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Electrodeposited $CdSe_{0.5}Te_{0.5}$: photoelectrochemical solar cells

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$CdSe_{0.5}Te_{0.5}$ thin films have been prepared by electrodeposition. The films were characterized by X-ray diffraction, energy dispersive X-ray fluorescence microanalysis, scanning electron microscopy, optical absorption techniques, Auger electron analysis and electron probe microanalysis. Photoelectrochemical cell performance after electrode annealing and photoetching treatments is reported.

1. Introduction

Electrodeposited $CdSe_{1-x}Te_x$ thin films are possible candidates for a stable and efficient liquid junction solar cell. Electrodeposition could be a cost-effective technology for production of terrestrial photoelectrochemical (PEC) cells. CdSe and CdTe form solid solutions over their entire composition range. Therefore, it is of interest to prepare photoelectrochemical cells based on electrodeposited $CdSe_{1-x}Te_x$ thin films. When $CdSe_{1-x}Te_x$ is used as a photoanode in polysulphide electrolytes, higher efficiencies [1] are obtained than in the case with CdSe [2–7].

It is the aim of this paper to report and discuss the results obtained only with electrodeposited $CdSe_{0.5}Te_{0.5}$ thin films. The band gap of a $CdSe_{0.5}Te_{0.5}$ thin film cell is close to that of CdTe, which provides an optimal match with the solar spectrum and thus facilitates its efficient utilization. According to Tai *et al.* [8], the band gap of $CdSe_{0.5}Te_{0.5}$ alloys varies in the range 1.35–1.45 eV, depending on the crystal structure of the alloys.

The electrodeposition technique presented in this paper has certain features different from the electrodeposition techniques reported earlier, particularly in solution preparation [9, 10]. In the present investigation, $CdSe_{0.5}Te_{0.5}$ thin films are obtained from the plating solution at a pH of about 2, under constant stirring, and in the absence of any Triton X-100. The main importance of stirring is to get pinhole-free, uniform, thin films. The initial speciation of TeO_2 with NaOH permits introduction of a higher TeO_2 concentation in the deposition bath. Photoelectrochemical solar cells have been fabricated from the electrodeposited $CdSe_{0.5}Te_{0.5}$ thin films on titanium substrates. The electrodes have been characterized using X-ray diffraction, energy dispersive X-ray fluorescence microanalysis, scanning electron microscopy (SEM), optical absorption techniques, Auger electron analyses and electron probe microanalyses.

2. Experimental details

$CdSe_{0.5}Te_{0.5}$ thin films were prepared from a plating solution containing 5×10^{-4} M tellurium dioxide solution, 5×10^{-4} M selenium dioxide solution and 5×10^{-2} M cadmium acetate solution. The pH of the deposition mixture was adjusted to between 2.5 and 1 by dilute sulphuric acid (1 : 10). Tellurium dioxide solution was prepared by dissolving TeO_2 powder in NaOH solution (10% by weight). The titanium substrates were cleaned in 10% hydrofluoric acid, then preheated for 2 min in an argon stream containing 0.5% oxygen at 650° C. Deposition was carried out under constant stirring and in the temperature range 40–60° C under potentiostatic conditions. The counter

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Table 1. Conditions for the electrodeposition of $CdSe_{0.5}Te_{0.5}$ thin films

Substrates	*Average plating current densities ($mA\ cm^{-2}$)*	*Potential (w.r.t SCE)*	*pH*	*Temperature (° C)*
Titanium (area: $4.5\ cm^2$)	8.8	−1 V	1.8	40
Titanium (area: $17\ cm^2$)	7	−850 mV	1.3	40
Molybdenum (area: $3\ cm^2$)	8	−850 mV	1.8	40

electrode was platinum while a saturated calomel electrode was used as the reference electrode. Plating conditions are presented in Table 1. The deposited films were cleaned with distilled water and immersed in a polysulphide solution (1 M Na_2S, 1 M NaOH, 1 M S) to dissolve any free selenium or tellurium that was present [11]. The deposited films were annealed at 650° C for 15 min in an argon stream containing 0.5% oxygen. The annealed films were etched in 0.1 N HCl and subsequently photoetched in 0.1 N HCl for a few seconds under a light intensity of $80\ mW\ cm^{-2}$ [19].

The front-wall cells, constructed from the electrodeposited films, were illuminated under artificial sunlight using a W-Iodine projector having a light intensity approximately equivalent to $80\ mW\ cm^{-2}$. The PEC cells were fabricated using electrodeposited $CdSe_{0.5}Te_{0.5}$ thin films as photoanodes, platinum as reference electrode and sulphide brass gauze as counter electrode [12]. The *I–V* characteristics of the PE cells were recorded using argon-purged polysulphide solution without any stirring of the electrolyte solution. The polysulphide solution was prepared from 2 M KOH, 2 M Na_2S and 2.6 M S.

2.1. *Instrumentation*

X-ray diffraction data were obtained using a Philips diffractometer with CuK_α radiation. Energy dispersive analysis of X-ray fluorescence (EDAX) and SEM were performed on a Philips Model P505 unit. The transmission measurements were carried out using a Beckman Model 5240 spectrophotometer. Film thicknesses were measured on an Alpha-Step Profiler (Tencor Instruments Inc., California). A Princeton Applied Research (PAR) system consisting of a Model 173 potentiostat/galvanostat, Model 175 Universal Programmer and a Model 179 digital coulometer was employed for the electrodeposition. Electron microprobe analysis was performed on a Cameca Model MBX, by using wavelength dispersive X-ray fluorescence spectroscopy (WDS).

3. Results and discussion

The electrochemistry of the deposition process and the cyclic voltammetric behaviour of TeO_2-containing electrolytes have been presented elsewhere [13]. The X-ray diffractogram (Fig. 1) was obtained for films annealed at 650° C for 1 h in an argon atomosphere. The $CdSe_{1-x}Te_x$ films

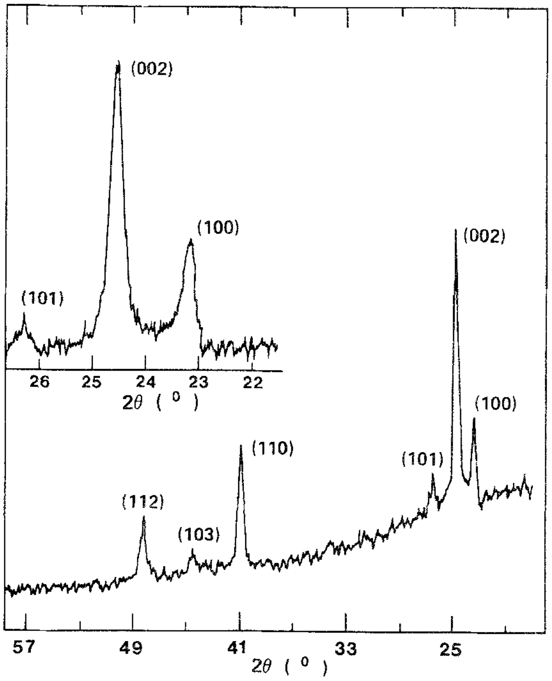

Fig. 1. X-ray diffraction pattern of a $CdSe_{0.5}Te_{0.5}$ thin film on a titanium substrate.

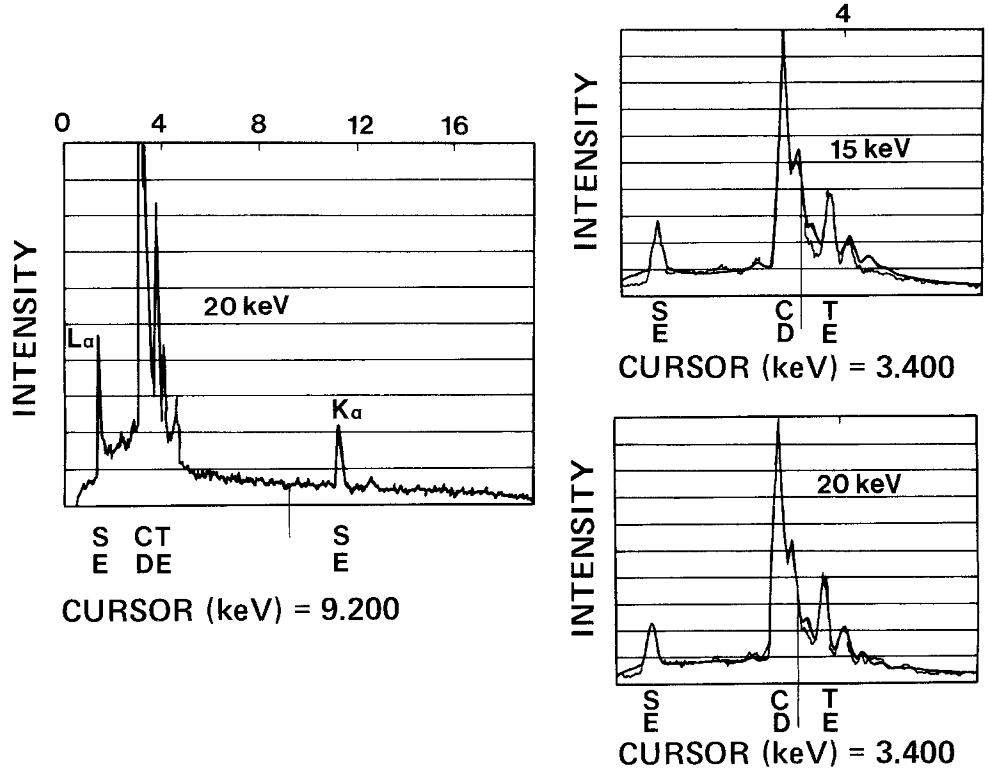

Fig. 2. Energy dispersive analysis (EDAX) of a $CdSe_{0.5}Te_{0.5}$ thin film.

have the hexagonal structure. From the X-ray diffraction data (Fig. 1), it is clear that the electrodeposited $CdSe_{1-x}Te_x$ thin films are single-phase compounds. The lattice constants were calculated from the following conventional equation [14]:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{\ell^2}{c^2} \tag{1}$$

where d = distance between lattice planes; h, k, l = Miller indices; a, c = lattice constant. The calculated lattice parameters for the a-axis and c-axis were 4.4 and 7.25 Å, respectively. The composition of the films was calculated from Vegard's rule [15], expressed as follows

$$a_{\mathrm{CdTe}}x + (1 - x)a_{\mathrm{CdSe}} = a_{\mathrm{obtained}} \tag{2}$$

$$c_{\mathrm{CdTe}}x + (1 - x)c_{\mathrm{CdSe}} = c_{\mathrm{obtained}} \tag{3}$$

The composition obtained from Equation 2 (when a_{obtained} is 4.4 Å) is $CdSe_{0.5}Te_{0.5}$, while the composition calculated from Equation 3 (when c_{obtained} is 7.25 Å) is $CdSe_{0.49}Te_{0.51}$. The relative selenium and tellurium contents of the films matches (fairly closely) the concentrations of SeO_2 and TeO_2 in the electroplating solution. Characterization of the films was also carried out by the EDAX/SEM techniques (EDAX results are given in Fig. 2). The intensity was recorded for a period of 90 s by using an electron beam voltage of 20 or 15 keV. The working distance and tilt angle were 12 mm and 30° (on the screen), respectively. The ratio of Cd : Se : Te obtained from the intensities by applying ZAF correction [13, 16] is 1 : 0.52 : 0.48. The average grain size obtained from SEM pictures taken of the annealed/photoetched films deposited on titanium substrates (Fig. 3a, b) was 8000 Å. The bandgap obtained from transmission measurements was 1.55 eV (Fig. 4). The stoichiometry of the layers was confirmed by wavelength dispersive electron microprobe measurements (system run conditions: 20 keV electron beam, 29 nA beam current and 30 μm beam size) (Fig. 5). A typical Auger electron spectrum (AES) and the depth profiles (peak to peak height and atom concentration) for the film

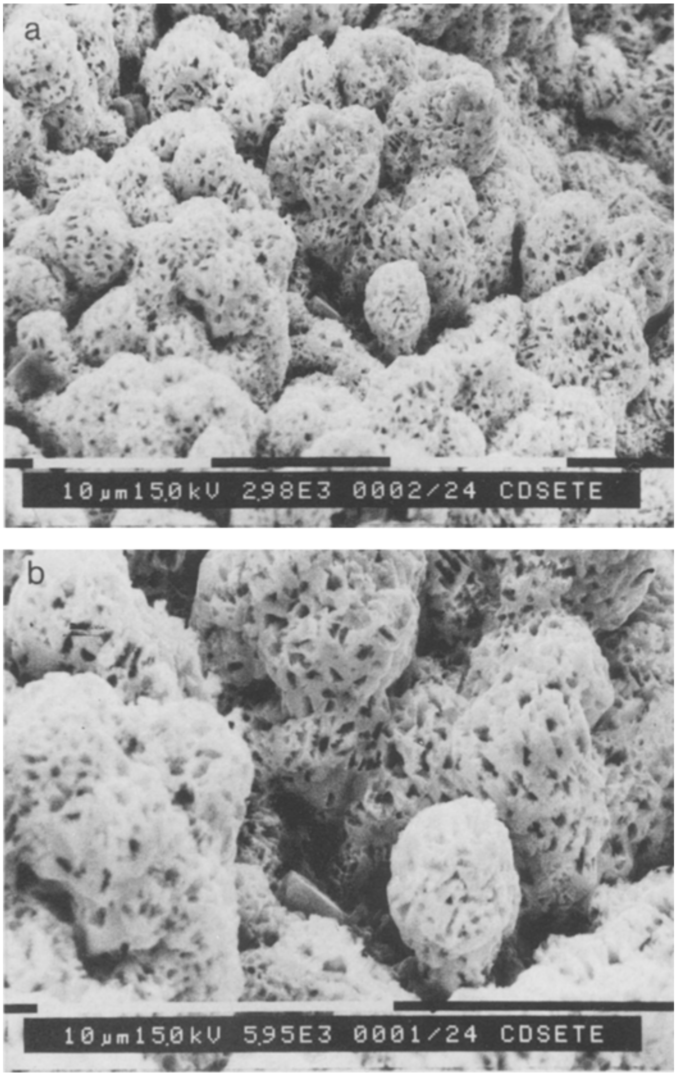

Fig. 3. SEM pictures (15.0 kV) at two magnifications of an electrodeposited CdSe$_{0.5}$Te$_{0.5}$ thin film on titanium substrates; after photoetching in 1.0 N HCL.

electrodeposited on molybdenum substrate are shown in Fig. 6a–c, respectively. The different composition (as compared with the WDS measurement) was obtained mainly because of the use of a non-optimized sensitivity factor. AES analysis showed that the composition of the film was consistent with the increase of the film thickness.

Fig. 7 represents typical *I–V* characteristics of the front-wall cells made from electrodeposited CdSe$_{0.5}$Te$_{0.5}$ films on 4.5 cm^2 titanium substrates. Curve I shows the efficiency (only 0.47%) of the cells fabricated using the as-deposited film. Curve II shows that the cell efficiency improves to 2.5% when the films were annealed in argon gas containing 0.5% oxygen for 15 min at a temperature of 650° C. Conversion efficiencies of up to 4.9% (Curve III) were achieved after photoetching the annealed films in 1.0 N HCl. *I–V* characteristics of the cells, fabricated using 17 cm^2 titanium substrates are shown in Fig. 8. Curve I, Curve II and Curve III show the characteristics of the as-deposited, annealed and annealed/photoetched films. The films were annealed at 650° C in argon gas containing 0.5% oxygen for 20 min. The photoetching treatments were carried out in 1.0 N HCl solution for a few seconds under 300 mV bias voltage. Table 2

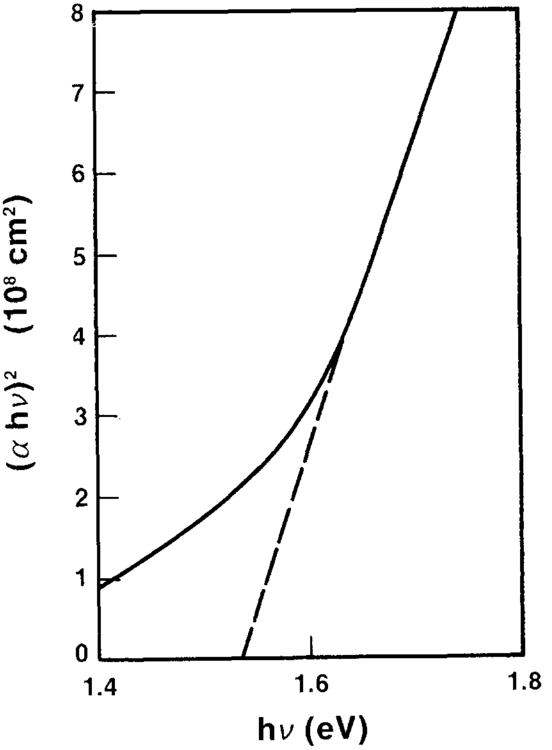

Fig. 4. Variation of $(\alpha h\nu)^2$ as a function of energy hν for a $CdSe_{0.5}Te_{0.5}$ thin film (direct bandgap).

summarizes the performance of the various photoelectrodes tested in this study. The large area cell efficiencies are significantly lower than those of cells using small area photoelectrodes. This loss in conversion efficiency could arise partially from inefficiency in carrier collections for the large area cells and from polarization losses at the counter electrode.

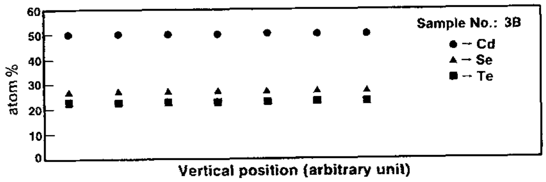

Fig. 5. Electron probe microanalysis (WDS) of a $CdSe_{0.5}Te_{0.5}$ thin film. Sample 3A: average Cd, 49.96 ± 3.21; average Te, 22.93 ± 1.47; average Se, 27.11 ± 1.74. Sample 3B: average Cd, 50.28 ± 2.55; average Te, 23.44 ± 1.19; average Se, 26.28 ± 1.33. (All values in atom %.)

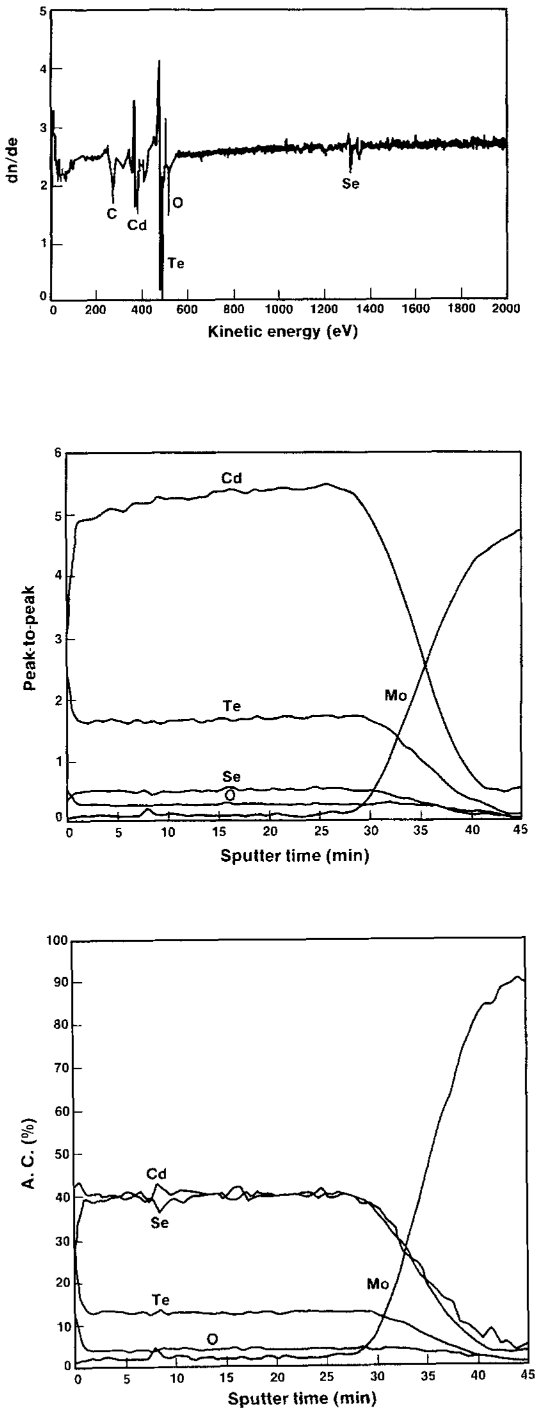

Fig. 6. (a) Auger electron spectrum of an electrodeposited $CdSe_{0.5}Te_{0.5}$ thin film on molybdenum substrate. (b) Auger depth profile (peak-to-peak height) of an electrodeposited $CdSe_{0.5}Te_{0.5}$ thin film on molybdenum substrate. (c) Auger depth profile (atom concentration) of an electrodeposited $CdSe_{0.5}Te_{0.5}$ thin film on molybdenum substrate.

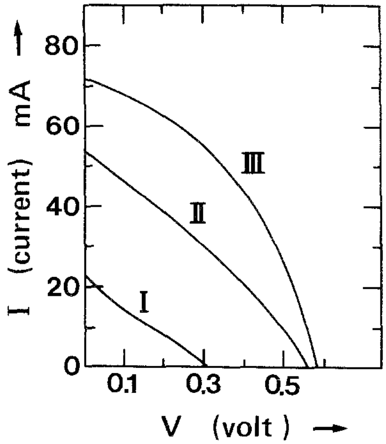

Fig. 7. *I–V* characteristics for electrodeposited $CdSe_{0.5}Te_{0.5}$ thin film deposited on titanium substrates (area: 4.5 cm^2). I, the as-deposited film; II, annealed film; III, annealed and photoetched film.

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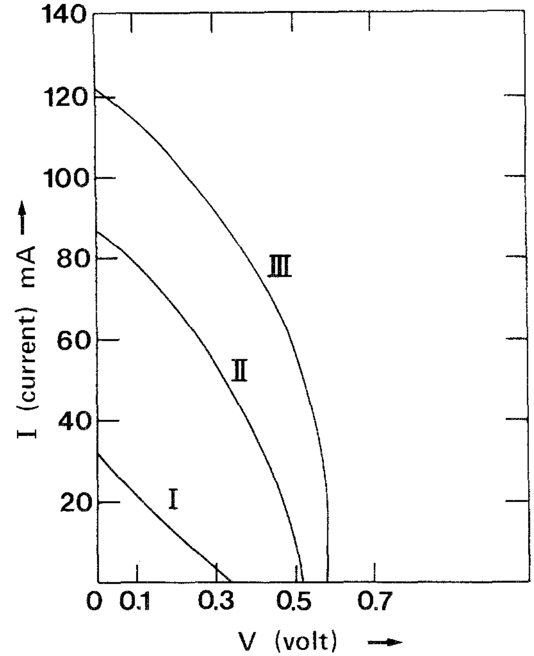

Fig. 8. *I–V* characteristic for electrodeposited $CdSe_{0.5}Te_{0.5}$ thin film deposited on titanium substrates (area: 17 cm^2). I, the as-deposited film; II, annealed film; III, annealed and phtoetched film.

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Table 2. Performance of the photoelectrodes in the PEC cell systems

Substrates	*Electrodes*	J_{sc} (*mA*)	V_{oc} (*Volts*)	*Fill factor*	*Efficiency*
Titanium (area: 4.5 cm^2)	As-deposited films	23	0.3	0.25	0.47
	Annealed films*	54	0.56	0.30	2.52
	Annealed (as above) and photoetched under 300 mV bias voltage in 1 N HCl	71	0.58	0.43	4.9
Titanium (area: 17 cm^2)	As-deposited films	33	0.32	0.24	0.18
	Annealed films†	87	0.53	0.28	1.0
	Annealed (as above) and photoetched under 300 mV bias voltage in 1 N HCl	122	0.57	0.40	2

* Annealed in argon gas containing 0.5% oxygen for 15 min at a temperature of 650° C.
† Annealed in argon gas containing 0.5% oxygen for 20 min at a temperature of 650° C.

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