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PHOTOELECTROCHEMICAL PROPERTIES OF CHEMICALLY DEPOSITED CD1-XFEXS THIN FILMS.

Physics

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ABSTRACT

The photoelectrochemical properties on chemically deposited Cd1-xFexS thin films with $0 \leq x \leq 1$ have been studied to asses its suitability to convert solar energy into electrical energy. The electrode was prepared from an aqueous alkaline medium consisting of Cd2+ and Fe2+ ions simultaneously in a definite volume stoichiometric proportion. The photoelectrochemical (PEC) cell of the configuration Cd1-xFexS / 1M (NaOH + Na2S + S) / C is fabricated to study the current-voltage (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 25 mW/ cm2 light intensity and are observed that Voc and Isc increased with the photoelectrode composition 'x', attained a maximum at x = 0.3 and decreased thereafter. The power conversion efficiency (η) and fill factor (ff) are found to be 3.03% and 43.2% respectively for the composition parameter x = 0.3. The other cell parameters like barrier height (ΦB), series and shunt resistances (Rs and Rsh), diode ideality factor (n) and flat band potential (Vfb) have been determined with respect to the composition parameter 'x'. The photoelectrochemical study shows that as deposited Cd1-xFexS thin films exhibit n-type conductivity.

KEYWORDS

Photoelectrochemical cell, Cd1-xFexS electrodes, efficiency, fill factor.

INTRODUCTION

Ternary semiconductors are gaining much importance due to their wide spectrum utility in various optoelectronic devices such as IR detectors, photoconductive, photovoltaic cells, light amplification, LED's, lasers, PEC cells [1-3] and is an efficient absorbers in visible region of the solar spectrum [4]. The semiconductors CdS and FeS are highly sensitive to light radiations, so due to the practical applications, the study of the photoelectrochemical properties of their mixed thin structures has technical as well as scientific importance. In photoelectrochemical studies, the parameters like resistivity, optical band gap, optical absorption, thermoelectric power and grain size of photoelectrode material has great influence on the open circuit voltage and short circuit current of the cell [5]. The efficiency and stability of PEC cell depends strongly on choice of the material [6], preparation conditions of the photoelectrodes, electrolytes and the experimental conditions which were optimized during the experiment [7]. The composite / mixed ternary semiconductor materials efficiency convert solar energy into electrical are [8] due to the fact that properties of the ternary material can be easily tailored to the desired level by changing the composition parameter 'x' with the compositional variation of CdS and FeS in the $Cd_{1-x}Fe_xS$, it is possible to alter the optical, electrical and structural properties since these properties depend on the Cd / Fe ratio. Thus with an optimum value of the composition parameter 'x', suitably prepared $Cd_{1-x}Fe_xS$ will act as an efficient photoconductor which are extremely useful in solar cell applications [9]. Therefore, it is proposed to prepare $Cd_{1-x}Fe_xS$ thin film photoelectrodes and study their photoelectrochemical properties such as photovoltaic power output and I-V characteristics. The PEC parameters include measurement of open circuit voltage (V_{oc}), short circuit current (I_{sc}), junction ideality factor (n), fill factor (FF), conversion efficiency (η), series and shunt resistances (R_s and R_{sh}) are discussed on the basis of composition parameter 'x'.

2. Experimental details

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

The polycrystalline $Cd_{1-x}Fe_xS$ thin film photoelectrodes with $0 \leq x \leq 1$ have been prepared on fluorine doped tin oxide (FTO) coated glass substrate by simple and inexpensive chemical bath deposition method. Equimolar cadmium sulphate, iron sulphate and thiourea solutions were used as the basic source materials. All the chemicals used were of analytical reagents grade (AR). The deposition was carried out at the deposition temperature 70 ^{0}C. The ultrasonically cleaned FTO glass substrates were attached to a specially designed substrate holder and were kept rotating at a speed of 60 rpm. The deposition time selected was 60 min. After 60 min. the samples were detached from the system and preserved in dark desiccator.

2.2. Fabrication and characterization of PEC cell.

A photoelectrochemical cell was fabricated using a standard three electrode configuration with $Cd_{1-x}Fe_xS$ thin film as an active photoanode of area 1×1 cm^2, graphite as counter electrode and standard calomel electrode (SCE) as a reference electrode. The redox electrolyte used was aqueous 1M polysulphide (NaOH + Na_2S + 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 0.2 cm. The area of the semiconductor thin film other than that in contact with electrolyte was covered by insulating material to avoid any contribution due to base contact of oxide material with the electrolyte and its interface in the measured values of net photocurrent density. For measurement of the power out put characteristics, a two electrode configuration consisting of the thin film photoelectrode 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 25 mW/cm^2. The illumination intensity was measured with a (Meco) Lux meter. Various current and voltages were measured by the 61/2 digit, HP 34401. Mott-Schottky plots were plotted using LCR (Aplab model 4912) at built in frequency 1 Khz.

3. RESULTS AND DISCUSSION

3.1. Conductivity type of $Cd_{1-x}Fe_xS$ films.

Photoelectrochemical cell with configuration $Cd_{1-x}Fe_xS$ / (1M NaOH + 1M Na2S + 1M S) / graphite was formed. For all the PEC cell it is observed that even in dark, a dark voltage V_D and a dark current I_D is developed, and the polarity of this voltage is negative towards the $Cd_{1-x}Fe_xS$ electrodes. The origin of this voltage is due to the difference between two half cell potentials in PEC cells [6,10] and can be written as

$$E = E_{graphite} - E_{(Cd1-xFexS)} \quad \text{(1)}$$

Where $E_{(Cd1-xFexS)}$ and $E_{graphite}$ are half cell potentials developed on $Cd_{1-x}Fe_xS$ and graphite electrode respectively.

When the above junction is illuminated with light intensity of 25 mW/cm^2, the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were increased with negative polarity towards $Cd_{1-x}Fe_xS$ electrodes. Thus the cathodic behaviour of photovoltage of the semiconductor is observed which indicates that the chemically deposited $Cd_{1-x}Fe_xS$ films are of n-type. [11].

3.2. Current-voltage Characteristics

The current voltage relation for n- $Cd_{1-x}Fe_xS$ cells devised with a photoelectrode of varying composition parameter 'x' has been studied. When a semiconductor material is immersed into the solution of a redox electrolyte, the movement of charge 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. For n-type material, the electrons move deep into the bulk, while holes move to the surface of the semiconductor causing the redox reactions in a counter field which is maximum at the open circuit condition called '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 [12-14]. Fig.1 shows I-V characteristics of the n- $Cd_{1-x}Fe_xS$ PEC cell in dark and under illumination (25 mW/cm^2). The non-symmetric nature of the I-V curve in forward and revere bias shows the rectification property of semiconductor-electrolyte junction. Under light illumination, shift of I-V curve in the fourth quadrant indicates that the cell can work as generator of electricity. The junction parameter can be obtained by using a simple diode equation as

$$I = I_0 (e^{qv/nkT} - 1) \quad (3)$$

Where n is junction ideality factor, I_0 is the reverse saturation current, v is the applied forward bias voltage, q is the charge on electron and I is the forward current in dark.

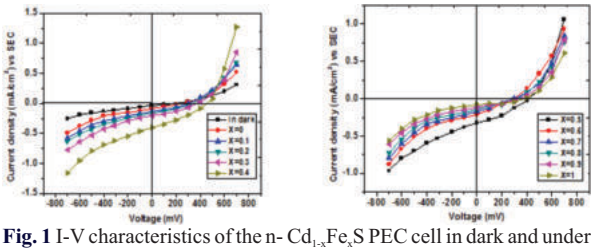

Fig. 1 I-V characteristics of the n- $Cd_{1-x}Fe_xS$ PEC cell in dark and under illumination

Table 1. Estimated photoelectrochemical parameters of $Cd_{1-x}Fe_xS$ PEC cells.

Composition x	I_{sc} (μA/cm^2)	V_{oc} (mV)	FF (%)	η (%)	R_s (Ω)	R_{sh} (kΩ)	n_d	n_L	ϕ_b (eV)	V_{fb} (Volt)
0	268	213	35.8	0.51	260	3.36	2.46	1.96	0.52	0.85
0.1	305	238	37.9	1.44	192	2.88	2.31	1.67	0.49	0.91
0.2	521	272	39.4	2.07	156	2.45	2.06	1.51	0.47	0.99
0.3	834	368	43.2	3.03	122	2.14	1.83	1.42	0.43	1.10
0.4	748	343	42.7	2.73	163	2.36	1.54	1.38	0.44	1.05
0.5	692	328	42.6	2.32	175	2.48	1.62	1.46	0.47	1.02
0.6	638	280	41.1	1.84	186	2.66	1.76	1.55	0.48	0.98
0.7	556	268	39.1	1.46	198	2.78	1.88	1.78	0.51	0.96
0.8	448	256	38.3	1.10	210	2.92	1.97	1.83	0.53	0.93
0.9	371	245	37.5	0.85	232	3.10	2.11	1.91	0.55	0.88
1	319	237	36.7	0.64	240	3.25	2.25	2.05	0.56	0.82

Fig. 2 shows the plot of log I against voltage (V) in dark. The plot shows linear behaviour. The junction ideality factor (n_d) was calculated and listed in table 1. The higher values of n_d may be due to the series resistance effect and carrier recombination at the semiconductor electrolyte interface.

Under illumination, I and V are replaced by I_L and V_L respectively. The current I_L is given by

$$I_L = I_0 (\exp [eV_L / n_L kT] - 1) - I_{ph} \quad (4)$$

It is observed that the values of junction ideality factor are greater than ideality value.

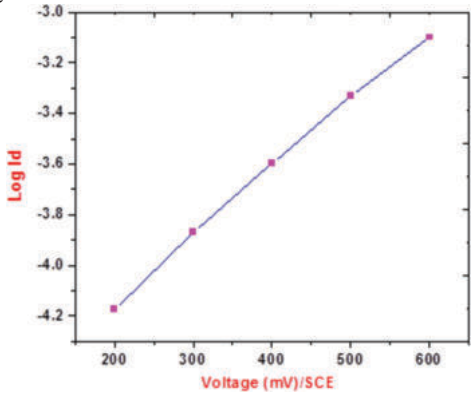

Fig. 2 Plot of log I against voltage (V) in dark.

3.3. Capacitance-voltage characteristics

The capacitance-voltage measurements give useful information regarding the donor concentration (N_D) and type of conductivity exhibited by the film. Fig. 3 shows the Mott-Schottky (MS) plots of the n- $Cd_{1-x}Fe_xS$ / sulphide / polysulphide electrolyte system for FTO coated glass substrate based PEC cells in the dark. The value of flat-band potential (V_{fb}) has obtained at $1/C_s^2 = 0$ on the potential axis according to the well known Mott-Schottky relation [15-16]

$$1/C_s^2 = [2/\varepsilon_0 \varepsilon_s q N_D][V - V_{fb} - (k\beta T/q)] \quad (5)$$

Where C_s is the space charge capacitance, V_{fb} is the flat band potential, ε_0 is the permittivity of free space, ε_s is the static permittivity of the semiconductor and N_D is the donor concentration and q is the charge on electrons. The valued of V_{fb} varies from 0.85 to 1.10 volts and is maximum for the cell having composition parameter x = 0.3. The values of n_d are obtained from M-S plot are given in table 1. The values of n_d are found to decrease with increase in composition parameter 'x' reaches a value 1.83 at x = 0.3 and thereafter go on increasing with further increase in x.

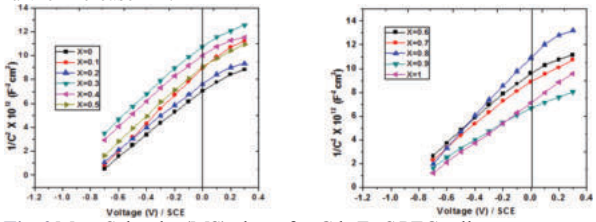

Fig. 3 Mott-Schottky (MS) plots of n- $Cd_{1-x}Fe_xS$ PEC cells

3.4. Photovoltaic Power Output Characteristics

Photovoltaic output characteristics were studied under light intensity of 25 mW/cm^2. Typical photocurrent versus photovoltage characteristics of n- $Cd_{1-x}Fe_xS$ / polysulphide under light illumination is shown in fig. 4. It is found that both the I_{sc} and V_{oc} increases with increase in composition parameter 'x' attain a maximum values at x = 0.3 and then decrease with further increase in 'x'.

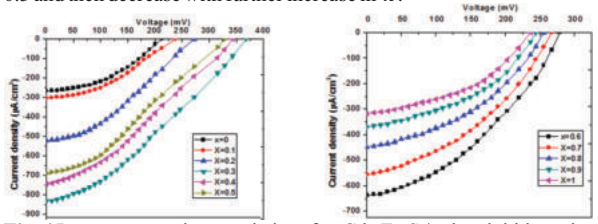

Fig. 4 Power output characteristics of n- $Cd_{1-x}Fe_xS$ /polysulphide under light illumination

The photovoltaic efficiency (η%) was calculated from the relation [17]

$$\eta = (I_{sc} \times V_{oc} \times ff / P_{input}) \times 100 \quad (6)$$

Where P_{input} is the power density of incident radiation.

The fill factor (ff) was obtained from the formula [18]

$$ff = (V_m \times I_m / V_{oc} \times I_{sc}) \quad (7)$$

Where Im and Vm are values of maximum current and maximum voltage, which can be extracted from the PEC solar cell.

Series resistance R_s and the shunt resistance R_{sh} were calculated from the slopes of the power output curves using the relations [18]

$$[dI/dV]_{I=0} \approx 1/R_s \quad (8)$$

$$[dI/dV]_{V=0} \approx 1/R_{sh} \quad (9)$$

The parameters estimated from the power output plots for n- $Cd_{1-x}Fe_xS$ thin films are given in table 1. The maximum power conversion efficiency (η) is found to be 3.03% for composition parameter x = 0.3. The increase in efficiency with increase in composition parameter may be attributed to increase in grain size of the film up to x = 0.3, thereafter as grain size decreases efficiency also decreased. Though the obtained efficiency is very less, there is a scope for the improvement of the efficiency. The series and shunt resistances are found to be 122 Ω and 2.14 kΩ respectively for x = 0.3.

4. CONCLUSION

The n- $Cd_{1-x}Fe_xS$ thin films can be deposited on to conducting FTO-coated glass substrates using simple chemical bath deposition

technique. As-deposited $Cd_{1-x}Fe_xS$ thin films are n-type polycrystalline and photoactive. The results indicated that for composition parameter x = 0.3 the efficiency and fill factor were increased to 3.03% and 43.2% respectively. The observed enhancement is due to increased open-circuit voltage, improved grain quality and improved photoelectrode absorption.

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