

SYNTHESIS AND CHARACTERIZATION OF CdS n-TYPE OF SEMICONDUCTOR THIN FILMS HAVING NANOMETER GRAIN SIZE

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We deposited CdS n-type of semiconductor films on different substrates by Chemical Bath Deposition Technique. Structural, Surface Morphology and Optical properties of as deposited CdS films were investigated by XRD, SEM, FTIR and UV-VIS Spectrophotometer. It is found that, the average grain size of CdS in the films is 08 to 130nm. The band gap was also calculated from the equation relating absorption coefficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the CdS in the films. We also observed that, the change in preparation parameters affects the deposition rate of thin films. The physical conditions were kept identical while growing all the samples. The investigation of the effect of the synthesis method on the grain size and the effect of grain size on the properties of semiconductor is under consideration.

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1. Introduction

Cadmium Sulfide are compound semiconductors with a wide range of potential applications. This material have exist in cubic or hexagonal forms and are wide- direct-band gap semiconductors. The CdS is an excellent material used with the semiconductor cadmium telluride to fabricate solar cells given its optimal band gap energy (2.42 eV) for optical windows, while great importance in the optoelectronic applications and a diverse range of applications for thin films of this semiconductor including as waveguides, heterojunction devices and in thin-film electroluminescent displays in which it is the most commonly used host material [1]. Applications in optoelectronic methods or photovoltaic devices is another area receiving attention , In CdS based solar cells, the use of wider band gap materials such as ZnS or CdZnS could lead to decreases in window absorption losses and improvements in the short circuit current of the cells [1,5].

In this work we report the preparation of the CdS n-type semiconductor thin films having a nanometer grain size by using Chemical Bath Deposition (CBD) Technique. The CBD is one of the most convenient, reliable, simplest, inexpensive method and useful for large area industrial applications as well as preparation of thin film at close to room temperatures. The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapor phase synthetic routes to semiconductor materials, such as CVD, MBE and spray pyrolysis. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD to coat large areas, in a reproducible and low cost process.

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Another advantage of CBD method with respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates.[1,5]

The main objective of the present work is to develop, the CADMIUM based binary and ternary II–VI compounds n-type of semiconductors **CdS** thin films by using **CHEMICAL BATH DEPOSITION (CBD)** Technique. Structural, Surface Morphology and optical properties of as deposited CdS films were investigated by XRD, SEM, FTIR and UV-VIS Spectrophotometer.

2. Experimental

Thin films of CdS were deposited from a solution of analytical grade CdSO₄ (Cadmium Sulphate) a Cd⁺⁺ ion source and Thiourea as a S⁻ ion source in an alkaline solution of Ammonia. Commercial glass slides, used as substrates, were cleaned in acetone and methanol ultrasonically, and finally, again washed with methanol ultrasonically before use. After cleaning the glass slides were kept vertically in a closed beaker with the help of a special holder which is attached to AC Motor having a constant speed of 60 r.p.m. We have a Double distilled water in a beaker and then added CdSO₄ of particular molarity as a Cd⁺⁺ ion source slowly under Magnetic stirring. Add liquid Ammonia slowly to the solution for adjusting the pH of solution which is measured on pH meter, providing the temperature to the solution by means of heating coil. Add Thiourea (SC (NH₂)₂) of particular molarity as a S⁻ ion source was slowly poured into the solution only when the appropriate temperature i.e. 60°C was reached. Finally the temperature was kept constant with the help of a temperature controller in the range 70°C to 72°C. The time for the deposition was varied from 10 to 60 Min after achieving constant temperature. After the deposition, the CdS films were washed with methanol ultrasonically to remove the loosely adhered CdS particles on the film and finally dried in air. The same procedure is repeated for different time durations [3,4].

The crystallographic structure of films was analyzed with a diffractometer (XPERT-PRO) by using Cu-K α lines ($\lambda = 1.54 \text{ \AA}$). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. Surface morphology were examined by JEOL model JSM - 6400 Scanning Electron Microscope. IR spectra of representative sample 0.1M was recorded with the FTIR-8400S (SHIMADZU, Japan). The absorbance vs the wavelength was recorded with the UV-VIS spectrometer (Perkin Elmer: Lambda 35) in the wavelength range 200–600 nm for a different molarities. Also we were changing the different parameters such as Time, Molarities, pH and Temperature and note the effects of deposition rate of thin films.

3. Results and discussion

All the measurements were done at room temperature for the films deposited by chemical route. The thickness of the films was measured by the micro-weighing method.

3.1 XRD studies

The X-ray diffractogram of CdS films show broadened diffraction profiles (figure 1). It is observed that XRD patterns show a preferred orientation along (002) plane. The grain size of the nanocrystalline films is estimated using the Scherrer formula [8],

$$D = K\lambda/\beta_{2\theta} \cos\theta$$

where K is a constant taken to be 0.94, λ the wavelength of X-ray used ($\lambda = 1.54 \text{ \AA}$) and $\beta_{2\theta}$ the full width at half maximum of (002) peak of XRD pattern, Bragg angle, 2θ , is around 26.5°. The grain sizes were found to be within the range 08 to 113nm.

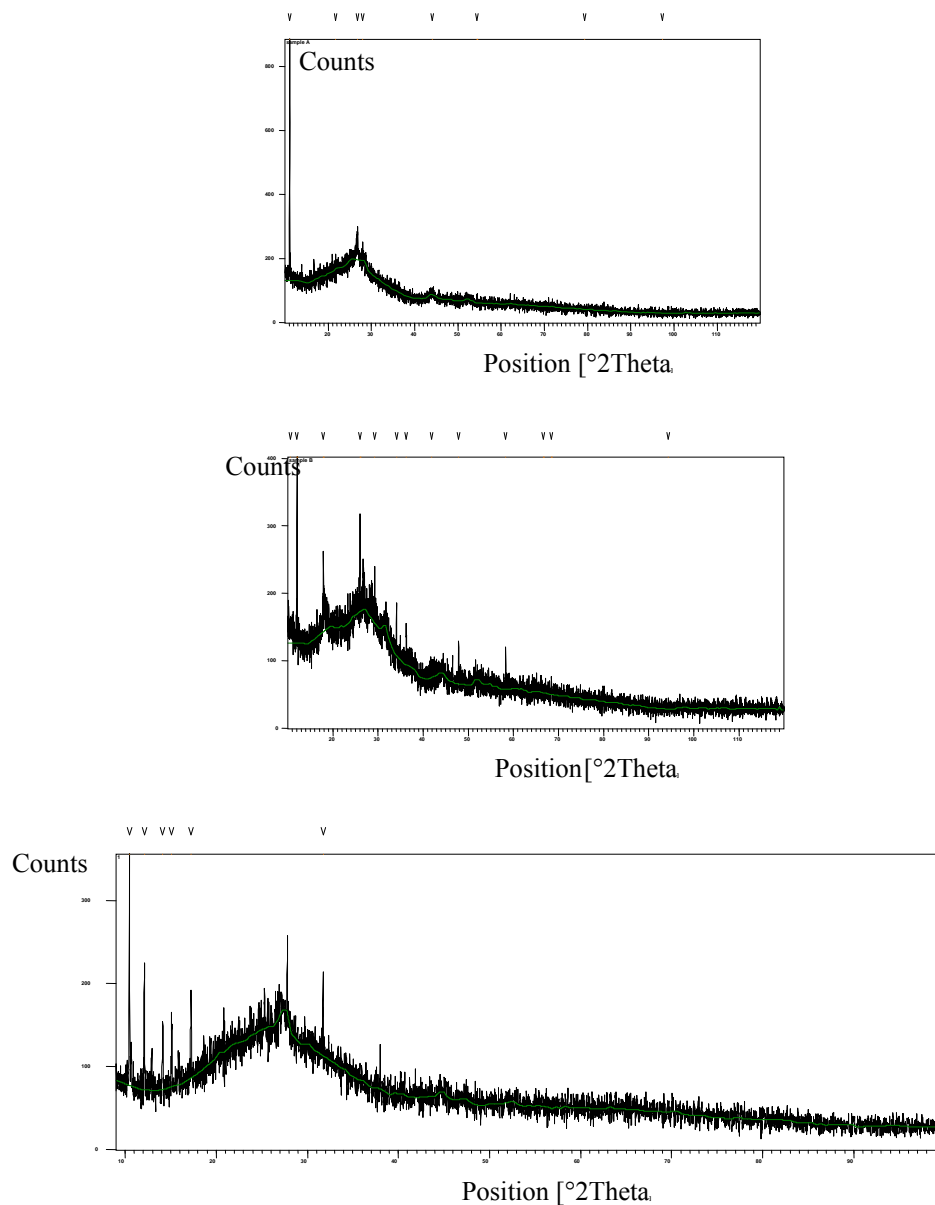


Fig. 1. XRD of CdS nanocrystalline films.

3.2 SEM analysis

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Figure 2 shows the surface morphology of CdS thin films deposited at 345K temperature observed by SEM. From the micrographs, it is observed that the ‘as-deposited’ films are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the substrates well. From the figure, we clearly observe the small nanosized grains engaged in a fibrous- like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films. From these images, it can be seen that the grain sizes of the films are not uniform. Therefore, from Figure 3, we estimated the grain sizes from different grains within the films and found to be about 08 to 130 nm. It is found that, the grain size of CdS thin films , from XRD and SEM are nearly equal it is given in Table 1.

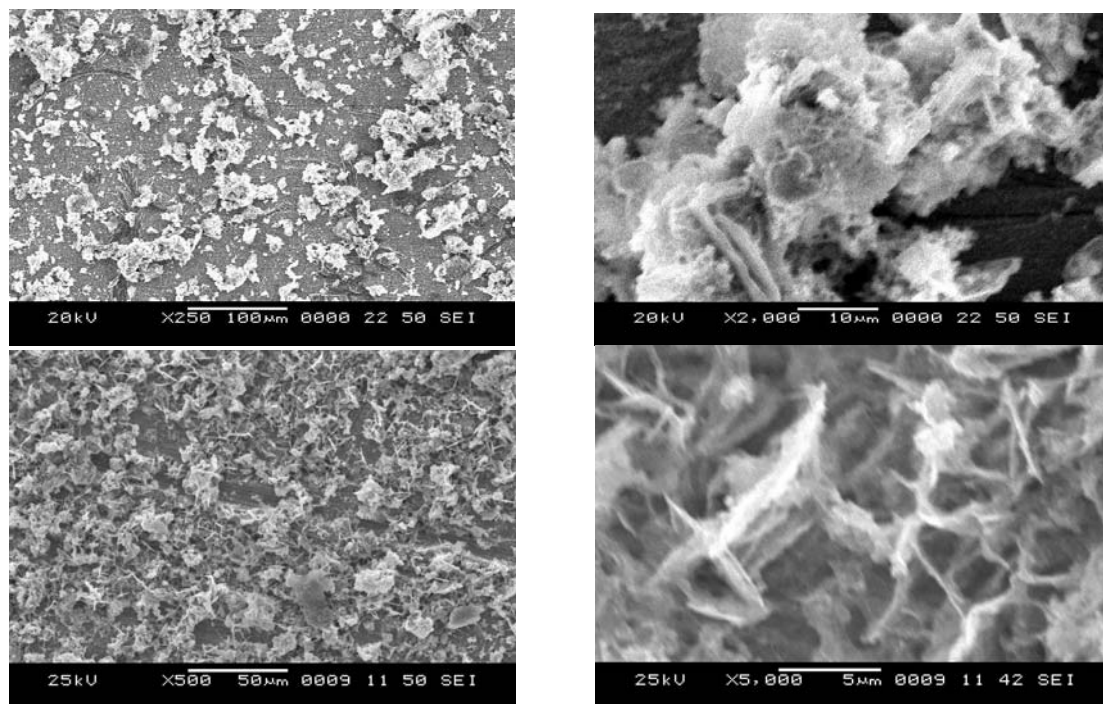


Fig. 2. SEM of CdS nanocrystalline films at different magnitudes.

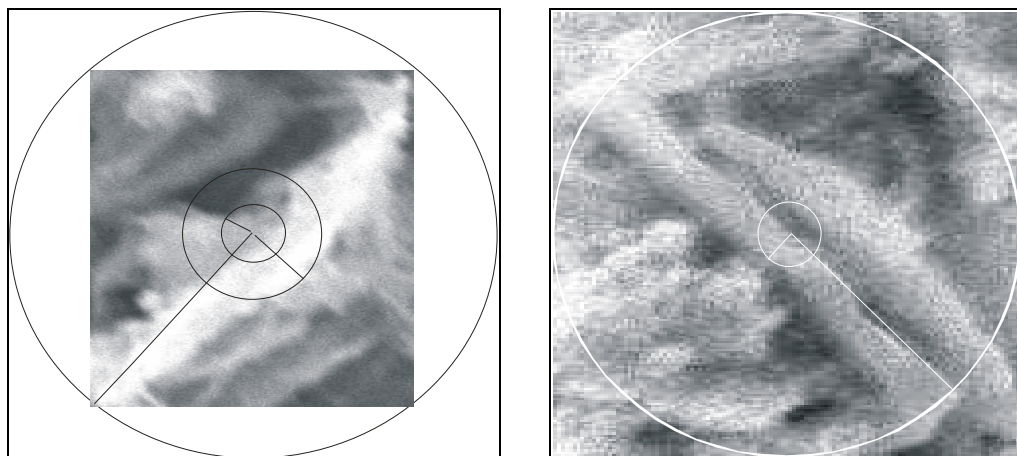


Fig. 3. Determination of Grain size from SEM.

Table 1. Values of Grain sizes of CdS thin films from XRD and SEM

Sample No.	Grain Size from XRD(nm)	Grain Size from SEM (nm)
01	8.11	8.0
02	13.90	16.22
03	24.33	27.03
04	59.93	64.90
05	113.32	129.80

3.3 IR spectra

IR spectra of CdS nanoparticles, is presented in figure 4. The IR frequencies along with the vibrational assignments for CdS nanoparticles are given in table 2. The band at 3584.82 cm^{-1} are due to O-H stretching vibrations of water molecules. The band at 2746.73 cm^{-1} are due to C-H stretching vibrations (Tang et al 2005). The bending vibrations of C=N appeared at 1574.93 cm^{-1} . CdS particles showed two stretching bands of C-O at 1182.4 and 1282.71 cm^{-1} . Trace amount of SO_4^- as impurity is seen as there are small absorptions around 1018.4 cm^{-1} (Williams and Fleming 2004). At 668.36 cm^{-1} and 703.8 cm^{-1} , there are medium to strong bands which have been assigned to Cd-S stretching (Periasamy et al 1997). The vibration absorption peak of the Cd-S band is at 262.33 cm^{-1} (Martin et al 1982; He et al 2003) [13-16].

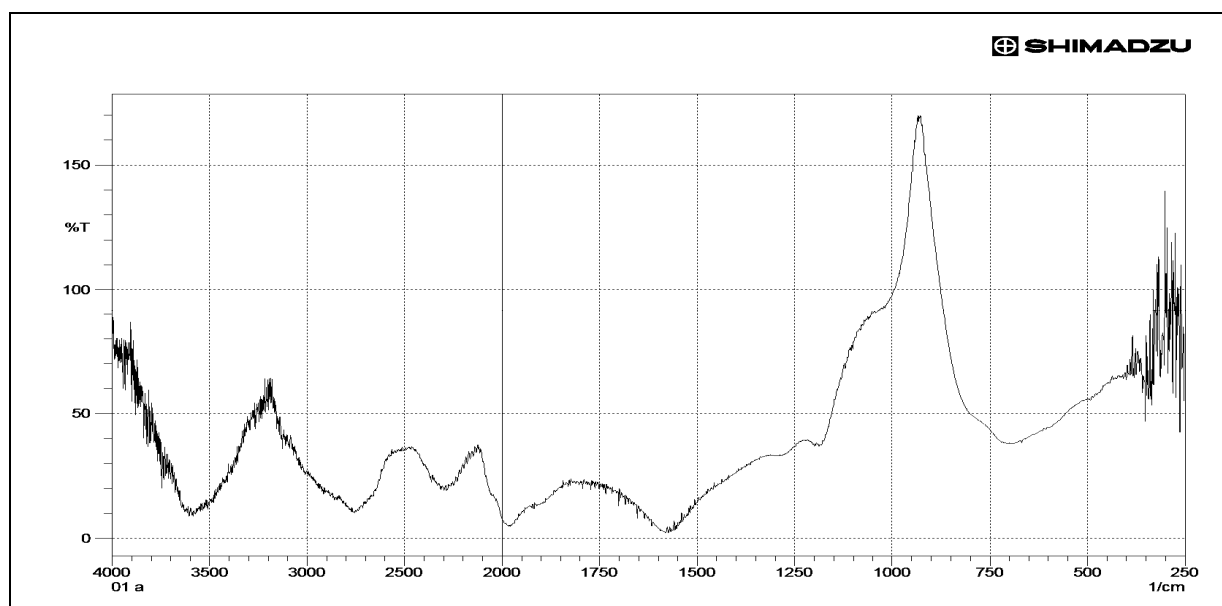


Fig. 4. IR spectra of CdS film for 0.1 M molarity.

Table 2. Positions and Vibrational Assignments of CdS film from IR spectra.

Positions (cm^{-1})	Intensities	Assignments
3584.82	Strong	O-H stretching
2746.73	Strong	C-H Stretching
1574.93	Strong	C=N stretching
1182.4 1282.71	Doublet Medium	C-O stretching
1018.4	Weak (trace)	SO_4^-
668.36 703.8	Doublet Medium	Cd-S stretching
262.33	Medium	Cd-S Stretching

3.4 Absorption studies

The UV absorption spectra of CdS thin films taken at room temperature are shown in figure 5. From the spectrograph the absorption edge of the samples are found to occur in the range 350–450 nm for nanocrystalline films. Absorption spectrum shows a clear shift to the lower wavelength side over bulk crystallites at ~ 515 nm. This blue shift of the absorption edge indicates decrease of the crystallite sizes of the samples. CdS is a typical direct band gap n- type of semiconductor. According to Tauc relation, the absorption coefficient for direct band material is given by (Tauc 1974; Sharma et al 1992)

$$\alpha = c(h\nu - E_g)^{1/2} / h\nu$$

where α is the absorption coefficient, c a constant, $h\nu$ the photon energy and E_g the band gap. The spectrographs were studied using the standard relation. A graph between $h\nu$ vs $(\alpha h\nu)^2$ is plotted and shown in figure 6. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap of film materials. The band gap of the films are determined from the plots which are found to be within 2.5–3 eV. The band gap increases with the decrease of crystallite size. The increment in band gap is approximately inversely proportional to the square of the crystallite size based on the effective mass approximation (Brus 1986).

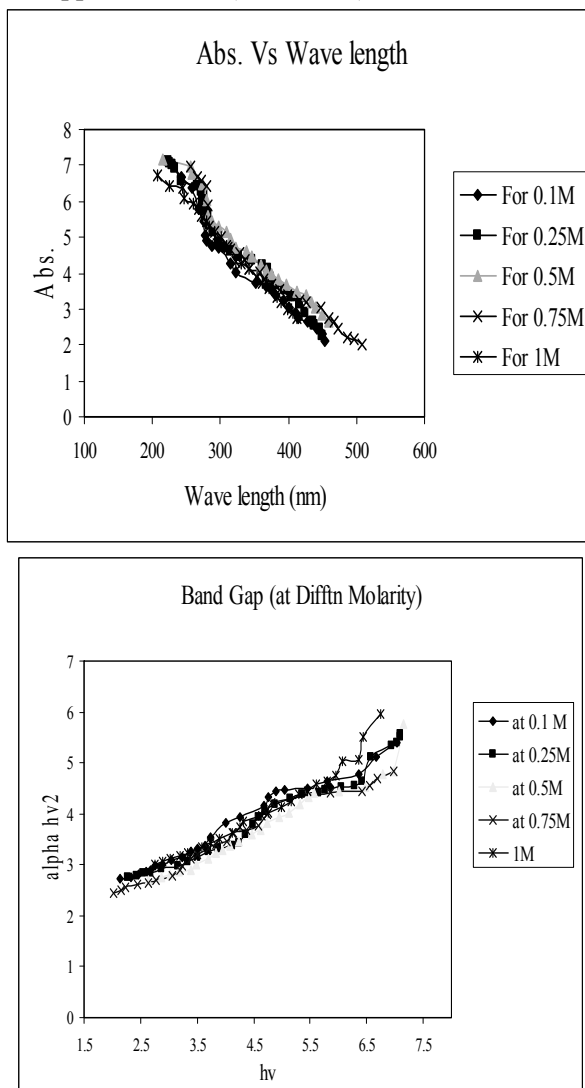


Fig. 5 and 6 : UV absorption spectra and band gaps of CdS films for different molarities.

4. Conclusions

Thin films of CdS prepared by CBD technique are found to be nanocrystalline. The crystallite sizes measured by XRD studies are found to be within 08–113 nm, and from SEM are within 08–130 nm. XRD shows that samples are of single cubic phase, which is important for device performance. SEM studies show presence of long tubes and irregular distributions of particles. FTIR spectroscopy showed the bonding peaks and the percentage transmittance, the films were found to have high transmittance in the range between 82 and 100% in the UV-VIS-NIR regions; hence, they could be effective as thermal control window coatings for cold climates and antireflection coatings. The UV absorption studies on films clearly show an increase in band gap with reduction in particle size as compared to bulk materials, and this fact supports the formation of nanocrystallites in these films. The overall deposition technique clearly observed that higher molarity facilitates the growth of nanocrystallite in CdS films.

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