, 28.36°, 36.78°, 43.23°, 48.08°, 53.08°, 58.53°, 66.33° and 69.43° corresponding to the planes of (303) ^{Ortho}, (101) ^{H}, (220) ^{C}, (1003) ^{H}, (201) ^{H} and (104) ^{H} for 1M of cadmium molar concentration CdS films. The prominent peaks exist at an angle of 2θ = 26.29°, 28.2°, 44.04°, 47.04°, 52.98° and 61.10° corresponding to the planes of (303) ^{Ortho}, (101) ^{H}, (220) ^{C}, (1003) ^{H}, (201) ^{H} and (104) ^{H} for 2M of cadmium molar concentration CdS films. And at higher molar density it produces CdO cubic crystalline at an angle of 30° and 33° corresponding to the planes of (111) ^{C} and (111) ^{C}.

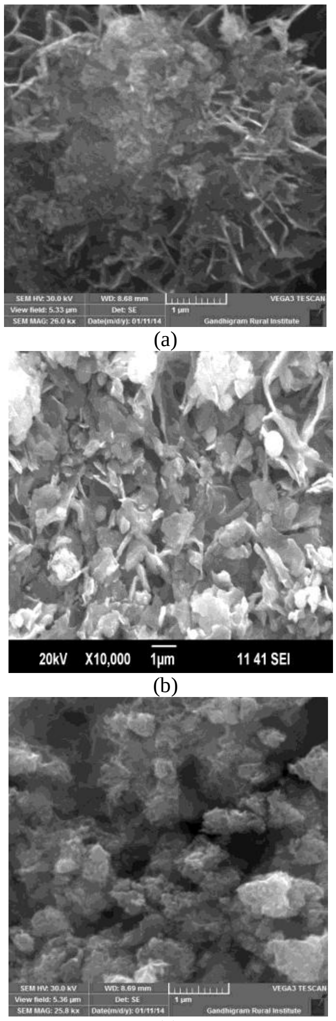
Table 1 XRD parameters of CdS thin films

Cation	strain (ξ) x 10^{-1} $lines^{-2}$ m^{-4}	Grain Size (D) m	Dislocation Density (δ) lines/m^2
0.5 M	1.11	6.81x10^{-9}	2.16x10^{8}
	1.24	7.45x10^{-9}	1.80x10^{8}
	1.37	7.49x10^{-9}	1.78x10^{8}
	1.08	4.01x10^{-9}	6.23x10^{8}
	1.82	1.70x10^{-8}	3.46x10^{7}
Average	**1.32**	**8.55x10^{-9}**	**2.46x10^{8}**
1 M	1.93	9.07x10^{-8}	1.22x10^{6}
	1.96	1.37x10^{-7}	5.40x10^{5}
	1.98	1.68x10^{-7}	3.60x10^{5}
	1.90	3.72x10^{-8}	7.24x10^{6}
	1.96	8.70x10^{-8}	1.32x10^{6}
	1.96	6.35x10^{-8}	2.48x10^{6}
	1.96	8.28x10^{-8}	1.46x10^{6}
	1.96	6.78x10^{-8}	2.17x10^{6}
	1.97	6.91x10^{-8}	2.10x10^{6}
Average	**1.95**	**8.91x10^{-8}**	**2.10x10^{6}**
2 M	1.95	1.17x10^{-8}	7.40x10^{5}
	1.97	1.64x10^{-7}	3.70x10^{5}
	1.98	2.86x10^{-7}	1.20x10^{5}
	1.98	1.44x10^{-7}	4.80x10^{5}
	1.98	1.48x10^{-7}	4.60x10^{5}
	1.98	1.54x10^{-7}	4.20x10^{5}
Average	**1.97**	**1.69x10^{-7}**	**4.32x10^{5}**

From the XRD spectrum, it clearly indicates that the diffraction peak intensity increases as the Cd^{2+} ion concentration of the bath solution increases. This is an indication of the crystallinity improvement with increasing Cd^{2+} ion concentration. Similar results have been observed by literatures [4-6]. The broad background is due to the amorphous glass substrate and also possibly due to some amorphous phase in the thin films [7]. Using the size of the crystalline, the dislocation density and strain has been calculated and are represented in table1.

B. Surface Morphology

Fig. 2 depicts the surface morphology of CdS thin films deposited from different cation (Cd^{2+} ions) concentration of the bath solution.



(a) (b) (c)

Fig. 2 SEM images for CdS thin films with different molar concentration in the bath solution (a) 0.5M (b) 1M (c) 2M

From the SEM analysis all the deposited films shows that the distributions of grains are not uniform throughout all the regions. But the films are without any void, pinhole or cracks, so that they cover the substrates well. We clearly observe the small grains engaged in a fibrous like structure, which clearly indicates the glassy nature along with amorphous phase of CdS thin films [8]. The SEM study also indicates that the decrease in the cadmium content improves the surface smoothness. Crystalline size also improves with increasing cation (Cd^{2+} ions) concentration [9]. The evidence from XRD analysis also depicts the same.

C. Films Thickness (T)

Fig. 3 depicts the crystalline growth is strongly influenced by the molarity of cadmium source. The deposition rate increases with increasing cation (Cd^{2+} ions) concentration, the terminal thickness increases with increasing cation (Cd^{2+} ions) concentration from 1.29nm to 4.53nm according to the concentration from 0.5M to 2M.

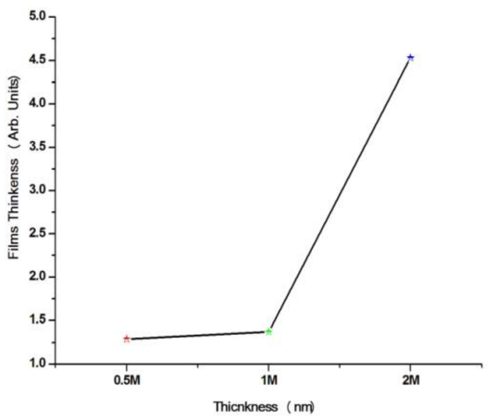


Fig. 3 Films thickness variation with of cation concentration

D. Optical Properties

The study of optical absorption is important property to understand the behavior of chalcogenide thin films.

1) Absorption:

The absorption spectra of coated CdS films are portrayed in Fig. 4. Absorbance peak intensity of the films increases by increasing the cation (Cd^{2+} ion) concentrations in the solution, which increases the grain size because of the decrease in the density of the nucleation centers. Thus a smaller number of centers start to grow, ensuring in large grains. Hani H. Ahmed also reported the same [10]. Rising and falling of the absorbance values during the continuous increase in cation (Cd^{2+} ions) concentration is due to the phase transition of CdS crystalline.

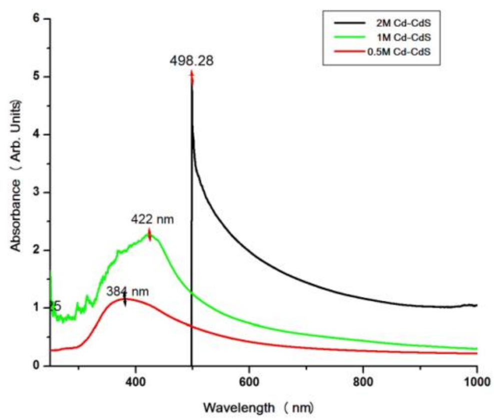


Fig. 4 Optical absorption spectra of CdS thin films

The absorption edge shifted to lower energy with cation (Cd^{2+} ions) concentration. This may be due to the modulation of band gap caused by Cd substitution.

The optical direct band gap (Eg) of the films can be estimated by extrapolated linear portion of $(\alpha h\nu)^2$ vs. hν plots using the Tauc relation [3]. The related plots are shown in Fig. 5. It was found decrease from 2.55eV to 2.12eV by increasing the Cd^{2+} ion concentration, where increasing Cd^{2+} ion concentration tend to increase in grain size i.e. crystalline size is inversely proportional to the bandgap of the films. These are in good harmony with the pervious reported by others [11-12].

The bandgap decrease, it could be due to the increase of density of localized state in the conduction band. It was confirmed by Hasnat and Podder, 2013 [13] reports and thickness of the films.

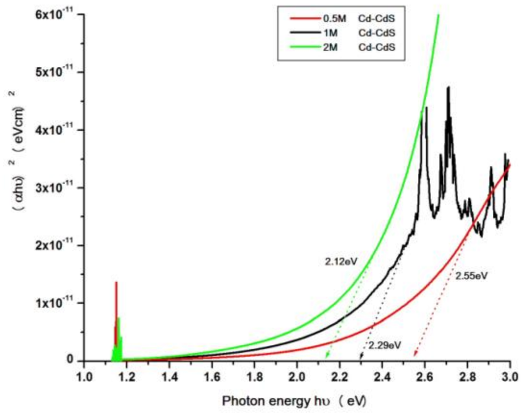


Fig. 5 Bandgap of CdS thin films

2) Refractive Index:

Refractive index is calculated using energy bandgap by various effective methods [14] and the values are tabulated. From the table 2, the refractive index of the specimens shown, refractive index is directly depend on cation density in the solution i.e., refractive index has smallest variation with cation (Cd^{2+} ions) concentrations in the same manner in bath solution.

Table 2 Refractive index of CdS thin films with various cation concentrations.

Cation	Bandgap (Eg eV)	Refractive Index		
		Ravindra	Herve and Vandamme	Moss
0.5M	2.55	2.47	2.49	2.55
1M	2.29	2.63	2.59	2.62
2M	2.12	2.73	2.66	2.67

It is slightly increased when the cation density increases. And also refractive index of the films is directly related with thickness of the films. Refractive index increases from 2.47 to 2.73 by increasing film thickness from 1.29µm to 4.59µm. Yunus Akaltun *et al.*, 2011 [14] also reports that the refractive index increases with increasing film thickness.

3) Optical Conductivity:

Variation of optical conductivity of the material versus photon energy deposited at different cation (Cd^{2+} ions) concentration is shown in the Fig. 6. The optical conductivity decreases exponentially with photon energy and cation (Cd^{2+} ions) concentrations in the bath solution.

The optical conductivity of the specimens vary with photon energy in similar manner, decreased sharply from various values of $3.09*10^4 s^{-1}$ at 3.06eV for 0.5M cation (Cd^{2+} ions) concentrated CdS films, $5.781*10^3 s^{-1}$ at 2.95eV for 1M cation (Cd^{2+} ions) concentrated CdS films and $6.33x10^2 s^{-1}$ at 3.2eV for 2M cation (Cd^{2+} ions) concentrated CdS films and various maximum values are obtained. After this, fluctuations were observed. From the graph, optical conductivity decreased in high cation (cadmium) content i.e. optical conductivity decreases with increasing crystalline of the films. It was confirmed from XRD analysis.

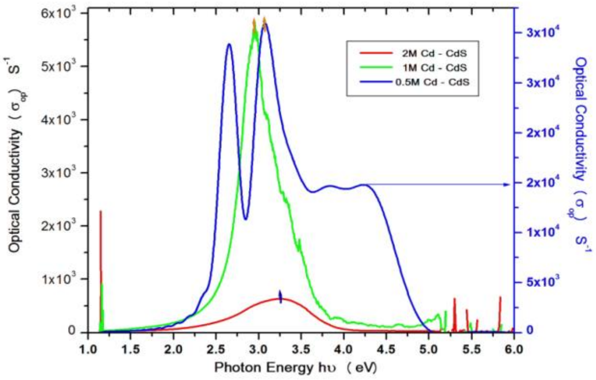


Fig. 6 The optical conductivity of CdS thin films with different cation concentration.

The overall conductivity increased with the increase in film thickness. The increase in conductivity due to increasing thickness may be attributed to the increasing number of sulphur vacancies present in the sample [13].

4) Photoluminescence:

The photoluminescence emission spectra of base responded CdS thin films are portrayed in Fig. 7.

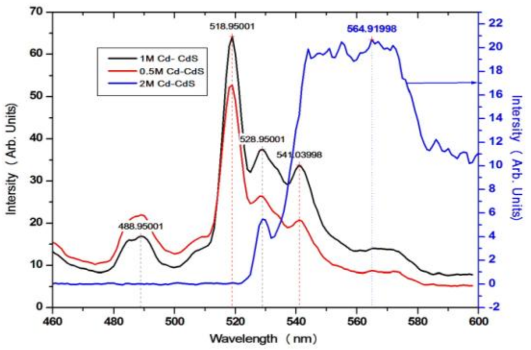


Fig. 7 PL spectra of CdS films with different cation concentration excitation at 2.5eV.

PL spectra have been recorded with an excitation wavelength of 310nm. It can be observed that all the PL spectra of the samples exhibits only green emission peaks at 489nm (2.53eV), 518nm (2.38eV), 529nm (2.34eV) and 541nm (2.29eV), except 2M of cation concentrated CdS films. That the high cation concentration CdS films exhibit both green and yellow band emission peaks at 541nm (2.29eV) and 565nm (2.19eV). From spectral analysis the sample 2M of Cd^{2+}-CdS produce lower energy shifted peaks when compared with low concentration samples. Which means the particles size is increased when cation (Cd^{2+} ions) concentrations are increased. It was confirmed from XRD, SEM and red shifted UV-Vis absorbance spectra.

CONCLUSIONS

The deposited CdS thin films were prepared with different cation (Cd^{2+} ions) concentration by chemical bath deposition methods. Deposited CdS thin films have the crystalline size which lies in the range from 8.9nm-185nm. Cation (Cd^{2+} ions) concentration, which can improved the crystalline size are inferred by XRD and SEM. The absorption edge is red shifted with respective CdS that indicate the increase of particle size. The bandgap and optical conductivity are decreased with increase in cation (Cd^{2+} ions) concentrations in the bath solution. Refractive index increases from 2.47 to 2.73 by increasing cation density in the solution. At the high concentration of cation can produce yellow band emission at 564nm in CdS films..

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