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Structural transformation of dip coated CdS thin films during annealing

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The present paper discusses structural transformation of CdS thin films during annealing and the consequent changes in their optical properties. CdS thin films are grown by the chemical bath deposition technique. The optical band gap is found to reduce on annealing and the change is attributed to the structural transformation of CdS from cubic to hexagonal phase.

1. Introduction

In recent years extensive research has gone on into the area of preparation and characterization of CdS thin films owing to its promising applications in the field of photovoltaic devices. A variety of techniques, such as thermal evaporation [1], sputtering [2], chemical spray pyrolysis [3] and chemical bath deposition (CBD) [4] have been used for depositing CdS thin films. Of these, the chemical bath deposition process is a relatively simple method and has attracted a lot of attention on account of the low cost and the possibility of forming films having large areas. CdS thin films of good quality, adherence and reproducible properties have been grown by the CBD technique. The CdS thin films prepared by this technique are found to be either in the metastable cubic phase or a mixture of cubic and hexagonal phases [5, 6]. Recent studies [7, 8] indicate a transition from the cubic phase to the stable hexagonal phase on thermal annealing and a consequent change in the optical band gap.

The present paper discusses the effect of thermal annealing on the optical properties of CdS thin films prepared by the CBD technique. X-ray diffraction (XRD) evidence for the conversion of CdS from cubic to hexagonal phase is presented. Scanning electron microscopy is used to characterize the microstructure of the as-deposited and annealed films and the results of these investigations are also discussed in the paper.

2. Experimental procedure

CBD was carried out by the decomposition of cadmium acetate (1 M) and thiourea (1 M) in alkaline medium (NH_4OH) to yield cadmium and sulphur ions. Triethanolamine was added to control the release of the Cd ions. The bath temperature during deposition was maintained at 333 K and the pH of the solution was slightly above 10. Cleaned glass substrates were held vertically in the bath. The thicknesses of the films were controlled by changing the dipping time and were measured using a Sloan 5050 Dektak depth profilometer. The films were subjected to thermal annealing in air at 673 K for different times. Microstructural characterization of the films was carried out using a Philips 501 scanning electron microscope. XRD studies on the samples were carried out using a Philips PW 1730/10 X-ray diffractometer. Optical absorption spectra of the films were recorded using an Ultraviolet–visual-near infrared (CHIMITO) spectrophotometer working in the transmission mode.

3. Results and discussion

Fig. 1 shows the optical absorption spectra of as-deposited and annealed film in the wavelength range 400–800 nm. It is seen from the optical absorption spectra that the band edge shifts on annealing towards the higher wavelength side indicating the reduction in the band gap value.

CdS is a direct band gap material and for a direct allowed transition, the absorption coefficient is given by

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

where $h\nu$ is the photon energy and E_g is the energy gap. The optical band gap is obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $h\nu$ to $\alpha = 0$. Fig. 2 gives the $(\alpha h\nu)^2$ versus $h\nu$ plot for the as-deposited CdS thin film and that annealed at 673 K for 3 h. It is evident from Fig. 2 that the optical band gap values of the as-deposited and annealed samples are 2.3 and 2.2 eV, respectively. The optical band gap shows a systematic decrease as a function of annealing time (Fig. 3). Such a decrease could be caused either by grain growth or any phase transition during annealing. Further investigations were carried out in order to

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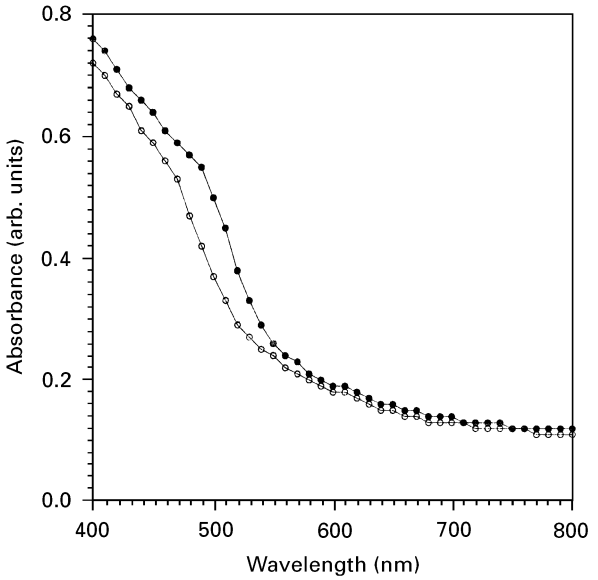

Figure 1 Optical absorption spectra of (○) as-deposited and (●) annealed (at 673 K for 3 h) CdS thin film.

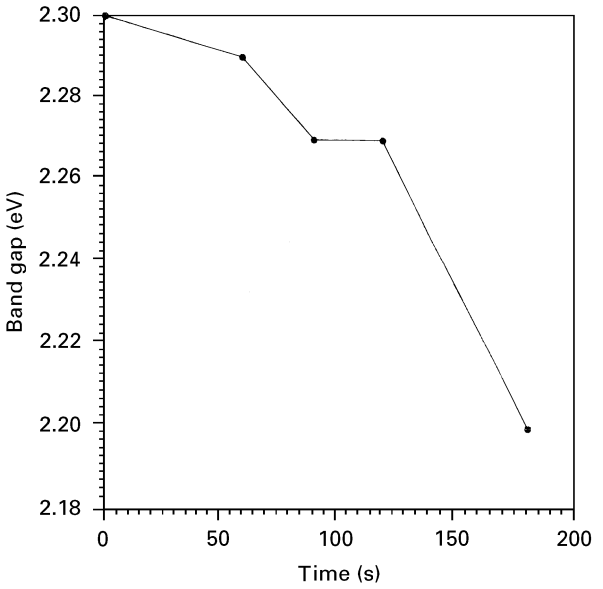

Figure 3 Variation of band gap, E_g, with annealing time.

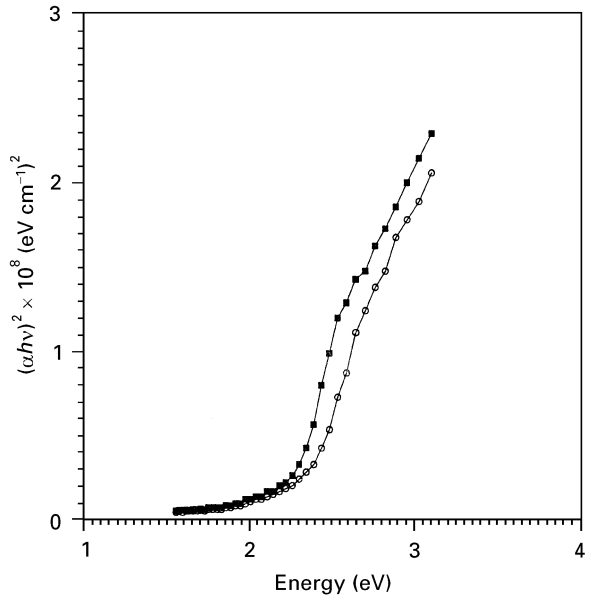

Figure 2 Variation of $(\alpha h\nu)^2$ with energy of (○) as-deposited and (●) annealed (at 673 K for 3 h) CdS thin film.

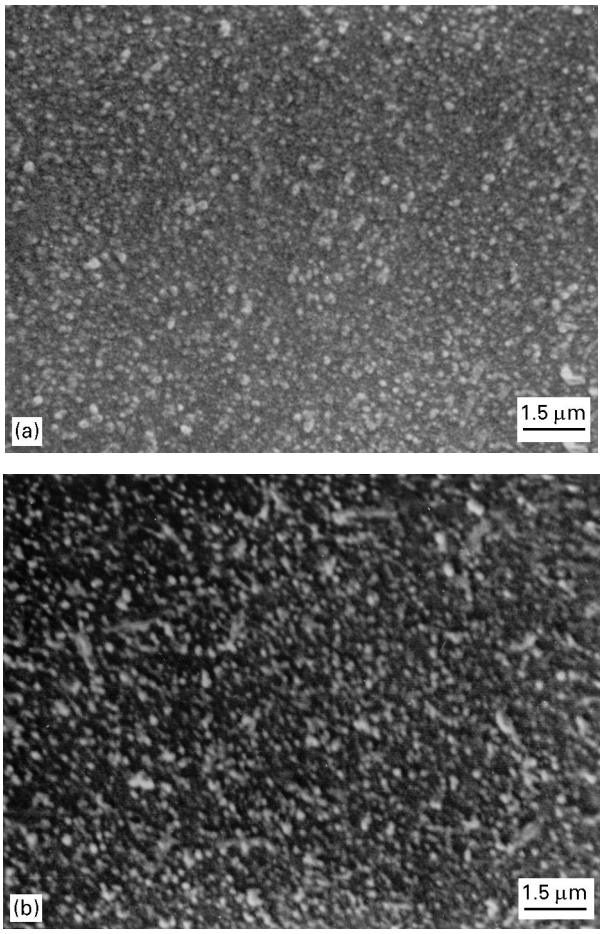

Figure 4 Scanning electron micrographs of (a) as-deposited and (b) annealed (at 673 K for 3 h) CdS thin film.

identify the exact cause of the changes in the optical properties of CBD CdS thin films.

Fig. 4 shows the scanning electron micrographs of the as-deposited CdS thin film and after annealing at 673 K for 3 h. The microstructure of the as-deposited film shows uniformly dispersed small clusters on the film. No qualitative changes in the microstructural features are seen on annealing. The cluster size remains more or less unaltered.

In the present study in order to verify whether cubic–hexagonal transformation has taken place during annealing, we have carried out XRD studies on the films. Because it is difficult to get good XRD patterns from thin films, we have carried out XRD analyses on thick films (1.8 μm). CdS films of 1.8 μm thickness were coated on glass substrates by continuous dipping for 2 h at 333 K. Fig. 5 shows the XRD patterns of the as-deposited and annealed films. The XRD pattern from the as-deposited film is given in Fig. 5a. It can be seen from the XRD pattern that the film is in the cubic phase and there is no preferential orientation as has been reported [9] earlier in the case of vacuum evaporated thin films. The peak at 29.3° does not

correspond to any of the CdS phases, but could be indexed as the (1 1 1) of thiourea, which is one of the chemicals used in the bath. On annealing at 673 K for 3 h in air we get the diffraction pattern given in Fig. 5b. The appearance of a number of lines that belong to the hexagonal phase, including many that exclusively belong to the hexagonal phase, confirms that phase transition from cubic to hexagonal phase has occurred on annealing. A few peaks corresponding to Cd_2SiO_4 are seen in Fig. 5b. The formation of cadmium silicate could have taken place due to the reaction between the substrate and the CdS thin film. Similar observation of the formation of cadmium silicate has been reported [8] by other investigators who also carried out annealing of CdS thin films on glass substrates.

The decrease in the optical band gap observed in the present study during annealing could be attributed to the cubic–hexagonal transformation. It is well known that the optical band gap and the unit cell volume has an inverse relationship.

The slightly higher unit cell volume of the hexagonal phase as compared with the cubic phase may explain the difference in the optical band gap of the two phases. The difference in the optical band gap of the cubic and hexagonal phase is about 0.1 eV, which agrees very well with the change observed in the present study.

The effect of thermal annealing on the optical band gap of CBD CdS thin films is reported by Angel *et al.* [7]. They have carried out photoacoustic spectroscopy to determine the change in the band gap of the CdS caused by annealing. The observed reduction in the band gap in the above studies is about 0.1 eV on annealing at 573 K for 50 h. The authors have attributed the change in the band gap to the cubic–hexagonal phase conversion based on XRD evidence.

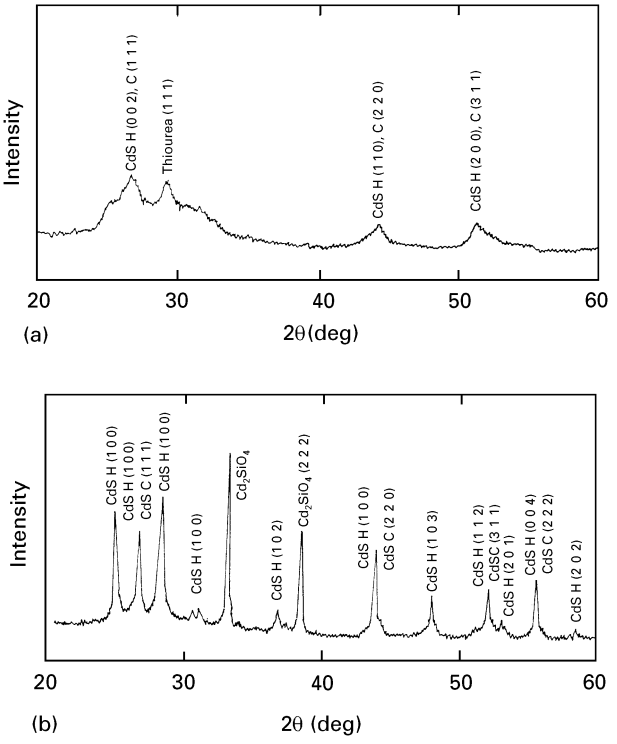

Figure 5 XRD (CuK_α radiation) patterns of (a) as-deposited and (b) annealed (at 673 K for 3 h) CdS thin film.

An alternative explanation for the decrease in the band gap during annealing may be offered based on possible increase in the grain size of the CdS during thermal annealing. The effect of grain size on the optical band gap arises out of quantum confinement effects and had been investigated by Yu *et al.* [10]. They carried out a transmission electron microscopic (TEM) investigation of the grain size of CdS thin films and tried to correlate the grain size with optical band gap. They could observe that there was a decrease of about 0.1 eV in the band gap when the grain size increased from 5 to 25 nm. At 25 nm grain size they observed that the band gap was within 0.01 to 0.02 eV of the bulk value. We have not carried out detailed characterization of the grain size using TEM in the annealed and as-deposited samples. However, an estimate of the average size of the grains could be obtained from the XRD pattern using the Sherrer formula,

$$D = 0.94\lambda/\beta\cos\theta \qquad (2)$$

where D is the grain size, β is the full-width at half-maximum (FWHM), 2θ is the Bragg angle and λ is the wavelength of the X-rays.

The estimated grain size of the as-deposited films is about 7 nm. The lines in the XRD pattern of the annealed sample are considerably sharp indicating the grain growth. The approximate grain size in the annealed sample turns out to be larger than 2.25 nm. One may be tempted to attribute the observed optical band gap shift of 0.1 eV to the grain coarsening effects, especially as the magnitude of the shift matches well with that measured by Yu *et al.* However, such an explanation is not tenable in the present case due to the following reasons. First, we observe clear evidence for a cubic to hexagonal phase transition during annealing. Such a transition can account for the band gap shift from 2.3 to 2.2 eV. Second, the band gap value due to coarsening slowly approaches the bulk value and never goes below the bulk value. The observed value of the optical band gap in the annealed film is well below 2.4 eV, the band gap of the cubic phase single crystal. Thus we might reasonably conclude that the observed band gap shift can be attributed to cubic–hexagonal phase conversion.

4. Conclusions

The effect of annealing on the optical properties of CBD grown CdS thin films is studied. Thermal annealing is found to remove the strain present in the CdS films. The optical band gap of the films shows a reduction from 2.3 to 2.2 eV, which is attributed to the cubic–hexagonal phase transition caused by thermal annealing.

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References

1. K. H. NORIAN and J. W. EDINGTON, *Thin Solid Films* **75** (1981) 35.
2. W. H. LEIGHTON, *J. Appl. Phys.* **44** (1973) 5011.
3. S. PENCE, C. W. BATES Jr and L. VARNER, *Mater. Lett.* **23** (1995) 195.
4. K. I. GRANCHAROVA, J. G. BISTREV, L. J. BEDIKJAN and G. B. SPASOVA, *J. Mater. Sci. Lett.* **12** (1993) 852.
5. M. NAGAO and S. WATANABE, *Jpn J. Appl. Phys* **7** (1968) 684.
6. I. KAUR, D. K. PANDYA and K. L. CHOPRA, *J. Electrochem. Soc.* **127** (1980) 943.
7. O. Z. ANGEL, L. HERNANDEZ, O. DE MELO, J. J. ALVARADO-GIL, R. LOZADO-MORALES, C. FALCONY, H. VARGAS and R. RABIREZ-BON, *Vacuum* **46** (1995) 1083.
8. O. Z. ANGEL, J. J. ALVARADO-GIL, R. LOZADO-MORALES, H. VARGAS and A. FERRIERA DE SILVA, *App. Phys. Lett* **64** (1994) 291.
9. R. SAGAR and M. P. SHIVASTAVA, *Phys. Lett. A* **183** (1993) 209.
10. I. YU, T. ISOBE and M. SENNA, *Mater. Res. Bull.* **30** (1995) 975.

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