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Characteristics of CdS films brush electrodeposited on low-temperature substrates

K.R. Murali[a,*], S. Kumaresan[b], J. Joseph Prince[c]

[a]*Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi 630006, India*
[b]*Department of Physics, Saranathan College of Engineering, Trichy, India*
[c]*Department of Physics, Bharathidasan School of Engineering and Technology, Trichy, India*

Abstract

Cadmium sulfide films were deposited by the brush plating technique on titanium and conducting glass substrates using a current density of $80\,mA\,cm^{-2}$. X-ray diffraction studies indicated the polycrystalline nature of the films. As the deposition temperature decreased, the peaks were broad indicating the formation of nanocrystallites. Optical absorption measurements yielded band gap values in the range of 2.60–3.00 eV as the deposition temperature decreases. XPS studies confirmed the formation of CdS. Atomic force microscope studies indicated the roughness of the films decreases with decrease of deposition temperature. The films have exhibited photoresponse without any pre-heat treatment.

Keywords: CdS; II–VI; Thin films; Brush plating

1. Introduction

The study of the physical properties of CdS films is a subject of current interest. Possessing a wide fundamental band gap, they have been used in a large variety of applications such as electronic and optoelectronic devices [1]. Polycrystalline CdS thin films are generally used in CdTe solar cells, as a window material for transmitting the light absorbed by CdTe and also as the n-type material for p–n junction of the solar cells [2–4]. Requirements of the CdS films are that they should be conductive ($\sim 10^{16}$ carrier/cm^3), thin to allow high transmission (50–100 nm), and uniform to avoid short circuit effects. Techniques like molecular beam epitaxy (MBE) [5–7], metal organic vapor phase epitaxy (MOVPE) and metal organic chemical vapor deposition (MOCVD) [8,9], close-spaced sublimation (CSS) [10], chemical bath deposition (CBD) [11–13], electrodeposition and successive ionic layer adsorption and reaction (SILAR) [14,15], screen printing [16], and physical vapor deposition (PVD) [17] have been employed for the deposition of CdS films. In this work, the brush plating technique has been employed for the deposition of CdS films on low-temperature substrates. The structural, optical, morphological, and photoelectrochemical properties of the films are reported and discussed.

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*Corresponding author. Tel.: +91 45 65 227550; fax: +91 45 65 227553.
E-mail address: muraliramkrish@gmail.com (K.R. Murali).

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2. Experimental methods

CdS films were prepared on conducting glass and titanium substrates using selective plating technique. The precursors used for the deposition of CdS were 0.5 M $CdSO_4$, 0.1 M sodium thiosulfate and triply distilled water to make up the solution to 10 ml. The cotton wrapped graphite anode was dipped in the precursor mixture and brushed on the stainless steel substrates. The films were deposited at a current density of 80 mA cm^{-2} at different temperatures in the range 5–50 °C. The deposition current density was fixed based on our earlier experience with brush-plated films [18]. It took 20 min to deposit a film of thickness 3.0−5.0 μm (thickness estimated from gravimetry). The films were characterized by X-ray diffraction using Phillips X-ray diffraction unit. Optical absorption measurements were made on the films deposited on conducting glass substrates using a U3400 Hitachi UV–Vis–NIR spectrophotometer. Surface morphology of the films were studied by MolecularImaging systems Atomic Force Microscope. Laser Raman studies were made using 18 mW He–Ne laser of a Renishaw Invia Raman system. Photoelectrochemical measurements were made using an ORIEL 250 W Tungsten Halogen lamp.

3. Results and discussion

The XRD pattern of the CdS films deposited on low-temperature substrates is shown in Fig. 1. The prominent peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3), (1 1 2), and (0 0 3) of the hexagonal phase are observed in all cases. It is observed that as the substrate temperature increases, the width of the peak decreases due to improved crystallinity. The lattice constants ‘a’ and ‘c’ calculated using the XRD data are 4.14, and 6.75 Å, which are in close agreement with the ASTM data. The crystallite size calculated with the Debye Scherrer equation using the built in software of the XRD equipment is found to increase with increase of substrate temperature (Table 1). EDAX studies indicated the composition of the films to be Cd (64.1%) and S (35.9%).

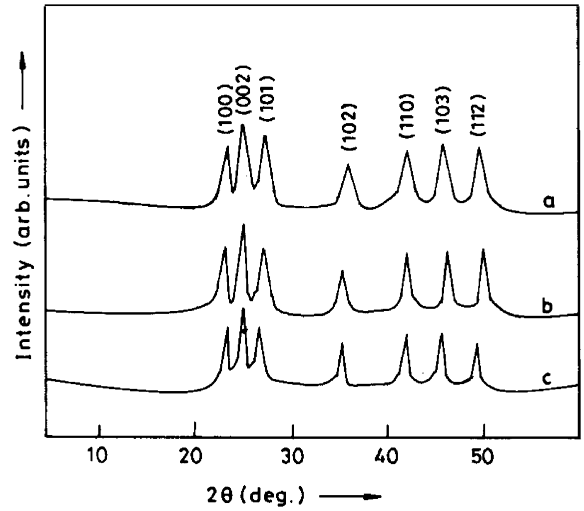

Fig. 1. XRD pattern of CdS films deposited at different temperatures: (a) 5 °C, (b) 15 °C, (c) 30 °C.

XPS studies show the binding energies of the Cd ($3d_{5/2}$ and $3d_{3/2}$) and S ($3d_{5/2}$ and $3d_{3/2}$) levels of the as-deposited CdS films as well as the films annealed at different temperatures. As shown in the

Table 1
Variation of crystallite size with substrate temperature

Substrate temperature (°C)	Crystallite size (nm)
5	15
15	25
30	40

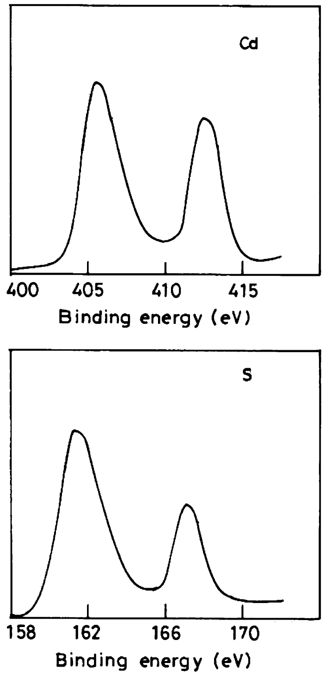

Fig. 2. XPS of CdS films deposited at 5 °C.

Fig. 2, the peak energy levels associated with the Cd ($3d_{5/2}$ and $3d_{3/2}$) appeared at 405, and 411.7 eV, respectively, these values are in close agreement with the literature values. The figure also shows the binding energies of S ($3d_{5/2}$ and $3d_{3/2}$) levels at 168.0, and 173.0 eV, respectively. There was no shift in the XPS pattern corresponding to the oxidation of selenium. Only the area under the peaks slightly decreased for the annealed films. Atomic concentration measurements made on the annealed samples yielded an apparent Cd/S ratio of 1.62, this calculation is based on the consideration of the area sensitivity factors for Cd and S and agrees very well with the composition estimated by EDAX measurements.

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. A plot of $(\alpha h\nu)^2$ vs $h\nu$ for the films deposited at different substrate temperatures is shown in Fig. 3. The plot is linear indicating the direct band gap nature of the films. Extrapolation of the line to the $h\nu$ axis indicated a direct band gap in the range 2.60–3.00 eV as the substrate temperature is decreased. This is due to the decrease in particle size with decrease of temperature. The variation of band gap at various substrate temperature is due to the variation of crystallite size with substrate temperature. Strong and weak confinements were noticed for the films. For strong confinement, the exciton energy is given by

$$E_s = E_g + h^2\pi^2/2\mu^2 - 1.786e^2/4\pi\varepsilon_0\varepsilon R - 0.248E^*_{Ry},$$

where E_g is the band gap of bulk CdS, the first term is related to the quantum localization energy, the second term represents the Coloumb energy and the third term represents the correlation energy in which E^*_{Ry} is the effective Rydberg energy and can be written as

$$\{\mu e^4/2(4\pi\varepsilon_0\varepsilon)^2h^2\},$$

where μ is the reduced effective mass, ε is the dielectric constant for CdS and ε_0 is the permittivity of free space. The estimated band gap of 2.80, 2.60,

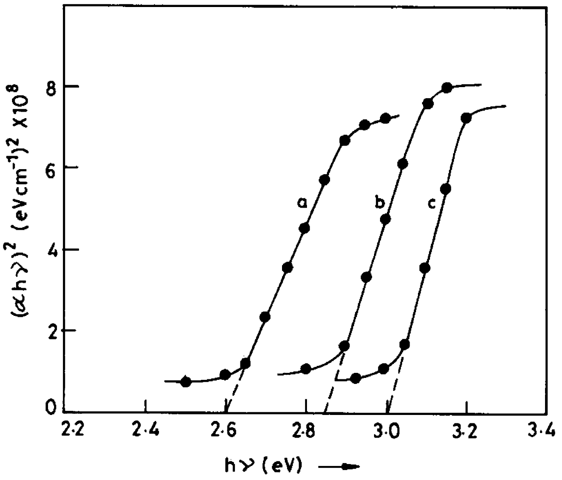

Fig. 3. $(\alpha h\nu)^2$ vs $h\nu$ plot of CdS films deposited at different temperatures: (a) 30 °C, (b) 15 °C, (c) 5 °C.

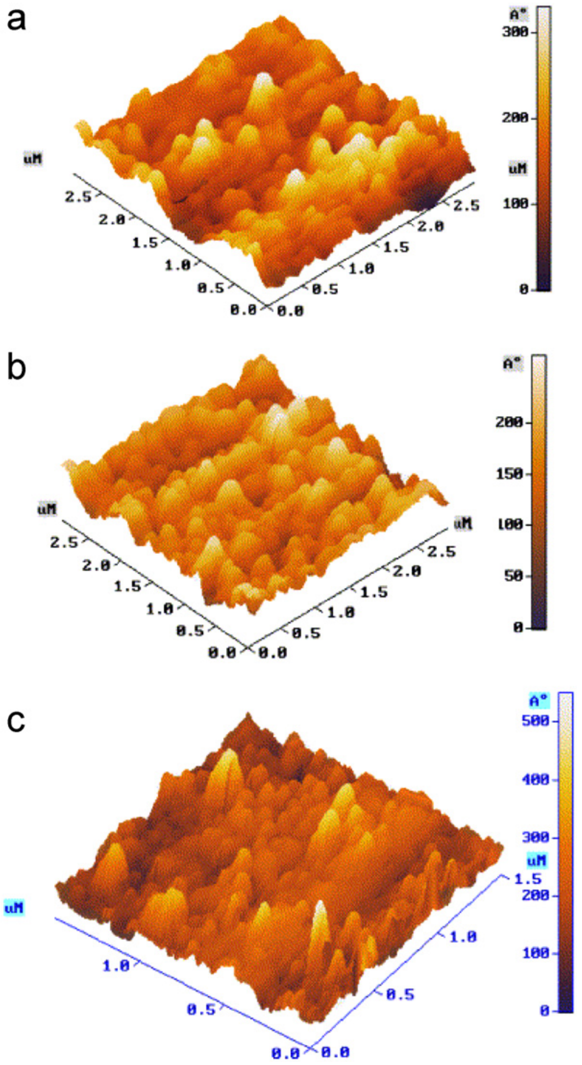

Fig. 4. Atomic force micrograph of CdS films deposited at different temperatures: (a) 30 °C, (b) 15 °C, (c) 5 °C.

and 2.40 eV due to strong confinement matches with the band gap value obtained from absorption measurements for the films deposited at 5, 15, and 30 °C, respectively.

Surface morphology of the films deposited at different temperatures is shown in Fig. 4. AFM images are characterized by slight surface roughness with a uniform crack-free, densely packed microstructure. The surface roughness (RMS) of the films is calculated by using the equipment's software routine. The surface roughness of films deposited at different temperatures is 4.86, 3.65, and 2.3 nm, respectively. Thus, surface roughness, decreases as temperature of deposition decreases. This is due to the fact that with a decrease in temperature, the grain size decreases and surface morphology becomes smoother.

Laser Raman studies indicated LO phonons corresponding to CdS. Upto fourth order phonons are observed in all the cases. Fig. 5 shows the Raman spectra of the films deposited at different temperatures. The intensity of the Raman peaks increased with increase of substrate temperature as is evident from the intensity counts in the x-axis.

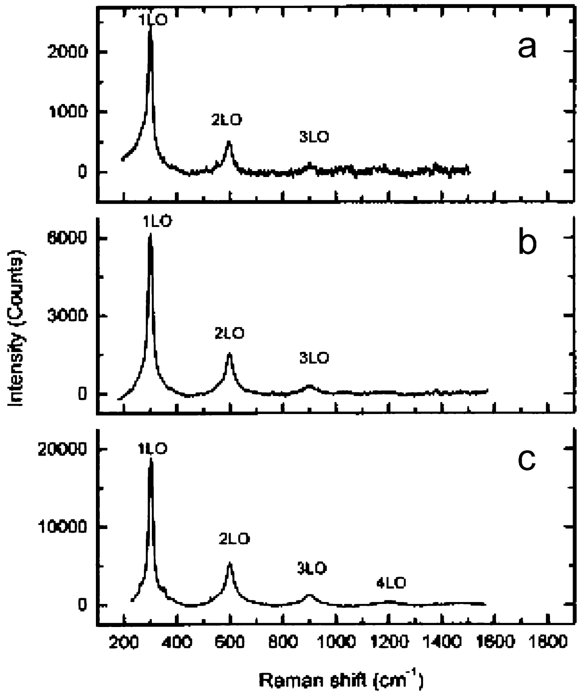

Fig. 5. Raman spectra of CdS films deposited on different substrate temperatures: (a) 30 °C, (b) 15 °C, (c) 5 °C.

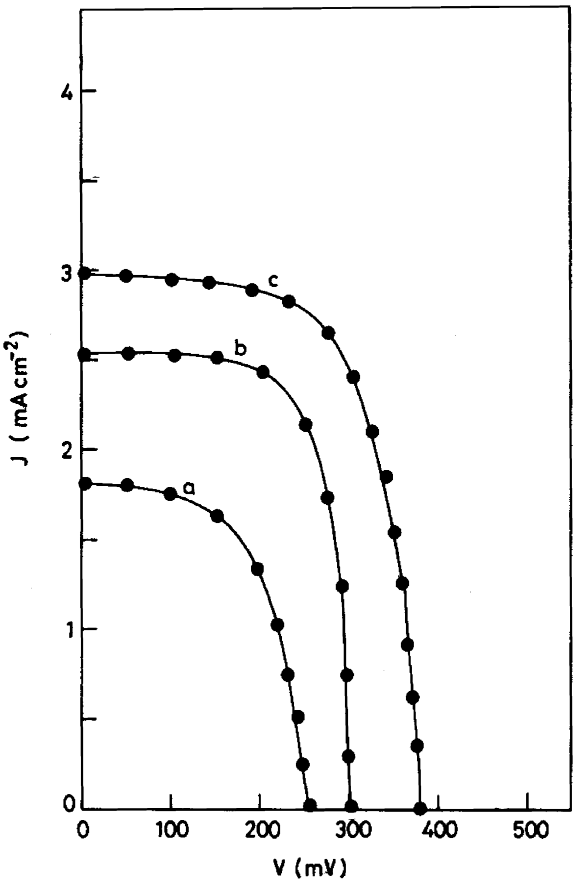

Fig. 6. Load characteristics of CdS films deposited on different substrate temperatures: (a) 5 °C, (b) 15 °C, (c) 30 °C.

Photoelectrochemical cells were made using the films as photoelectrodes of active area 0.01 cm^2, graphite as counter electrode and 1M polysulfide as redox electrolyte (1 M Na_2S, 1 M NaOH, and 1 M S). The as-deposited films exhibited weak photoresponse. Fig. 6 shows the load characteristics of the films deposited at different temperatures measured at 60 mW cm^{-2}. The values of the output parameters are higher than the earlier reports [19], in earlier studies, the films were heated in air/argon atmosphere to induce photoresponse but in the present work the as-deposited films have exhibited photoresponse without any heat treatment step. The mechanism responsible for the photoactivity in Cd chalcogenides is due to chalcogen vacancies [20], in earlier reports photoactivity has been reported only after heat treatment. During heat treatment the concentration of the chalcogen vacancy attains the desired value for inducing photoactivity in the films. In the present work the deposition process itself incorporates the desired concentration of the sulfur vacancy which results in photoactivity even without heat treatment. Upon heat treating the films the photoactivity further increases.

4. Conclusion

The results of this investigation indicates that the brush plating technique can be used to deposit nanocrystalline CdS films useful for photovoltaic applications.

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