SHORT COMMUNICATION

Cd(SeTe) septum photoelectrochemical cells

K. R. MURALI, V. SUBRAMANIAN, N. RANGARAJAN, A. S. LAKSHMANAN, S. K. RANGARAJAN

Central Electrochemical Research Institute, Karaikudi 623 006, India

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1. Introduction

The construction of semiconductor septum cells emerges from the idea of a pigmented bilayer lipid membrane (BLM) separating two aqueous solutions containing redox agents [1, 2]. However, from a practical point of view, the efficiencies reached with such systems are very low (below 0.1%). Attempts have been made to improve the system by using polycrystalline semiconductors in place of pigmented BLM [3]. Earlier reports on septum cells were based on CdSe in pellet form or slurry coated films [4, 5]. Septum cells based on electrodeposited Cd(SeTe) films are reported here for the first time.

2. Experimental details

The films used in this work were prepared by a selective plating technique from an electrolyte containing 0.1 M $CdSO_4$, 0.066 M SeO_2 and 0.033 M TeO_2, on conducting SnO_2 and titanium substrates. The films were adherent and had a thickness around 5.0 μm. They were annealed in argon for 20 min at 550° C and were further annealed at 300° C under a vacuum of 10^{-6} Torr for 30 min.

Diffuse reflectance measurements on the films were made using a Hitachi U3400 UV–VIS–NIR spectrophotometer. The films were characterised by X-ray diffraction studies using CuK_α radiation and surface morphology was examined by a 35 CF JEOL scanning electron microscope.

A schematic of the septum cell is shown in Fig. 1. The septum of Cd(SeTe) film on titanium substrate (5 cm^2) was positioned firmly in a groove in the PVC cell with PVC solution. The solvent was allowed to evaporate. After drying, 1 M alkaline polysulphide was added to one compartment (photoexposed side) and different electrolytes $CdCl_2$, $CuSO_4$, $CuCl_2$ and $Cu(NO_3)_2$ to the other. Graphite was used as the counter electrode on the photoexposed side and either graphite, platinum, copper or cadmium was used as electrode on the other. Digital HIL meters were used for the measurement of current and voltage. The light source was a 250 W ORIEL tungsten halogen lamp. The photon flux was measured by a CEL Suryamapi.

3. Results and discussion

Among the film compositions prepared that corresponding to hexagonal polycrystalline $CdSe_{0.21}Te_{0.79}$, having a band gap of 1.45 eV, gave the best output in the conventional PEC cell.

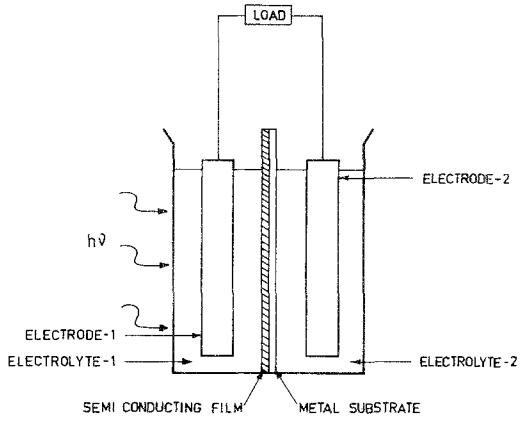

Fig. 1. Schematic of a septum cell.

Structure and composition were determined from X-ray data (Fig. 2) and applying Vegard's law. The band gap was deduced from optical absorbance measurements. Hence a composition of $CdSe_{0.21}Te_{0.79}$ was used throughout for the fabrication of septums.

The SEM (Fig. 3) showed a smooth and uniform surface with a grain size distribution around 1.0 μm.

The resistivity of the as deposited films was found to be around 120 Ω cm. The heat-treated films showed a resistivity around 20 Ω cm.

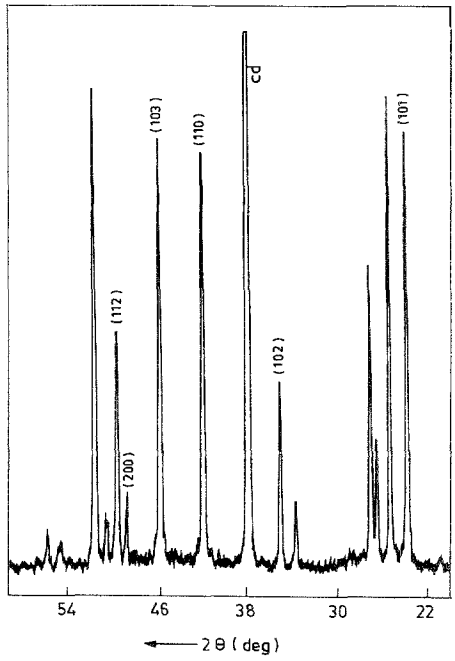

Fig. 2. X-ray diffractogram of $CdSe_xTe_{1-x}$ film.

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Table 1. Output parameters of $CdSe_{0.21}Te_{0.79}$ septum. Intensity: 45 mW cm^{-2}.

System	I_d (*mA*)	V_d (*mV*)	I_l (*mA*)	V_l (*mV*)	V_{oc} (*mV*)	I_{sc} (*mA*)	J_{sc} (*mA cm^{-2}*)
C|0.5 M $CdCl_2$|Ti|Cd(SeTe)|PS|C	−0.8	−700	1.15	517	1217	1.95	0.39
Pt|0.5 M $CdCl_2$|Ti|Cd(SeTe)|PS|C	−0.2	−735	0.51	520	1255	0.71	0.14
Cd|0.5 M $CdCl_2$|Ti|Cd(SeTe)|PS|C	−2.5	−380	6.3	650	1030	8.8	1.80
C|0.5 M $CuCl_2$|Ti|Cd(SeTe)|PS|C	−1.2	−90	1.65	240	330	2.85	0.57
Pt|0.5 M $CuCl_2$|Ti|Cd(SeTe)|PS|C	−0.5	−160	0.54	130	290	1.04	0.21
Cu|0.5 M $CuCl_2$|Ti|Cd(SeTe)|PS|C	−3.2	−290	9.55	590	880	12.75	2.55
C|0.5 M $CuSO_4$|Ti|Cd(SeTe)|PS|C	−0.01	−250	0.39	60	310	0.40	0.08
Pt|0.5 M $CuSO_4$|Ti|Cd(SeTe)|PS|C	−0.08	−225	0.167	70	295	0.247	0.05
Cu|0.5 M $CuSO_4$|Ti|Cd(SeTe)|PS|C	−2.1	−10	4.4	290	300	6.5	1.3
C|0.5 M $Cu(NO_3)_2$|Ti|Cd(SeTe)|PS|C	−0.2	−140	0.5	16	156	0.7	0.14
Pt|0.5 M $Cu(NO_3)_2$|Ti|Cd(SeTe)|PS|C	−0.08	−150	0.2	15	165	0.28	0.06
Cu|0.5 M $Cu(NO_3)_2$|Ti|Cd(SeTe)|PS|C	−1.0	−25	2.6	180	205	3.6	0.72

PS = 1 M polysulphide
$V_{oc} = V_l - V_d$; $I_{sc} = I_l - I_d$.

When the Cd(SeTe) film-electrolyte interface is illuminated, electron-hole pairs are generated. The electrons move through the bulk of the n-type semiconductor and the titanium substrate and reach the other compartment. There the electrons reduce metal ions to the metal. This process can be used to recover precious metals from industrial wastes. The hole, on the other hand, travels to the surface of the semiconductor and oxidizes the sulphide ions. The photovoltage and photocurrent values with different metal salt solutions in the second compartment are given in Table 1. A photovoltage as high as 1.03 V and a photocurrent density of 1.80 mA cm^{-2} were obtained when Cd/$CdCl_2$ was used in the second compartment. It is observed that the photovoltage obtained with platinum, graphite or the respective metal electrodes contacting the electrolyte in the second compartment does not follow a systematic variation. However, the photocurrent was found to be highest when the electrode was reversible to the cation in solution. Of the graphite and platinum electrodes, the former yielded a higher photocurrent output.

When Cu/$CuCl_2$ was used in the second compartment, copper deposition was observed on the Ti surface facing the $CuCl_2$ solution and it was found that the copper electrode had turned slightly greyish, indicating the probable formation of copper oxide.

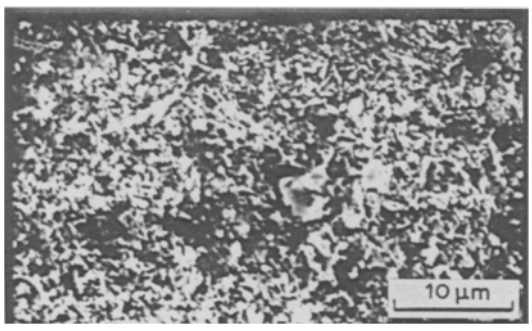

Fig. 3. SEM of $CdSe_{0.21}Te_{0.79}$ film.

Table 2. Effect of photoetching: [Cd\|$CdCl_2$\|Ti\|$CdSe_xTe_{1-x}$\|polysulphide\|C]

Duration of photoetching (*s*)	V_{oc} (*mV*)	J_{sc} (*mA cm^{-2}*)
0	1.03	1.8
15	1.075	1.9
30	1.1	2.02
45	1.2	2.12
60	1.3	2.24

The load characteristics of the cell with the following configuration is shown in Fig. 4.

C\|polysulphide\|CdSeTe\|Ti\|$CuCl_2$\|Cu

A fill factor of 0.32, V_{oc} of 0.83 V, J_{sc} of 2.53 mA cm^{-2} and efficiency of 1.49% were obtained under an illumination of 45 mW cm^{-2}.

The output of the septum cell after photoetching in 1 : 5 HCl for different times in the range 15–60 s is shown in Table 2. Both V_{oc} and I_{sc} increase gradually with increase in photoetching time. A 60 s photoetch yielded a 24% increase in photocurrent and a 26%

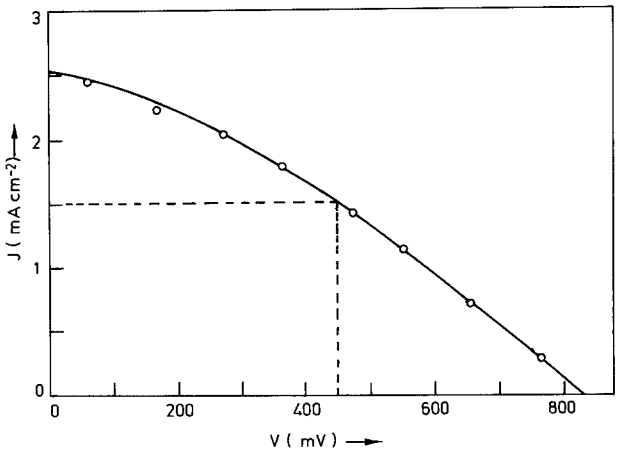

Fig. 4. Load characteristics of the cell under illumination: FF = 0.32, ΔV_{oc} = 830 mV, ΔJ_{sc} = 2.53 mA cm^{-2}, η = 1.49%.

increase in photovoltage. This increase may be attributed to the increase in photoresponse of the semiconductor electrode with increase in photoetching time.

The septum cell of the configuration mentioned earlier was tested under sunlight for 15 days. Negligible variation in the approximate photo-output for daylight hours for the length of period studied was noticed indicating good electrode stability. Long term stability studies are planned.

4. Conclusion

Electrodeposited $CdSe_xTe_{1-x}$ films are shown to be promising semiconductor septum electrodes. Further work to improve the efficiency of the light conversion capability of the system is in progress.

References

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