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CHARACTERISTICS OF BRUSH ELECTRODEPOSITED CdS FILMS

K.R.MURALI*, MARY MATHELINE[a], RITA JOHN[b]
Electrochemical Materials Science Division
Central Electrochemical Research Institute, Karaikudi – 630 006, India
[a]Dept of Physics, Dept of Physics, J.A.College for Women(Autonomous), Periyakulam, India
[b]Department of Physics, University of Madras, Chennai – 600 025, India

CdS films were deposited by the brush electrodeposition technique on conducting glass and titanium substrates at different current densities in the range of 30 – 300 mA cm^{-2} and at 80˚C. The films exhibited polycrystalline structure with the cubic phase. After post heat treatment in argon atmosphere the crystal structure changed to hexagonal. The band gap of the films was around 1.39eV. The refractive index value decreases from 2.6 to 1.57 as the wavelength increased from 550 nm to 1000 nm. The electrical conductivity varied in the range of 0.1 to 20 ohm cm as the annealing temperature is increased. The value of carrier density decreases from 3.13 x 10^{18} to 2.7 x 10^{17} cm^{-3} with increase of annealing temperature.Laser Raman studies indicated LO phonon peaks at 150 cm^{-1} and 600 cm^{-1}.

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1. Introduction

Cadmium sulphide (CdS) is an important direct band gap II-VI semiconductor and low cost, large area thin film formulation of CdS is necessary for technological applications in solar cells for photoelectric conversation [1], light emitting diodes for flat panel displays [2] and transistors for electronic switches [3]. CdS thin films are deposited using various techniques such as vacuum evaporation [4], RF sputtering [5], chemical vapour deposition [6], spray pyrolysis [7], molecular beam epitaxy [8],electrodeposition [9] and chemical bath deposition [10, 11]. In this work, the brush plating technique has been employed for the deposition of CdS films.

2.Experimental

CdS films were prepared on conducting glass and titanium substrates using selective/brush plating technique. The precursors used for the deposition of CdS were 0.2 M $CdSO_4$, 0.2 M sodium thiosulphate and triply distilled water to make up the solution to 10 ml. The films were deposited at 80˚C and at different current densities in the range 50 mA cm^{-2} to 300 mA cm^{-2}. The films were characterized by x-ray diffraction studies using Philips x-ray diffractometer and CuKα radiation. Optical studies were made using a Hitachi U3400 UV-VIS-NIR spectrophotometer. Surface morphology was studied by Molecular imaging systems Atomic force microscope. Electrical properties of the films were studied by Hall measurements. Thickness of the films measured by surface profilometer is 0.95 microns.

* Corresponding author: muraliramkrish@gmail.com

3. Results and discussion

X-ray diffraction (XRD) patterns of cadmium sulphide films deposited at different current densities is shown in Fig.1. The films exhibit polycrystalline nature with peaks corresponding to the cubic phase. The intensity of the peaks increased with deposition current density. The XRD patterns of the films post heat-treated at different temperatures in the range 450 - 550°C are shown in Fig.2. Peaks corresponding to the hexagonal phase were observed. As the heat treatment temperature increases, the crystallinity of the films also increased as evidenced by the sharpness of the XRD peaks. Peaks corresponding to (100), (002), (101), (110), (103) and (112) reflections were observed. The lattice parameters calculated from the XRD data are a = 4.145 Å and c = 6.752 Å. These values are found to be in close agreement with the ASTM data. The crystallite size calculated using the Debye-Scherrer's equation is indicated in Table.1.

Table 1. Crystallite size of CdS films deposited at a current density of 300 mA cm^{-2}

Annealing temperature(˚C)	Crystallite size(nm)
450	50
475	70
500	85
525	95
550	105

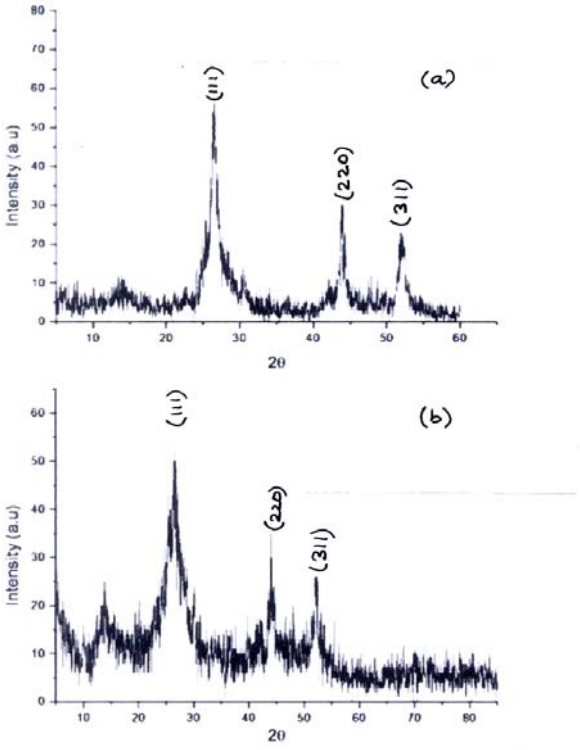

Fig.1 - XRD patterns of CdS films deposited at different deposition current densities (a) 50 mA cm^{-2} (b) 300 mA cm^{-2}

EDAX studies indicated the composition of the films annealed at 475^{o}C to be Cd (60.1%) and S (39.9%). For the films annealed at 550°C, the concentration varied slightly and it was Cd (62.2%) and S (37.8%)(Fig.3).

Optical absorption measurements were made on the CdS films deposited on conducting glass substrates. Substrate absorption, if any was corrected by placing an uncoated conducting glass substrate in the reference beam. Fig.4 shows the transmission spectra of CdS films deposited at a current density of 300 mA cm^{-2}. The spectra exhibited interference fringes and the value of the refractive index was estimated by the envelope method[12,13] as follows:

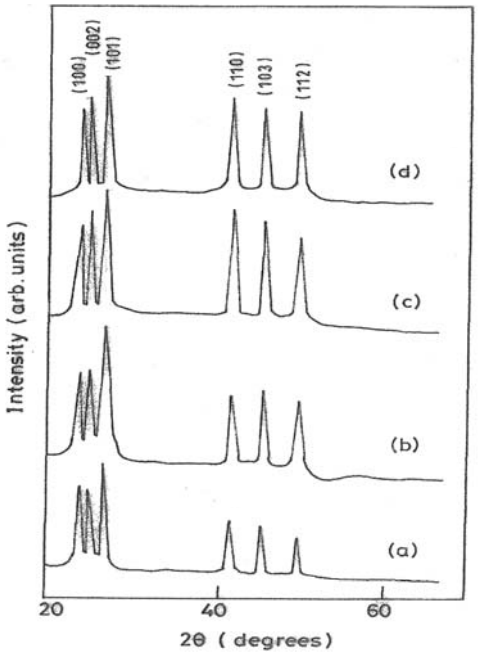

Fig. 2 - XRD patterns of CdS films annealed in argon atmosphere at different temperatures (a) 450°C (b) 500°C (c) 525°C (d) 550°C.

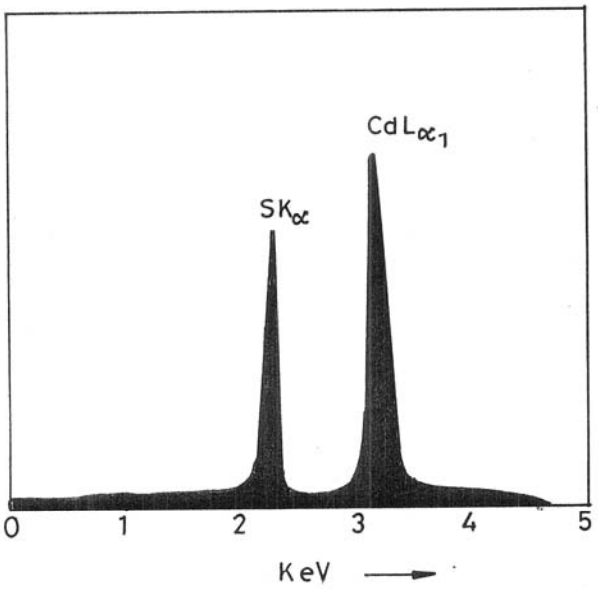

Fig.3. EDAX spectrum of CdS films heated at 550 °C

$$n = [N + (N^2 - n_s^2)]^2$$

$$N = (n_s^2 + 1)/2 + 2n_s(T_{max} - T_{min})/ T_{max} T_{min}$$

where n_s is the refractive index of the substrate, T_{max} and T_{min} are the maximum and minimum transmittances at the same wavelength in the fitted envelope curve on a transmittance spectrum. The extinction coefficient was calculated by trhe following equation,

$$k = \alpha\lambda/4\pi$$

$$\alpha = 1/d \ln \{ (n-1)(n-n_s)/(n+1)(n-n_s)\} [(T_{max}/T_{min})^2 + 1]/[(T_{max}/T_{min})^2 - 1]$$

$$d = (\lambda_1\lambda_2)/2n(\lambda_2 - \lambda_1)$$

where 'α' is the absorption coefficient and 'd' is the film thickness, λ_1 and λ_2 are the wavelengths at the two adjacent maxima or minima. Using the envelope method, the refractive index was calculated for the films. The variation of refractive index with wavelength is shown in Table.2. Fig.5 shows the $(\alpha h\nu)^2$ vs $h\nu$ plot of the CdS films annealed at 550°C. The energy gap obtained from the wavelength at which onset of maximum absorption is obtained corresponds to 2.39 eV. This value is similar to the values obtained on thin film CdS deposited by other techniques[7,9,10]. Hall measurements were made on the films adopting the following procedure [12]. In this method, the CdS layer is mechanically transferred from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [13,14]. The electrical properties of the CdS layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. The influence of annealing temperature on the resistivity of the films is depicted in Fig.6. The magnitude of the resistivity varies from 0.1 to 20 ohm cm as the annealing temperature is increased.

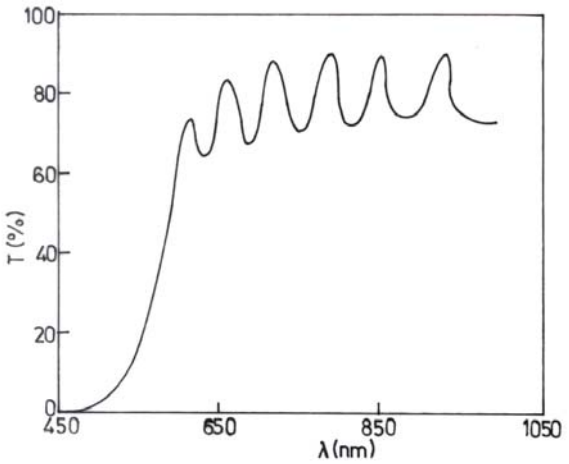

Fig.4. Transmission spectra of CdS films deposited at 300 mA cm^{-2}

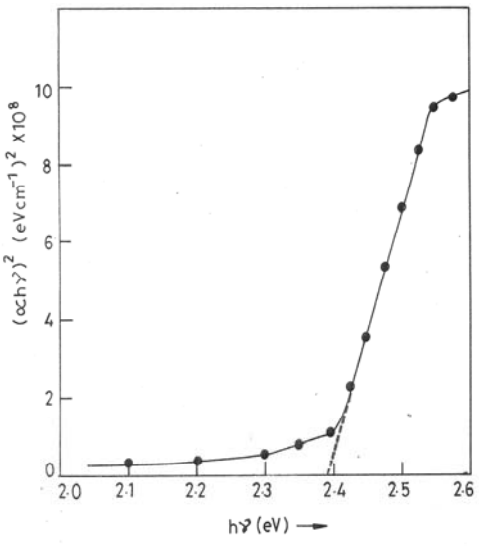

Fig. 5. $(\alpha hv)^2$ vs hv plot of the CdS films annealed at 550 °C

Table 2. Variation of Refractive index with wavelength

Wavelength(nm)	Refractive index
550	2.6
600	2.4
650	2.2
700	2.1
750	1.9
800	1.8
850	1.65
900	1.60
950	1.58
1000	1.57

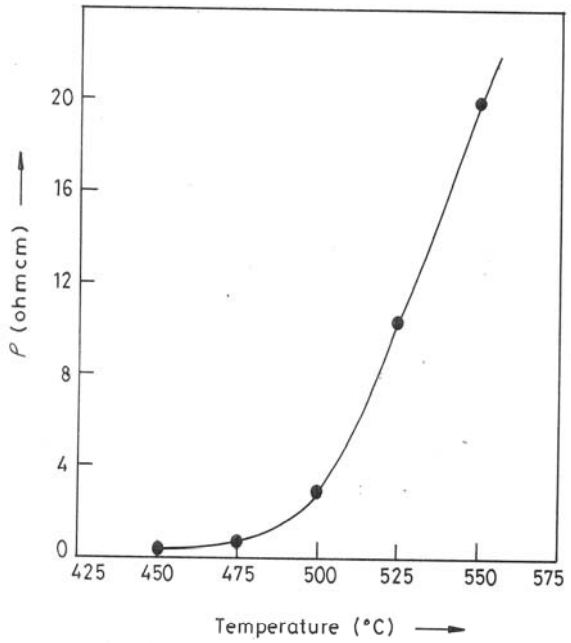

Fig.6. Variation of resistivity of CdS films with post annealing temperature

Fig.7 shows the variation of Hall mobility (μ_H) of all the films with annealing temperature. It was observed that the mobility decreases initially and then attains a constant value as the annealing temperature increases.

Fig.8 shows the variation of carrier concentration N with the annealing temperature. It is evident from the figure that the carrier concentration decreases from 3.13×10^{18} to 2.7×10^{17} cm^{-3}.

The result that the resistivity increases with increase of annealing temperature may be due to the change in film stoichiometry (excess cadmium or sulphur vacancies, which are electron donor sites that provide the additional carriers and decrease the resistivity). In addition, CdS dissociates during annealing by evaporation modifying the ratio of Cd/S. Further, during annealing oxygen fills the S vacancies in CdS and as these donor sites are eliminated, the free carrier concentration is reduced. Invariably, the absorbed oxygen offsets the decrease in resistivity due to the excess carriers provided by the excess cadmium obtained on heat treatment resulting in a net increase of resistivity.

The grain boundaries between the crystallites dominate the electrical properties of the polycrystalline thin film semiconductors [15]. Traps at the grain boundaries are responsible for the potential barrier that limits carrier mobility.

The room temperature Raman spectra of the CdS films deposited at different deposition current densities are shown in Fig.9. The Raman spectra of the CdS films exhibit a well-resolved line at approximately 300 cm^{-1}, corresponding to the first order scattering of the longitudinal

optical (LO) phonon mode. CdS can take both hexagonal wurtzite and cubic zinc blende structures,

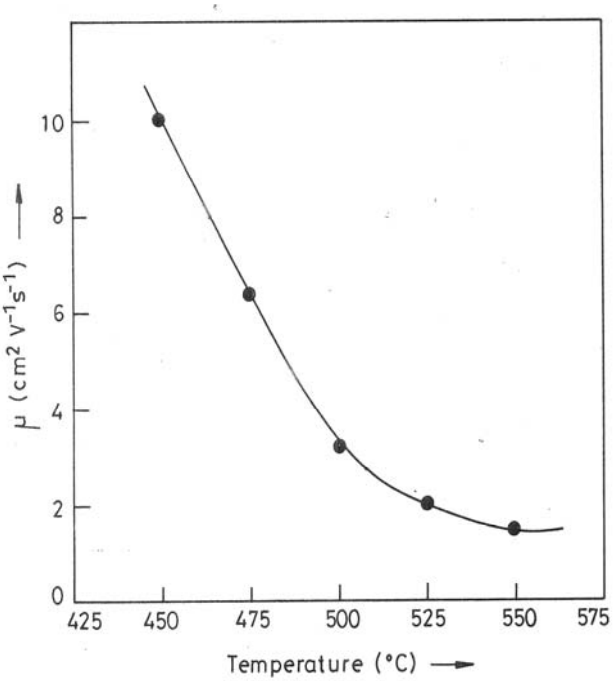

Fig.7. Variation of mobility of CdS films with post annealing temperature

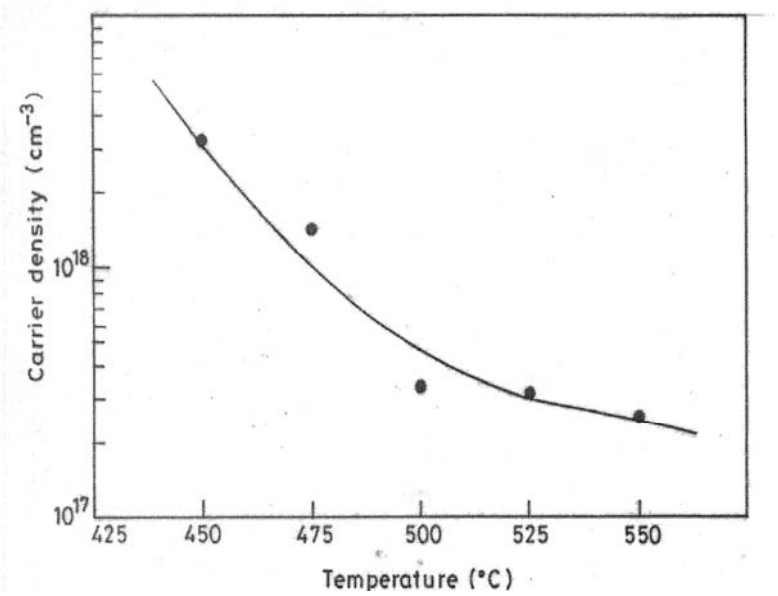

Fig.8. Variation of Carrier density of CdS films with post annealing Temperature.

and it was reported that for both the structures, the zone-center longitudinal-optical A1(LO) phonon frequency is about 305 cm^{-1}[16,17]. The FWHMs of the 1 LO peak are 27.8, 23.7, and 20.6 cm^{-1}, for the films deposited at 50 mA cm^{-2}, 150 mA $cm^{-2}$and 300 mA cm^{-2} respectively. These values are much larger than that (6.5 cm^{-1}) for melt grown single-crystal CdS. Usually, very large width indicates poor crystallinity (lack of long-range order) in the films, but the well-defined peak indicates the crystalline nature of the films. Hence, the large FWHM in the present case can be attributed to a polycrystalline effect in the films. The broad second-order scattering of LO phonons is also visible at approximately 600 cm^{-1}, regardless of deposition temperature. The main characteristic of the Raman spectra of our films is the broadening of the LO peak in the samples

deposited at lower deposition temperatures. The peak position did not change much with change in deposition temperature and remained almost constant.

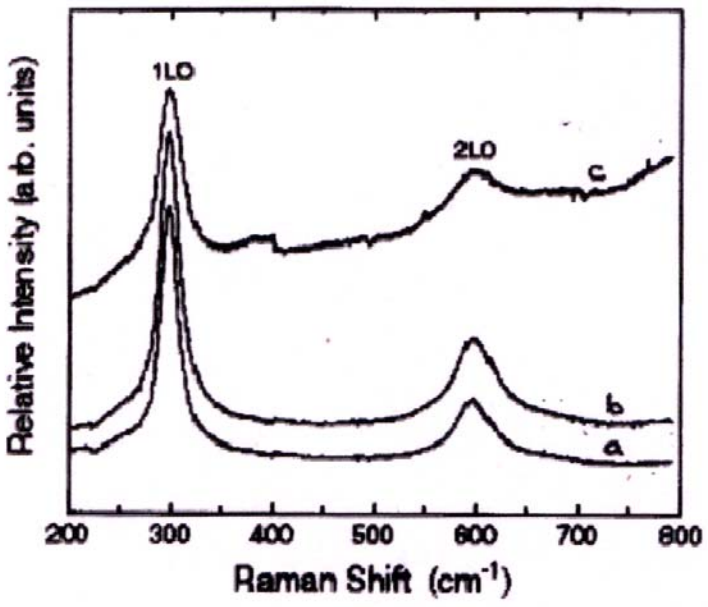

Fig.9. Laser Raman Spectra of CdS films deposited at different deposition current densities (a) 50 mA cm^{-2} (b) 150 mA cm^{-2} (c) 300 mA cm^{-2}

4.Conclusions

This study clearly indicates that CdS films with low resistivity can easily be prepared by the brush plating technique. The refractive index of the films is 2.6. The films are transparent in the visible region.

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