Photoelectrochemical Cells using Electrosynthesized Cadmium Sulphide and mixed Sulphide of Bismuth (III) and Cadmium (II) as Photoelectrodes.

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Abstract: Attempts have been made to enhance the conversion efficiency of photoelectrochemical cell using electrolytically deposited CdS semiconductor electrode in sulphide–polysulphide electrolyte. In the present investigation the thin film of polycrystalline CdS and mixed sulphide of Cd(II) and Bi(III) have been synthesised electrochemically onto conducting glass substrate by co-depositing one and both the metals and anodising the film in electrolyte bath containing aqueous solution of Na_2S. The cell configuration is photoelectrode / NaOH (1M) + S (1M) + Na_2S (1M) / Pt. The performance parameters of the cell include measurements of photocurrent, photovoltage, fill factor, cell efficiency, flat band potential, band gap energy, ideality factor, stability and study of I-V characteristics in dark.

Keywords: Electrodeposition, Liquid junction, Chalcogenide, Photoanode, Thinfilm.

1.Introduction

Metal chalcogenides are potential candidates for solar energy conversion as they are efficient absorbers in the visible and near infrared regions of solar spectrum [1–6]. Low fabrication cost, ease in operation, availability of materials, relatively no lattice mismatch, make these materials more attractive and acceptable to most of the researchers in the field of photovoltaic technology, Among the several chalcogenides, CdS and Bi_2S_3 have been studied extensively as individual binary components for thin film applications in energy conversion [7–14]. Study on their composite film materials is now becoming the recent trend in the field of photovoltaic research [15–18].

Different processes have been reported earlier for the deposition of CdS thin films [19–22]. In the present study the cost effective, simple electrodeposition method for preparation of thin film of simple and composite chalcogenides of Cd (II) and Bi (III) is employed and the prepared electrodes in the form of thin films are used as photoelectrodes while fabricating photoelectrochemical (PEC) cells using sodium polysulphide electrolyte as a medium of charge transport from one electrode to another.

2. Experimental section

2.1. Thin film deposition:

Cadmium Sulphide thin films were obtained on conducting glass substrates using electrodeposition method form an electrolytic bath containing molar aqueous solution of Cadmium sulphate followed by anodisation of electrodeposited Cadmium metal already washed with distilled water, using unimolar aqueous solution of Sodium sulphide as anodizing electrolyte. The mixed sulphide semiconductor of Cd (II) and Bi (III) were prepared by codepositing both the metals from an electrolyte bath containing equimolar aqueous solution of both Bi (III) and Cd (II) in the ratio 1:2. The detail methods of preparation of thin films were same as in our earlier papers (23-24). In order to optimize the different deposition parameters such current density, time, temperature etc, several trials were conducted to get uniform, polycrystalline deposit well adhered to the substrate surface. After deposition the thin films were thoroughly washed in distilled water and dried in room temperature in dark for one night. All chemicals used in our experiment were of Analytical reagent grade (AR).

2.2. Fabrication and characterization of PEC cell

The photoelectrochemical Cell was devised in an H-shaped flat surface glass vessel by combining either simple or composite electrode system as photosensitive electrode (test electrode) with a Platinised Platinum (Pt/Pt) foil electrode as the counter electrode (CE) in Sodium sulphide / polysulphide redox electrolyte containing unimolar solution of NaOH, S and Na_2S. The photoelectrode was illuminated by a 200W tungsten filament lamp connected to a stabilised power supply. The power output characteristic of the photoelectrochemical cells were obtained at a constant illumination of $20mW/cm^2$ as measured by calibrated solar intensity meter "Suryamapi" (obtained

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from central electronic Ltd India). The exposed surface area of the photoelectrode was 2.0cm^2. The photocurrents and photopotentials were noted for various intensities from 5mW/Cm^2 to 100mW/Cm^2.The spectral photoresponse of the photocells were studies in the range of wavelengths from 400nm to 750nm. A wire wound potentiometer was used to vary the voltage across the junction and the current flowing through the junction was measured with the help of a current meter. A saturated calomel electrode (SCE) was used as the reference electrode (RE) in (I-V) study. photoelectrochemical behaviours of the semiconductor – liquid electrolyte junction solar cells have been studied by measuring junction ideality factor both in dark and light (n_d and n_L), fill factor (ff), power conversion efficiency (n), Series resistance (R_S), Shunt resistance (R_{SH}), band gap energy (E_g), and flat band potential (V_{fb}).

The PEC cell with configuration is:

photoanode / NaOH (1M) + S (1M) + Na$_2$S (1M) / Pt.
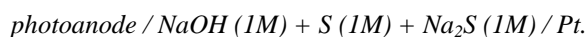
2.3. Thickness measurement

The average thickness of the deposited semiconductor thin films was measured gravimetrically using the following equation.

$$t = w/Ad$$

Where t = thickness of the deposited film.

W = weight of the deposited compound.

A = total area of the deposited film.

D = density of the film assuming that the density of the film is the density of the bulk.

The thickness of CdS and mixed CdS-Bi$_2$S$_3$ the films have been found to be 3.3µm and 4 µm.

3. Results and Discussion

Some dark voltage (V_d) and dark current (I_d) were observed with working electrodes (CdS, mixed CdS-Bi$_2$S$_3$) being used as negative polarity and platinised platinum as the positive polarity end. The dark voltage though very small, may be attributed to the difference between the two half cell potentials of 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 electrodes are of n-type.

The Fig.1 of dark Current–voltage (I–V) curves of PEC cells for both the electrodes are non-symmetrical indicating the formation of rectifying type junction [25].
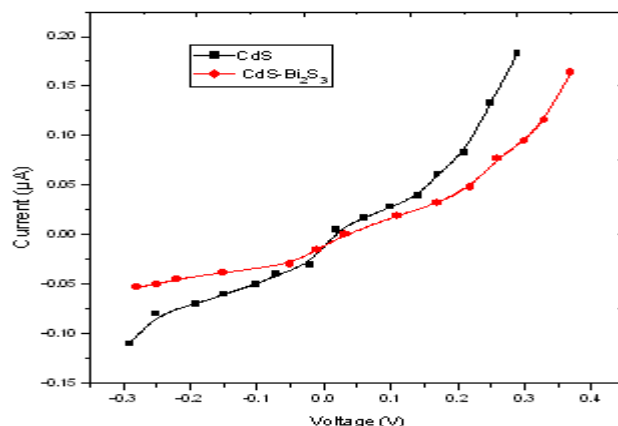

Figure 1: I-V Charactristics of CdS and CdS-Bi$_2$S$_3$

The plots of log I with voltage have been shown in Fig.2 from which the junction ideality factors (n_d) can be determined from the plots using the equation (1):

$$V_{OC} = \frac{n_d}{q} kT \; ln \frac{I_{SC}}{I_0} \qquad (1)$$

Where

V_{OC} = Open circuit voltage.

n_d = Junction ideality factor.

q =charge on electron.

k =Boltzmann constant.

T =temperature.

I_{SC} = Short circuit current.

I_0 =reverse saturation current density.

The ideality factors for CdS and mixed CdS-Bi$_2$S$_3$ were found to be 4.46 and 5.2. The higher value of n_d in mixed CdS-Bi$_2$S$_3$ attributes the dominance of series resistance as well as structural imperfection. It also implies average transfer through the semiconductor electrolyte interface with major role from surface states and deep traps [26].
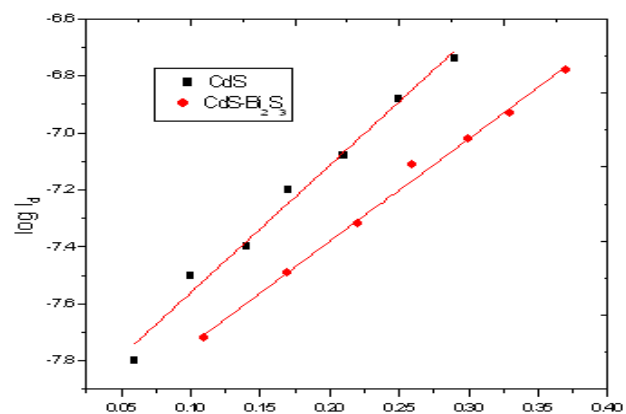

Figure 2: Determination of ideality t factor of CdS and CdS-Bi$_2$S$_3$.

The photovoltaic power putout characteristics for the PEC

cells using CdS and mixed CdS-Bi$_2$S$_3$, under illumination of 20mW/cm^2 have been determined from the current-voltage (I-V) plots as shown in Fig.3.
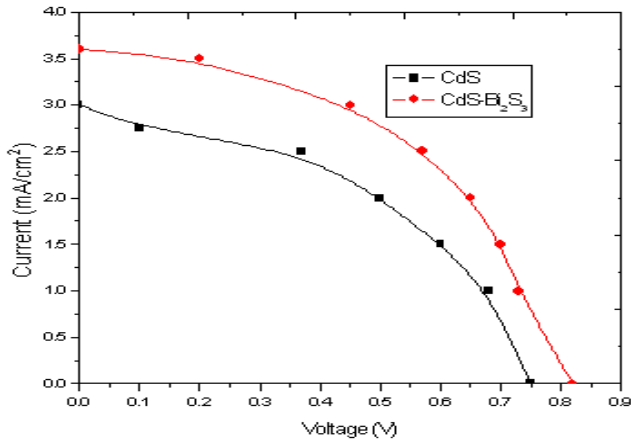

Figure 3: Power output curve for CdS and CdS-Bi$_2$S$_3$.

The efficiencies and fill factors have been calculated using the equations 2 &3: [7]

$$n = \frac{I_m \times V_m}{P_{input}} \qquad (2)$$

$$ff = \frac{I_m \times V_m}{V_{OC} \times I_{SC}} \qquad (3)$$

Where   I$_m$ = Current obtained at the maximum power point on the photovoltaic power output curve.

V$_m$ = Voltage obtained at the maximum power point on the photovoltaic power output curve.

P$_{input}$ = Power density of incident light.

V$_{OC}$ = Open circuit voltage.

I$_{SC}$ = Short circuit current.

And the values are found to be for 5.16 and 7.26 with corresponding fill factor values .46 and 0.49 for CdS, and mixed CdS-Bi$_2$S$_3$ respectively. The higher efficiency of mixed CdS-Bi$_2$S$_3$ as compared to CdS may be due to high shunt resistance, low series resistance, low band gap and interface states which are responsible for recombination mechanism. The values of series resistance and shunt resistance have been calculated from the equations 4 & 5: [7].

$$\left(\frac{dI}{dV}\right)_{I=0} \cong \frac{1}{R_S} \qquad (4)$$

$$\left(\frac{dI}{dV}\right)_{V=0} \cong \frac{1}{R_{Sh}} \qquad (5)$$

Where
R$_s$ =Series resistance.

And R$_{sh}$ is the shunt resistance.

For CdS and mixed CdS-Bi$_2$S$_3$ and found to be 63 & 85.7 Ω and 517 &1.288 kΩ respectively.

The photoresponse of the PEC cells using CdS, and mixed CdS-Bi$_2$S$_3$ have been studied by measuring open circuit voltage and short circuit current against light at different intensities. Fig. 4 shows variation of shot circuit current (Isc) for CdS, and mixed CdS-Bi$_2$S$_3$ as a function of light intensity, whereas, Fig. 5 shows the variation of open circuit voltage as a function of light intensity.
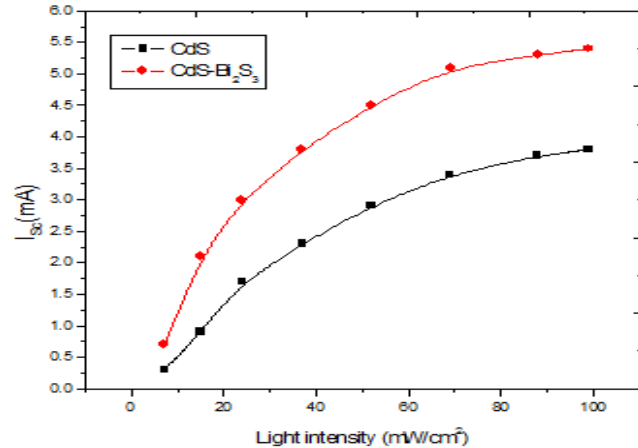

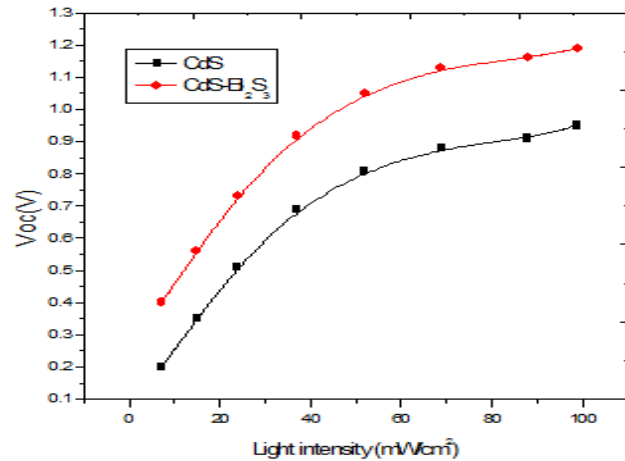**Figure 4:** Photoresponse as a function of short circuit for CdS and CdS-Bi$_2$S$_3$.

Figure 5: Photoresponse as a function of short circuit for CdS and CdS-Bi$_2$S$_3$.

The photoresponse measurements showed a logarithmic variation of open circuit voltage with the incident light intensity. However, at higher intensities, saturation in open circuit voltage was observed, which can be attributed to the saturation of the electrolyte interface, charge transfer and non-equilibrium distribution of electrons and holes in the space charge region of the photoelectrode. But short circuit current follows almost a straight line path. The photoelectrode–electrolyte interface can be modelled as a Scotty barrier solar cell [27]. A plot of log Isc against Voc should give a straight line and from the slope of the line the lighted ideality factor can be determined using the equation 6: [4]

$$V_{OC} = \frac{n_L}{q} kT \ln \frac{I_{SC}}{I_0} \qquad (1)$$

The plot of log Isc with Voc for CdS, and mixed CdS-Bi$_2$S$_3$ photoelectrode is shown in Fig. 6. The lighted ideality factors are found to be 5.17 and 3.4.
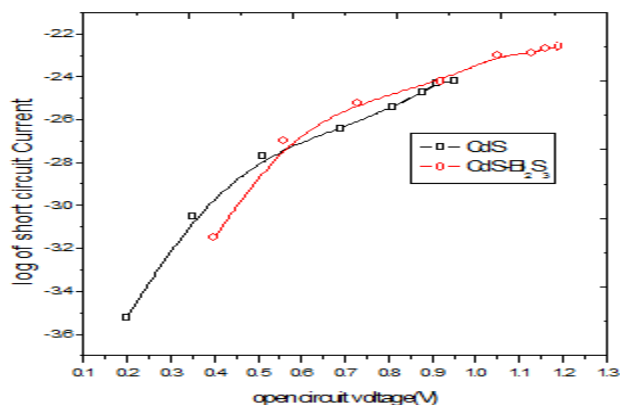

Figure 6: Determination of ideality factor of CdS and CdS-Bi$_2$S$_3$ in light.

The spectral responses of the cells have been studied plotting short circuit current against wavelength fig.7.
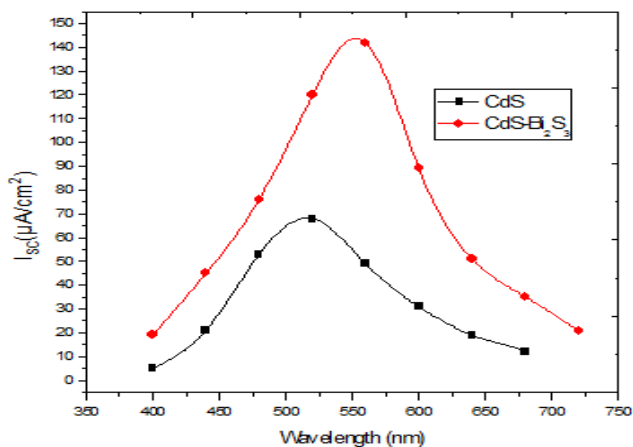

Figure 7: Spectral response of CdS and CdS-Bi$_2$S$_3$.

The decrease of I$_{sc}$ towards shorter wavelength of the peak for CdS, and mixed CdS-Bi$_2$S$_3$ may be due to absorption of light in electrolyte and high surface recombination of photogenerated carrier by surface state. The decrease of I$_{sc}$ towards longer wavelength of the peak may be attributed due to transition between defect levels. The peak values can also be used to calculate band gap energy, which are found to be 2.4 and 2.15eV. The increase of efficiency of PEC cell while using mixed CdS-Bi$_2$S$_3$ may also be due to decrease of band gap.

The flat band potential of a semiconductor gives information of the relative position of the Fermi levels in photoelectrode as well as the influence of electrolyte and charge transfer process across the junction. This is also useful to measure the maximum open circuit voltage that can be obtained from a cell. The flat band potential of the semiconductors have also been determined from the plot of (I$_{ph}$)^2 against voltage (fig.8) and found to be .72 and .78V w.r.t. SCE for CdS, and mixed CdS-Bi$_2$S$_3$ respectively which are the measure of electrode potential at which band bending is zero.
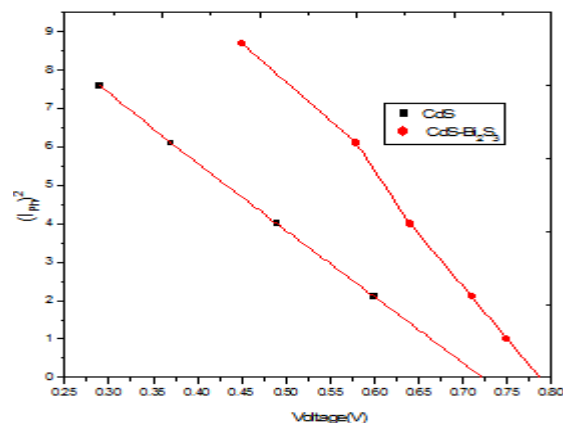

Figure 8: Determination of V$_{fb}$ for CdS-Bi$_2$S$_3$ phtoelectrode.

Table 1: performance parameters of the synthesized photoelectrodes CdS and CdS-Bi$_2$S$_3$.

Electrode Thickness	CdS 3.3µm	CdS-Bi$_2$S$_3$ 4µm
n_d	4.46	5.2
n_L	6.3	6
R_S	63 Ω	85.7 Ω
R_{SH}	517 kΩ	1.288 kΩ
FF	.46	.49
V_{FB}	.72V	.78V
E_g	2.4 eV	2.15 eV
V_{oc}	.75	.82
I_{sc}	3,0	3.6
(η)	5.16	7.26

4. Conclusion

CdS and Mixed CdS–Bi$_2$S$_3$ thin films can be successfully grown by the help of simple and cost effective electrochemical technique. The improved performance of the mixed CdS-Bi$_2$S$_3$ Semiconductor electrode is due to decrease in band gap energy, higher flat band potential, smaller electron affinity of the mixed electrode materials, higher shunt resistance and low series resistance. In our investigation, dark current observed was virtually negligible indicating no dissolution of the photoelectrode materials. The photocurrent was observed with illumination for 14 hours and found to be nearly constant indicating stability of the electrode. The optical studies revealed that the energy band gap of mixed CdS–Bi$_2$S$_3$ thin film has

close match with the solar spectrum, which may be useful in production of optoelectronic devices.

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