Structural, optical and photoelectrochemical properties of brush plated CdSe$_x$ Te$_{1-x}$ thin films

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CdSe$_x$Te$_{1-x}$ films have been deposited by the brush plating technique for the first time, on titanium and conducting glass substrates at room temperature. These films were annealed in argon atmosphere at 475°C for 15 min. Their structural, optical and photoelectrochemical (PEC) properties are presented and discussed. The power conversion efficiency has been found to be 9.0% at 60 mW cm^{-2} white light illumination. A peak quantum efficiency of 0.7 has been obtained for the films of composition CdSe$_{0.7}$Te$_{0.3}$. Donor concentration of 10^{17} cm^{-3} and electron mobility of 60 cm^2 V^{-1} sec^{-1} were obtained. © *2003 Kluwer Academic Publishers*

1. Introduction

Thin films of cadmium chalcogenides have received much attention for their application in electro optic devices, PEC cells and solar cells [1]. CdSe and CdTe form CdSe$_x$Te$_{1-x}$ solid solution throughout the entire composition range, the bandgap and lattice parameters of which can be varied by changing the relative amounts of chalcogenides. CdTe has an optimum bandgap for solar cell applications but is unstable in all redox electrolytes [2]. CdSe is more stable than CdTe but the efficiency is expected to be limited by its bandgap. Power conversion efficiencies upto 12% have been reported for CdSe film electrodes and upto 8% for polycrystalline CdSe$_{0.6}$5Te$_{0.35}$ electrodes which has an optimal bandgap similar to that of CdTe and shows a stability comparable to CdSe in sulphide-polysulphide electrolyte [3].

Several deposition techniques have been employed for the preparation of CdSe$_x$Te$_{1-x}$ films [3–7]. The brush plating technique also called the swab plating technique, is a simple, convenient and low cost method for obtaining large area films. This technique has been employed for the first time by the author in producing these films for application in solar energy conversion. Under identical deposition conditions, compared with the conventional electrodeposition technique which takes about one hour to obtain 2.0 μm thick film, the brush plating technique takes only 20 min to obtain 5.0 μm thick films, of good quality.

The objective of this paper is to study the structural, morphological, optical and photoelectrochemical properties of CdSe$_x$Te$_{1-x}$ films obtained by the brush plating technique.

2. Experimental

CdSe$_x$Te$_{1-x}$ films of 5.0 μm in thickness were deposited on Ti and conducting glass substrates of 1 cm^2 in area by the brush plating technique, at room temperature. Pretreatment of the Ti substrate was found to be an essential step to obtain very good adhesion. The presence of TiO$_2$ on the surface was found to reduce the PEC conversion efficiency of the films. Ti substrates were degreased first with trichloroethylene, then etched for 30 s in a solution containing equal volumes of 2:1 HNO$_3$ and 1:1 HCl and finally treated for 30 s in 10% by volume of NaOH. The plating bath consisted of 0.25 M CdSO$_4$, 0.01 M SeO$_2$ and 0.01 M TeO$_2$ (pH about 4). The brush anode consisted of a graphite sheet wrapped at one end with cotton. The area of the anode could be varied depending on the cathode area to be coated. The anode and cathode were connected to a dc power supply. The anode was wetted by the plating solution and the substrate was brushed with it. The rate of motion of the brush was around 4 cm min^{-1}. The current density was maintained at 80 mA cm^{-2}. Deposition took place at a very rapid rate. CdSe$_x$Te$_{1-x}$ films of thickness 5.0 μm were obtained after 20 min. Thickness of the films were estimated by gravimetry. A large number of films (>50) were prepared.

Films were annealed at 475°C in an argon atmosphere for 15 min under controlled rate of heating and cooling. The argon used for annealing contained a few ppm of oxygen. After annealing the thickness of the films were around 4.5 μm. Structural characterization was carried out by X-ray diffraction (XRD) studies using Cu K$_\alpha$ radiation. Morphological studies were carried out employing a 35CF JEOL scanning electron microscope. Film thickness was calculated from the mass of the deposit and the density of the bulk CdSe$_x$Te$_{1-x}$ [10]. Optical absorption studies were made employing a Hitachi U 3400 UV-Vis—near IR spectrophotometer for films deposited on SnO$_2$ substrate. Resistivity of the films was measured with an Agronic digital micro ohm meter, model 53C. For measuring the cross plane resistance, an indium contact was applied on the

top of the entire $CdSe_xTe_{1-x}$ film. The PEC cell consisted of the annealed $CdSe_xTe_{1-x}$ film and graphite sheet as photo and counter electrodes respectively in 1 M alkaline polysulphide, which is 1 M with respect to NaOH, Na_2S and S solution. The light source was a 250 W ORIEL quartz tungsten halogen lamp. The photon flux was measured by a CEL suryamapi (light intensity measuring instrument).

3. Results and discussion

The XRD pattern of the as deposited as well as the annealed film is shown in Fig. 1. Peaks corresponding to the hexagonal phase are observed. Elemental Cd, Se or Te was not observed in the diffractogram. Since the thickness of the films is quite high, peaks corresponding to the Ti substrate were not observed. The peaks were found to increase in height after annealing, thus indicating the improved crystallinity of the annealed films. The composition of the films estimated from EDAX measurement is $CdSe_{0.7}Te_{0.3}$. This composition is in close agreement with that estimated from Vegard's law. Films of other compositions were also prepared by varying the concentrations of SeO_2 and TeO_2 solutions, however, results are presented only for $CdSe_{0.7}Te_{0.3}$ films since they exhibit maximum photoactivity.

Fig. 2a and b indicate the surface morphology of the as-deposited and heat treated $CdSe_{0.7}Te_{0.3}$ films. It is observed that the as deposited films exhibit fine grains (Fig. 2a), while after heat treatment the grain size is found to increase (Fig. 2b). The average grain size increased from 1.0 μm–3.0 μm after heat treatment.

Optical absorption studies were carried out using an identical uncoated SnO_2 substrate in the reference beam. A plot of $(\alpha h\nu)^2$ vs. $h\nu$ (Fig. 3) gives a straight line. Extrapolation of the line to the energy axis yields a direct band gap of 1.54 eV.
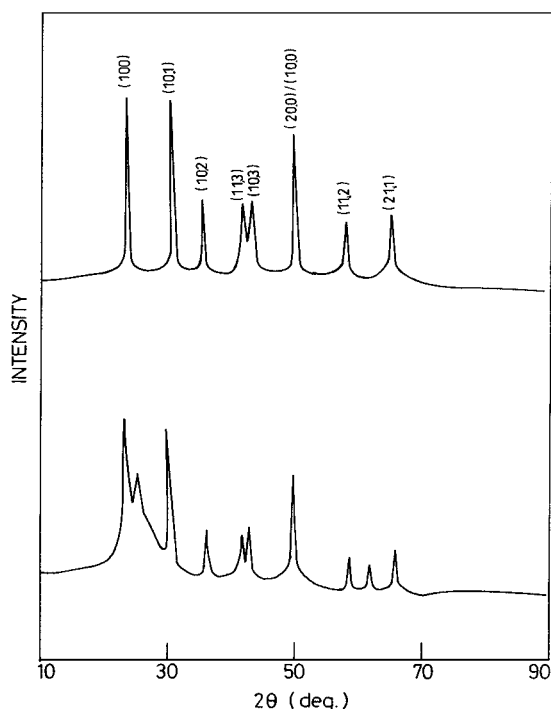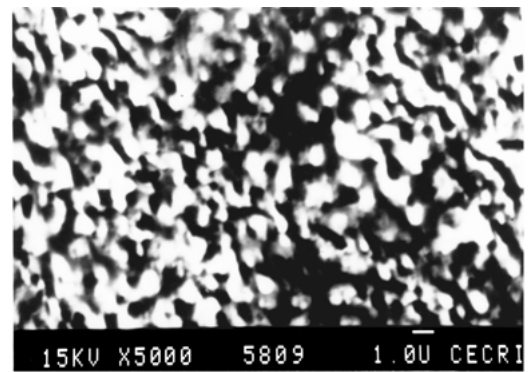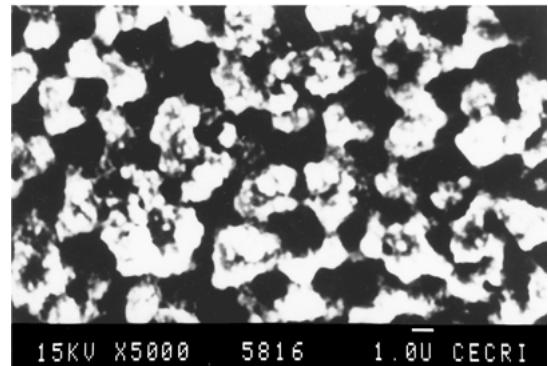

(a)

(b)

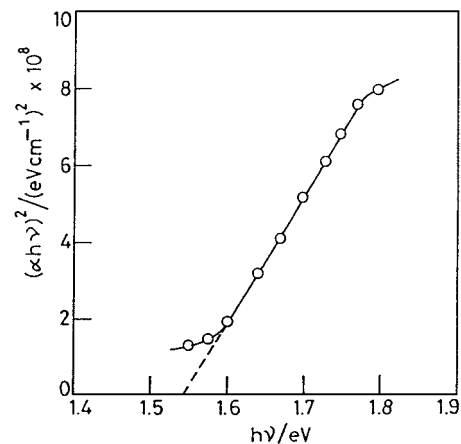*Figure 2* Scanning Electron Micrograph of brush plated $CdSe_{0.7}Te_{0.3}$ film: (a) as deposited and (b) heat treated.

Figure 3 Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for brush plated and post heat treated $CdSe_{0.7}Te_{0.3}$ film.

It was found that the brush plating technique is highly reproducible and reliable. The efficiency of the as deposited electrodes was limited by the small grain size and low electrical conductivity, so further annealing and etching treatments were essential for realizing high conversion efficiencies. It was also noticed [8], that during annealing, oxygen is necessary for reasonable conversion efficiencies. Chemisorbed oxygen is an effective electron acceptor compensating the excess concentration of free electrons, thereby controlling the donor concentration [9]. The power output characteristics of the PEC cell employing the $CdSe_{0.7}Te_{0.3}$ film annealed at $475°C$ is shown in Fig. 4. The film was given a chemical etching treatment followed by PEC etching. Photoetching was done in 1:10 HCl at an illumination of
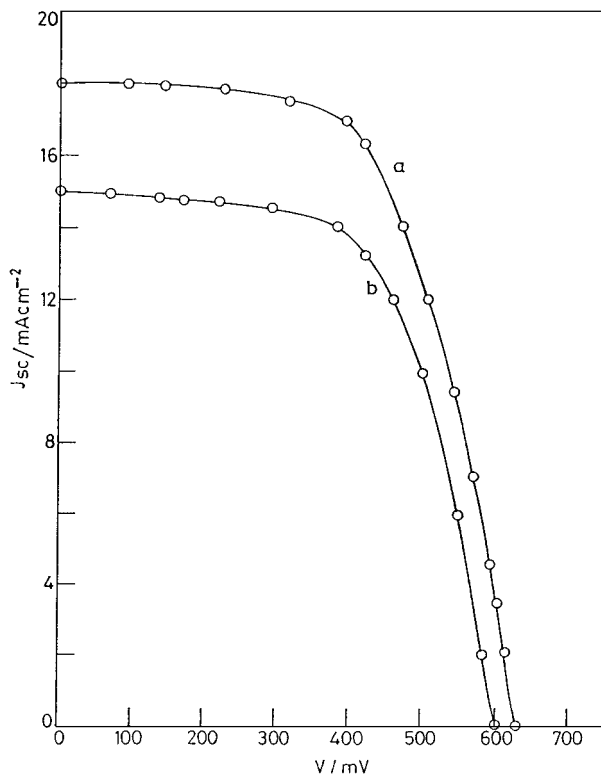

Figure 1 XRD pattern of brush plated $CdSe_{0.7}Te_{0.3}$ film: (a) as deposited and (b) heat treated.

Figure 4 Power output characteristics of PEC cell at 60 mW cm^{-2} illumination in 1 M polysulphide: (a) chemical etch and (b) photo etch.

100 mW cm^{-2} white light for different duration in the range 0–80 s by shorting the photo and counter electrodes. A PEC cell with a typical brush plated CdSe$_{0.7}$Te$_{0.3}$ film which was chemically etched gave an open circuit voltage (V_{oc}) of 600 mV, a short circuit current density (J_{sc}) of 15 mA cm^{-2}, a fill factor of 0.6 and a conversion efficiency (η) of 9.0% under an illumination of 60 mW cm^{-2}. The photo etched film yields a V_{oc} of 630 mV, a J_{sc} value of 18 mA cm^{-2}, a fill factor of 0.6 and a conversion efficiency of 11.3%. Photo etching leads to an increase in surface area which gives rise to enhanced current [11]. Photo etching also leads to selective attack [3] of surface defects not accessible to the chemical etchants. The effect of duration of photo etching on V_{oc} and J_{sc} are shown in Fig. 5. As illustrated, both voltage and current are found to increase upto 60 s and then decrease afterwards. The decrease
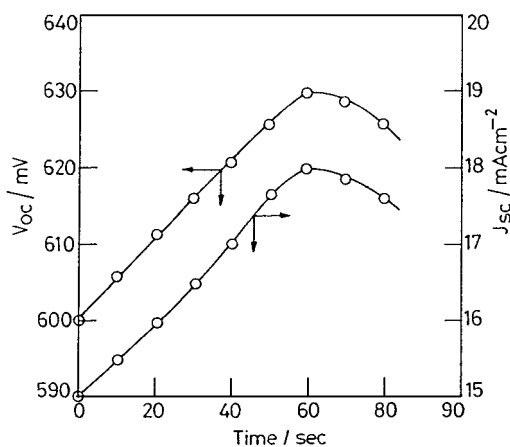

Figure 5 Dependence of V_{oc} and J_{sc} on photoetching duration for the heat treated films.
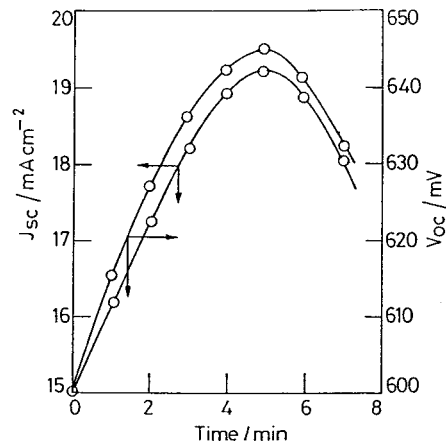

Figure 6 Effect of Cu modification (0.01 M CuCl$_2$ dipped) on V_{oc} and J_{sc} for the heat treated film.

is attributed to separation of grain boundaries due to prolonged photo etching.

Fig. 6 shows the influence of copper modification. Both V_{oc} and J_{sc} are altered when the CdSe$_{0.7}$Te$_{0.3}$ film is dipped in cupric chloride solution (0.01 M) and then employed in the PEC cell. Their values increase with the duration of dipping upto 5 min and decrease afterwards. The increase is attributed to surface modification by Cu$^+$ ions which decrease the number of recombination centers. Above a certain concentration of Cu$^+$ ions, obtained after 5 min in the present case, the decrease in voltage and current may be due to additional acceptor centers due to Cu$^+$ ions induced on the film surface. Hence, optimum dipping time is essential to obtain maximum effect.

The as grown electrodes were found to be stable for more than two years in the alkaline polysulphide solution. After removing the electrodes from the cell, the thickness of the film was found to be 4.5 μm. The surface was characterized by x-ray diffraction and it exhibited a pattern similar to Fig. 1. Further, the composition estimated by EDAX was CdSe$_{0.7}$Te$_{0.3}$, thus indicating the absence of photodegradation.

The Mott-Schottky plot of the CdSe$_{0.7}$Te$_{0.3}$/ polysulphide electrolyte system for titanium substrate based PEC cells was studied in the dark. The value of the flat band potential, V_{fb} was obtained at $1/C_{sc}^2 = 0$ on the potential axis according to the well known Mott-Schottky relation [12, 13],

$$1/C_{sc}^2 = [2/\varepsilon\varepsilon_0 q N_D][V - V_{fb} - kT/q] \qquad (1)$$

where C_{sc} is the space charge capacitance, V_{fb} the flat band potrential, ε the dielectric constant of the semiconductor, ε_0 the permittivity of free space and N_D the donor concentration.

Mott-Schottky plots were obtained at different frequencies (Fig. 7). A small frequency dispersion is observed in agreement with earlier workers [14–18]. Such dispersion may be due to surface roughness and the existence of electrolyte ions in the region close to the surface, whose mobility is not so high when compared with electrons or holes in the semiconductor. It may be recalled that the effective mass of holes/electrons is
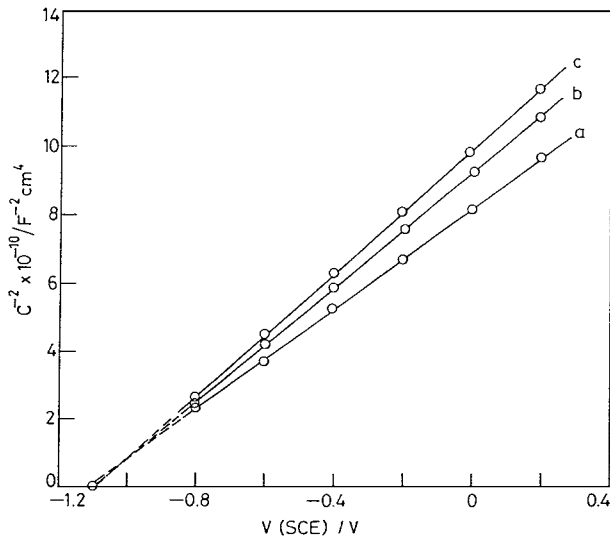
Figure 7 Mott-Schottky plots of CdSe$_{0.7}$Te$_{0.3}$/polysulphide PEC cell at different frequencies: (a) 1 kHz, (b) 10 kHz, and (c) 20 kHz.

much lower than those of the ions in the electrolyte. Thus, regarding the changes in frequency, the response of the low mobility ions of the electrolyte at the interface between the semiconductor and the electrolyte to the ac signal is slower, leading to a frequency dispersion. The frequency dispersion in the Mott-Schottky plots will be minimum for those systems where the surfaces are absolutely smooth so that the area of the electrolyte in contact with the semiconductor surface is almost the same. In that case, the total capacitance is given by [19]:

$$C = (1/C_{sc} + 1/C_{DL})^{-1} \sim C_{sc} \qquad (2)$$

where C is the total capacitance, C_{sc} the space charge capacitance and C_{DL} is the solution side double layer capacitance. In the capacitance measurement technique, say for an n-type semiconductor electrolyte junction, the participating entities are electrons at the surface of the semiconductor and the ions on the redox electrolyte side. As is well known, the mobility of electrons exceeds by several orders of magnitude the mobility of ions in solution. So the response of he electrons to the applied sinusoidal signal is much faster than that of the ions in the electrolyte.

Now, if the semiconductor is etched in the dark or if it is photo etched, the effective area of the semiconductor—electrolyte junction is modified, i.e., the effective area on the electrolyte side increases, leading to a great enhancement in C_{sc} compared to C_{DL}.

The active area (region) responsive to the ac signal is much greater than the geometrical area of the semiconductor in contact with the electrolyte due to etching or photo etching of the semiconductor surface, leading to a situation where the double layer capacitance can no longer be neglected and in fact becomes dominant in the expression for the total junction capacitance, so we can write,
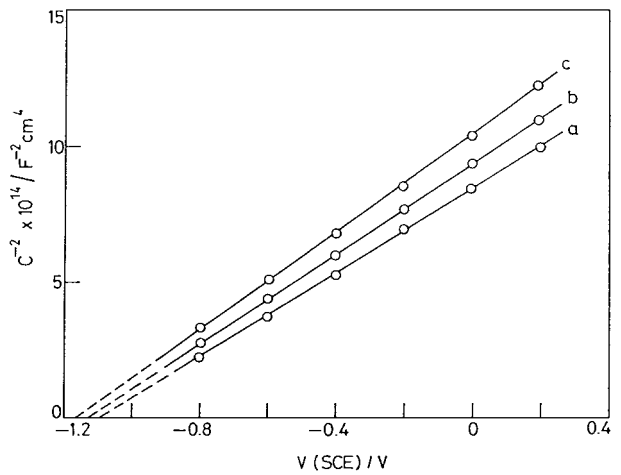
$$C \sim C_{DL} \qquad (3)$$

Figure 8 Mott-Schottky plots of CdSe$_{0.7}$Te$_{0.3}$/polysulphide PEC cell after photoetching at different frequencies: (a) 1 kHz, (b) 10 kHz, and (c) 20 kHz.

Thus, for the semiconductor electrolyte junction with rough semiconductor surfaces, the Mott Schottky plots do exhibit frequency dispersion [19, 20]. Fig. 8 shows the Mott-Schottky plots after photo etching the film. Flat band potentials in the range −1.1 V to −1.15 V (SCE) are obtained. The value of the donor density was estimated from the slope of the Mott-Schottky plots and is found to be 2.0×10^{17} cm^{-3}.

The quantum efficiency (ϕ) is influenced by the depletion layer width in the semiconductor, which in turn, is dependent on conductivity [21]. Quantum efficiency has been evaluated employing the following expression [22, 23].

$$\phi = 1240 \, J_{sc}/\lambda P \qquad (4)$$

where J_{sc} is the short circuit current density expressed in A cm^{-2}, λ is the wavelength expressed in nm and P is the incident light intensity expressed in W cm^{-2}. Fig. 9 shows the variation of quantum efficiency with wavelength in the range 600–850 nm. No corrections have been made for solution or window absorption, or for window or sample reflection. A peak quantum efficiency of 0.70 is observed at 810 nm.

The photocurrent, which is separated from the dark current [24], follows the Gartner's photocurrent
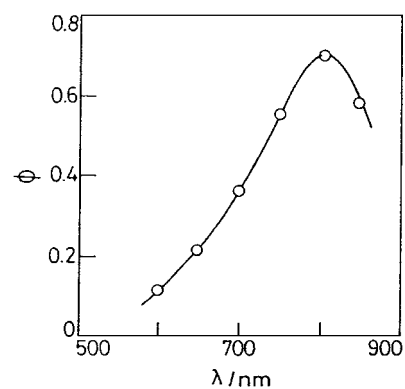

Figure 9 Variation of quantum efficiency vs. wavelength for the PEC cell employing the heat treated CdSe$_{0.7}$Te$_{0.3}$ electrode.

equation for a metal/semiconductor junction:

$$\phi = 1 - e^{-\alpha W}/(1 + \alpha L_p) \qquad (5)$$

where W is the width of the space charge layer, given by,

$$W = [(2\varepsilon\varepsilon_o/qN_D)(V - V_{fb})] \qquad (6)$$

where q is the electronic charge, α the absorption coefficient, L_p the minority carrier diffusion length (holes), ε the dielectric constant of the semiconductor, ε_o the permittivity of free space, V the electrode potential, V_{fb} the flat band potential and N_D the donor density. By choosing a wavelength of relatively weak absorption so that $\alpha L_p \ll 1$ and $\alpha W \ll 1$ [25], the following relationship is obtained:

$$\phi = \alpha L_p \qquad (7)$$

Hence,

$$\phi^{-1} = (\alpha L_p)^{-1}$$

A plot of ϕ^{-1} vs. α^{-1} yields a straight line, L_p is obtained from the inverse of the slope and is found to be 0.2 μm.

The results obtained in this work are higher than the previous reports. It is worth noting that CdSe$_{0.65}$Te$_{0.35}$ electrodes, prepared by cathodic electrodeposition gave V_{oc} of 0.51 V, J_{sc} of 18 mA/cm^2 and an efficiency of 5.82%, while a value of 0.1 μm was obtained for the minority carrier diffusion length [26].

The cross plane resistivity is found to be 1 ohm cm and the in plane resistivity was found to be 0.5 ohm cm. This shows that the surface contains more donors than the bulk. Employing the cross plane resistivity value, the mobility of electrons was found to be 60 cm^2 V^{-1} s^{-1}.

4. Conclusions

The present study indicates that the simple and reproducible brush plating technique can be successfully employed for the preparation of device quality films. The films exhibited improved crystallinity after heat treatment. High values of output parameters were obtained by this technique. The electrodes were found to be stable for more than two years. The quantum efficiency as well as the power conversion efficiency is comparable with the earlier reports.

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