International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 4, Issue 9
September 2017

Structural and Optical Properties of CdS Thin Films Prepared by Chemical Bath Deposition Technique

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Abstract

Chemical bath deposition (CBD) technique was used to deposit nano-structured cadmiumsulphide (CdS) thin films on pre-treated glass substrates. The films are studied using the X-ray diffraction (XRD) , scanning electron microscopy (SEM) and optical absorption and transmission techniques. The XRD shows that the films are polycrystalline and isa mixture of cubic and hexagonal phases, which agrees with the earlier report of CdS thin film.The average grain size of the film is about 39.14 nm. SEM studiesindicate thatthe grains are seen to be spherical and symmetrical, not uniformly distributed and not well connected to each other. The EDAX spectrum shows that the film contain the elements Cd and S as expected. Optical study shows that thefilm has a band gap of 3.15 eV.

Keywords: Chemical bath deposition, EDAX, Nanocrystalline, SEM, Thin films, XRD.

1. Introduction

In the present development of technology, nano - structured CdS thin films has gained considerable research attention and has been becoming a promising candidate for various applications. CdS films belong to the II-VI semiconductor compounds and they are highly reproducible, stable and cost effective material for optoelectronic devices, photovoltaic industry and optical detectors etc. [1-5]. They are also widely used in photonic devices like light emitting diodes [6], solar cells [7], and lasers [8]. But poor conductivity of CdS filmsas low as 10^{-8} $(\Omega m)^{-1}$has been reported [9]. Such limitations in properties can be varied over several orders of magnitude by considering doping of different dopants to different extends and annealing the sample at different temperatures[10]. In order to enhance applications in different fields, we must study doping and annealing effects on CdS thin films.

There are various techniques to prepare CdS thin films such as spray pyrolysis [11], chemical bath deposition [12-15], successive ionic layer adsorption and reaction [16], etc. 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 [17]. CBD can be used to deposit any compound that satisfies four basic requirements: simple precipitation, highly insoluble in the solution, chemically stable in the solution, and a slow reaction with production of free anion[18].

The CBD reactions are carried out in alkaline solution. A complexing agent is added to prevent the precipitation of metal hydroxides. The complexing agent also reduces the concentration of free metal ions, which in turn helps to prevent rapid bulk precipitation of the desired product.

In this study, chemical bath deposition technique was adopted for the deposition of nano-structured thin films of CdS and the structural, morphological, compositional and optical properties of the films are investigated .

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2. 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 indetergent 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. Acqueous 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 stirrer they are stirred at room temperature for hours to get homogeneous solutions. Under the stirring condition, NH3solution (25%) [SDFCL] is slowly added drop by drop to $CdCl_2$ so that the colour 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 [19-20]:

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 :

$$NH_3 + H_2O \rightarrow N\overset{+}{4} + OH^-$$

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).

3. Result and Discussion

3.1 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 andρ is the density of CdS, then the film thickness is calculated as

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$$t = \frac{W_2 - W_1}{\rho} \text{ X } 10^{-4} \mu$$

The thickness of the prepared film is found to be t = 0.545 μ

3.2 Structural Characterisation and Particle size analysis:

The X-ray diffraction pattern of the prepared samplesis shown in figure 1. The diffraction peaks of CdS film shows that the samples are polycrystalline in nature with mixed phase of hexagonal and cubic structures with preferred grain orientation s along (111),(200), (220), and (112), which is in agreement as reported by earlier workers like Ghosh et.al.[21]. 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).

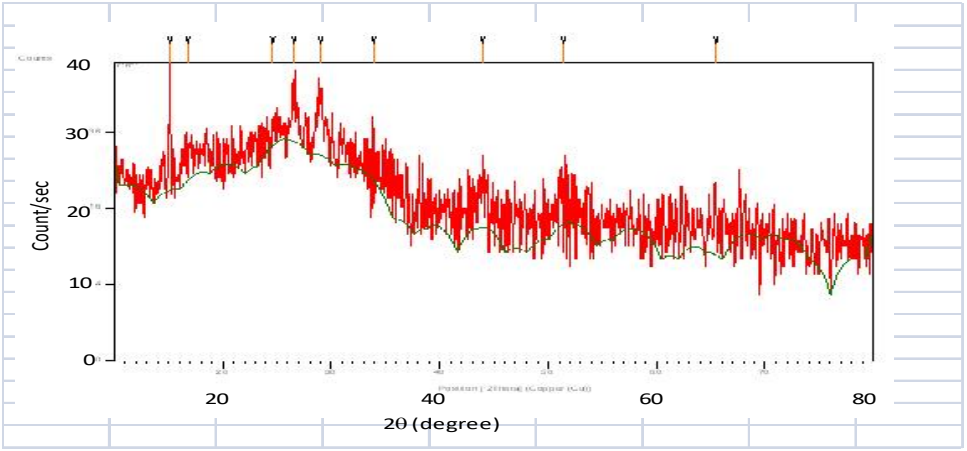

Figure 1: XRD pattern of 0.5 M CdS thin film.

The grain size or particle size (D) of the particles was estimated from the Debye- Scherrer's formula [22],

$$D = \frac{0.9\ \lambda}{\beta \cos\theta}$$ (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 [23]:

$\delta = \frac{1}{D^2}$ Where D is the grain size.

The microstrain was calculated by the formula [23]:

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

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

hkl (planes)	2θ(positions of peaks)	d (Å) (interplanar distance)	Average D value (nm)	Average of δ value (line^2/m^2)	Average value of ε
(111)	26.5668	3.35251 (cubic)	39.14425	0.652627×10^{15}	2.611266×10^{-3}
(200)	29.0423	3.07213 (cubic)			
(220)	43.9473	2.05863(cubic)			
(112)	51.4250	1.77547 (hexagonal)			

Table 1 : Diffraction peaks, d- values, average particle size, average dislocation density (δ) and average microstrain(ε) of 0,5 M CdS thin film.

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3.3 Surface Morphology Studies :

Scanning Electron Micrographs of the prepared CdS sample is 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

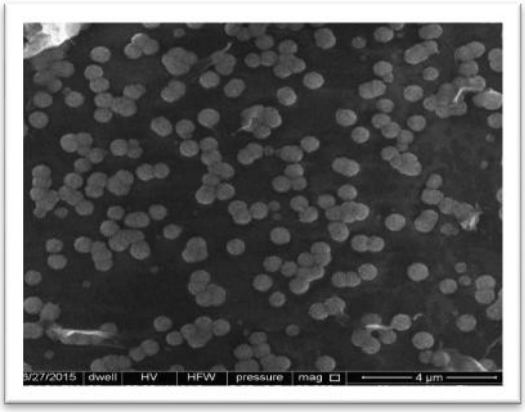

Figure 2: SEM picture of 0.5M CdS thin fim.

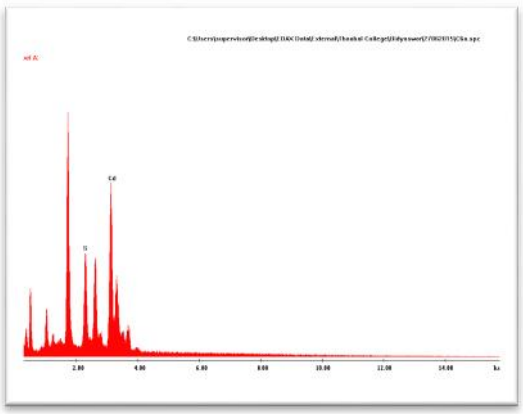

Figure 3 : EDX spectrum of 0.5 M CdS thin film.

3.4 Compositional Studies :

Figure 3 shows the elemental composition i.e. EDX analysis of the CdS thin films. The EDX indicates that the products consist of Cadmium and Sulfur elements as expected. The Silicon signal appears from the glass substrate.

Percentage of the main compositional elements is shown in table 3.

Element	Weight(%)	Atomic(%)	[Cd]/[S]
S	14.93	38.08	
Cd	85.07	61.92	1.6257
Total	100	100	

Table 3: Percentage of main elements in prepared CdS thin films.

3.5 Optical Studies :

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

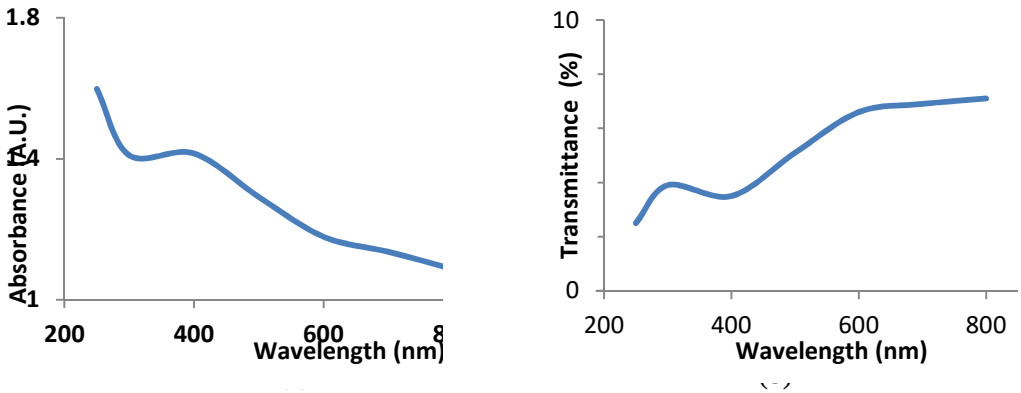

Figure 4:Optical (a) absorbance (b) transmittance spectrum of 0.5M CdS fi

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Figure 4(left) & 5(right):absorbance and transmittance curves as a function of wavelength for the nanocrystallineCdS thin film.

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 co-efficientα, the incident photon energy hυ and optical band gap $E_g$is related by the equation [24]

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

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 characterises 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 = $\frac{1}{2}$

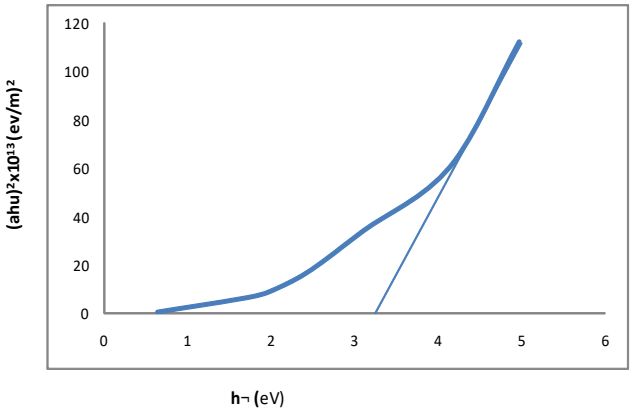

Figure 6: Optical energy gap of 0.5MCdS thin film.

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 value of E_g was found to be 3.15 eV.

4. Conclusion

Nanocrystalline thin films of CdS 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. The SEM photograph of the CdS thin film indicates that the morphology of the particles are spherical and symmetrical and it is concluded that the film follows a multi-layer growth pattern. The EDAX spectra shows that the film contains the elements Cd and S as expected. The optical absorbance study shows that the prepared film has a band gap of 3.15 eV.

5. Acknowledgements

The authors are thankful to Luminescence Dosimetry Laboratory, Thoubal College, Thoubal, Manipur, sponsored by AERB/CSRP, Mumbai, for allowing to use its facilities. The authors are also grateful to Scanning Electron Microscope and X-Ray Diffraction Laboratories of Manipur University, Imphal, for providing the XRD and SEM (along with EDX) facilities of prepared samples and Institute of Biotechnology , Thoubal College, Thoubal, Manipur for allowing us measurement of optical properties

of thin films. One of the authors Kh.Kamala Devi, thanks UGC (NERO) Office Guwahati, for providing financial support in the form of Minor Research Project.

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