Effect of annealing temperature on structural and Raman spectroscopy analysis of nanostructured CdS thin films

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Abstract. Nanocrystalline CdS thin films were deposited on glass substrates using the sol-gel spin coating method. The structural properties and surface morphology of the CdS thin films were characterized by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Atomic force microscopy (AFM). XRD studies revealed that all the films exhibit cubic structure with a (1 1 1) preferential orientation. The diffraction peak (1 1 1) shifts towards higher 2\textdegree value with increasing annealing temperature from 150 \textdegree C to 350 \textdegree C. The Raman spectra shows the intense and broad peaks at \textasciitilde302 and \textasciitilde603.5 cm\textsuperscript{-1}, which are assigned to fundamental optical phonon mode (LO) and first overtone mode (2LO) of CdS.

1. Introduction
Cadmium sulfide (CdS) has been studied extensively for various applications such as solar cells, photovoltaic devices and photosensors because of its high transmittance in visible and high reflectance in the infrared region, high absorption coefficient, high electron affinity, low resistivity and easy of making an Ohmic contact \cite{1, 2}. CdS is an n-type semiconductor with a direct band gap of 2.42 eV (in cubic phase) and 2.57 eV (in hexagonal phase) at room temperature. For solar cells applications, CdS films need to have a suitable conductivity (>10\textsuperscript{16} carriers/cm\textsuperscript{3}), and adequate thickness to allow high transmission and good uniformity to avoid electrical short-circuit effects \cite{3}. CdS thin films have been prepared by several methods such as spray pyrolysis \cite{4}, spin coating\cite{5}, RF sputtering\cite{6}, pulsed laser ablation\cite{7}, screen printing\cite{8}, successive ionic layer adsorption and reaction (SILAR)\cite{9, 10}, electro deposition \cite{11}, chemical bath deposition (CBD) \cite{12, 13}, close-spaced sublimation (CSS) \cite{14}, metal organic chemical vapor deposition (MOCVD) \cite{15, 16}, molecular beam epitaxy (MBE) \cite{17, 18}. Among these methods sol – gel spin coating method had many advantages such as low cost, simplicity and its ability to obtain uniform films with good adherence and reproducibility. In this work the effect of annealing temperature on structural and surface morphological properties of sol-gel spin coated CdS thin films were reported.

2. Experimental details
The preparation of nanocrystalline CdS thin films had been done with the following steps: at first, polyethylene glycol (PEG 200, SDFCL) sol was prepared by mixing 0.6 mL of PEG with 8.9 mL of ethanol and 0.5 mL of acetic acid under stirring, which was continued for 90 minutes. Cadmium nitrate and thiourea were used as precursors for incorporation of Cd and S, respectively. These
precursors were dissolved in ethanol with stirring for 90 minutes. The as-prepared solution was slowly added to the PEG sol with vigorous stirring for 6 h in order to obtain the final sol ready for depositing CdS thin films. The spin coating method was used to prepare CdS thin films on the glass substrates. The substrates had been rotated with a speed of 1000 rpm for 45 s. After the deposition, the samples were annealed for the removal of solvent and residual organics and film densification. The films were post-annealed in air at 150, 250 and 350 °C respectively for one hour. X-ray diffraction data of CdS thin films were obtained with the help of a X-ray diffractometer (Bruker AXS D8 Advance) with CuKα radiation (λ=0.154 nm) X-ray source. Surface morphological studies were carried out using a Field Emission Scanning Electron Microscope (JEOL Model JSM - 6390LV). The surface topography of the CdS thin film samples has been studied using AFM (Park XE-100: Atomic Force Microscopy). The Raman spectrum for CdS thin films were recorded at room temperature by micro-Raman spectroscopy using Renishaw Invia Raman microscope (Renishaw plc, Gloucestershire, UK) with 514-nm excitation wavelength of an Ar ion laser.

3. Results and discussion

The X-ray diffraction patterns of CdS thin films annealed from 150 to 350 °C is shown in figure 1. The diffraction peaks at 27.33°, 44.7°, and 52.8° corresponding to (1 1 1), (2 2 0) and (3 1 1) planes (JCPDS 21-0829) of the cubic phase. It is observed that the intensity of diffraction peak (2 0 0) decreases with increase of annealing temperature from 150 to 350 °C. It is clearly observed that the intensity and sharpness of diffraction peak corresponding to the plane (1 1 1) increases with the increase of annealing temperature which confirms that the crystallinity of the films is improved. The angle 2θ shifts towards higher angles with the increase of annealing temperature from 150 to 350 °C.

![Figure 1. XRD patterns of CdS thin films annealed at different temperatures.](image)

The crystallite size (D) of the CdS thin films were determined using the Scherer formula [19]

\[
D = \frac{K\lambda}{\beta\cos\theta} \text{ nm} \quad (1)
\]
where $K = 0.94$ is a constant, $\lambda$ is the wavelength of X-ray ($\lambda = 0.154$ nm) and $\beta$ is the full width at half maximum of (1 1 1) peak in radians, $\theta$ is the Bragg angle. The crystallite sizes are found to be in the range of 18.7–26.6 nm. The crystallite size of CdS thin films increases with the increase of annealing temperature. Similar results have been shown by earlier literature Bilgin et al. [20] and Barote et al. [21].

The thickness ($t$) of the films is an important parameter for the analysis of physical properties. The thickness of CdS films was measured with the help of a weight difference method using a sensitive electronic balance, in this method the substrate was weighed before ($m_1$) and after the deposition ($m_2$) and the thickness of the films was obtained from the relation [22]

$$t = \frac{(m_1 - m_2)}{\rho a} \quad (2)$$

where $\rho$ is the density of the film material (g/cm$^3$) and $(a)$ is the area of the film (in cm$^2$). The thickness of CdS thin films are found to be 1260, 1170, 1160 Å respectively. The number of crystallites per unit area ($N$) of the films was determined using the following relation [23]

$$N = \frac{t}{D^3} \quad (3)$$

where $t$ is the thickness of the film.

The micro strain ($\varepsilon$) in the thin films was determined using the formula [24]

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (4)$$

The dislocation density ($\delta$) is defined as the length of dislocation lines per unit volume. It has been estimated using the relation [25]

$$\delta = \frac{n}{D^2} \quad (5)$$

where $n$ is a factor that equals unity when the dislocation density is minimum and $D$ is the crystallite size. Dislocation density ($\delta$) gives information regarding the amount of defects in a crystal. The calculated microstructural parameters of CdS thin films are presented in table 1. The small values of dislocation density obtained in the present study confirm the good crystallinity of the thin films fabricated by spin coating technique. As the annealing temperature increases the dislocation density ($\delta$) decreases which may lead to reduction in the concentration of lattice imperfections.

| Annealing temperature ($^\circ$C) | Lattice constant (nm) | Crystallite size (nm) | Microstrain, $\varepsilon \times 10^3$ (lin.$^{-1}$.m$^{-4}$) | Dislocation density, $\delta \times 10^{16}$ (lin.m$^{-2}$) | Number of crystallites per unit area |
|-------------------------------|----------------------|----------------------|--------------------------------|--------------------------------|----------------------------------|
| 150                           | 0.5682               | 18.7                 | 0.247                          | 0.468                          | 5.98                             |
| 250                           | 0.5656               | 22.8                 | 0.250                          | 0.476                          | 4.05                             |
| 350                           | 0.5651               | 26.6                 | 0.290                          | 0.644                          | 3.86                             |

Figure 2 illustrates the surface morphology of nanocrystalline CdS thin films deposited on glass substrates. FESEM micrographs of CdS thin films reveal that the grains are in spherical shape and a homogeneous film without cracks and free from holes. It can be easily understood that the shape and arrangement of the grains are highly influenced by the growth mechanism. In accordance with the X-ray diffraction, FESEM micrograph was also approved the nanocrystalline formation of CdS thin film. The formation of the nanoparticle with size dependent properties makes the thin film useful in
sensors and optical devices. Figure 3 shows the AFM images of nanocrystalline CdS thin films annealed at 250 °C and 350 °C. It clearly shows a hummock-like surface topography with smooth, homogeneous, uncracked, compact and dense. The average roughness and rms roughness values of CdS thin films post-annealed at 250 °C and 350 °C are found to be 2.84 nm and 3.68 nm.

Figure 2. FESEM images of CdS thin films post-annealed at different temperatures.

Figure 3. AFM images of CdS thin films annealed at 250 °C and 350 °C.

Figure 4 shows the Raman spectra of nanostructured CdS thin films annealed at different temperatures. Raman spectrum of thin film deposited on glass substrate had two peaks, 1LO and 2LO which belong to the first and second longitudinal optical phonon modes. The 1LO peak is strong while
the 2LO peak is weak which corresponds to the fundamental and overtone modes respectively [26]. Intensities of the fundamental and first overtone of the LO phonons were used for qualitative understanding of electron–phonon interaction in small particles. Raman spectrum of the CdS thin films annealed at different temperatures displayed a single fundamental band at 300 cm\(^{-1}\) (1LO) and overtone mode at about 600 cm\(^{-1}\) (2LO). It was observed that the Raman spectrum contained overtones of weaker intensities than the fundamental [27], which is in good agreement with the earlier reports made by Rajalakshmi et al. [28], Zhang et al. [29] and Oladeji et al. [30] for CdS nanoparticles. A substantial frequency shift (~3.5 cm\(^{-1}\), 1 cm\(^{-1}\), 3.3 cm\(^{-1}\)) for the 1LO phonon (301.5 cm\(^{-1}\), 304.1 cm\(^{-1}\), 301.7 cm\(^{-1}\)) from CdS bulk [31] of about 305 cm\(^{-1}\) was observed for the CdS films annealed at 150, 250, 350 °C. The observed Raman shift towards lower frequency might be due to the electron-phonon interaction caused by the reduction of particle size [32]. The second-order scattering of LO phonon is also visible at approximately 600 cm\(^{-1}\). As the particle size increases with the increase of annealing temperature, the intensity of 2LO line becomes stronger, while the 1LO line becomes weaker. The decreased peak intensity with annealing is attributed to the shift of the crystalline structure of CdS films to a more cubic phase [33].

![Figure 4. Raman spectrum of CdS thin films annealed at different temperatures.](image)

4. Conclusion
CdS thin films prepared by sol-gel spin coating method had a good adherence with the glass substrate. The effect of annealing temperature on the structural and surface morphological properties was studied. From the XRD patterns, it is observed that the CdS thin films have a preferred orientation along (1 1 1) plane with cubic phase structure. The crystallinity of the films became better at higher
annealing temperature. FESEM images of nanocrystalline CdS thin films revealed that the grains are uniformly distributed and spherically shaped. The Raman peaks appearing at 302 cm\(^{-1}\) and 603.5 cm\(^{-1}\) were attributed to 1LO and 2LO phonons indicating the growth of CdS thin films with a crystalline quality.

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