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Chemical bath deposition of CdS thin films and their partial conversion to CdO on annealing

K L NARAYANAN, K P VIJAYAKUMAR, K G M NAIR*† and G V N RAO†

Department of Physics, Cochin University of Science and Technology, Cochin 682022, India
†Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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Abstract. CdS thin films prepared by chemical bath deposition technique are characterized using X-ray diffraction, optical absorption spectrometry and scanning electron microscopy. The results of the annealing studies on the films in flowing argon and air atmospheres are also presented in this paper. The resistivity has drastically reduced on annealing in flowing air which is attributed to the partial conversion of CdS to CdO phase.

Keywords. Cadmium sulphide; chemical bath deposition; annealing.

1. Introduction

Cadmium sulphide finds extensive applications in the area of solar cells and opto-electronic devices. The wide band gap (2·43 eV) makes it an ideal material for use as the window layer of heterojunction solar cells (Basol 1988; Das and Morris 1993).

Several techniques such as thermal evaporation (Hayashi *et al* 1988), RF sputtering (Martil *et al* 1984), pulsed laser evaporation (Kwok *et al* 1988), chemical vapour deposition (CVD) (Canevari *et al* 1984) and chemical bath deposition (CBD) (Chopra *et al* 1982) have been used for forming CdS thin films. Among these various processes, chemical bath deposition is advantageous on account of the low cost and its suitability for forming large area thin films. CdS thin films deposited by chemical bath deposition are normally found to have high resistivity ($\sim 10^7$ ohm cm) (Melo *et al* 1994). There have been several reports of the formation of conducting CdS during annealing of the chemical bath deposited CdS thin films (Jayakrishnan *et al* 1994; Tomas *et al* 1995). Transformation of the as deposited cubic phase of CdS to hexagonal phase during annealing has also been reported (Zelaya-Angel *et al* 1995).

The present paper reports the preparation of CdS thin films on glass substrates by CBD technique. The authors have tried out various deposition conditions to study the influence of the bath parameters on the film quality. The films grown by this technique were characterized by several techniques such as X-ray diffraction, scanning electron microscopy, energy dispersive analysis of X-rays (EDAX) and optical absorption spectrometry. The effect of annealing on the structure and electrical properties of the films are also discussed in this paper.

*Author for correspondence

2. Experimental

The reaction mixture used for chemical bath deposition of CdS thin films consisted of aqueous solutions of cadmium chloride and thiourea along with triethanolamine. Ammonia was added to the bath to maintain the pH value of the solution at about 10. The bath temperature was maintained at 333 K. Thin films of CdS were deposited on well cleaned glass substrates kept vertically in the bath. The dipping time was varied from 30 min to 140 min. The thickness of the films was measured with the help of a SLOAN DEK-TAK 3030 profilometer. X-ray diffraction studies were obtained using a Siemens D-500 X-ray diffractometer. CuK_{α} radiation was used for the diffraction studies. Optical absorption measurements were done on the samples in the range 400–1100 nm using the Chimito UV-VIS-NIR spectrometer. Annealing was carried out in both flowing air and argon atmospheres. Resistivity of the annealed samples was measured in the Van der Pauw geometry at room temperature. Scanning electron microscopic investigations were carried out using the Philips 501 SEM. Energy dispersive analysis of X-rays (EDAX) attached to the SEM was employed to carry out the elemental analysis of the thin films.

3. Results and discussion

CdS thin films were deposited using chemical baths containing various molar concentrations of cadmium and sulphur compounds. The films deposited in baths containing equimolar concentration of cadmium chloride and thiourea were found to have good uniformity and adhesion characteristics. The film thickness depended on the time of dipping. The thickness of the films was measured as a function of deposition time and the results are given in figure 1, from which one can see that there is a linear dependence of the film thickness on the deposition time. The films were found to be highly resistive, with the resistivity in the range of 10^5 to 10^9 ohm cm.

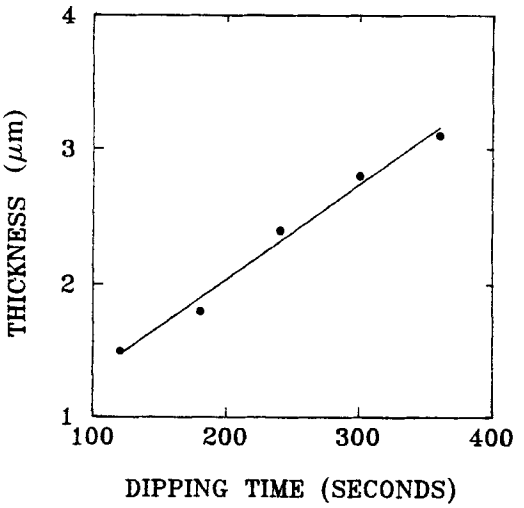

Figure 1. The figure shows the linear variation of film thickness with dipping time.

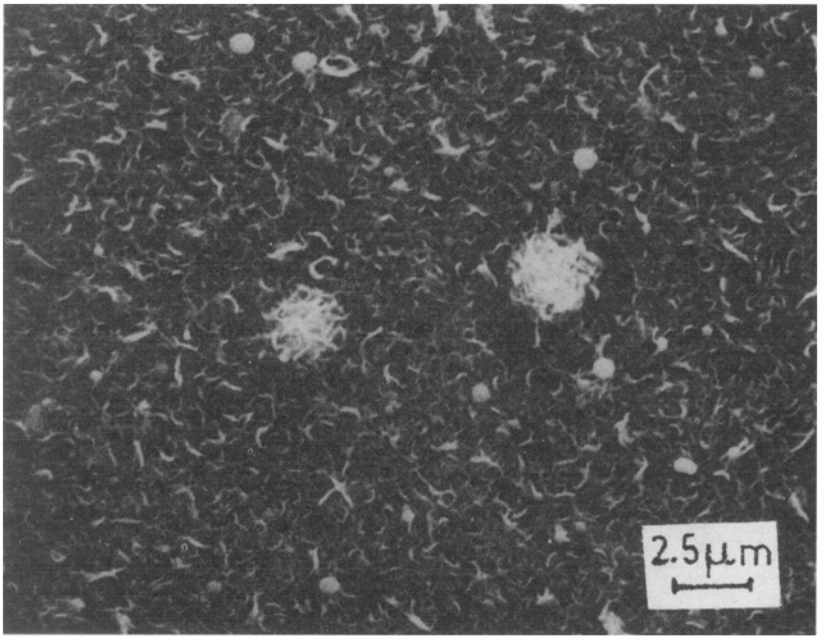

Figure 2. Scanning electron micrograph of as deposited CdS thin film.

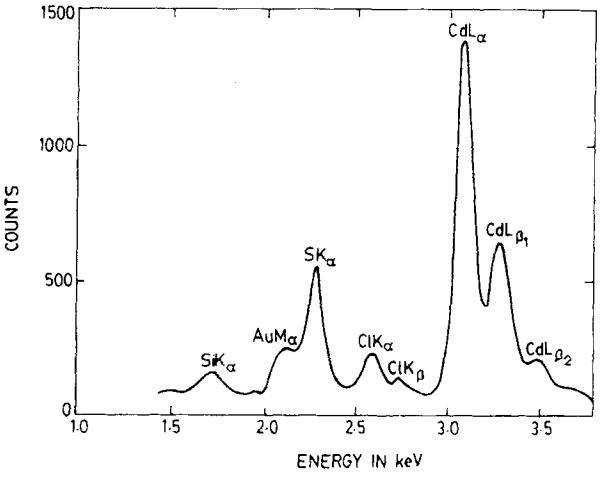

Figure 3. EDAX spectrum of a typical as deposited CdS thin film.

The morphology of the CdS thin films was studied using scanning electron microscopy. Figure 2 shows the SEM micrograph of a typical CdS thin film. It is seen from the scanning electron micrographs that the CdS thin film is uniform with a few isolated clusters on it. The clusters have an approximate size of 2 to 3 microns. These few well marked regions of high density growth (clusters) may be attributed to the local variation in the growth conditions. The chemical homogeneity of the films was checked using EDAX. The EDAX spectra were taken at various locations on the film. Figure 3 shows a typical EDAX spectrum of the film. The composition was found to be

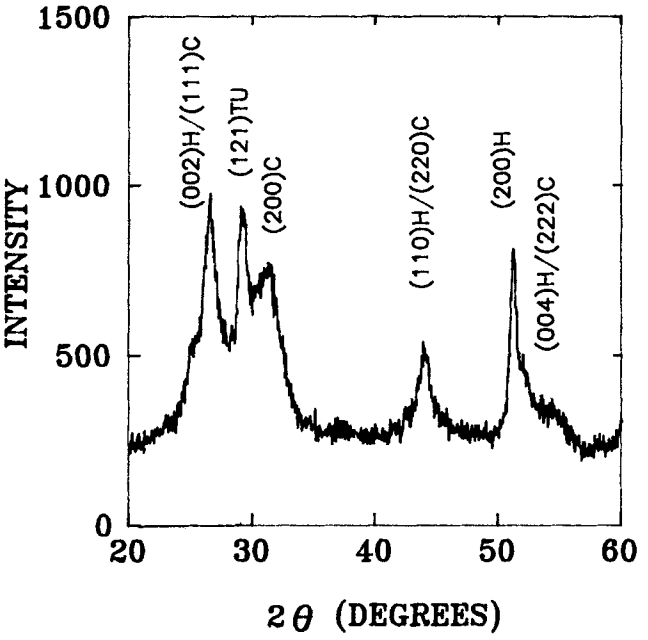

Figure 4. X-ray diffraction pattern of as deposited CdS thin film (CuK_α radiation used). The pattern has peaks corresponding to both cubic (C) and hexagonal (H) phases indicating that the film is a mixture of both phases.

homogeneous across the film as evidenced by the same ratio of cadmium X-ray counts to sulphur X-ray counts at various locations. EDAX spectra of the clusters reveal that they have the same composition as the rest of the film confirming that the clusters are densely packed microcrystallites of CdS and is not made up of any impurity. The small contamination of chlorine seen on the film is attributed to cadmium chloride which is one of the reagents used for the deposition. EDAX spectra also show the presence of small amounts of gold and silicon. The gold peak arises from the thin gold film coated on the samples prior to SEM observations for better conductivity and contrast. The silicon peak probably arises from the substrate which is glass.

The X-ray diffraction pattern of the as prepared film is shown in figure 4. The films are crystalline and the analysis of X-ray patterns reveals the presence of both hexagonal and cubic phases of CdS. Similar observations were earlier reported by Kaur *et al* (1980). The peaks in the diffraction pattern in figure 4 are quite broad, possibly due to fine crystallite size. The particle size d can be evaluated using the Debye Scherer formula

$$d = 0{\cdot}94\lambda/B\cos\theta,$$

where 2θ is the Bragg angle, B, the full width at half maximum and λ the wavelength of the X-ray used. The average particle size in the as deposited film works out to be around 7 nm. The high resistivity could be partially attributed to the extremely small grains.

The peak at 28·4° in figure 4 does not belong to CdS and is attributed to thiourea. The thiourea contamination in CdS thin films prepared by this method is inevitable as it is one of the main ingredients in the bath. However thiourea is volatile and gets removed during annealing at higher temperatures.

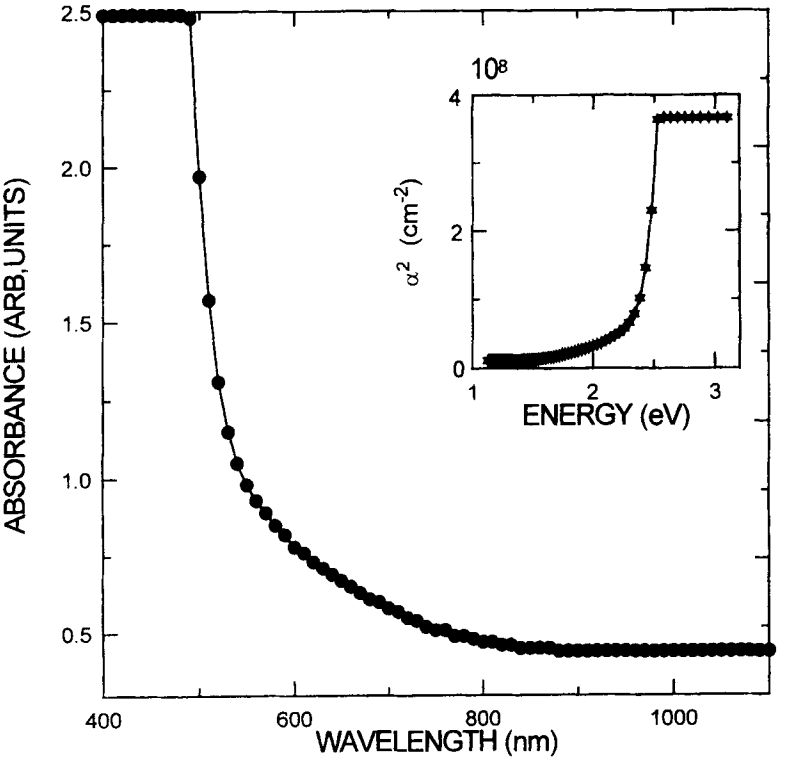

Figure 5. Optical absorption spectrum of as deposited CdS thin film (inset shows the plot of $(\alpha)^2$ versus $h\nu$).

The optical absorption spectra of the as deposited CdS film is given in figure 5. CdS is a direct band gap material and the absorption coefficient α is related to band gap by

$$\alpha \propto (h\nu - E_g)^{1/2}.$$

The band gap can be obtained by extrapolating the linear portion of the α^2 vs energy plot (inset of figure 5) to the energy axis. The optical band gap of the films was found to be 2·35 eV.

The annealing of the films in air atmosphere (673 K, 2 h) resulted in drastic reduction of the resistivity of the films. The resistivity of the films dropped to 0·2 ohm cm. In order to understand the origin of such a large change in the resistivity, the X-ray diffraction studies were carried out on the annealed samples. Figure 6 shows the X-ray diffraction pattern of the film annealed in flowing air. The most striking feature of the XRD pattern is the sharpening of all the peaks indicating grain growth. The estimate using the Debye Scherer formula gives a grain size of 35 nm in the annealed samples as against 7 nm in the as deposited samples. Further examination of the XRD pattern indicates the partial conversion of cubic phase to the hcp phase of CdS as evidenced by several peaks which belong exclusively to the hexagonal phase. Such conversion has been recently reported by several investigators (Zelaya-Angel *et al* 1994, 1995). The appearance of the peaks at $2\theta = 32{\cdot}9°, 38{\cdot}2°$ and $55{\cdot}2°$ indicate the formation of CdO phase. The authors attribute the increase in the electrical conductivity to the formation of cadmium oxide phase, as

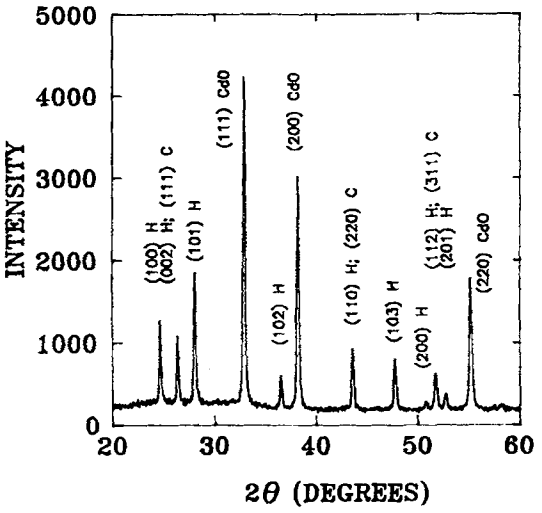

Figure 6. X-ray diffraction pattern of CdS thin film annealed in flowing air atmosphere for 2 h at 673 K.

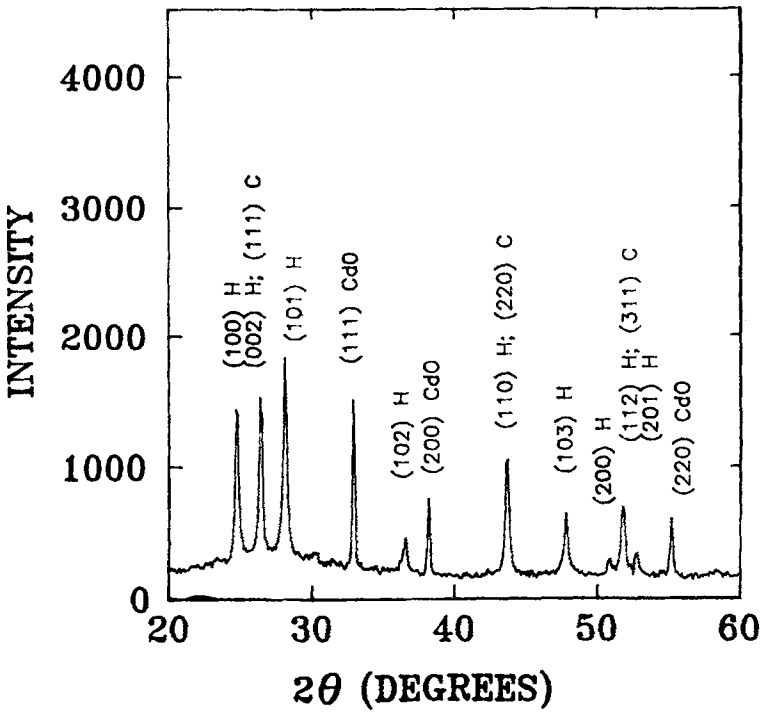

Figure 7. X-ray diffraction pattern of CdS thin film annealed in oxygen deficient atmosphere for 2 h at 673 K.

the grain growth and the conversion to hcp phase are unlikely to substantially alter the resistivity of the films.

In order to confirm this, annealing was carried out under inert atmosphere. The phase transformation to hcp and the grain growth were seen in the case of the films

subjected to argon annealing. However, the films did not become conducting confirming that the observed conductivity of the air annealed films were solely due to the formation of CdO phase.

It is interesting to note that the resistivity decrease is seen only in the case of films annealed in flowing air or oxygen where considerable fraction of CdS gets converted to CdO. This is probably because a continuity between the various CdO grains is required for obtaining good conductivity. Such a condition is achievable only when a substantial volume fraction of CdS gets converted to CdO, rather than when CdO is present as isolated islands in an insulating CdS matrix. Figure 7 shows an XRD of a film annealed in an oxygen deficient atmosphere by passing commercial grade argon through the furnace. The CdO phase is still present as can be made out from the presence of the characteristic peaks at $2\theta = 32{\cdot}9°, 38{\cdot}2°$ and $55{\cdot}2°$. The phase could have formed due to the presence of oxygen impurity in the gas used for flushing the furnace. However, the intensities of the CdO peaks are small compared to the case of annealing in flowing air, indicating much lower volume fraction of CdO. This film was having high resistivity of the order of 10^7 ohm cm. The CdO phase in this case could have formed as isolated island on the insulating CdS matrix, which probably explains why the resistance remains high despite the formation of the conducting CdO phase. Several previous investigators have reported the formation of highly conducting CdS phase on annealing (Nair *et al* 1994). It has been reported by Jayakrishnan *et al* (1994) that low resistivity CdS films of cubic phase have been formed on rapid thermal annealing of dip coated CdS films. They have shown that rapid thermal annealing of dip coated films in vacuum resulted in the reduction of the film resistivity from 7×10^7 ohm cm to 0·16 ohm cm. They (Jayakrishnan *et al* 1994) have attributed this reduction to the effect of desorption of adsorbed oxygen, which according to them acts as trap for mobile charge carriers in CdS. Such a drastic reduction in resistance was not observed when they carried out slow thermal annealing in a vacuum of 10^{-2} mbar which they ascribe to surface contamination due to slow annealing in vacuum. We have not carried out

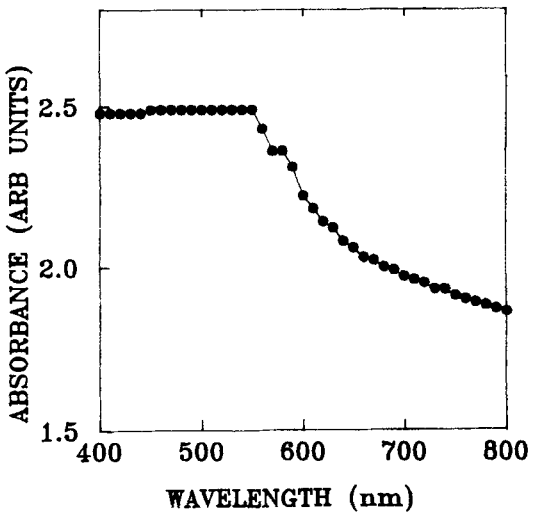

Figure 8. Optical absorption spectrum recorded for the typical annealed CdS thin film. It can be seen that the absorbance has increased considerably on annealing.

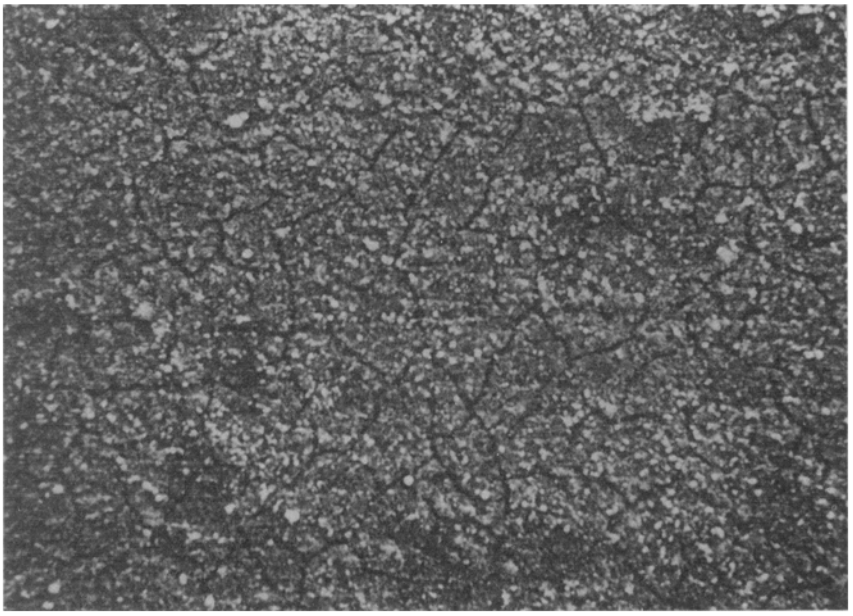

Figure 9. Scanning electron micrograph of annealed CdS thin film. It can be seen from the micrographs that the cracks are developed on annealing. These cracks are responsible for higher absorbance values.

rapid thermal annealing of dip coated samples. However, we carried out annealing in a vacuum furnace at a vacuum of 10^{-5} mbar, so as to avoid contamination effects. Though the time of annealing is much larger (150 min) than the rapid thermal annealing (1 min), the vacuum in our case is better by three orders of magnitude and any results of oxygen desorption could have manifested in our case also. However the films were highly resistive even after annealing quite in disagreement with the results of Jayakrishnan *et al* (1994). XRD pattern (not shown here) did not show the presence of CdO phase. We have observed reduction in resistivity only when substantial conversion of CdO phase is formed.

Nair *et al* (1994) have reported the formation of CdO on air annealing of dip coated CdS thin films. These results are in agreement with our study. They have also observed the formation of CdO phase in the annealed films which became conducting. One of the main problems associated with the annealing of the dip coated films is the deterioration of the optical transmission. Figure 8 shows the optical absorption spectrum of a CdS thin film after annealing. Large increase in the optical absorption is seen. The SEM micrograph of the annealed film is shown in figure 9. Large number of cracks are visible in the micrograph, presumably created during annealing due to thermal stresses. The reduction in the optical transmission may be attributed to the reduction in the film quality.

4. Summary and conclusions

The bath parameters for the preparation of CdS thin films of good adhesion and uniformity have been standardized. Air annealing increases the conductivity of the

films. The reduction in resistivity occurs when substantial fraction of the film is converted to CdO. Grain growth occurs during annealing as suggested by the sharpening of the XRD patterns.

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