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Structural and Optical Characterization of Chemically Prepared Barium Doped CdS Nanostructured Thin Films

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Abstract: - Pure and Barium doped Cadmium Sulphide (CdS) nanostructured thin films are deposited on pre-treated glass substrates by the simple chemical bath deposition (CBD) technique. The films are characterized using X- ray diffraction (XRD), scanning electron microscopy (SEM) and optical absorption and transmission techniques. The XRD study shows that the pure and doped films are polycrystalline and is a mixture of cubic and hexagonal phases. The average grain of films was found to increase with the doping of Barium. The SEM studies indicate that the grains are seen to be spherical. An EDAX spectrum confirms that the films contain the elements Cd, S and Ba as expected. The optical investigation shows a small decrease in the band gap value for the doped films. The pure and 0.5% Badoped films were found to have a band gap of 3.15 eV and 3eV respectively. As the films show good response to the light, they will be useful for photo sensors and photovoltaic devices.

Keywords: *- Cadmium sulphide, chemical bath deposition, nanomaterial, photo sensor.*

I. INTRODUCTION

Materials and structures with low dimensions have excellent properties which enabled them to play a crucial role in the rapid progress of the field of science. Advances in low dimensional semiconducting materials resulted in the development of a wide range of electronic and optoelectronic devices that affected many aspects of the technological society. The group II-VI compound semiconductors CdS have attracted considerable interest because of their wide applications in optoelectronic devices [1]. Study of preparation and properties of this compound for their possible application in solar cells, light emitting diodes and non-linear optical devices has been increasing in recent years [2-3]. Among the many techniques of preparing thin films, the chemical bath deposition (CBD) technique has drawn a special attention because this technique has many advantages such as no requirement for sophisticated instruments, minimum material wastage and economical way of large area deposition. The film deposited by this method has better photoconductivity and improved morphological properties such as roughness and pinhole density as compared with film processed by other techniques [4]. Deposition of thin films of metal sulfides, selenides and oxides, together with some miscellaneous compounds on substrates by CBD technique has been a long practice [5-6]. In the CBD technique, the film quality, structure, morphology, electrical conductivity, electronic and optical properties depend on the starting material, complexing agent used, the bath parameters like deposition time, pH value etc. In addition, doping process has the ability to change the entire properties of the semiconducting material. Doping with different material or element to different extents has also found to alter the properties of pure CdS thin films [7-8]. The addition of Mn on CdS by using spray prolysis, show a fall in the values of optical band gap and electrical resistance [9]. Ni doped CdS film show excellent photoconductivity properties [10]. Doping of Cu results into change of CdS semiconducting material from n to p- type decreasing the band gap [11]. The particle size of CdS was found to be increased on doping Pb, although the band gap is decreased [12]. Thus, in order to enhance applications in different fields, we must study doping effects on CdS thin films. In this study, nano-structured pure and Ba doped CdS thin films are prepared using the chemical bath deposition technique and investigated their structural, morphological, compositional and optical properties.

II. EXPERIMENTAL DETAILS

The commercial microscope's ordinary glass slides (GEMS) of size 75mm x 25mm x 1.25mm were used as a substrate for film deposition. The substrate was submerged into acquariga (1: 3; NHO_3: HCl) for about 48 hours to dissolve the maximum amount of impurities. Next, the substrates were washed with clean tap water and then it is submerged in detergent solution for 30 min. The substrates are then rinsed with clean tap water and then with double distilled water. Finally the substrates were washed with acetone to remove oily content and then rinsed with double distilled water for two times and dried in oven. Chemicals of analytical reagents grade are used for the sample preparation. Aqueous solutions of 25mL$CdCl_2$ (0.5 M), [Merck, India] and 25 mL Thiourea [$SC(NH_2)_2$] (0.5 M) [CDH, India] are taken separately in two beakers. Using magnetic stirrers they are stirred at room temperature for hours to get homogeneous solutions. Under the stirring condition, NH3 solution (25%) [SDFCL] is slowly added drop by drop to $CdCl_2$ so that the color becomes milky white and the Ph value of the solution becomes 10. Then, the stirred homogeneous 25mL aqueous Thiourea solution was added to the $CdCl_2$ solution and stirring continued for about 5 minutes. Glass substrates were then immersed vertically into the solution. After 20

hours, the slides are taken out and washed with double distilled water and dried in the oven at room temperature. The reaction mechanism of the above process is as follows [13-14]: Thiourea $[(NH_2)_2CS]$ hydrolyses in solution to give S^{2-} ions according to:

$$(NH_2)_2CS + 2\,OH^- \rightarrow CH_4N_2O + HS^-$$
$$HS^- + OH^- \rightarrow H_2O + S^{2-}$$

Again, ammonia hydrolyses in water to give OH^- ions according to:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

When ammonia solution is added to Cd^{2+} salt solution $Cd(OH)_2$ starts precipitating ,i.e.

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2$$

This $Cd(OH)_2$ precipitate dissolves in excess ammonia solution to form the complex Cadmium tetra – amine ions $[Cd(NH_3)_4]^{2+}$

$$Cd^{2+} + 4\,NH_3 \rightarrow [Cd(NH_3)_4]^{2+}$$

Finally the CdS thin film is formed according to :

$$[Cd(NH_3)_4]^{2+} + S^{2-} \rightarrow CdS + 4NH_3$$

The reaction shows that the main role of NH_3 concentration in the bath is as complexing agent for the Cd^{+2} ions.

The film thickness was determined by the gravimetric method using electronic precision balance (model: MAB – 182). The crystal structure and orientation of the prepared CdS films were investigated by X-ray diffraction method. The X-ray diffraction patterns were recorded using X- ray diffractometer (model: Philips XPERT- PRO) with CuK_α radiation (λ= 1.54060Å) and the analysis of the surface morphologies were performed with a scanning electron microscope (model: FEI Quanta -250). The composition of the CdS films was determined by studying the energy dispersive X- ray fluorescence of the samples using EDAX-SL, Ametek. The optical absorbance and transmittance were measured using UV – Visible double beam spectrophotometer (model: Systronic – 2203).

III. RESULT AND DISCUSSION

3.1.1 Film thickness measurement

The film thickness was determined gravimetrically by measuring the change in weight of the substrate due to film deposition , the area of deposition and using the known density of CdS (4.84 gm/cm^3). If W_1 and W_2 are the weights of the substrate before and after film deposition in gram, A is the area of film deposition in cm^2 and ρ is the density of CdS, then the film thickness is calculated as

$$t = \frac{W_2 - W_1}{\rho A} \times 10^{-4} \mu m$$

The thickness of the prepared CdS films was found to be 0.545μm and 0.520 μm for the un-doped and 0.5% Ba doped respectively.

3.1.2 Structural Characterisation & Particle size analysis

The X-ray diffraction pattern of the prepared samples is shown in figure 1. The diffraction peaks of un-doped and Ba doped CdS films show that the samples are polycrystalline in nature with mixed phase of hexagonal and cubic structures with preferred grain orientations along (111),(200), (220), (112), (100), (002), etc. which are in agreement as reported by earlier workers like Ghosh et.al.[15]. The intense peak oriented along (111) lattice plane indicates that the growth of the grains is parallel to the substrate. The peaks in the spectrum is also verified with the known patterns of standard X- Ray diffraction data file (JCPDS file No. 10-454,cubic, JCPDS6 – 314, hexagonal).

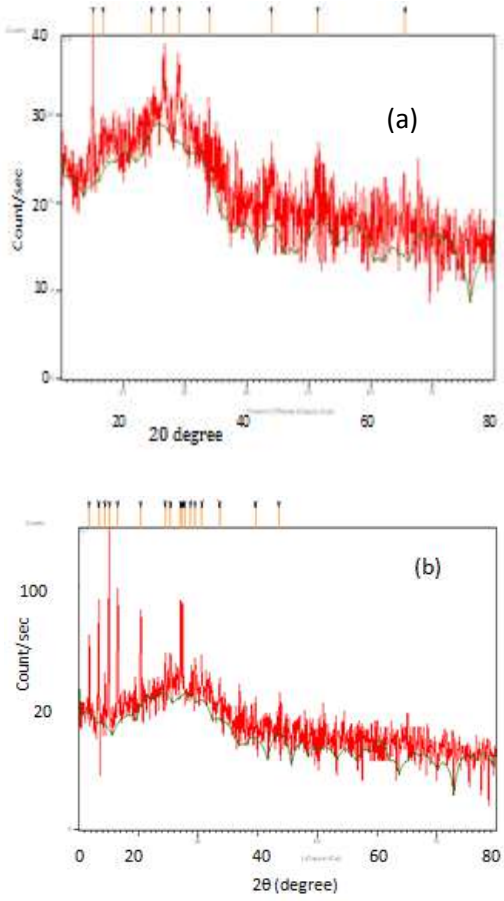

Figure 1 XRD pattern of 0.5 M CdS thin film (a) un-doped (b) 0.5% Ba doped.

The grain size or particle size (D) of the particles was estimated from the Debye- Scherrer's formula [16],

$$D = \frac{0.94\lambda}{\beta \cos\theta} \text{ (for spherical crystallites)}$$

where 2θ is the diffraction angle, λ is the X-ray wavelength used (1.54060Å for CuK_α) and β (in radian) is the full width at half maximum (FWHM) of the diffraction peak for which the particle size is to be calculated. The dislocation density was calculated by the relation [17]:

$$\delta = \frac{1}{D^2}$$

where D is the grain size. The micro strain was calculated by the formula [17]:

$$\varepsilon = \frac{\beta \cos\theta}{4}$$

The average grain size, the dislocation density (δ) and the micro strain (ε) are shown in table 1.

Table 1: Diffraction peaks, d- values, average particle size, average dislocation density (δ) and average micro strain (ε) of pure and 0.5% Ba doped 0.5M CdS thin film.

	hkl	2θ degree positions of peaks	d Å (inter planar distance)		Average		
					D (nm)	δ (line^2/m^2)	ε
0.5M Pure CdS	111	26.5668	3.35251	cubic	39.14425	0.652627x10^{15}	2.611266x10^{-3}
	200	29.0423	3.07213	cubic			
	220	43.9473	2.05863	cubic			
	112	51.4250	1.77547	hexagonal			
0.5% Ba Doped 0.5M CdS	100	24.4974	3.63083	hexagonal	40.12562	0.621092x10^{15}	0.959515x10^{-3}
	002	25.3905	3.50510	hexagonal			
	200	29.4689	3.02863	cubic			
	210	33.5560	2.66849	cubic			
	110	43.5130	2.07814	hexagonal			

3.2 Surface Morphology Studies

Scanning Electron Micrographs of the prepared CdS (0.5 M), un-doped and Ba doped samples are shown in figure 2. It shows that the morphology of the particles are nearly spherical in shape and are not well connected to each other.

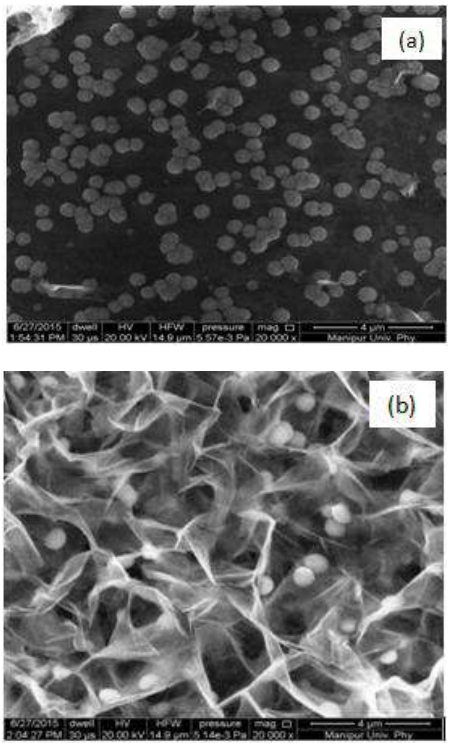

Figure 2 SEM picture of 0.5M CdS thin films: (a) Un-doped (b) 0.5% Ba doped

3.2.1 Compositional Studies

Figure 3 shows the elemental composition i.e. EDAX analysis of the un-doped and Ba doped CdS thin films. The EDAX indicates that the products consist of Cadmium, Sulfur and Barium elements as expected. The Silicon signal appears from the glass substrate.

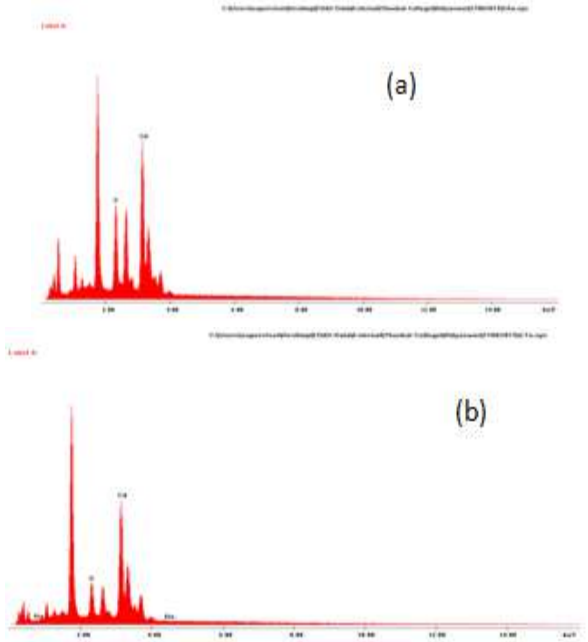

Figure 3 EDAX spectrum of 0.5 M CdS thin film: (a) Un-doped (b) 0.5% Ba doped Percentage of the main compositional elements is shown in table 3.

Table 2 Percentage of main elements in prepared un-doped and Ba doped CdS thin films.

Element	Weight (%)		Atomic (%)		[Cd]/[S]	
	Pure 0.5M CdS Film	Doped 0.5% Ba 0.5M CdS	Pure 0.5M CdS Film	Doped 0.5% Ba 0.5M CdS	Pure 0.5M CdS Film	Doped 0.5% Ba 0.5M CdS
S	14.93	8.60	38.08	24.84		
Cd	85.07	90.10	61.92	74.28	1.6257	2.9903
Ba	-	1.30	-	0.88		
Total	100	100	100	100		

The optical absorbance and transmittance of the CdS films were observed using the UV-V double beam spectrophotometer (Systronics – 2203).

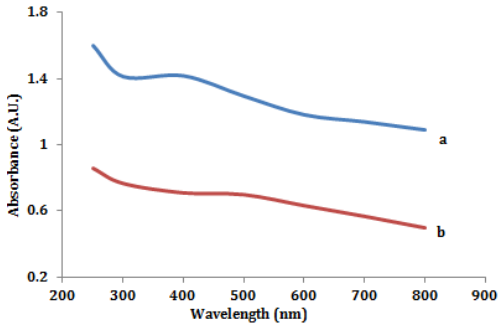

Figure 4 Absorbance spectrum of 0.5M CdS film: (a) Un-doped (b) 0.5% Ba doped

The optical absorbance is a powerful method to determine the energy band gap, as the absorption in this UV-V region corresponds to electronics energy transition

in the material. Figure 4 and 5 show the absorbance and transmittance curves as a function of wavelength for the nanocrystalline un-doped and Ba doped CdS thin films.

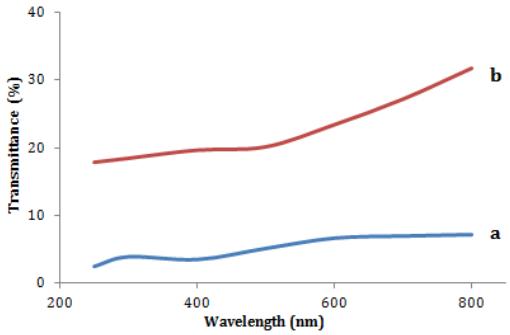

Figure 5 Transmittance spectrum of 0.5M CdS film:(a) Un-doped (b) 0.5% Ba doped

The absorption coefficient α is given by the relation

$$\alpha = 2.3026 \left(\frac{A}{t}\right)$$

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

In semiconductors, the absorption coefficientα, the incident photon energy hυ and optical band gap E_g is related by the equation [18]

$$\alpha h\upsilon = k(h\upsilon - E_g)^n$$

where υ is the frequency of the incident photon, h is Planck's constant, k is a constant which is different for different transition and n is the number which characterizes the optical processes. The value n is such that n = $\frac{1}{2}$ for a direct allowed transition, 2 for the indirect allowed transition, $\frac{3}{2}$ for a forbidden direct transition and 3 for a forbidden indirect transition. For CdS, the value of n = $\frac{1}{2}$

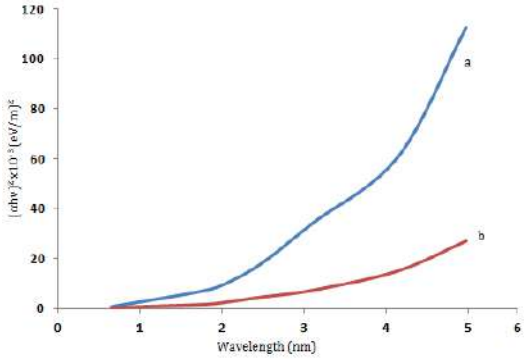

Figure 6: Optical energy gap of 0.5M CdS thin film: (a) Un-doped (b) 0.5% Ba doped

The band gap of the films was determined by plotting a graph between $(\alpha h\upsilon)^2$ and (hυ). It is shown in figure 6. The band gap energy E_g was estimated by extrapolation of linear part of curve to energy axis. The values of Eg were found to be 3.15 eV and 3 eV for the un-doped and 0.5% Ba doped 0.5M CdS thin films respectively.

IV. CONCLUSION

Nanocrystalline thin films of CdS (0.5M) are successfully deposited on pre treated glass substrate by using the chemical bath deposition technique. Structural, morphological, compositional and optical studies were carried out. Structural analysis indicates that the prepared films is polycrystalline and is a mixture of cubic and hexagonal phases. The average particle size as estimated from XRD peaks was found to be 39.14425 nm and 40.12562 nm for the un-doped and 0.5% Ba doped CdS thin films respectively. Thus, there is a slight increase in the size of the Ba doped particles. The SEM photographs of the CdS thin film indicate that the morphology of the particles are spherical and symmetrical and it is concluded that the films follow a multi-layer growth pattern. The morphological and structural properties of CdS are found to be doping depended. The EDAX spectra show that the respective films contain the elements Cd, S and Ba as expected. The optical absorbance studies show that the prepared films have a band gap of 3.15 eV and 3eV for the un-doped Ba doped CdS films respectively. The films show good response to the light and hence they can be employed in photo-sensors and photovoltaic devices. The results suggest that doping of CdS thin films may be further investigated for applications in the development of solar cells, sensors and fuel cells.

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