

## PHOTOELECTROCHEMICAL STUDIES ON POLYCRYSTALLINE CdS (CHEMICAL BATH DEPOSITION) AND CdSe (CHEMICAL BATH AND ELECTRO DEPOSITION) THIN FILM ELECTRODES

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### Summary

The photoelectrochemical behaviour of polycrystalline CdS and CdSe thin film electrodes prepared by a chemical bath deposition (CBD) method has been examined in an aqueous sulfide-polysulphide electrolyte. The open circuit voltage, short circuit current, flat band potentials, and efficiencies are reported. The CBD technique is simple and promising for the preparation of polycrystalline metal chalcogenides. The behaviour of CdSe prepared by electrodeposition has also been examined.

### 1. Introduction

In recent years, there has been considerable activity in the study of photoelectrochemical (PEC) solar cells containing a semiconductor/electrolyte junction [1 - 5]. Semiconductors have been used either as single crystals or in the polycrystalline form [4, 5]. While measurements on single crystals are undoubtedly reliable, polycrystalline materials have been found to yield efficiencies close to that of single crystal values and might prove economical. Polycrystalline thin film electrodes, mainly CdS and CdSe, are usually prepared by either chemical vapour deposition, spray pyrolysis, electrochemical deposition or vacuum evaporation. Miller and Heller [6] first reported the formation of CdS by anodisation of cadmium sheet in Na<sub>2</sub>S. The CdS films have also been deposited cathodically from aqueous electrolytes containing Cd<sup>2+</sup> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Recently, Tsou and Cleveland [7], using CdS thin films prepared by spray and vacuum deposition techniques in PEC cells, obtained power conversion efficiencies in the range 0.038 - 0.054%.

Russak *et al.* [8] reported 5% efficiency for CdSe thin film electrodes prepared by co-deposition of Cd and Se metal by vacuum evaporation, and films prepared by spray pyrolysis techniques achieved 5.2% efficiency [9].

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Recently, Miller and Haneman [10] prepared CdSe thin films on Ti and Ni substrates by cathodic electrodeposition from a stirred electrolyte solution containing HCl, CdCl<sub>2</sub> and SeO<sub>2</sub> with a carbon counter electrode, and achieved efficiencies of about 3%. A method in which a slurry of CdSe semiconductor is painted onto a substrate and sintered at 400 °C has been examined recently [11, 12]. A chemical bath deposition (CBD) technique, originally proposed by Kitaev and co-workers [13, 14] and extended by Chopra *et al.* [15], has been employed by many workers. Efficiencies in the range 0.011 - 5.5% have been reported for PEC cells with an aqueous electrolyte [16 - 18]. Recently, however, the CBD method has been improved to enable large area CdSe semiconducting films to be produced [19].

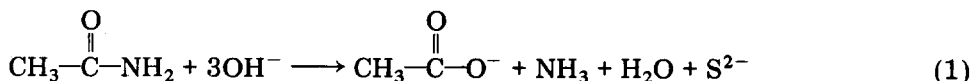
In this paper we report the results of studies of the photoelectrochemical behaviour of cells containing electrodes prepared by the CBD technique. We also compare the performance of a PEC cell containing anodically deposited CdSe with one containing CdSe prepared by CBD.

## 2. Experimental

### *Chemical bath deposition (CBD) of CdS and CdSe*

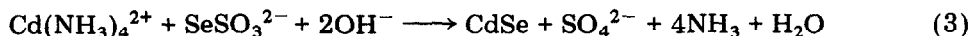
The thin film deposition of CdS and CdSe was completed in a glass beaker containing the reaction mixture. The substrates used were (2 cm × 5 cm) plates, of either SnO<sub>2</sub>-coated glass or titanium, which had to be suspended along the wall of the beaker. The reaction mixture was thermostatically controlled and stirred continuously to ensure a uniform deposition. The CdS thin films were prepared on a titanium substrate by a modification of the method proposed by Pavaskar *et al.* [20].

For each deposition, 10 ml of CdSO<sub>4</sub> (1.0M) and 50 ml of 2.0M ammonia were mixed in a 250 ml beaker to form Cd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, to which 10 ml of 0.5M thioacetamide solution was added. The reaction mixture was stirred at a constant temperature of 80 - 85 °C, and the thin films were deposited in about 45 min on substrates which had been cleaned by boiling in 0.1M H<sub>2</sub>SO<sub>4</sub> and washed in double distilled water. After deposition had been completed the films on the substrates were then washed several times in more double distilled water before being dried and stored in a desiccator. The reaction mechanism for the formation of CdS from thioacetamide and Cd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> is:



The constant, 80 - 90 °C, temperature, and clean substrates were essential to ensure a uniform coating.

Polycrystalline CdSe thin films were prepared by the CBD technique described by Fofanov and Kitaev [13]. The reaction mixture consisted of 10 ml of CdSO<sub>4</sub> (0.2M), 20 ml of NH<sub>4</sub>OH (0.5M), 10 ml of sodium selenosulphate (0.2M) with 10 ml of 0.1M Na<sub>2</sub>SO<sub>4</sub> added and maintained at a pH between 11 and 12. The substrates to be deposited were immersed in the solution which was again stirred and maintained at a temperature between 80 and 85 °C. A thin film of CdSe was deposited on the substrates after about 30 min. According to the reaction scheme (eqn. (3)), SeSO<sub>3</sub><sup>2-</sup> undergoes rapid hydrolysis to give Se<sup>2-</sup>, which reacts with Cd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> to precipitate CdSe. By suppressing the hydrolysis of SeSO<sub>3</sub><sup>2-</sup> (eqn. (4)) by the addition of Na<sub>2</sub>SO<sub>4</sub>, however, the formation of Se<sup>2-</sup> could be controlled and the deposition rate of the CdSe reduced.



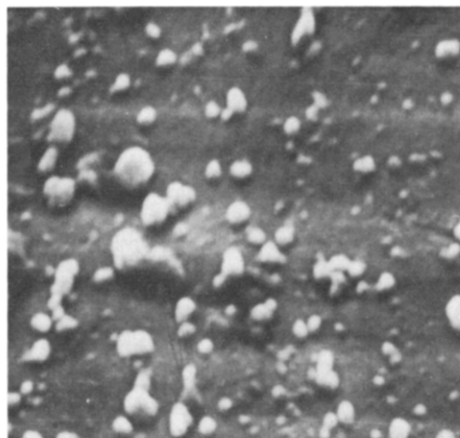
Similar observations were made by Fofanov and Kitaev [13] in the deposition of lead chalcogenides. The CdSe electrodes thus prepared were washed thoroughly, dried at 100 °C, and stored in a desiccator.

#### *Electrodeposition of CdSe thin films*

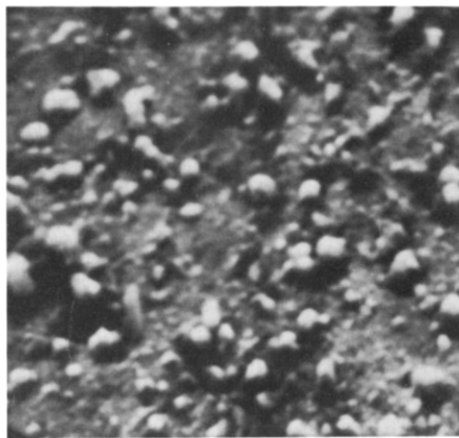
Hodes *et al.* [21] first reported the cathodic deposition of CdSe from an aqueous solution containing Cd<sup>2+</sup> and SeO<sub>2</sub> in acid medium. Later, Tomkiewicz *et al.* [22], studied the performance of cathodically deposited CdSe films in liquid junction solar cells. The reaction sequence for the formation of CdSe by the reduction of H<sub>2</sub>SeO<sub>3</sub> in the presence of Cd<sup>2+</sup> in 0.1M H<sub>2</sub>SO<sub>4</sub> has also been reported by Kazacos and Miller [23], but the performance of this type of electrode was not reproducible and they are unsuitable for use in PEC cells. Recently, Boudreau and Kauh [24] pointed out that the concentration of Cd<sup>2+</sup>, H<sub>2</sub>SeO<sub>3</sub>, and the current density are highly critical parameters in obtaining a stoichiometric CdSe film using cathodic deposition.

In the following, we present a method for the anodic formation of CdSe in which the above parameters are not critical. The first step in the anodic formation of CdSe is to plate cadmium metal on to a cleaned titanium electrode. It was found that a solution containing 20 ml of 0.02M CdSO<sub>4</sub>, 10 ml of 0.1M ethylenediaminetetraacetic acid (EDTA) and 0.1% gelatin gave a uniform, bright, polycrystalline coating of cadmium after passing 10 mA/cm<sup>2</sup> for 20 min. The surface layer was then converted to CdSe by anodizing it for 10 min at +0.6 V with respect to a saturated calomel electrode (SCE) in 2M KOH saturated with selenium. Excess selenium, which passivates the electrode surface, was removed by washing the electrode with a hot 1M KOH solution and then with a 1M Na<sub>2</sub>S solution. Finally, the electrodes were washed with double distilled water, dried at 100 °C and stored in a desiccator.

The thickness of the CdS and the CdSe films was estimated to be 1 - 10  $\mu\text{m}$ , based on the weight gain of the substrates during deposition. The CdS and CdSe films were uniform and adhered strongly to the substrate and resisted abrasion. The 'd' values were calculated from the X-ray diffraction patterns for CdS and CdSe; they corresponded to an hexagonal phase for CdS, and a mixed phase consisting of hexagonal and cubic phases for CdSe. The scanning electron micrographs of the CdS and the CdSe films (Fig. 1(a), (b)) showed that the surface was uniform without any voids or cracks. The scanning electron micrographs of the CdS and CdSe surfaces (Fig. 1(c), (d)) following heat treatment at 300  $^{\circ}\text{C}$  for five hours in an inert atmosphere



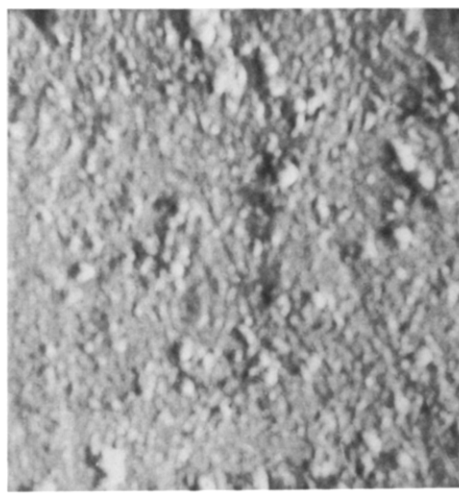
(a)



(b)



(c)



(d)

**Fig. 1. Scanning electron micrographs. (a) CdS, (b) CdSe, films prepared by chemical bath deposition; (c) CdS, (d) CdSe, films after heat treatment at 400  $^{\circ}\text{C}$  for 2 h ( $10^{-3}$  Torr).**

showed that the grain size had increased. The heat treatment also increased the adherence of the films to their substrate.

For the electrochemical measurements, the  $I$ - $V$  curves were obtained using an activated carbon sheet (3 cm  $\times$  5 cm) counter electrode. The electrolyte was a solution of 1M NaOH, 0.5M Na<sub>2</sub>S and 0.5M S for the CdS cells [2]. With the CdSe PEC cells, however, the electrolyte also included 0.05M Se, as this was found to protect the CdSe electrode from photocorrosion.

For the photoelectrochemical measurements, a conventional three-electrode system was used, with a semiconductor working electrode, a platinum foil counter electrode and an SCE reference electrode [25]. All the measurements were made at room temperature under a nitrogen blanket. The semiconductor thin film electrode was illuminated through an optically flat Pyrex window. The cyclic voltammetry was semi-automated using a ramp function generator and an X-Y recorder [25], although the cell potential and currents were monitored with a digital multimeter.

### 3. Results and discussion

#### *CdS PEC cell*

The potentiostatic current-voltage curves of CdS thin film electrodes in the dark and under illumination in polysulfide-sulfide electrolyte are shown in Fig. 2. It can be seen that appreciable currents were measured with no illumination above  $-0.8$  V with respect to SCE (Fig. 2(c)) for an untreated electrode (before annealing and etching). It is possible that this indicates the oxidation either of the electrolyte or of the titanium substrate. The CdS thin films heated in nitrogen at 300 °C and etched in 0.1M HCl for a few seconds show much less dark current (Fig. 2(d)). The  $I$ - $V$  curves for treated and untreated electrodes under illumination are shown in Figs. 2(a)

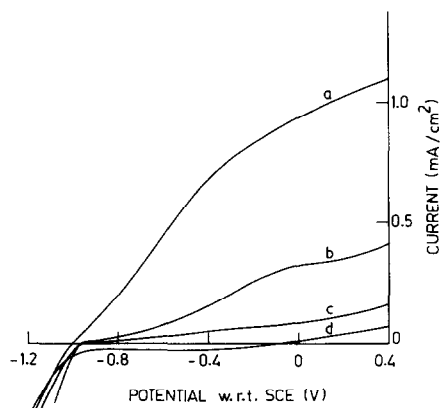


Fig. 2. Potentiostatic  $I$ - $V$  curves for thin film CdS electrodes on titanium (scan rate 5 mV/s). (a) Illuminated after heat treatment; (b) illuminated immediately after preparation; (c) in the dark immediately after preparation; (d) in the dark after heat treatment.

and (b), respectively. It can be seen that the onset of the photocurrent of an untreated electrode is not very sharp and the photocurrents are also much less than those for a treated electrode. The  $I-V$  curves of a treated CdS (Fig. 2(a)) electrode show a sharp onset of photocurrent at  $-1.05$  V with respect to SCE which can be taken as the flat band potential (defined as the potential where there is no field at the semiconductor-liquid interface) of the CdS electrode, and is comparable with the value in the same electrolyte ( $-1.2$  to  $-1.3$  V with respect to SCE) for the single crystal [2]. A black deposit of cadmium metal, due to the reduction of the CdS film, was noticed when a cathodic bias equal to, or greater than,  $-1.3$  V was applied to the thin film electrode.

The variation of the photocurrent of the etched polycrystalline CdS electrode with wavelength did not differ substantially from that of etched single crystal electrodes [2]. The maximum photo-response was found to be at about 500 nm, which corresponds to a band gap of 2.4 eV.

The stability of thin film CdS electrodes in a sulfide/polysulfide electrolyte was checked by measuring the short circuit photocurrent ( $I_{sc}$ ) and the open circuit voltage ( $V_{oc}$ ) for treated and untreated electrodes over about 10 h: the results are shown in Fig. 3. While, for the untreated electrode, the  $V_{oc}$  and  $I_{sc}$  values are 295 mV and 0.26 mA, respectively, they are 430 mV and 0.94 mA for a treated electrode. A small decrease in the  $I_{sc}$  after continuous illumination for 10 h was observed for an untreated electrode.

The power characteristics of a thin film CdS electrode in polysulfide/sulfide electrolyte using a carbon counter electrode are shown in Fig. 4. An unannealed, unetched, chemically deposited CdS film on Ti exhibits (Fig. 4(a)) a reasonable open circuit voltage of 295 mV. The fill factor (FF),

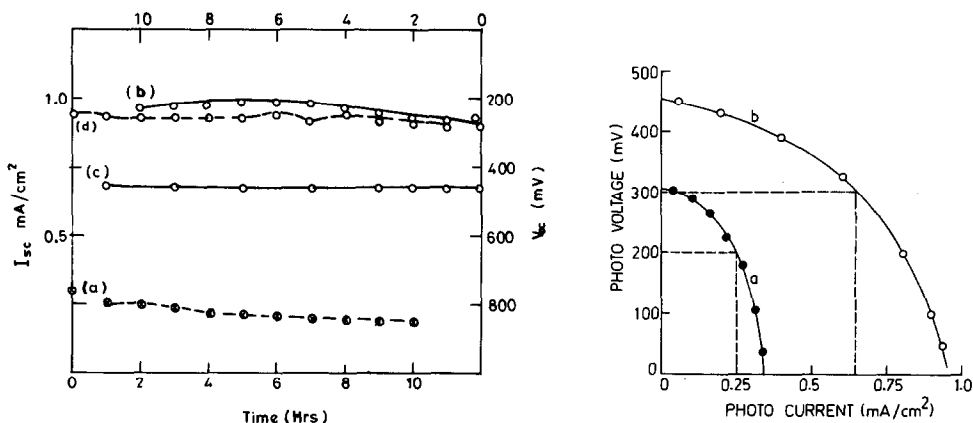


Fig. 3. Short circuit photo-current ( $I_{sc}$ ) and open circuit photo-potential ( $V_{oc}$ ) as a function of time for a CdS film. (a)  $I_{sc}$  for untreated; (b)  $V_{oc}$  for untreated; (c)  $V_{oc}$  for treated; (d)  $I_{sc}$  for treated.

Fig. 4. Power characteristics for CdS/ $\text{Na}_2\text{S}$  (0.5M), NaOH (1.0M), S (0.5M)/C PEC cell. (a) Untreated electrode; (b) treated electrode.

a characteristic parameter for a PEC cell equal to 1 for an ideal semi-conductor/electrolyte junction, was calculated by the relation  $FF = (I \times V)_{\max} / I_{sc} \times V_{oc}$ , where  $(I \times V)_{\max}$  is the maximum power output of the cell and was found to be  $\sim 0.3$ .

On the other hand, films annealed at 300 °C and etched in 0.1M HCl for 30 s deliver a photo-potential of 455 mV and have an improved fill factor of 0.42. The estimated efficiencies of cells containing treated and untreated CdS film electrodes are 0.27 and 0.10%, respectively. These values are better than those reported by Tsou and Cleveland [7] with spray deposited (0.038%) and vacuum deposited (0.054%) CdS film PEC cells.

### CdSe PEC cell

The potentiostatic  $I$ - $V$  characteristics of thin film CdSe electrodes prepared by the chemical bath deposition method have been examined in the dark and under illumination. The results are shown in Fig. 5. The dark current for a CdSe electrode prepared by anodic deposition is as high as 1 mA/cm<sup>2</sup> at zero applied bias (Fig. 5(a)), indicating the occurrence of some electrode reactions in the dark. This electrode did not give proper  $I$ - $V$  characteristics under illumination (Fig. 5(c)), although after annealing under nitrogen atmosphere at 300 °C for 5 h and treating the surface with 1.0M ZnCl<sub>2</sub> solution there was an improvement (Fig. 5(b)). The dark current decreased from 1 mA to 20  $\mu$ A following this treatment and higher photocurrents were observed (Fig. 5(d)). The flat band potentials for anodically deposited CdSe electrodes and for thin film CdSe electrodes prepared by CBD (-1.28 V and -1.32 V with respect to SCE, respectively) are close to those reported in the literature for single crystals [8]. The CdSe films prepared by CBD, however, give much higher photocurrents and better

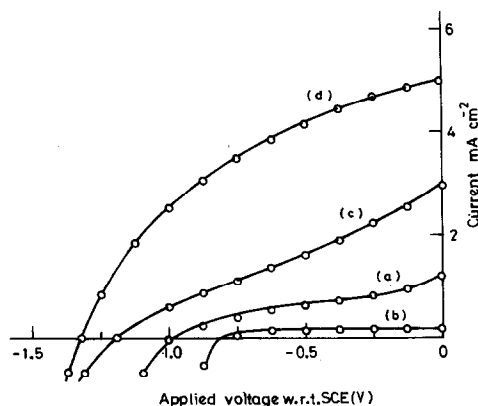


Fig. 5.  $I$ - $V$  characteristics of n-CdSe thin film electrode (prepared by electrochemical deposition). (a) Untreated electrode in the dark; (b) treated electrode in the dark; (c) untreated electrode under illumination; (d) treated electrode under illumination.

potentiostatic  $I$ - $V$  characteristics than the anodically formed CdSe thin films.

The spectral response of CdSe electrodes prepared by both techniques, after surface treatment and annealing, was similar, although the photo-response of the CdSe electrodes prepared by the CBD technique was better. The electrodes did not respond to wavelengths below 475 nm; possibly because of electrolyte adsorption. Maximum photo-response was observed at around 700 - 715 nm, which corresponds to a band gap of about 1.7 eV.

The characteristics of a range of PEC cells with thin film CdSe electrodes prepared by CBD and by anodic deposition are shown in Table 1 at different stages of preparation. It can be seen that the open circuit photo-voltage and short circuit photo-current of those prepared by CBD, after annealing and surface treatment, are higher than those formed anodically, after similar treatment. The 1.95% efficiency obtained in this investigation for polycrystalline PEC cells is comparable with those CdSe electrodes prepared by other methods.

TABLE 1

Characteristics of PEC cells with CdSe thin film electrodes prepared by two different methods

	Chemical bath deposition			Anodic deposition		
	Immediately after preparation	After annealing	After annealing and etching	Immediately after preparation	After annealing	After annealing and etching
$V_{oc}$ (mV)	312	415	510	315	430	440
$I_{sc}$ (mA/cm <sup>2</sup> )	2.95	4.10	5.02	1.45	2.50	2.80
$P$ (mW/cm <sup>2</sup> )	0.13	0.52	0.98	0.08	0.36	0.45
Fill factor	0.14	0.31	0.39	0.18	0.34	0.37
Efficiency (%)	0.27	1.02	1.95	0.16	0.74	0.90

The results obtained on PEC cells containing CdS and CdSe thin film electrodes demonstrate that the CED technique is a promising method for obtaining better quality films for use in PEC cells. The method is simple and less time consuming. Annealing and etching the films help improve the efficiencies, probably because of increased grain size and decreased film resistance.

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