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Photoelectrochemical cells based on CdSe films brush plated on high-temperature substrates

K.R. Murali[a,*], A. Austine[b], B. Jayasutha[b], D.C. Trivedi[a]

[a]*Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi 630006, India*
[b]*Department of Physics, J.J. College of Engineering, Trichy, India*

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Abstract

CdSe thin films were brush plated on substrates maintained at temperatures in the range 30–90 °C from the precursors. The films exhibited hexagonal crystal structure. Optical band gap of 1.65 eV was obtained. XPS measurements indicated the formation of CdSe. Capacitance–voltage measurements indicated the films to exhibit n-type behaviour. A carrier density of $10^{17}\,cm^{-3}$ was obtained. Photoelectrochemical cells have exhibited higher efficiency compared to earlier reports on brush-plated films. Spectral response measurements indicated a peak quantum efficiency of 75% at 1.65 eV.

Keywords: CdSe; Thin films; Brush plating; Photoelectrochemistry

1. Introduction

CdSe is a direct band gap semiconductor belonging to the II–VI group and possessing excellent optoelectronic properties. Thin film transistors and image intensifier tubes have been fabricated with this material. It is also a very stable photoanode in wet photovoltaic cells. Several physical and chemical techniques are available for the growth of thin films of CdSe [1–9]. Though results on brush-plated

*Corresponding author.
E-mail address: muraliramkrish@gmail.com (K.R. Murali).

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CdSe films have been reported earlier [10], the films were deposited on room-temperature substrates. To our knowledge this is the first report on CdSe films grown by the brush plating technique on substrates maintained at high temperatures.

2. Experimental methods

CdSe films were brush plated on to titanium and conducting glass substrates maintained at different temperatures in the range 30–90 °C. The precursors used were 0.5 M $CdSO_4$ and 0.1 M SeO_2. A current density of 100 mA cm^{-2} was employed and the plating time was 10 min. Thickness of the films was measured by the weight difference method. The thickness was found to vary in the range of 3.0–5.0 μm as the substrate temperature increased. The films were characterized by X-ray diffraction technique using Philips X-ray diffractometer with Cu Kα radiation. Optical absorption measurements were made on the films using Hitachi UV-VIS-NIR spectrophotometer. XPS studies were made on the films using ESCALAB. EDAX measurements were also made. Preliminary studies on the photoelectrochemical properties of the films were made in 1 M polysulphide electrolyte (1 M NaOH, 1 M Na_2S and 1 M S) under illumination from an ORIEL tungsten halogen lamp.

3. Results and discussion

XRD patterns of the films deposited at different substrate temperatures are shown in Fig. 1. The prominent peaks corresponding to *d*(1 0 0),(0 0 2),(1 0 1),(1 1 0),(1 0 3) and (1 1 2) are observed in all cases. It is observed that as the substrate temperature increases, the intensity of the peaks also increase and the width of the peak decreases due to improved crystallinity. The lattice constants '*a*' and '*c*' calculated using the XRD data are 4.304 and 7.044 Å, which are in close agreement with the ASTM data. After annealing the films, the XRD peaks became sharper but only slightly increased in intensity. After photoetching, the XRD pattern was similar to the annealed films. The crystallite size calculated using the Debye Scherrer equation is found to increase with increase of substrate temperature (Table 1).

To examine the chemical composition of the films, the XPS spectra of the CdSe films grown at different bath temperatures were measured and are indicated in Fig. 2. The figure exhibits the detailed spectra of Cd3d and Se3d regions respectively. The two strong peaks at 411.8 and 405.1 eV correspond to $Cd3d_{3/2}$ and $Cd3d_{5/2}$ binding energies. The peak at 54.3 eV, measured in the Se energy region is attributed to the Se3d transition. The energies for Cd and Se are in good agreement with the literature [11]. XPS studies on the annealed films indicated a reduction in the area under the Se curve. This is supported by the results of EDAX studies wherein a slight excess of Cd was observed. After photoetching, the area under the Se curve did not decrease further. EDAX measurements on the films deposited at 50 °C, indicated Cd (50.2%) and Se(49.8%), as the substrate temperature increased to 90 °C, the selenium concentration increased slightly(Cd—49.2% and Se—50.8%). After annealing, the

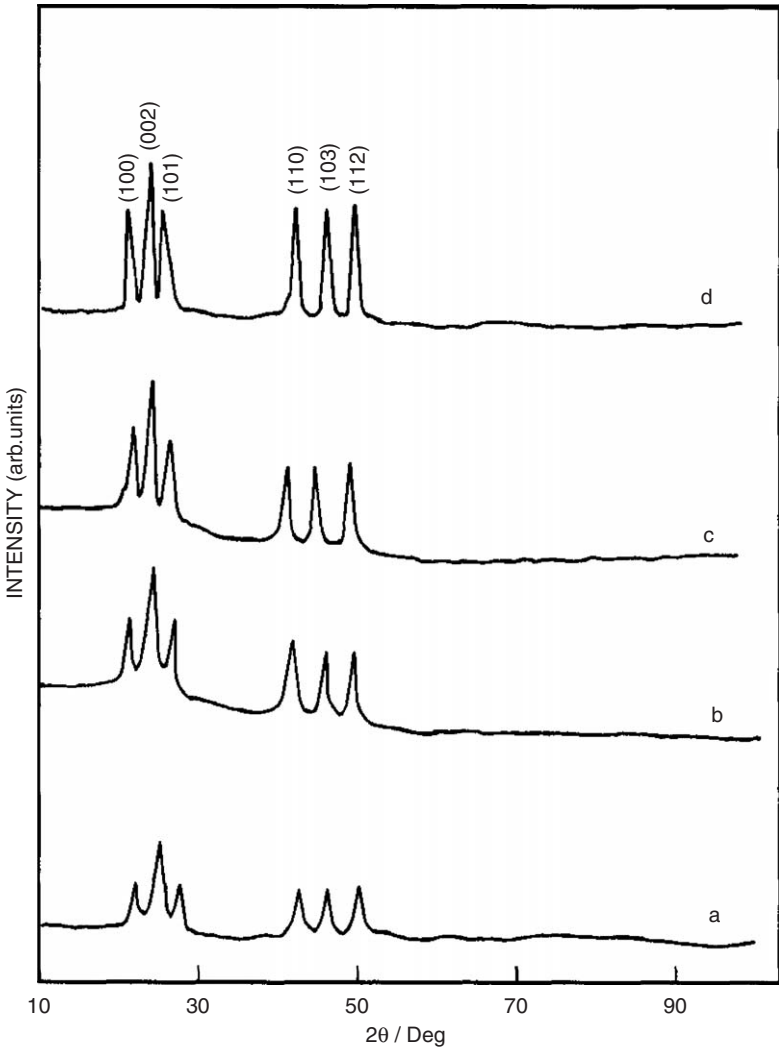

Fig. 1. X-ray diffraction pattern of CdSe films plated at different substrate temperatures (a) 30 °C (b) 50 °C (c) 70 °C and (d) 80 °C.

Table 1
Variation of crystallite size with bath temperature

Bath temperature (°C)	Crystallite size (nm)
30	100
50	150
70	230
80	340
90	450

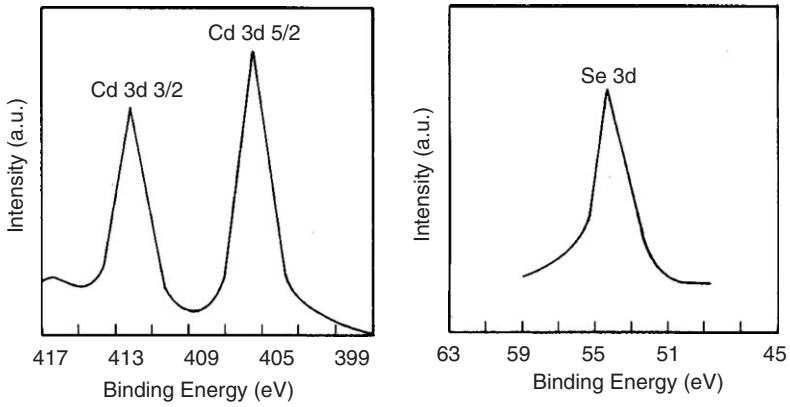

Fig. 2. (a) and (b) XPS spectra of CdSe films deposited at a substrate temperature of 90 °C.

composition of the films indicated a slight excess of Cd(Cd—50.4%, Se—49.6%).Hot probe measurements indicated n-type behaviour.

Optical absorption measurements were made at room temperature by placing an uncoated identical conducting glass substrate in the reference beam. A plot of $(\alpha hv)^2$ vs. hv for the films deposited at a substrate temperature of 90 °C is shown in Fig. 3. The plot is linear indicating the direct band gap nature of the films. Extrapolation of the line to the hv-axis indicated a direct band gap of 1.65 eV. The band gap of the films after anneal and etch did not change.

Cross plane resistivity measurements were made on the films by evaporating indium contacts on the surface of the film. The cross plane resistivity was found to increase from 50 to 120 Ω cm with increase of substrate temperature. This may be due to the increase in selenium concentration and decrease in cadmium concentration for the high-temperature deposited films. Photoelectrochemical cell studies were made on the films deposited at high temperatures, while the low-temperature grown films did not exhibit any photoresponse, those deposited at 90 °C exhibited a weak photoactivity, photovoltage of 250 mV and photocurrent of 100 μA were obtained. Earlier work on brush-plated films [10], did not exhibit any photoactivity, since the films were deposited at room temperature. Photoactivity was induced in the above samples by annealing them in argon and an efficiency of 7.0% was obtained after annealing and photoetching. To improve the photoactivity of the films obtained in the present study, they were heat treated in argon atmosphere in the temperature range 475–550 °C for 10 min. The output was observed to increase with increase of heat treatment temperature till 525 °C, beyond which the output is found to decrease due to a slight change in the stoichiometry. Amongst the films, those deposited at 90 °C have exhibited maximum photoactivity, hence the results are presented only for these films. The load characteristics of the films deposited at 90 °C and post-heat treated at 525 °C are shown in Fig. 4. The output parameters were V_{oc} of 0.6 V, J_{sc} of 15 mA cm^{-2}, ff of 0.66 and efficiency of 9.0%. The films were photoetched in 1:10 HCl at an illumination of 100 mW cm^{-2} white light in the range 0–80 s by shorting

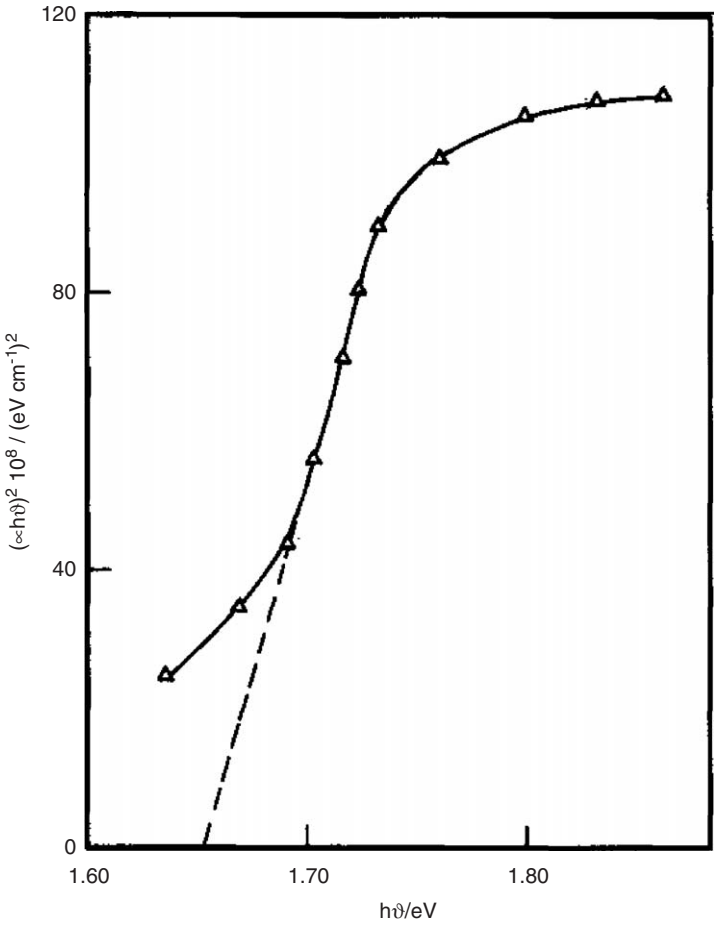

Fig. 3. $(\alpha h\nu)^2$ vs. $h\nu$ plot of CdSe films deposited at a substrate temperature of 90 °C after heat treatment at 525 °C.

the photo- and counter-electrodes. The output was found to increase after photoetching. The open circuit voltage increased from 0.6 to 0.63 V, the short-circuit current increased from 15 to 18 mA cm^{-2} and the efficiency increased from 9% to 11.3%. Photoetching leads to an increase in surface area which gives rise to enhanced current [12]. Photoetching also leads to selective attack [5] of surface defects not accessible to chemical etchants. The results of this investigation are higher than those reported earlier for brush-plated films [10]. The cells were found to be stable for more than 1 year. Capacitance–voltage measurements were made on the films in 1 M sodium sulphate electrolyte. The nature of the plot (Fig. 5) indicates n-type behaviour, agreeing well with hot probe measurements. The value of the carrier density calculated from the slope of the plot is found to be in the range of 10^{17} cm^{-3}. The V_{fb} value for the films annealed and photoetched was −1.20 V vs. SCE and N_d

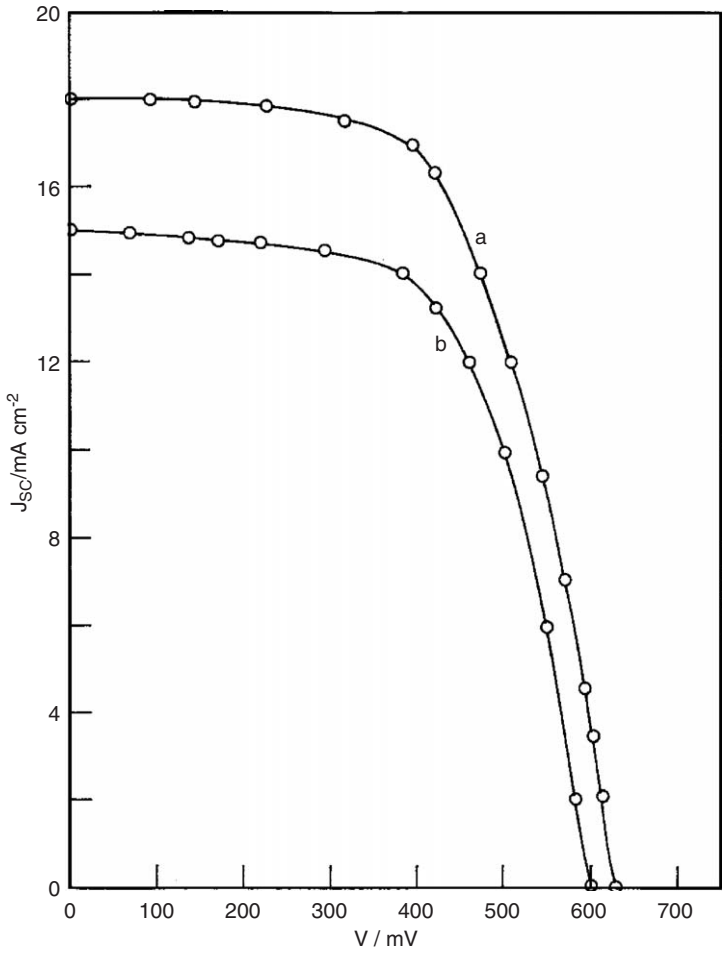

Fig. 4. Power output characteristics of CdSe electrodes deposited at 90 °C and post annealed at 525 °C (a) photoetched and (b) chemical etch.

value only slightly changed. Spectral response measurements were made on the films in the wavelength range 300–900 nm. The response peaked at 1.65 eV corresponding to the band gap of the semiconductor. A value of 0.75 was obtained for the quantum efficiency calculated from the photocurrent maximum value obtained at 1.65 eV.

4. Conclusions

The results of this investigation clearly point to the possibility of depositing highly efficient and stable photoelectrodes. The results of this investigation are higher than those reported earlier on films brush plated at room temperature and post annealed.

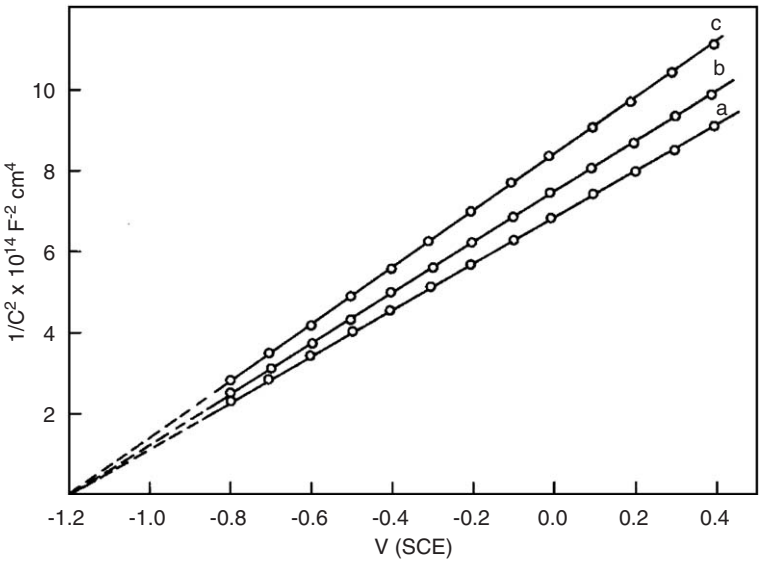

Fig. 5. Capacitance–voltage plot of CdSe film deposited at (a) 30 °C (b) 80 °C and (c) 90 °C after heat treatment at 525 °C.

Moreover, the process is being scaled up for production of large area commercial devices. Preliminary results on 25 cm^2 area photoelctrodes have indicated a conversion efficiency of 7%.

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