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DYE SENSITIZATION OF PHOTOELECTROCHEMICAL (PEC) CELL USING ELECTRODEPOSITED n-CdS AND MIXED CdS-CdSe THIN FILM

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CdS, CdSe and mixed CdS-CdSe thin film electrodes have been prepared electrochemically for their use in photoelectrochemical cells. These films were obtained on clean Nickel substrates. Mixed CdS-CdSe semiconductor electrode was prepared by dipping electrode in an aqueous solution of sodium selenosulphite(Na_2SeSO_3).The conversion efficiency of the PEC cell could be enhance by adding thymol blue as sensitizer to the S^{-2}/Se^{-2} redox electrolytes

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1. Introduction

Cadmium chalcogenide such as CdS, CdSe and their mixtures are important semiconducting materials for their use in photoelectrochemical (PEC) cells as photoanode[1-3,5-7]. Bard and co-workers [8] suggested that the addition of small amount of CdSe to CdS electrode greatly improves the solar to electrical energy conversion efficiency of CdS in semiconductor-liquid electrolyte junction PEC cell. They have prepared the Sulphide-Selenide mixtures by mechanically mixing the polycrystalline CdS and CdSe followed by sintering the mixed materials. Many studies were conducted utilizing dyes to sensitize reaction at photo electrodes in PEC cells [9,10]. Thin film of n-CdS and n-CdSe have been prepared by different methods like chemical bath deposition method, chemical vapor deposition method, spray pyrolysis, electrodeposition etc[4,11-13].

This paper presents the photo electrochemical behavior of CdS, CdSe and mixed CdS-CdSe thin film electrodes prepared in two steps. Electrodeposited cadmium metal is anodized in sodium sulphide solution to get CdS film and in sodium seleno-sulphite solution to get CdSe film. The mixed CdS-CdSe film is prepared by simply dipping electrodeposited CdS electrode in aqueous sodium seleno-sulphite

The aim of this present study is to use the above thin film semiconductor electrodes in fabricating a photo electrochemical(PEC) cell with as suitable power conversion efficiency paying attention to the role of dye as regards to its sensitization effect for improving maximum efficiency. The performance parameters include the measurement of open circuit voltage(V_{oc}), short circuit current(I_{sc}), fill factor(ff), conversion efficiency(η), flat band potential(V_{fb}) and optical band gap energy(E_g).

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2. Experimental

The semiconductor materials were deposited in the form of thin film on clean Nickel substrates (previously etched in 3% dilute HCl for ten minutes) electrochemically under galvanostatic condition. For the preparation of CdS film, Cadmium metal was deposited on the substrate (1cm^2 geometrical area) using a deposition bath containing 1 molar cadmium sulphate solution at 30^0C ±1 by passing a current density of 20mA/cm^2 for 45 minutes with slow stirring. The substrates were used as cathode and a platinized platinum electrode of 1 cm^2 geometrical area used as the anode. The deposited thin film was washed with deionized water and was anodized in a unimolar alkaline solution of sodium sulphide at a current density of 20mA/cm^2 for 30 minutes. The thin film of CdSe was prepared by anodizing the deposited cadmium film in an aqueous solution of sodium seleno-sulphite (Na_2SeSO_3). The mixed CdS-CdSe thin film semiconductor was prepared by dipping the electrodeposited cadmium sulphide electrode in aqueous solution of sodium selenosulphite of 0.4 molar concentration for a period of 30 minutes at 80^0C. Sodium selenosulphite solution being prepared by refluxing 4gm of selenium powder with 12.5gm of anhydrous sodium sulphite in 100 ml deionised water for 4hours.

All deposited films were washed with deionised. Dried in air and finally annealed in air for half an hour at 500^0C. The thickness of the deposited films was found to be 2-4 μm.

The photo-electrochemical cell (PEC) was formed by combining the semiconductor electrode (used as working electrode, WE) with a platinized platinum electrode of 1cm^2 geometrical area (used as counter electrode,CE) in a polysulphide electrolytes containing 1M NaOH, 1M S 1M Na_2S. The semiconductor photo electrodes were irradiated with a500 w tungsten filament lamp conneted to stabilized power supply. The intensity of the illuminating light was measured with the help of a calibrated solar intensity meter "Suryamapi"(obtained from central electronic Ltd, India). Other experimental details were given elsewhere[14]. The electrode potentials were measured versus a calomel electrode (SCE). The PEC cell was a double-compartment cell having the following configuration,

$$WE / 1M (Na_2S, S, NaOH) //0.5N K_3Fe(CN)_6/Pt$$

3. Results and discussion

The simple two step method of preparation of CdS and CdSe thin film on Nickel substrate involves the electrodeposition of thin film of cadmium metal and subsequent anodization of the deposited film from aqueous Sulphide and Selenide bath respectively. Thin film of CdSe was prepared by anodizing electrodeposited cadmium metal in an aqueous solution of sodium seleno-sulphite which involves the following reaction,

$$Se + SO^{2-}_3 \leftrightarrow SeSO^{2-}_3 \quad (1)$$

$$SeSO^{2-}_3 + 2e^- \leftrightarrow Se^{2-} + SO^{2-}_3 \quad (2)$$

$$Cd + Se^{2-} \leftrightarrow CdSe + 2e^- \quad (3)$$

The formation of mixed CdS-CdSe thin film was achieved by dipping the electrodeposited CdS in sodium selenosulphite solution at80^0C. In this case most probably the smaller sulphide ions, (ionic radius = 1.7A^0) were replaced by larger selenide ions (ionic radius = 1.84A^0). Formation of mixed CdS-CdSe may be as follows

$$SeSO^{2-}_3 + OH^- \leftrightarrow SO^{2-}_4 + HSe \quad (4)$$

$$HSe^- + OH^- \leftrightarrow H_2O + Se^{2-} \quad (5)$$

$$CdS + Se^{2-} \leftrightarrow CdSe + S^{2-} \quad (6)$$

The chemical deposition of thin film of CdSe on glass substrate from solution containing Cd (II) ions through steps (4) and (5) has been studied in detail by Kainthla et al [4]. the thermodynamics feasibility of step (6) is estimated by ΔG^0_{298}, which seemed to be about 6 kcal/mole [15].

3.1 Conductivity type

Some dark voltage (V_d) and dark current (I_d) were observed with working electrode (CdS, CdSe, mixed CdS-CdSe) being used as negative polarity and platinised platinum as the positive polarity end. The dark voltage though very small, may be atrrbuted to the difference between the two half cell potentials and the PEC cell i.e $E_{cell} = E_{Pt/Pt} - E_{WE}$, where $E_{Pt/Pt}$ and E_{WE} are the half cell potentials (reduction potential) when dipped in the polysulphide redox electrolyte. On illumination of the semiconductor-electrolyte junction the magnitude of voltage increases with negative polarity towards the semiconductor thin film electrode indicating that the conductivity of SC electrode is of n-type

3.2 Spectral measurement

Fig (1) gives the photo response of the CdS and CdS-CdSe thin film electrodes prepared by electrodeposition method in the electrolyte containing 1M NaOH and 1MNa_2S. The photoresponse of CdS was observed at wavelength shorter then 550 nm where as photoresponse of mixed CdS-CdSe electrode appeared at a wider range of wavelength due to the formation of a solid solution after annealing. The existence of solid solution in the sintering film of CdS-CdSe obtained by electrophoretic deposition has been confirmed earlier[16]. The onset of photocurrent starts at a higher wavelength in case of mixed CdS-CdSe electrode indicating a decrease in band gap energy of the mixed SC materials. The higher photocurrent of mixed CdS-CdSe based PEC cell might be due to the lower E_g value as compared to simple CdS.

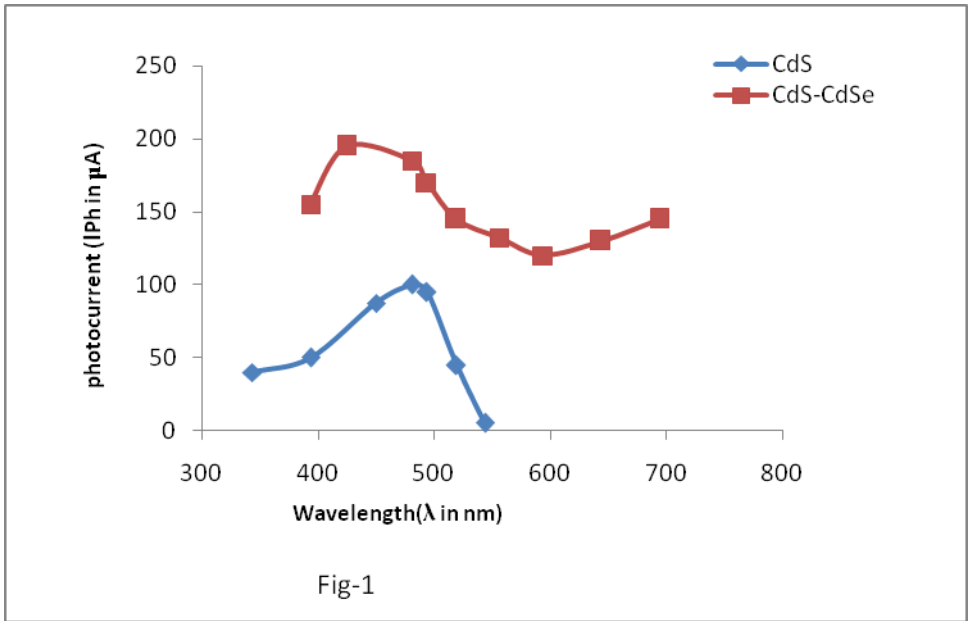

Fig (1) Spectral response of thin film CdS and CdS-CdSe electrodes in 1M Na_2S and 1M NaOH electrolytes.

3.3 Power output characteristics:

The power output characteristics of the photo electrochemical (PEC) cell were determined from the current-voltage (I - V) plot as shown in Fig (2), of the cell using thin film CdS, CdSe, mixed CdS-CdSe electrodes in sulphide-polysulphide redox electrolytes at an illumination intensity of 40mW/cm^2. The mixed CdS-CdSe thin film electrode based PEC cell was found to have better optical to electrical conversion efficiency then that of the cells using simple CdS and CdSe thin film. The efficiencies of the cell using CdS, CdSe and mixed CdS-CdSe have been calculated to be 3.0, 2.42 and 4.42 with corresponding fill factor values 0.50, 0.55 and 0.59 respectively. The improved performance of mixed CdS-CdSe based PEC cell may be interpreted in term of (i) electron affinity (ii) band gap energy(E_g) (iii)flat band potential(V_{fb}) of the semiconductor electrode materials. A semiconducting photo anode should have as small as electron affinity as possible [17] to maximize the open circuit voltage (V_{oc}). Selenium is less electronegative than sulphur. So it is likely that the electronegativity of semi conducting material mass of CdS will decrease if sulphide ions are partially exchanged with selenide ions. The band gap energy (E_g) of CdSe (1.7eV) is less than that of CdS (2.4eV). Therefore it is expected that band gap energy of mixed CdS-CdSe would be less than that for CdS semiconducting materials. The band gap energy of mixed CdS-CdSe has been found to be 2.18eV.

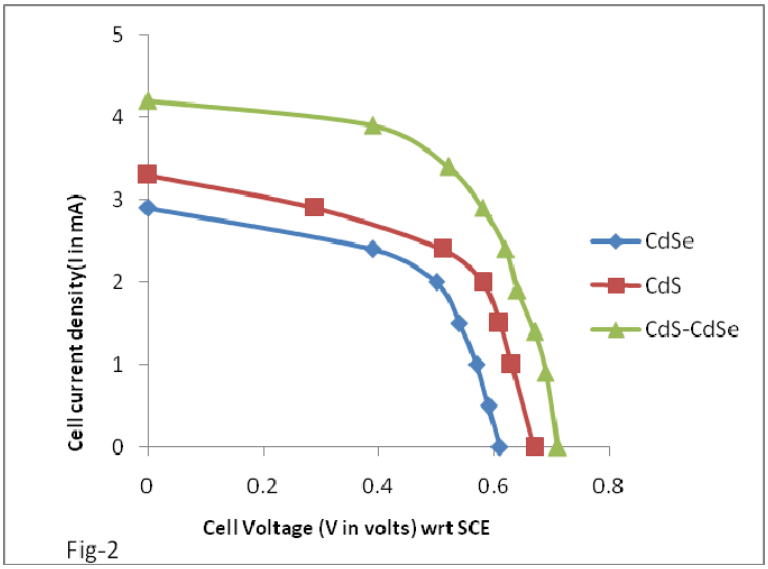

Fig (2) Current- Voltage (I-V) characteristic of thin film electrodes using 1M (Na_2S, NaOH and S)

M.A.Butler and D.S.Ginley [18] employed schotty barrier model to determine the flat band potential (V_{fb}) of a semiconductor electrode. A plot of the square of the photocurrent (I_{ph}) versus applied potential (V) will intercept the potential axis at the flat band potential (V_{fb}). Applying the data corresponding to Fig (2) of our experimental results it has been observed that I_{ph}^2 versus V plot as represented in Fig (3) is linear and extrapolated value of potential assumed to be V_{fb} (wrt SCE) shifts to more negative value for mixed CdS-CdSe electrode (V_{fb} = 0.67V) than that for only CdS (V_{fb} = 0.64V). Nousi et al.[19] reported a similar result with CdS and mixed CdS-CdSe prepared by sintering a mechanical mixture of CdS and CdSe.

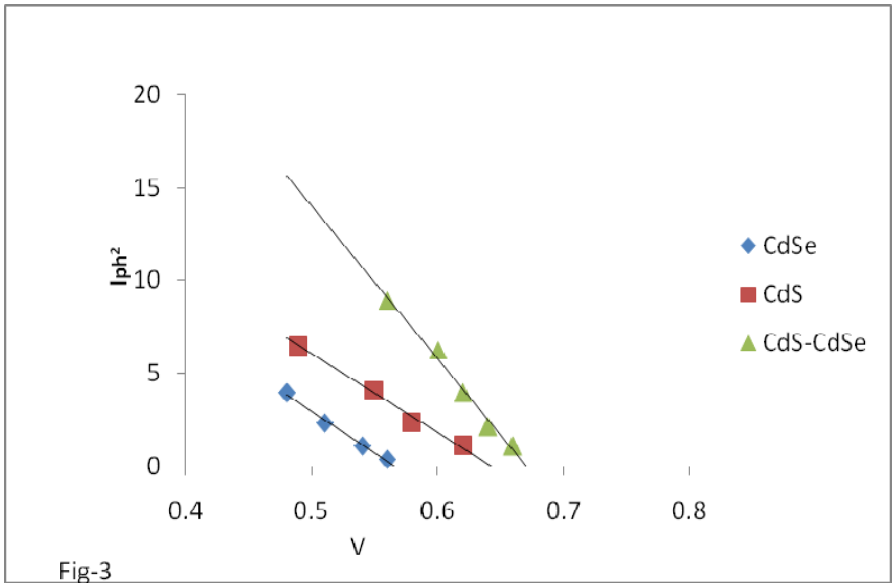

Fig (3) Square of photocurrent against applied potential (V) for the electrodesmention in fig (2)

The photo electrochemical (PEC) cell using thin film CdS and mixed CdS-CdSe electrodes have been studied by adding thymolblue dye ($C_{27}H_{30}O_{15}S$, λ_{max} = 594 nm) at a concentration of 2.5 $x10^{-5}$ molar to the sulphide-polysulphide redox electrolyte containing unimolar solution of sodium sulphide, sodium hydroxide and sulphur in the anodic compartment. The current-voltage (I-V) behavior of the above PEC cell having configuration

WE / 1M (Na_2S, NaOH, S, thymol blue //0.5 $K_3Fe(CN)_6$) /Pt

is represented in Fig (4). Due to the addition of the dye, the optical to electrical conversion efficiency (η) of the PEC cell using CdS Semiconductor electrode was found to increase magnificently. The efficiency and fill factor have been calculated to be 4.8 and 0.59 respectively as 3.0 and 0.50 for CdS based cell without dye. While adding the dye to the cell using mixed CdS-CdSe electrode, the efficiency was found to be 5% against 4.42% without dye. The fill factor for the cell with and without dye was fount to be 0.62 and 0.59 respectively. It has been stated that the present of dyes [20]. in solution, whose absorption band energies are lower than the band gap energy (E_g) of the semiconductor increases the photocurrent of the PEC cell. This is due to increase in the density of majority free carriers (in this case electron). The added dye molecules get deposited on the semiconductor surface. On illumination electrons are transferred from the excited dye molecules to the conduction band with higher rate. The efficiency of the PEC cell though found to increase on dye sensitization due to improvement in characteristics property of the semiconductor electrode, the values obtained were not very large. This may be due to surface states acting as recombination centers for electron-hole pairs.

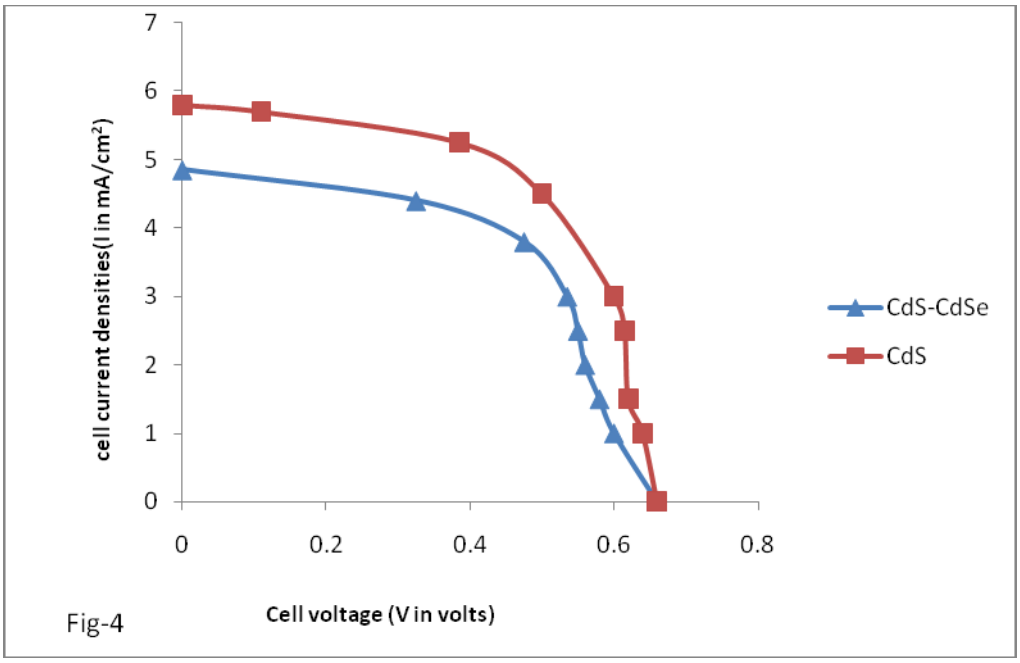

Fig (4) Power output characteristics of the PEC cell using thymolblue dye in 1M (Na_2S, NaOH, S) redox electrolytes

4. Conclusions

It has been shown that the two steps electro-deposition method is the most convenient way for thin film deposition of CdS, CdSe and mixed CdS-CdSe on to nickel substrate. Addition of a small amount of CdSe into CdS surface increases the photo response of Semiconductor electrode while using as photo anode in PEC cell. The improved performance of CdS-CdSe Semiconductor electrode is due to decrease in band gap energy, higher flat band potential and smaller electron affinity of the mixed electrode materials Addition of a small amount of suitable dye to the redox electrolyte could enhance the efficiency of the cells appreciably due to increase in the population of tmajority carriers.

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