Effect of precursor ratios on the structural, morphological and optical properties of CBD-CdS films

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Abstract. Cadmium sulfide (CdS) films were deposited on fluorine doped tin oxide (FTO) glass substrates by chemical bath deposition (CBD). X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), photoluminescence (PL), and Fourier transform infrared (FT-IR) analyses were employed to compare the structural, morphological, and optical properties of deposited films. The XRD studies confirmed the cubic crystalline nature of the deposited films, and the intensities of the peaks were found to vary for different precursor ratios. The results of SEM study show that the films were smooth and uniform. The RMS surface roughness values of the CdS films were found to be in the range of 25.42nm to 35.33nm. Energy band-gap values of the CdS films were found in the range of 2.32eV to 2.39eV. Two distinct bands (centred at 489nm and 556nm) were found in the PL emission spectra. S-C-N, Cd-S, and C-S vibrations were observed to dominate in the FT-IR spectra.

1. Introduction
The Cadmium sulfide (CdS) is one of the most popular II-VI group compound semiconductor due to its use in wide range of applications such as, light emitting diodes, optoelectronic devices, thin film solar cells, photo-degradation, and piezo-electronic devices [1-2]. CdS can be synthesized in different size and shape such as triangle, cube, sheet, tube, wire, film, rod, powder, fiber, etc. Multiple deposition techniques have been developed to deposit CdS films such as thermal evaporation, spray pyrolysis, electrodeposition, chemical bath deposition (CBD), molecular beam epitaxy [3-4]. CBD technique is easy to perform among these deposition techniques and can be implemented using low cost experimental set-up. The quality and applicability of CdS films is affected by various deposition parameters including deposition time, complexing agent, pH variation, bath temperature, and annealing treatments[5–6]. However, the effect of variations in cadmium (Cd) and sulfur (S) ratio has not been explored well in the literature. Therefore, we are reporting the rigorous study of variations in structural, morphological, and optical properties of CdS films due to changes in precursor ratio.

2. Experimental details
Fluorine doped tin oxide (FTO) coated glass slides were used as substrates. Cadmium acetate and thiourea were used as precursor materials. Amonia (NH₃) has been used as a complexing agent as it helps to maintain the pH of the solution too. Chromic acid, acetone, and double distilled water were used for the cleaning of all the required items before the film deposition. A hot plate magnetic stirrer was used to homogenize the solution. Three different solutions were prepared with different Cd/S ratios (a) 1:1, (b) 1:2, and (c) 1:3. Then, all the three solutions (with an FTO slide dipped inside) were
placed in the water bath for 1h at 70 °C. After the completion of deposition process, all the three CdS films were lifted carefully and washed ultrasonically in distilled water. X-ray diffraction (XRD) technique was used for structural analysis of the films. For the study of morphological behaviour of the films, scanning electron microscopy (SEM) and atomic force microscopy (AFM) characterization techniques were employed. UV-visible spectroscopy was used for the optical analysis of the films. Photoluminescence (PL) was used to study the luminescence behaviour of the films and Fourier transform infrared (FT-IR) spectroscopy was employed to analyse their infrared absorption spectra.

3. Results and discussions

3.1 Structural analysis

The XRD diffractograms of CdS films deposited for different precursor ratio is shown in figure 1. Film deposited for Cd/S ratio 1:2 and 1:3 have three characteristic XRD peaks (111), (200) and (220). But the film deposited for Cd/S ratio 1:1 has only (111) and (200) characteristic peaks[7]. Thus, all three films have cubic crystalline nature, but the intensity of peaks is different for different film. The film deposited for Cd/S ratio 1:1 and 1:3 are poorly crystallized as compared to the film deposited for CdS ratio of 1:2. It suggests that the crystalline behaviour of CBD-CdS films depends on the precursor ratio. The crystalline sizes of films deposited for Cd/S ratio 1:1, 1:2, and 1:3 are calculated by Scherrer formula, which are found as 60.28nm, 65.34nm, and 52.47nm, respectively. Hence, the crystallite size estimation also suggests that the film deposited for Cd/S ratio of 1:2 is more crystalline than the other two films.

![XRD patterns of CdS films deposited for Cd/S ratio (a) 1:1, (b) 1:2, and (c) 1:3.](image)
3.2 Surface morphology
The surface morphology of the CdS films deposited for different Cd/S ratio is shown in figure 2. As shown in SEM micrographs (figure 2) of the CdS films, one can easily notice that the precursor ratio affects the morphology of the films significantly. The film deposited for Cd/S ratio of 1:2 shows the better morphological behaviour as compared to other two films. The RMS surface roughness values of films deposited for Cd/S ratio 1:1, 1:2, and 1:3 are found as 30.36 nm, 25.42nm, and 35.33nm, respectively. These values have been calculated from the AFM analysis using the instrument’s software and the corresponding AFM images are shown in figure 3. The smoothness and low roughness of the film surface suggests that the film is suitable for optoelectronic applications[8-9].

![Figure 2. SEM images of CdS films deposited for Cd/S ratio (a) 1:1, (b) 1:2, and (c) 1:3.](image)

![Figure 3. AFM images of CdS films deposited for Cd/S ratio (a) 1:1, (b) 1:2, and (c) 1:3.](image)

3.3 Optical analysis
The optical transmission spectra of CdS films deposited for different Cd/S ratio is shown in figure 4. It shows that the transmittance values of the films varied from 60% to 90%, specifically in the longer wavelength region. Due to its better morphology and smoothness on the surface, the film deposited for Cd/S ratio of 1:2 exhibits better transmission behaviour as compared to other two films. The optical band-gap energy of the CdS films has been estimated from the Tauc’s plot as shown in figure 5. The band-gap energy of the films deposited for Cd/S ratio of 1:1, 1:2, and 1:3 are found as 2.32 eV, 2.36 eV and 2.39 eV, respectively. The optical transparency and band-gap values matched pretty well with the literature [10].
Figure 4. Transmittance spectra of CdS films deposited for Cd/S ratio 1:1, 1:2, and 1:3.

Figure 5. Tauc’s plots of CdS films deposited for Cd/S ratio 1:1, 1:2, and 1:3.

3.4 PL study
Figure 6 presents the PL spectra of CdS films deposited for different Cd/S ratios. PL spectroscopy has been performed to study the luminescence spectra (Ex=442 nm) recorded in the wavelength range from 400nm (3.1eV) to 750nm (1.65eV). The structures of PL emission spectra of all three films exhibit the similar curve shapes, but the intensity of film deposited for Cd/S ratio of 1:2 is maximum suggesting that it has better PL behaviour as compared to other two films. Two distinct bands have been obtained in the PL spectra. The first stronger peak centred at 2.53 eV (489nm) is associated with the band to band transition and the second one centred at 2.23 eV (556nm) is attributed to radiative recombination of electrons and holes through surface/defect states [11].
Figure 6. PL spectra of CdS films deposited for Cd/S ratio 1:1, 1:2, and 1:3.

3.5 FT-IR study
The characteristic peaks exhibited by room temperature FT-IR spectra of deposited films are presented in figure 7. The absorption bands at 1448 and 1971 cm\(^{-1}\) are associated with the triple-bonded S–C–N vibrations. Band situated at 1642 cm\(^{-1}\) is associated with the bending vibrations of CdS. Another broad band at 1309 cm\(^{-1}\) is related with the C-S stretching bands. Some other weak bands observed between 684 and 917 cm\(^{-1}\) are associated with the stretching of C–O bond, C-S bond, O–H bond, and Cd-S bond of CdS. These findings are in good agreement with the previous studies [12-14].

Figure 7. FT-IR spectra of CdS films deposited for Cd/S ratio 1:1, 1:2, and 1:3.
4. Conclusions
Three CdS films with different Cd/S ratio have been deposited by CBD technique. Films showed cubic crystalline nature and the film deposited for Cd/S ratio of 1:2 exhibits best crystallinity. The SEM analysis showed that the morphological nature of films depends significantly on the Cd/S ratio and it varied with the change in the precursor ratio. AFM analysis confirms that the films deposited for 1:1 and 1:3 are rougher than the film deposited for Cd/S ratio of 1:2. Two bands (situated at 489nm and 556nm) are found in PL spectra of the CdS films. Stretching bands of C-S, O–H, C–O, S-C-N, and Cd-S bonds of CdS films are found in the FT-IR spectra.

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