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# PREPARATION AND CHARACTERIZATION OF CDS NANO-FILMS VIA SOL – GEL METHOD AT DIFFERENT ANNEALING TIME

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***Abstract*** **- Highly crystalline and transparent Cadmium Sulphide (CdS) thin films were deposited on microscopic glass substrates by sol- gel spin coating technique. Effects of annealing time on structural and optical properties of the films were studied. Data obtained from XRD patterns are used to identify the phase, crystal structure, grain size and lattice constants of the films. There is a preferential orientation of the crystallites in the film along c-axis (perpendicular to the plane of the substrate) producing a strong hexagonal (0 0 2) peak. The crystallite size obtained through the XRD analysis was found to increase with increase in annealing time, varying from 6.1 nm to 9.3 nm. The size of the particles estimated also from the band gap values obtained from optical study, using the Brus equation was found to be in the range of 5.0 nm to 9.6 nm. The photoluminescence spectra show presence of defect structures and the CdS emission spectral peaks are found to decrease in intensity, with increase in annealing time. These results suggest that the deposition of CdS thin films should be further investigated for application towards the fabrication of optoelectronic devices.**

***Keywords*** **- CdS Thin Films, Sol - Gel Process, Spin Coating Technique, XRD, AFM, Brus equation, PL**

## I. INTRODUCTION

The synthesis and study of binary metal chalcogenides of group II - VI semiconductors in a nanocrystalline form has been a rapidly growing area of research due to their important nonlinear optical properties [1, 2], luminescent properties [3, 4], quantum size effect [5] and other important physical and chemical properties [6]. Cadmium sulfide (CdS) with a wide band gap of 2.4 eV (in bulk) is a technologically important semiconductor material which has been studied for decades. CdS in a nanocrystalline thin film form can be prepared by a variety of methods (both physical and chemical) like sol - gel [7], electrostatic deposition [8], electrochemical method [9, 10], gas evaporation [11], CBD [12] etc. Among these the sol – gel spin coating method has many advantages such as simplicity, low cost, and its ability to obtain uniform films with good adherence and reproducibility [13].

In this paper, we report on the effect of annealing time on structural, surface morphological and optical properties of spin coated CdS thin films by sol- gel spin coating technique.

## II. EXPERIMENTAL DETAILS

*Synthesis of CdS Nanocrystals*

The preparation of the starting solutions and the process of coating of CdS films are shown below as a flowchart (Fig. 1). Glass micro slides of 2.5 cm x 2.5 cm were used as substrates. Prior to deposition the substrates were washed with soap solution, acetone and water then boiled in concentrated (2M) chromic acid and kept in distilled water for 24 hrs. Finally the substrates were ultrasonically cleaned in ultrasonic bath (SYSTRONICS) for 30 minute. Continuous films are formed onto the substrates by spin deposition of the material droplets at a spin speed of 1000 rpm for spinning time of 30 second.

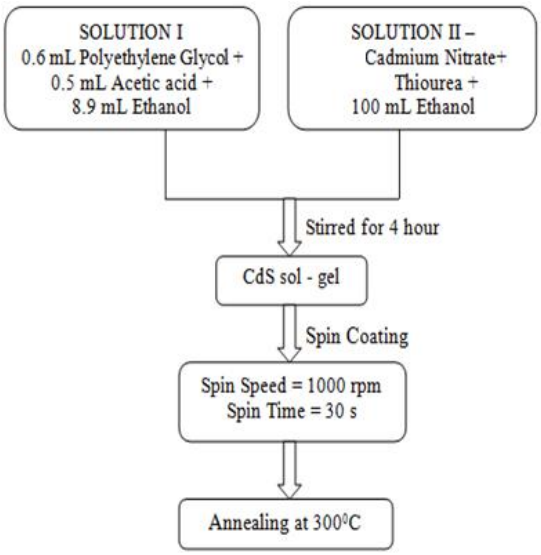


Fig. 1 Flowchart to prepare CdS thin films

After deposition, annealing of the samples was carried out to remove the solvent and organic residuals. In this work the films were post annealed in air at 300˚C for 45 minute. Annealing time is one of the parameters, which may influence the stiochiometry and structural properties of the films. So in order to study the influence of annealing time on the film properties, two more samples were prepared and annealed at 300˚C with the annealing time of 60 minute and 75 minute.

*Sample Characterization*

In order to study the structural, surface morphological and optical properties of the films, X- Ray Diffraction patterns, Atomic Force Microscopic image, Optical transmission spectra and Photoluminescence spectra were obtained using X'PERT PRO X – ray diffractometer, Scanning Probe Microscope, Schimadzu UV – VIS – NIR spectrophotometer and Shimadzu RF-5301 PC luminescence apparatus respectively. X- Ray diffractometer was operated at 40 KV and 30 mA with CuK$\alpha_1$ radiation of wavelength 1.5407Å. AFM surface topography has been studied using Digital Instruments Dimensions 3100 Scanning Probe Microscope operated in tapping mode. Transmission spectra were recorded in the range of 200 – 800 nm. The Photoluminescence (PL) study was carried out with a xenon lamp as light source and the used excitation wavelength was 380 nm.

## III. Results and Discussion

*X – Ray diffraction Analysis*

The XRD pattern of CdS thin films annealed for different annealing time such as 45 minute, 60 minute and 75 minute at 300°C were shown in Fig. 2. The XRD pattern shows only one peak that corresponds to the reflection (0 0 2) of hexagonal phase showing the preferential orientation of the film is along the (0 0 2) direction. However, we can observe also that the films have some amorphous component. The intensity of the (0 0 2) peak found to increase with increase in annealing time of the films.

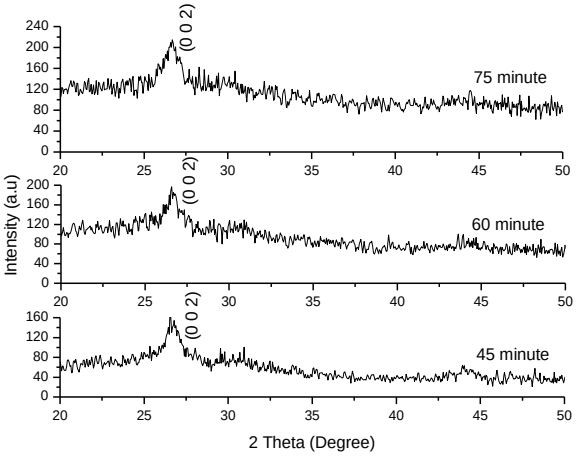


Fig. 2 XRD patterns of CdS thin films for different annealing time

The average crystallite sizes were obtained from the XRD pattern using the Debye - Scherrer's formula [14],

$$D = \frac{k\lambda}{\beta\cos\theta} \text{ (nm)} \qquad (1)$$

where, D is the average crystallite size, k is a constant taken to be 0.94, β is the full width at half maximum (FWHM), θ is the Bragg angle and λ is the wavelength of the X– ray source. As the annealing time is increased, it is seen that crystallite size of CdS increases from 6.1 nm to 9.3 nm [Table 1]. Thambidurai et al., [15] have also reported that the crystallite size increased with the increase of annealing time.

The lattice parameters 'a' and 'c' of the unit cell were evaluated by the relation [16],

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \qquad (2)$$

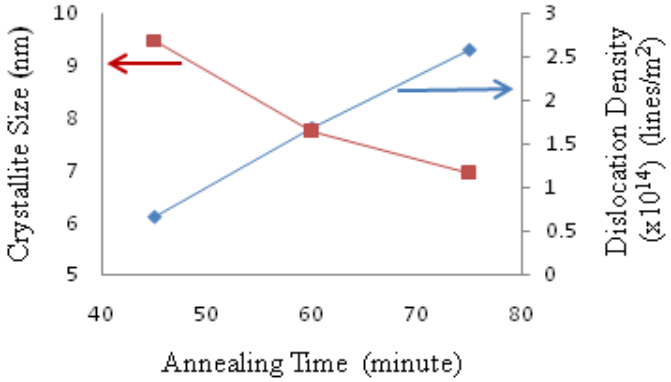


Fig. 3 Variation of crystallite size and dislocation density with annealing time

The observed XRD pattern and the lattice parameter value 'a' and 'c' are found to match well [Table 1] with the standard JCPDS data (File: 06 - 0314) and the similar result was reported in previous works also [15, 17].

The dislocation density (δ), defined as the length of dislocation lines per unit volume, has been estimated using the formula [18],

$$\delta = \frac{1}{D^2} \qquad (3)$$

where δ being the measure of amount of defects in a crystal. The calculated structural parameters are given in Table 1.

TABLE 1: STRUCTURAL PARAMETERS OF CdS THIN FILMS FOR DIFFERENT ANNEALING TIME

| Annealing Time (Minute) | 2 Theta (deg) | d – spacing (Å) | Unit cell Volume V (Å)$^3$ | Lattice Parameter | | Crystallite Size D (nm) | Dislocation Density δ (*$10^{14}$) (lines/m$^2$) |
|---|---|---|---|---|---|---|---|
| | | | | *a* (Å) | *c* (Å) | | |
| 45 | 26.72 | 3.34202 | ----- | ----- | 6.684 | 6.1 | 2.69 |
| 60 | 27.10 | 3.35383 | 98.606 | 4.120 | 6.708 | 7.8 | 1.64 |
| 75 | 26.52 | 3.35546 | 97.457 | 4.095 | 6.711 | 9.3 | 1.16 |
| JCPDS reference | 26.66 | 3.36700 | 99.448 | 4.136 | 6.713 | ----- | ----- |

Dislocation densities decrease with increase in annealing time, which shows to the reduction in the concentration of lattice imperfections and confirm the improvement in crystallinity of the thin films with annealing time. Figure 3 shows the variation in crystallite size and dislocation density according to annealing time.

*Surface Morphological Analysis*

AFM analysis of spin coated CdS thin fim annealed at 300°C for 75 minute (Figure 4) shows that the surface is composed of crystallites grouped together into larger agglomerates. The observation was carried out on several location of the film in order to obtain statistical average value and root mean square (RMS) value of surface roughness has been calculated by microscope software and is 63.7 nm.

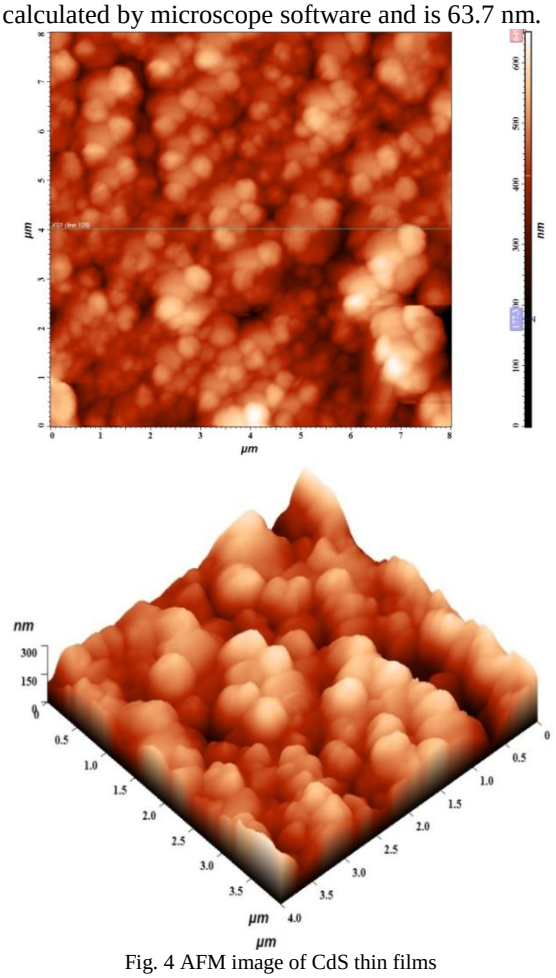


Fig. 4 AFM image of CdS thin films

The image reveals that the film is homogeneous without any cracks and is continuous with well connected grains.

*Optical Analysis*

The UV – Visible spectroscopic study of the spin deposited CdS thin films was done in the wavelength range of 200 – 800 nm. The band gap values of the CdS thin films were found from the Tauc's plots drawn for the UV – Vis spectroscopic data.

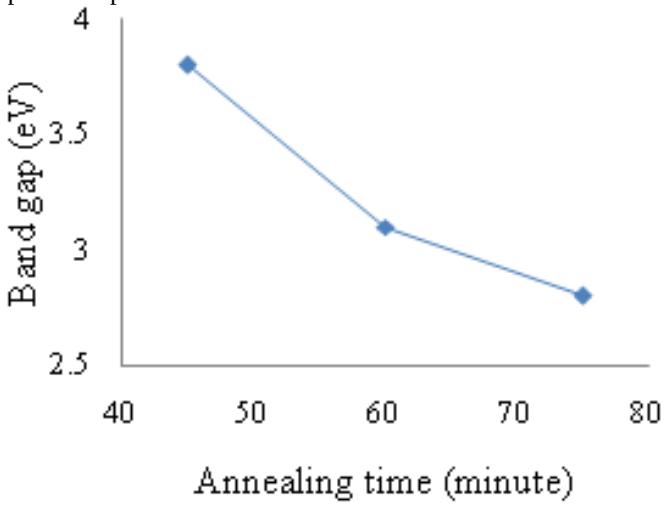


Fig. 5 Variation in band gap with annealing time

The calculated optical band gap values are found to be in the range of 2.8 to 3.8 eV and were also shown in Table 2.The optical band gap values obtained using the absorption spectra are greater than the bulk band gap (2.42 eV) and this indicates the formation of nanoparticles and presence of quantum confinement effect in the prepared CdS thin films. Figure 5 shows the variation of band gap with annealing time. As the annealing time increases the band gap decreases.

The size of the particles can also be estimated from the band gap values, using the Brus equation [19],

$$E_{th} = E_g + \frac{h^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{\varepsilon R} \qquad (4)$$

where $E_{th}$ is the band gap of the CdS thin film, $E_g$ is the band gap of bulk CdS (2.42 eV), h is the Planck's constant, $m_e$* is the effective mass of electron (0.9 me), $m_h$* is the effective

mass of hole (0.8 me), ϵ is the dielectric constant and R is the radius of the grains. The second term of equation (5) represents the kinetic energy of the confined exciton and the third term indicates the coulomb interaction of the electron with the hole. Here the coulomb interaction is negligible [20].

TABLE 2: OPTICAL PARAMETERS OF CdS THIN FILMS FOR DIFFERENT ANNEALING TIME

| Annealing Time (minute) | Optical Band gap (eV) | Particle size from band gap (nm) |
|---|---|---|
| 45 | 3.8 | 5.0 |
| 60 | 3.1 | 8.6 |
| 75 | 2.8 | 9.6 |

The particle size values obtained from the optical band gap calculated using Brus equation are shown in Table 2. The values obtained from the Brus equation well matched with the values obtained from XRD study using Debye Scherrer's formula and is represented in Figure 6.

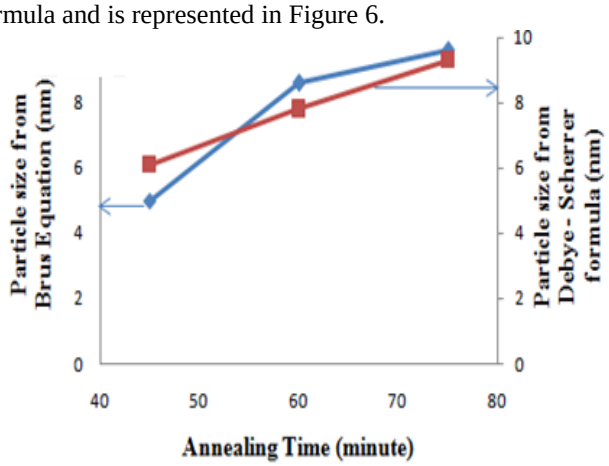


Fig. 6 Variation in particle size with annealing time

As the particle size obtained from the XRD and the optical absorption studies are found to be slightly larger than the Bohr radius, the strong confinement effect can be assumed to be prevalent in the prepared CdS nanocrystalline films.

*Photoluminescence Analysis*

PL spectra were recorded at room temperature with an excitation wavelength of 380nm. Figure 7 shows the photoluminescence (PL) emission spectra of the CdS thin films.

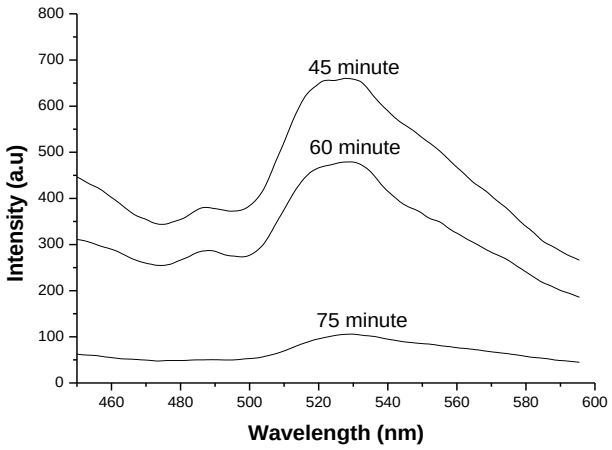


Fig. 7 Photoluminescence emission spectra of the CdS thin films

The PL emission spectra of spin coated CdS films found to exhibit two emission peaks centered at 488 nm and 527 nm which are green and yellow emission bands of CdS respectively. Similar observation has been reported in earlier works [21]. In CdS films defects found to consist of cadmium vacancies, sulphur vacancies, interstitial cadmium and sulphur atoms adsorbed on the surface. The green band composed of a peak centered at around 527 nm originated from radiative recombination [22], which was related to the grain size distribution.

As the size of the grains decreased, the ratio of surface to volume of the grains got increased which led to enhancement of the green band intensity, which may be explained by the fact that more Cd interstitials were trapped on the grain boundaries. The PL spectrum peak is found to broaden out with increase in annealing time. The inhomogeneous broadening of peaks can be attributed to higher concentration of defects. Bigger the nanocrystals the smaller the number of surface states induced is, and so defects are lower, which may result in the reduction of shallow – trap centers.

## IV. CONCLUSION

The structure of the annealed CdS films prepared by sol gel spin coating method analyzed by X-ray diffraction technique indicated the presence of the (0 0 2) crystal planes corresponding to CdS hexagonal structure. The values of the size of the CdS particles obtained from both Brus equation method and from Debye - Scherrer formula found to match well. The PL spectra showed that the peaks are found to broaden out with increase in annealing time. This study revealed that these films might be suitable for opto electronic devices.

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