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PHOTOELECTROCHEMICAL CHARACTERIZATIONS OF SPRAY DEPOSITED NANOSTRUCTURED $FeCdS_3$ THIN FILMS

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Nanostructured $FeCdS_3$ thin films were prepared by spray pyrolysis method using various complexing agents. The current voltage (I–V) characteristics of the films were studied for n-$FeCdS_3$/ polysulfide /graphite photoelectrochemical cell configuration. The fill factor (FF) and efficiency (η) for the cell have been estimated. It was found that PEC cell formed with the film deposited from acetic acid complex shows improvement in V_{oc}, I_{sc}, FF and ŋ %. The junction ideality factors, n_d and n_l was found 4.43 and 5.71 for EDTA and decreases to 4.04 And 5.39 respectively for the film deposited from acetic acid. The photovoltaic efficiency (η %) and fill factor (FF%) is 0.21 and 4.42 for the PEC cell formed from the $FeCdS_3$ film deposited from EDTA complex and it increases to 0.41 and 43.47 respectively for cell formed from the film deposited using acetic acid.

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1. Introduction

Research on pollution free solar energy conversion devices particularly photoelectrochemical (PEC) cells has gained importance in the last few decades. The nanostructured semiconductor thin film introduces deep changes in its photoelectrochemical properties. As compare to bulk, nanostructured materials exhibit significant change in their properties, viz. band gap, porosity and surface area, which are important for PEC performance [1-4]. Many binary and ternary nanostructured semiconductor thin films, especially from the II and VI groups of the periodic table, are attracting attention of research community due to their potential use in fabrication of various semiconductor devices particularly photoelectrochemical solar cells. For PEC system semiconductor-electrolyte junction is formed by immersing semiconductor in an electrolyte. A space charge layer develops in the semiconductor adjacent to the interface with electrolyte. At equilibrium the Fermi level of the semiconductor and the redox potential of the solution are adjusted in the same level. When the semiconductor is illuminated, the Fermi level of the semiconductor will rise. This rise in Fermi level depends on the rate of charge transfer at the counter electrode. The electrons will move through load to the counter electrode and reduce the ions in the electrolyte. There are several advantages of PEC cells for solar energy conversation over photovoltaic devices. The main advantage is that energy can be stored in PEC devices in the form of conventional fuel. It do not contain solid-solid junctions and thus easy to fabricate and cost effective.

Even though the several research reports are available concerning the preparation and PEC properties of CdS and FeS_2 thin films, but no report is available on ternary $FeCdS_3$ [5-13]. In the present investigation, nanocrystalline $FeCdS_3$ films were deposited onto fluorine doped tin oxide

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(FTO) coated glass substrates using three different complexing agents by spray pyrolysis at 453 K temperature. Photoelectrochemical (PEC) properties of these $FeCdS_3$ nanocrystalline films were studied in polysulphide electrolyte.

2. Experimental details

By optimizing preparative parameters, such as deposition temperature (453 K), spray rate (6 mL/min), pH, etc., $FeCdS_3$ films were prepared by the chemical spray deposition method. To deposit FTO films 7.9 g of $SnCl_4$ $5H_2O$ was fully dissolved in 300 mL of ethanol and 5 mL of 7.5 M NH_4F [14]. This solution was sprayed on glass substrates kept at 405 K temperature to prepare FTO films. $FeCdS_3$ films were deposited by spraying the solution containing 10 mL of 0.1M Ferric Nitrate, 10 mL of 0.1M $CdCl_2$, 10 mL of 0.1M thiourea and 10 mL of 0.1M of complexing agents onto fluorine doped tin oxide (FTO) coated glass substrates. Films without complex and in presence of acetic acid, tartaric acid and EDTA were prepared. The film thickness was measured by weight difference method and found of the order of 137 nm. The photoelectrochemical (PEC) cell was fabricated in an H-shaped glass cuvette using one of the sample as an active photoelectrode, sodium polysulphide as redox electrolyte, and impregnated graphite rod as a counter electrode. A saturated calomel electrode (SCE) was used as reference electrode. The power output characteristics were obtained for all the cell configurations under a constant input light intensity of 80 $mWcm^{-2}$. The water lens was interposed between the lamp and the cell to avoid the heating of the cell. The distance between the photo-electrode and counter electrode was 0.3 cm. The photo anode area exposed to light was 1.5 × 1.5 cm i.e. 2.25 cm^2. The current-voltage (I-V) characteristics in the dark and under light illumination are studied. The fill factor (FF) and power conversion efficiency (η) of the cell were calculated from the photovoltaic output characteristics.

3. Results and discussion

In chemical spray pyrolysis method on the hot substrate cations Fe^{3+} and $Cd^{3+}$and anions S^{2-}, which are present in the spray solution, react with each other to give $FeCdS_3$. In presesce of acetic acid, tartaric acid and EDTA, the iron and caduium forms metal complex which decopses to liberate Fe^{3+} and Cd^{3+}ions for the film formation. Ultimetaly the rate of decomposition was governed by the presense of complex. The detail reaction mechanisum was given somewhere else. It was found that the $FeCdS_3$ films are nanocrystalline in nature with mixed phase of orthorhombic FeS_2 and hexagonal CdS. The films deposited using acetic acid and EDTA complex shows vertical rod-like and web-like architecture of $FeCdS_3$.

A PEC cell with configuration $FeCdS_3$ / NaOH - S -Na_2S/ $C_{(graphite)}$ was formed.

It was seen that even in the dark PEC cell gives some dark voltage, V_d and dark current, I_d with $FeCdS_3$ electrode as the negative and graphite electrode as the positive. The origin of this voltage is attributed to the difference between two half-cell potentials in the PEC cell, which can be written as,

$$E = E_{graphite} - E_{FeCdS_3} \quad (1)$$

The polarity of this dark voltage was negative towards semiconductor electrode. The sign of the photo voltage gives the conductivity type of $FeCdS_3$. This suggests that $FeCdS_3$ is an n-type conductor [15].

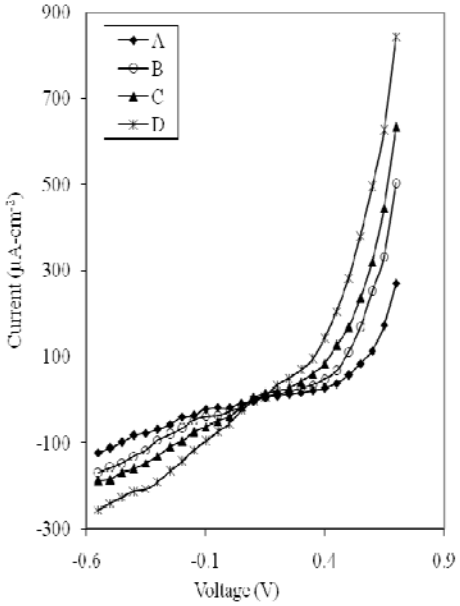

Fig. 1.Current–voltage characteristics in dark for $FeCdS_3$ polysulphide PEC cells formed from films deposited using complex: (A) EDTA; (B) Tartaric acid; (C) without complex; (D) Acetic acid.

The current–voltage (I–V) characteristics of PEC cells in dark and under illumination were examined with $FeCdS_3$ photoelectrode deposited using different complexing agents is shown Fig. 1 and 2. The origin of the dark voltage is attributed to the difference between Fermi levels of the semiconductor electrode/electrolyte. The dark current observed may be due to deterioration of the photoelectrode in dark. The non-symmetric nature of I -V curve (Figs 1 and 2) in forward and reserve bias shows the rectification property of the semiconductor electrolyte junction.

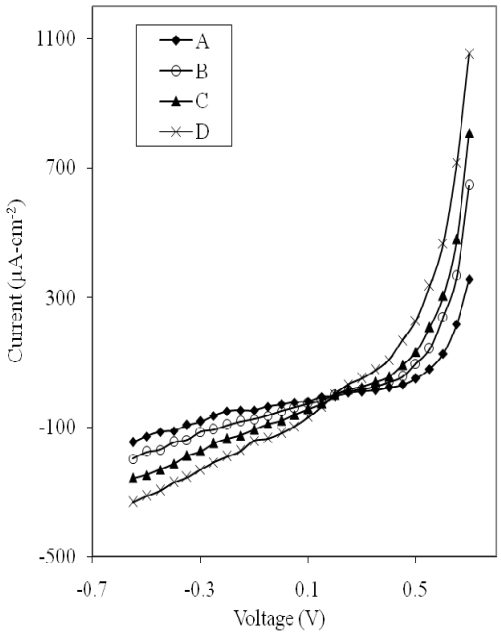

Fig. 2.Current–voltage characteristics under illumination for $FeCdS_3$ polysulphide PEC cells formed from films deposited using complex: (A) EDTA; (B) Tartaric acid; (C) without complex; (D) Acetic acid.

From I -V curve, the junction ideality factor in dark (n_d) and in light (n_l) were calculated for different films deposited from various complexes using the relation,

$$I = I_0\left[e^{\frac{eV}{nKT}} - 1\right] \quad (2)$$

where n is junction ideality factor, I_0 the reverse saturation current, V the forward bias voltage and I is the forward bias current. The values of junction ideality factors, n_d for dark and n_l under illumination were calculated from the graph of log I versus V (Fig. 3 and 4) and are listed in Table 1. The junction ideality factors, n_d and n_l was found 4.43 and 5.71 for EDTA and decreases to 4.04 And 5.39 respectively for the film deposited from acetic acid. The higher value of n_l is indicative of the series resistance effect and the carrier recombination at the semiconductor–electrolyte interface [16].

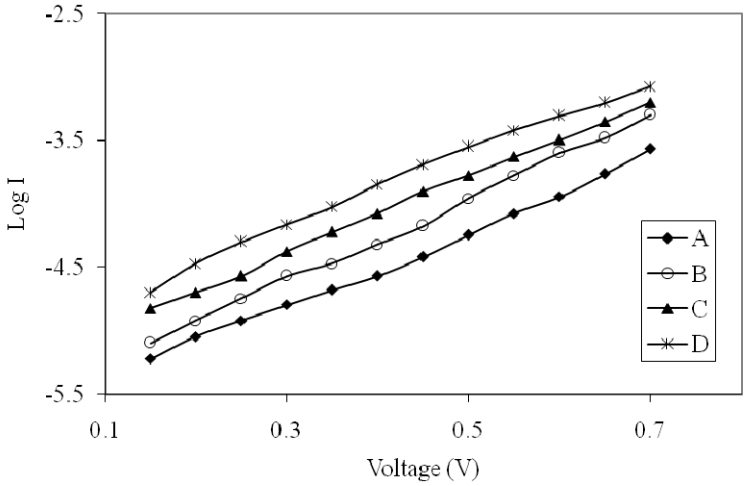

Fig. 3. Log I versus voltage plots for $FeCdS_3$ polysulphide PEC cells in dark formed from the films deposited using complex: (A) EDTA; (B)Tartaric acid; (C) without complex; (D) Acetic acid (derived from Fig. 1 with same notations)

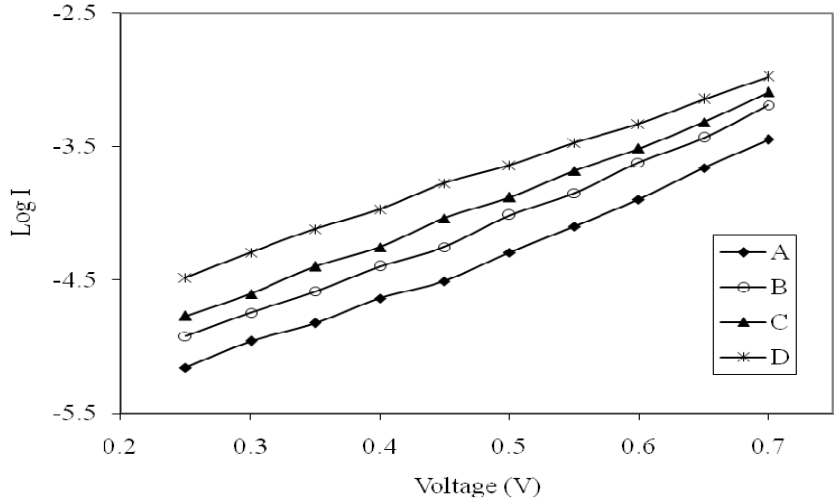

Fig.4. Log I versus voltage plots for $FeCdS_3$ polysulphide PEC cells under illumination formed from films deposited using complex: (A) EDTA; (B)Tartaric acid; (C) without complex; (D) Acetic acid (derived from Fig. 2 with same notations)

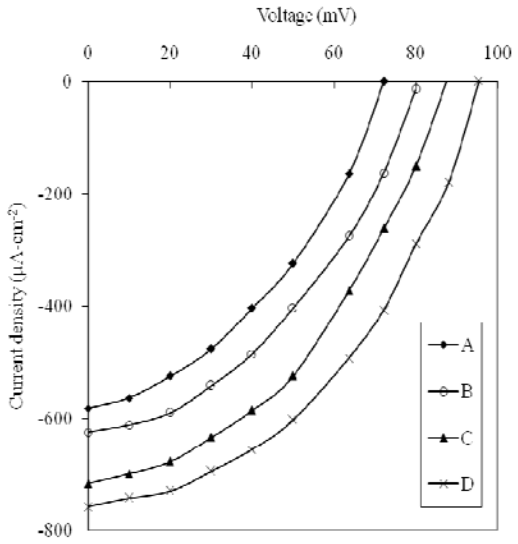

Fig. 5. Photovoltaic output characteristics for $FeCdS_3$ polysulphide PEC cells under illumination for various films deposited using complex: (A) EDTA; (B)Tartaric acid; (C) without complex; (D) Acetic acid

Table 1. Estimated important parameters from photovoltaic power output curves of $FeCdS_3$ PEC cells.

Film	Complex used	Ideality factor		I_{sc} ($\mu A/cm^2$)	V_{oc} (mV)	R_s (Ω)	R_{sh} (Ω)	(FF %)	(η %)
		n_d	n_l						
A	EDTA	4.43	5.71	555	72.2	52	556	40.42	0.21
B	Tartaric acid	4.36	5.68	625	80.6	53	769	40.30	0.25
C	-	4.22	5.55	699	89.4	50	588	42.67	0.33
D	Acetic acid	4.04	5.39	758	95.3	41	467	43.47	0.40

The photovoltaic output characteristics were studied under light intensity of 80 mW/cm^2. Fig. 3 shows photovoltaic power output curves for $FeCdS_3$ film deposited using different complexes. It is seen that the short circuit current (Isc) and open circuit voltage (Voc) depends on the complex used in deposition process. It is 555 $\mu A/cm^2$ and 72.2 mV for the film deposited from EDTA complex and increases to 758 $\mu A/cm^2$ and 95.3 mV for the film deposited from acetic acid, which may be attributed to variation in the stoichiometry with respect to the complex used in the deposition process. The photovoltaic efficiency (η %) was calculated from the relation [17],

$$\eta = \left[\frac{(I_{sc} V_{oc} FF)}{P_{hv}}\right] \times 100\ \% \qquad (3)$$

where P_{hv} is the power density of the incident radiation. The fill factor (FF) was calculated from the relation [18],

$$FF = \left[\frac{I_m V_m}{I_{sc} V_{oc}}\right] \times 100\ \% \tag{4}$$

where Im and Vm are, respectively the current density and voltage obtained at maximum power point on the photovoltaic power output curve. Series resistance (Rs) and shunt resistance (Rsh) were evaluated from the slopes of the power output characteristics using the relation,

$$R_s = \left[\frac{dV}{dI}\right]_{I=0}, \tag{5}$$

$$R_{sh} = \left[\frac{dV}{dI}\right]_{V=0}, \tag{6}$$

The parameters estimated from power output plots are shown in table 1. The maximum efficiency was obtained from $FeCdS_3$ film deposited on FTO coated glass substrate from acetic acid complex. The series resistance (Rs) and shunt resistance (Rsh) is 52 and 556 Ω for the PEC cell formed from the $FeCdS_3$ film deposited from EDTA complex and it decreases to 41 and 467 Ω respectively for cell formed from the film deposited using acetic acid. This may be due to the improvement of crystallinity and/or grain size.

4. Conclusions

$FeCdS_3$ films can be spray deposited onto FTO coated glass substrates using EDTA, tartaric acid, acetic acid complexing agents. From PEC studies, it is clear that $FeCdS_3$ is an n-type material. Photovoltaic power output characteristics showed better performance for the film deposited on FTO coated glass using acetic acid complex as compared to other complexes. The photovoltaic efficiency (η %) and fill factor (FF%) is 0.21 and 4.42 for the PEC cell formed from the $FeCdS_3$ film deposited from EDTA complex and it increases to 0.41 and 43.47 respectively for cell formed from the film deposited using acetic acid.

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References

[1] R.S. Mane, B.R. Sankapal and C.D. Lokhande, Mater. Chem. Phy., **60**, 196 (1999).
[2] S. Licht, Sol. Energy Mater. Sol. Cells, **38**, 305 (1995).
[3] Z. Loinzos, N. Syrcellis and G. Mourin, Thin Solid Films, **204**, 139 (1991).
[4] G. Hodes, I. Howeil and L. Peter, J. Electrochem. Soc., **139**, 3136 (1992).
[5] J.M. Dona and J. Herrero, J. Electrochem. Soc., **139**, 2810 (1992).
[6] K.K. Nanda, S.N. Sarangi, S. Mohanty and S.N. Sahu, Thin Solid Films, **322**, 21(1998).
[7] K.K. Nanda, S.N. Sarangi and S.N. Sahu, Appl. Surf. Sci., **133**, 293 (1998).
[8] K.K. Nanda and S.N. Sahu, Appl. Surf. Sci., **119**, 50 (1997).
[9] S.H. Pawar, C.H. Bhosale and L.P. Deshmukh, Bull. Mater. Sci., **8**, 419 (1986).
[10] N. Badera , B. Godbole , S.B. Srivastava , P.N. Vishwakarma , L.S. S. Chandra, D. Jain, M. Gangrade , T. Shripathib, V.G. Sathe and V. Ganesan Appl.Surf. Sci., **254,** 7042 (2008).
[11] I.J. Ferrer , P. Diaz-Chao, A. Pascual and C. Sanchez, Thin Solid Films, **511/512,** 177 (2006).
[12] S. Thanikaikarasan , T. Mahalingam, Soonil Lee, Hanjo Lim, S.Velumani and Jin Koo Rhee, Mater. Sci. Eng. B **174, 1/2**, 231(2010).
[13] P. S. Patil, Mater Chem Phys., **59**, 185 (1999).

[14] V.M.Nikale, N.S.Gaikwad, K.Y.Rajpure and C.H.Bhosale, Mater. Chem. Phys., **78**, 363 (2003).
[15] L.P. Deshmukh, V.S. Sawant and P.P. Hankare, Sol. Cells, **31**, 557 (1991).
[16] V. D. Dasand and L. Damodare J. Appl. Phys., **81**, 1522 (1997).
[17] T. J. Coutts, Solar Energy Mater., **50**, 99 (1978).