Photoelectrochemical properties of chemically deposited $Cd_{1-x}Mn_xS$ thin films

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ABSTRACT The Photoelectrochemical (PEC) properties of chemically deposited $Cd1_{-x}Mn_xS$ ($0 \leq x \leq 1$) thin films have been studied to convert solar energy into electrical energy. $Cd_{1-x}Mn_xS$ acts as photo anode inPhotoelectrochemical cells.PEC cell of configuration $Cd_{1-x}Mn_xS$ /1M ($NaOH+Na_2S+S$)/C is fabricated to study the I-V characteristics in dark and under illumination and capacitance voltage C-V characteristics in dark at room temperature. The photovoltaic power output curves have been obtained under illumination ($20mW/cm^2$). As composition x increases V_{oc} and I_{sc} was also increased and attains maximum at x = 0.6 and decreased thereafter. The power conversion efficiency (η) and fill factor (ff) are found to be 0.385% and 0.53 respectively for the composition x = 0.6. PEC cell parameters like series and shunt resistances (R_s and R_{sh}), junction ideality factor and flat band potential (V_{fb}) were also determined.

1. Introduction

Various semiconductor electrodes have been extensively studied for electrochemical photovoltaic in terms of sustained and efficient capture and conversion of solar energy. The properties of such systems are critically dependent on interface formed between the semiconductors [1]. Maximum utilization of solar spectrum and stability against anodic reactions forms a constraint in PEC cell over the materials selection. Hence, the efficiency and stability of PEC cell depends on the material properties, preparative conditions of the photo electrodes and electrolytes [2-3]. The recent trend is to develop low cost tailor made solar energy materials with selected combinations of these chalcogenides compounds expected to produce the desired level of Photoelectrochemical (PEC) properties such as high absorption of solar energy spectrum, compatible band gap energies. Among the several other chalcogenides, CdS and MnS have been studied extensively as individual binary components for thin film applications [4-10],

In this context, $Cd_{1-x}Mn_xS$ seems to be promising composition as its properties can be engineered to cope with the maximum utilization of solar spectrum. In present communication, we report the chemical synthesis of $Cd_{1-x}Mn_xS$ photo electrodes and their Photoelectrochemical properties with special reference to the PEC parameters.

2. Experimental details

2.1. Preparation of $Cd_{1-x}Mn_xS$ thin film electrodes

$Cd_{1-x}Mn_xS$ thin films (x= 0.2 through 1.0) was deposited on indium tin oxide (ITO) coated glass substrates. The cadmium sulphate ($CdSO_4$) used as a sources of Cd^{2+} ions and manganese sulphide ($MnSO_4$) used as a sources of Mn^{+2} ions, thiourea $(NH_2)_2CS$ is used as a source of S^{2-} ions. The ammonia (NH_3) and TEA were used as complexing agents to control the pH of the reaction. In the preparation of $Cd_{1-x}Mn_xS$ thin films, the conditions of deposition were kept same as that of CdS. However the molar value of Cd^{+2} and Mn^{+2} were varied in proportion to 1-x and x, and molar value of sulphide was kept constant throughout.

PEC cells for all compositions have been devised and characterized with special reference to the PEC parameters.

2.2. Fabrication and characterization of PEC cell

PEC cell was fabricated using a standard three electrode configuration with $Cd_{1-x}Mn_xS$ thin film as an active photoanode of area 2×2 cm^2, graphite as counter electrode and standard calomel electrode (SCE) as a reference electrode. The redox electrolyte used was aq.1M polysulphide ($NaOH+Na_2S+S$). Tungsten filament lamp of 100 W was used as a light source. The distance between the photo anode and counter electrode was kept 0.3 cm. The area of thin film that is not in contact with electrolyte was covered by insulating material. For measurement of the power output characteristics, a two electrode configuration consisting of thin film photo electrode and graphite as the counter electrode was used. Measurements for the power output characteristics and I-V plots were made at a fixed interval after waiting for sufficient time to equilibrate the system in dark as well as under illumination. The power output curves for various cell configurations were recorded under constant illumination intensity (20 mW/cm^2).

3. Results and discussion

3.1. Current-voltage characteristics

The current transport mechanism through semiconductor-electrolyte (S/E) interface can be defined by Butler-Volmer relation. Fig.1 shows I-V characteristics of $Cd_{1-x}Mn_xS$ PEC cell under illumination. The asymmetric nature of the I-V curve in forward and revere bias shows rectification property of semiconductor-electrolyte junction. Under illumination, I-V curve shift in fourth quadrant indicates proper cell functioning as electricity generator. The junction parameter in dark can be obtained by using diode equation as,

$$I = I_0(e^{qV/nkT} - 1)$$

Where the symbols have their usual meanings. Fig. 1 shows the linear behavior of I against V in dark. The n values (Table 1) were found to be higher than expected; indicating influenced current transfer across the semiconductor-electrolyte interface due to various recombination mechanisms and series resistance effect as a consequence of surface states [11].
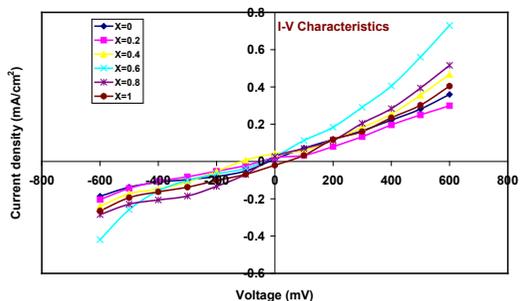
Fig. 1 I-V Characteristics of chemically deposited Cd$_{1-x}$Mn$_x$S thin film.

Table 1. Estimated important photoeletrochemical parameters for Cd$_{1-x}$Mn$_x$S thin film.

Composition	V$_{oc}$ (mV)	I$_{sc}$ (µA)	R$_s$ (Ω)	R$_{sh}$ (kΩ)	n$_L$	η%	ff	V$_{fb}$ (Volts)
X=0	275	125	533	16.0	1.80	0.084	0.49	0.750
X=0.2	280	151	516	10.2	1.72	0.108	0.51	0.785
X=0.4	292	367	375	3.63	1.68	0.277	0.52	0.815
X=0.6	**305**	**467**	**296**	**1.83**	**1.55**	**0.385**	**0.53**	**0.850**
X=0.8	260	300	321	4.20	1.74	0.187	0.48	0.825
X=1	174	294	375	7.31	1.84	0.092	0.36	0.790

3.2. Capacitance-voltage characteristics

The measurement of space charge layer capacitance with respect to applied potential is an another way of analyzing the semiconductor–electrolyte interface. Fig. 2 shows the Mott-Schottky (MS) plots of the Cd$_{1-x}$Mn$_x$S / sulphide / polysulphide electrolyte system for ITO coated glass substrate based PEC cells in the dark. The value of flat-band potential (V$_{fb}$), 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 [12], has obtained at 1/ C$_s^2$ = 0 on the potential axis according to the well known Mott-Schottky relation and values of V$_{fb}$ are tabulated in Table 1.
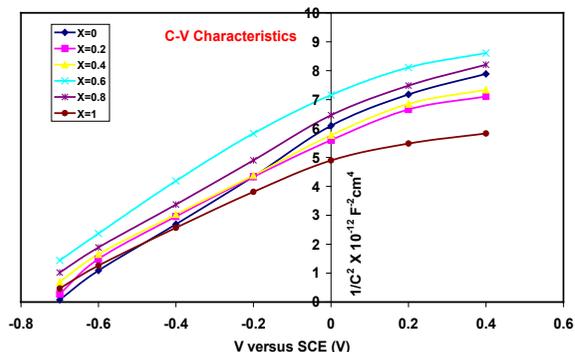

Fig. 2 shows the Mott-Schottky (MS) plots of the Cd$_{1-x}$Mn$_x$S system

3.3. Photovoltaic power output characteristics

Photovoltaic output characteristics (Fig. 3) were studied under

$$\eta = \frac{I_{sc} \times V_{oc} \times ff}{P_{input}} \times 100 \text{ Where, } P_{input} \text{ is the power density of incident radiation.}$$

$$ff = \frac{V_m \times I_m}{I_{sc} \times V_{oc}} \text{ Where, } I_m \text{ and } V_m \text{ are values of maximum current and maximum voltage.}$$
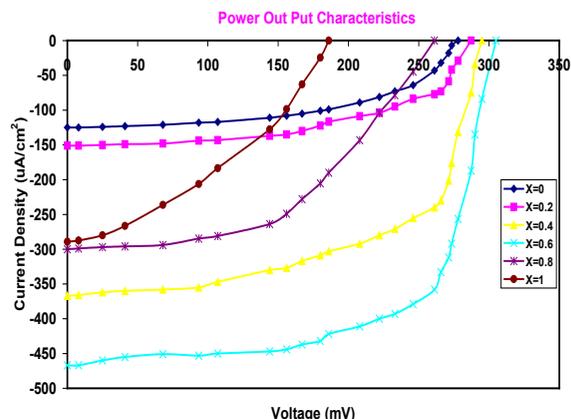

Fig. 3 Photovoltaic power output characteristics for Cd$_{1-x}$Mn$_x$S thin films

Series resistance (R$_s$) and the shunt resistance (R$_{sh}$) were calculated from the slopes of the power output curves.

$$\left[\frac{dI}{dV}\right]_{I=0} \approx \frac{1}{R_s} \quad \left[\frac{dI}{dV}\right]_{V=0} \approx \frac{1}{R_{sh}}$$

The power conversion efficiency (η) is found to increase with composition parameter 'x' up to 0.6. The synchronised increase in efficiency with increased composition may be attributed due to increase in grain size [13-14] of the film up to x = 0.6, and decrease thereafter is due to decreased grain size. The values of shunt resistances (R$_s$ and R$_{sh}$), junction ideality factor and flat band potential (V$_{fb}$) were also determined and given in Table 1.

4. Conclusion

The Cd$_{1-x}$Mn$_x$S thin films have been deposited on to conducting ITO-coated glass substrates using novel, inexpensive chemical deposition route. Efficiency and fill factor has been increased to 0.385 % and 0.53 respectively for x = 0.6. The highest value of flat band potential (850 mV) was observed for the cell with photo electrode composition equal to 0.6.

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