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### RESEARCH ARTICLE

#### PHOTOELECTROCHEMICAL SOLAR CELL APPLICATIONS OF CHEMICALLY DEPOSITED $Cd_{1-x}Mn_xS$ THIN FILMS

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#### Abstract

The  $Cd_{1-x}Mn_xS$  thin films were deposited by simple and cost-effective chemical bath deposition method. A photoelectrochemical (PEC) solar cell with configuration  $Cd_{1-x}Mn_xS | 1M (NaOH-Na_2S- S) | C$  is formed. The photo-voltage increases with polarity negative towards the  $Cd_{1-x}Mn_xS$  electrode, showing that  $Cd_{1-x}Mn_xS$  is of n-type semiconductor. The capacitance-voltage measurements give useful information regarding the donor concentration ( $N_D$ ) and type of conductivity. The values of  $V_{fb}$  varies from -750 mV to -850 mV. The junction ideality factors under light are calculated from the slope of the plot  $\log I$  against  $V$ , and have values from 1.86 to 1.53 for ITO substrates. The series and shunt resistances are found to be 296  $\Omega$  and 1.83 k $\Omega$  respectively for  $x = 0.6$

**Keywords:** PEC,  $Cd_{1-x}Mn_xS$  thin films, flat band potential, Ideality factor.

#### Introduction

Photoelectrochemical (PEC) cells of various designs have been used to convert solar energy into suitable forms for more efficient use (Mureramanzi and Tien 1986; Kalyanasundaram 1985; Gerischer 1979; Sawant *et al.*, 2007; Gratzel and Bunsenges 1980; Rajpure and Rajpure 2000). It is an alternative to the commercially available solid state junction photovoltaic cells for the direct conversion of sunlight

into electrical energy (Fujishima and Honda 1972; Gerischer 1982). Photoelectrochemical (PEC) cells have been widely studied for solar as well as non-solar applications. Cadmium chalcogenides in the form of single crystals, sintered pellets and polycrystalline materials have been employed in PEC cells (Pawar *et al.*, 2006). The efficiency and stability of PEC cells are strongly dependent on the preparation conditions of the photoelectrodes, electrolytes and on experimental conditions (Yadav *et al.*, 2008). These cells are simple in construction and

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have the advantage that they can be used for both electrical and chemical energy conversions. The basic requirement of a good PEC cell is thin film photoelectrode of low resistivity and of large grain size (Das and Damodare 1997). The large grain size leads to reduction of grain boundary area of thin films with important consequences for efficient energy conversion. The low resistivity of the photoelectrode minimizes the series resistance of the PEC cell.

### Experimental details

The polysulphide electrolyte solution was prepared in an aqueous medium. The basic ingredients used for the preparation of solution were as follows:

- (i) A. R. Grade Sodium sulphide ( $\text{Na}_2\text{S}$ ) supplied by S. d. fine Chem. Ltd., Boisar, Mumbai.
- (ii) A. R. Grade Sulphur powder (S) supplied by S. d. fine Chem. Ltd., Boisar, Mumbai.
- (iii) A. R. Grade Sodium hydroxide (NaOH) supplied by S. d. fine Chem. Ltd., Boisar, Mumbai.

One molar polysulphide electrolyte was made in double distilled water by adding appropriate amounts of sodium hydroxide and sodium sulphide at room temperature. In this solution, sulphur was added and mixture was stirred rigorously. Then mixture was filtered and stored in an air sealed bottle. The colour of the final solution was yellowish pink.

### Construction of photoelectrochemical (PEC) solar cell

A photoelectrochemical solar cell was fabricated using a standard three electrode configuration with  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  thin film as an active photoanode of area  $1 \times 1 \text{ cm}^2$ , graphite as counter electrode and standard calomel electrode (SCE) as a reference electrode. The redox electrolyte used was aqueous 1M polysulphide ( $\text{NaOH} + \text{Na}_2\text{S} + \text{S}$ ). A 100 W tungsten filament lamp was used as a light source. To prevent heating of the cell, water lens was interposed between the lamp and the cell. The distance between the photoanode and counter electrode was kept 0.3 cm.

## Results and Discussion

### Conductivity type

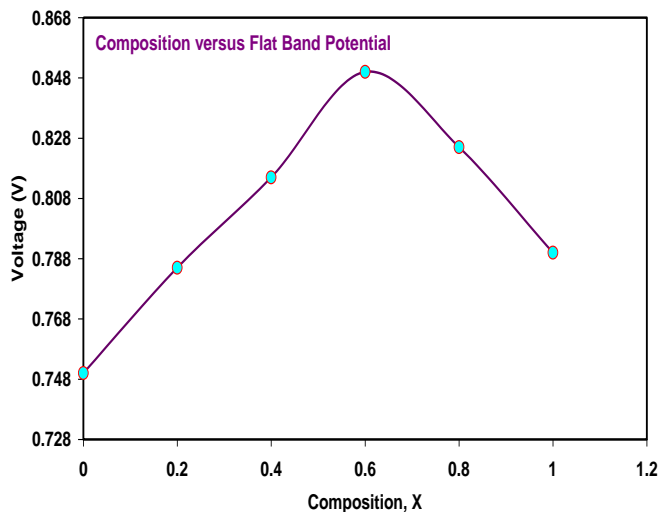
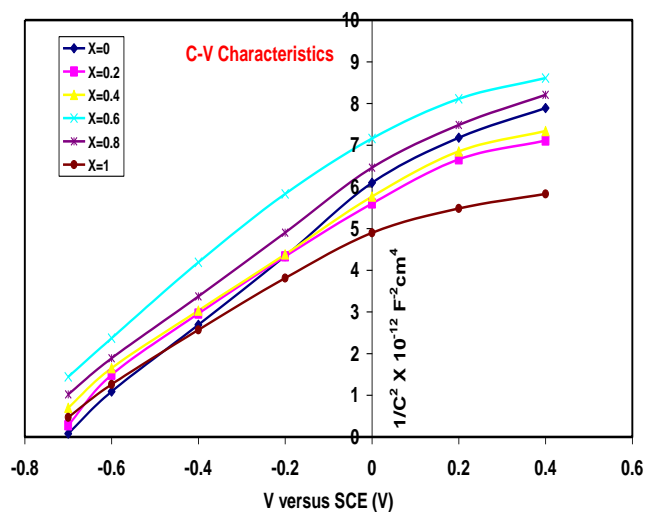
A photoelectrochemical (PEC) solar cell with configuration  $\text{Cd}_{1-x}\text{Mn}_x\text{S} | 1\text{M} (\text{NaOH}-\text{Na}_2\text{S}-\text{S}) | \text{C}$  is formed in order to check the type of conductivity exhibited by  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  thin films. It is observed that even in dark, PEC cell gives some dark voltage  $V_d$ . The polarity of this voltage is negative towards the  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  photoelectrode. The origin of this voltage is attributed to the difference between two half cell potentials in the PEC cell ( Chandra and Pandya 1982). When the junction is illuminated photovoltage increases with polarity negative towards the  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  electrode, showing that  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  is of n-type semiconductor (Janzen 1978).

### Capacitance-voltage (C-V) characteristics

The capacitance-voltage measurements give useful information regarding the donor concentration ( $N_D$ ) and type of conductivity exhibited by the film. Fig. 1 represents the Mott-Schottky (MS) plots of the n-  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  / sulphide / polysulphide electrolyte system for ITO coated glass substrate based PEC solar cells in the dark. The value of flat-band potential ( $V_{fb}$ ), which is the measure of maximum open-circuit voltage attainable from the cell and gives the information of the relative positions of the Fermi levels of the semiconductor and the electrolyte in terms of the band bending caused by surface interactions (Gerischer 1961) has obtained at  $1/C_s^2 = 0$  on the potential axis according to the well known Mott-Schottky relation.

$$\frac{1}{C_s^2} = \left[ \frac{2}{\epsilon_0 \epsilon_s q N_D} \right] \left[ V - V_{fb} - \left( \frac{kT}{q} \right) \right]$$

where  $C_s$  is the space charge capacitance,  $V_{fb}$  is the flat band potential,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_s$  is the static permittivity of the semiconductor and  $N_D$  is the donor concentration and  $q$  is the charge on electrons. The variation of  $V_{fb}$  with composition parameter 'x' is shown in Fig. 2. The values of  $V_{fb}$  varies from -750 mV to -850 mV.



**Fig. 1:** Mott-Schottky plots  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  ( $0.0 \leq x \leq 1.0$ ) / 1M polysulphide / C photoelectrochemical solar cell.

**Fig. 2** The variation of  $V_{fb}$  with composition parameter 'x'.

**Table 1** Photoelectrochemical performance parameters of chemical bath deposited  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  thin films.

Composition	$V_{oc}$ (mV)	$I_{sc}$ ( $\mu\text{A}$ )	$K_s$ ( $\Omega$ )	$R_{sh}$ ( $k\Omega$ )	$n_L$	$\eta\%$	ff	$V_{fb}$ (Volts)	Crystalline size from SEM (nm)
<b>X=0</b>	273	124	530	16.5	1.81	0.083	0.48	0.751	137
<b>X=0.2</b>	281	152	517	10.5	1.74	0.105	0.49	0.784	164
<b>X=0.4</b>	291	369	378	3.68	1.69	0.273	0.51	0.813	198
<b>X=0.6</b>	<b>303</b>	<b>465</b>	<b>294</b>	<b>1.84</b>	<b>1.53</b>	<b>0.382</b>	<b>0.54</b>	<b>0.851</b>	<b>212</b>
<b>X=0.8</b>	258	301	319	4.25	1.76	0.185	0.49	0.827	345
<b>X=1</b>	174	292	373	7.35	1.86	0.092	0.35	0.789	405

**I-V Characteristics of Cd<sub>1-x</sub>Mn<sub>x</sub>S photoanode:**

The current voltage (I-V) characteristics for n- Cd<sub>1-x</sub>Mn<sub>x</sub>S cells with varying composition (x) have been studied. When a semiconductor material is kept into the solution of a redox electrolyte, the motion of charge carriers occurs at semiconductor-electrolyte (S/E) interface generating the electric field at the interface.

When this interface illuminated by light of photon energy greater than optical gap of semiconductor, excess charge carriers are generated that are separated at the space charge region gives rise to open circuit voltage. This voltage acts as the driving force for further flow of electrons from semiconductor to the counter electrode whereas an electrolyte captures the holes ((Gerischer 1983; Aruchami *et al.*, 1982) The current transport mechanism through the interface can be defined by Butler-

Volmer relation [33] as

$$I=I_0 \left[ e^{\frac{(1-\beta)V_f}{RT}} \right] \left[ e^{\frac{\beta V_f}{RT}} \right]$$

Where, I<sub>0</sub> is equilibrium exchange current density, V the over voltage, β is a symmetry factor, R the universal gas constant and f is Faraday constant. When the symmetry factor (β) = 0.5, it corresponds to the presence of a symmetrical barrier height and yields a symmetrical I-V curve. When β>0.5, the I-V curves should not be symmetrical and the interface have a rectifying property called as Faradiac rectification (Gutierrez 1990).

The current –voltage characteristics of the PEC cell formed with n- Cd<sub>1-x</sub>Mn<sub>x</sub>S thin film electrodes deposited onto ITO for x=0.6 is shown in Figure 3. From these graphs it is inferred that the PEC cells act as a generator of electricity. The information of junction parameters can be obtained using a simple diode equation:

$$I=I_0 \left[ e^{\frac{eV}{nKT}} - 1 \right]$$

where,

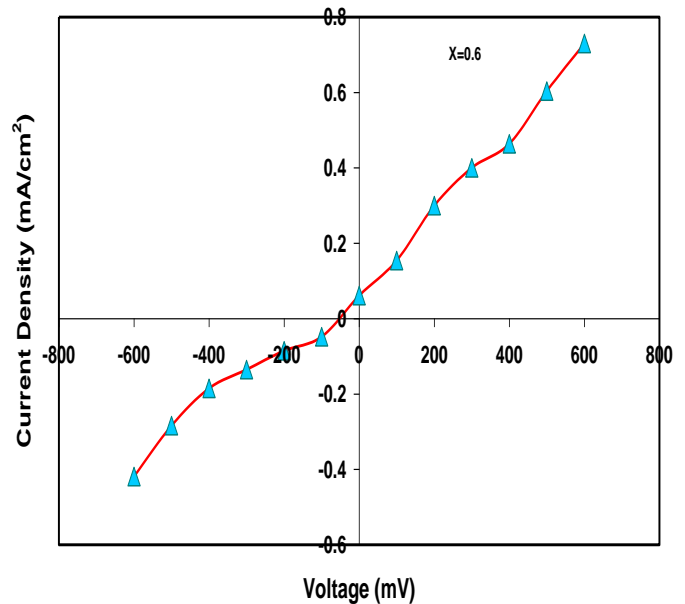
n is the junction quality factor

I<sub>0</sub> is the reverse saturation current,

V is the applied forward bias voltage and I, the forward current in dark.

Under illumination, V and I are replaced by V<sub>L</sub> and I<sub>L</sub> respectively.

The junction ideality factors under light [Figure 4] are calculated from the slope of the plot log I against V, and have values from 1.86 to 1.53 for ITO substrates. The higher value of n<sub>d</sub> is indicative of the series resistance effect and recombination mechanism at the electrolyte interface (Rajpure and Bhosale 2000; Sawant and Bhosale 2006; Coutts 1978; Lade *et al.*,2001; Deshmukh *et al.*,1990; Rajeshwar *et al.*, 1981)



**Fig. 3.** The current –voltage characteristics of n- Cd<sub>1-x</sub>Mn<sub>x</sub>S thin film electrodes deposited onto ITO for x=0.6

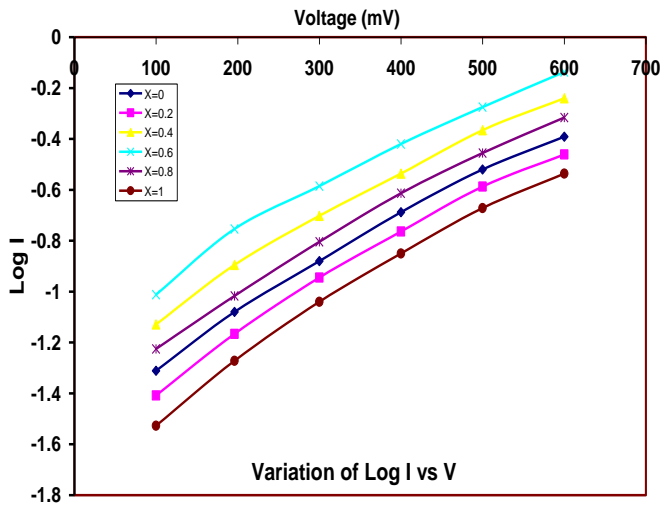


Fig. 4. The the plot log I against V of n- Cd<sub>1-x</sub>Mn<sub>x</sub>S thin film electrodes

**Photovoltaic Power Output:**

When a PEC solar cell is illuminated by means of a light of constant intensity, the current voltage characteristics shifts in fourth quadrant, and this behavior is in accordance with the theory of solar cells acting as electricity generator.

A PEC cell may operate over a wide range of voltages and currents. By increasing the resistive load on an irradiated cell continuously from zero (a short circuit) to a very high value (an open circuit), it is possible to determine the maximum power point ( P<sub>m</sub> = V<sub>m</sub> × I<sub>m</sub>), that is the load for which the cell can deliver maximum electrical power (Sankapal and Lokhande, 2001; Das and Damodare 1997; Coutts, 1978).

Photovoltaic output characteristics were studied under light intensity of 20 mW/cm<sup>2</sup>. Typical photocurrent versus photovoltage characteristics of n- Cd<sub>1-x</sub>Mn<sub>x</sub>S / polysulphide under light illumination is shown in Figure 5. It was found that both the I<sub>sc</sub> and V<sub>oc</sub> increases with increase in composition parameter ‘x’ attain a maximum values at x = 0.6 and then decrease with further increase in ‘x’.

We attribute the observed improvement to the increased short circuit current of the cell due to the increased photoelectrode absorption, decreased band gap of CdS and decrease in effective series resistance of a cell. These results are analogous to those reported by Mahapatra and Roy (Mahapatra and Roy1984) and Deshmukh et.al. for mixed materials.

The photovoltaic efficiency (η %) was calculated from the relation [45]

$$\eta = \frac{I_{sc} \times V_{oc} \times ff}{P_{input}} \times 100$$

where P<sub>input</sub> is the power density of incident radiation.

The fill factor (ff) was obtained from the formula (Coutts 1978)

$$ff = \frac{V_m \times I_m}{I_{sc} \times V_{oc}}$$

where I<sub>m</sub> and V<sub>m</sub> are values of maximum current and maximum voltage, which can be extracted from the PEC solar cell.

Series resistance R<sub>s</sub> and the shunt resistance R<sub>sh</sub> were calculated from the slopes of the power output curves using the relations (Coutts 1978; Barote 2011) and are tabulated in Table 1.

**Conclusion**

- Cd<sub>1-x</sub>Mn<sub>x</sub>S thin films were chemically deposited.
- Photoelectrochemical solar cell properties of Cd<sub>1-x</sub>Mn<sub>x</sub>S thin films were studied.
- A photoelectrochemical solar cell was fabricated using a standard three electrode configuration with Cd<sub>1-x</sub>Mn<sub>x</sub>S thin film as an active photoanode.
- It is observed that even in dark, PEC cell gives some dark voltage V<sub>d</sub>.
- The values of V<sub>fb</sub> varies from -750 mV to -850 mV.
- Photovoltaic output characteristics were studied under light intensity of 20 mW/cm<sup>2</sup>.

- $I_{sc}$  and  $V_{oc}$  increases with increase in composition parameter 'x' attain a maximum value at  $x = 0.6$

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