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PHOTOELECTROCHEMICAL (PEC) CELLS BASED ON NEBULISED SPRAY PYROLYSED Bi_2S_3 THIN FILMS

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Bi_2S_3 thin films are deposited on microscope glass slides and fluorine doped tin oxide (FTO) coated glass substrates by nebulised spray pyrolysis technique. The films are deposited at optimised deposition conditions. The films are characterized by X-ray diffraction and UV-Vis-NIR spectrophotometry and Atomic force microscopy. The photoelectrochemical properties of the films is analysed by capacitance-voltage measurements. Bi2S3 thin films coated on FTO coated glass substrates are used as photoanodes in a conventional two electrode electrochemical cell containing polysulphide electrolyte. The performance of the Bi2S3 photoanodes are analysed under different intensities of illumination. Cell parameters such as open circuit voltage, short circuit current,efficiency, fill factor, junction ideality factor are calculated. The efficiency of the PEC cell based on Bi_2S_3 photoelectrodes is 0.009% under an illumination intensity of $60 mW/cm^2$.

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1. Introduction

Solar energy is a potential source of renewable energy. The direct conversion of solar energy into electrical energy is achieved by photovoltaic cells. Electrochemical Photovoltaic (ECPV) Cells are cost effective alternatives for p-n junction solar cells. Though ECPV cells are economic, they suffer from very low efficiency when compared to their solid state counter parts. The performance of an ECPV cell can be improved by enhancing the properties of the semiconductor material which is used as the photoanode/cathode. The primary requirement for an ECPV cell is that the semiconductor material which is used as the photoanode should have a band gap in the range of 1.4-1.6 eV. Bismuth sulphide (Bi_2S_3) is a challenging material because of its midway band gap (E_g=1.7 eV), absorption coefficient of the order of 10^4-10^5 cm^{-1}, reasonable conversion efficiency and stability together with low cost[1].Reports are available on the properties of Bi_2S_3 thin films deposited by chemical bath deposition [2], spray pyrolysis [3], electrodeposition [4] , SILAR method [5], thermal evaporation [6] and reactive evaporation [7]. Spray pyrolysis is an economically viable and efficient technique for the large area deposition of thin films. Microstructure of the films have profound effect on the performance of the photoelectrodes. And hence in the present work an attempt has been made to deposit Bi_2S_3 thin films having novel microstructure and to analyse the performance of the films as photanodes in photoelectrochemical cell.

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2. Experimental

Bi_2S_3 thin films are deposited by nebulised spray pyrolysis technique at optimised deposition conditions. The film deposition conditions are given in table-1.Films are annealed at 300°C for an hour. Crystalline nature of the films are analysed by X-ray diffraction and optical band of the films is determined from optical transmittance measurements. Film microstructure is analysed by atomic force microscopy. Panalytical X-pert Pro X-ray diffractometer, Veeco (Nanosope-E) Scanning probe microscope and UV-Vis-NIR double beam spectrophotometer (JASCO V-570) are used for recoding the X-ray diffraction pattern, surface morphology and Optical transmittance of the samples respectively. Bi_2S_3 thin films coated on conducting glass substrates are used for studying the photoelectrochemical characteristics of the films. C-V measurement is carried out by forming a three electrode electrochemical cell with the configuration Bi_2S_3/1M NaOH-1M Na_2S-1M S/C in which calomel electrode and platinum electrode served as the reference and counter electrode respectively.

Table 1 film deposition conditions

Spray parameter	Condition
Concentration of the precursors	:0.2 M
Volume of spray solution for single spray process	:5 ml
Total volume of the solution sprayed for each deposition	:50 ml
Spray rate	:0.5ml/minute
Substrate nozzle distance	:5 cm
Substrate temperature	:300°C

The space charge layer capacitance of the junction as function of applied potential is recorded using Keithley (3330) LCR meter. The thin film of Bi_2S_3 is employed as a photoanode in an electrochemical photovoltaic cell with the configuration Bi_2S_3/1M NaOH-1M Na_2S-1M S/C. Platinum is used as the counter electrode and 1M NaOH-1M Na_2S-1M S is used as the electrolyte. The power output characteristic of the cell is studied by illuminating the cell with light of varying intensity.

3. Results and Discussion

3.1 Structural Properties

X-ray diffraction pattern of the Bi_2S_3 thin films deposited on glass substrates is shown in figure-1. Apprearence of prominent peaks in the X-ray diffraction pattern of the film is indicative of the polycrystalline nature of the film. Analysis of the X-ray diffraction data reveals that the films belong to bismuthinite phase of bismuth sulphide having orthorhombic crystal structure.

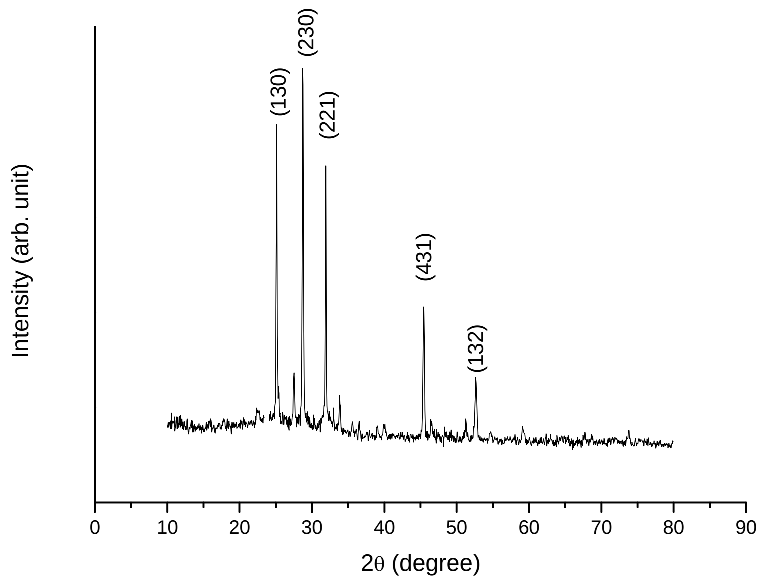

Fig. 1 XRD pattern of Bi_2S_3 thin film deposited by nebulised by spray pyrolysis

Three dimensional surface features of the film is analysed by atomic force microscopy. The atomic force micrograph (figure-2) of the film indicates the formation novel microcubes which are uniform in size and shape. This unique morphology may be attributed to the uniform and very fine spray droplets which are produced by using the small volume jet nebulizer. And hence it may be concluded that the use of small volume jet nebuliser can improve the microstructure of the film significantly which in turn can improve the performance of the film when used as photoelectrodes.

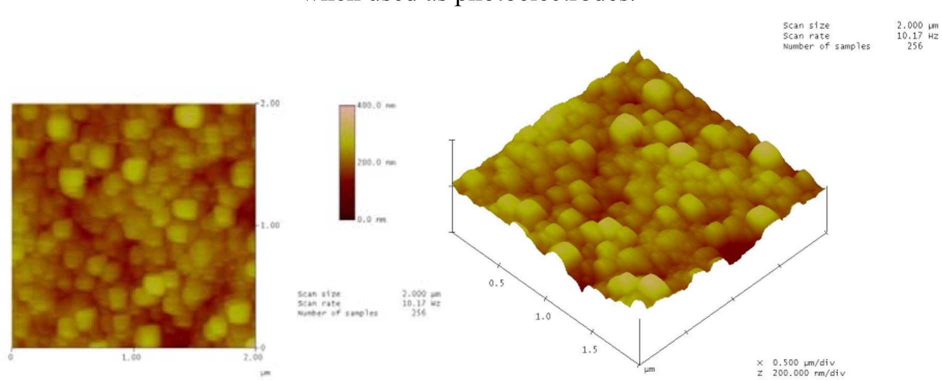

Fig. 2 Atomic force micrograph of Bi_2S_3 thin films deposited by nebulised spray pyrolysis

3.2 Optical Properties

Band gap is an important parameter which has a direct consequence on the conversion efficiency of a PEC cell. The nature of optical transitions taking place in the film is found by analysing the nature of the Tauc plot (figure 3). The linear nature of the plot in highly absorbing region indicates that the transitions taking place in the film are direct and allowed. The value of direct band gap of the film is 1.7 eV.

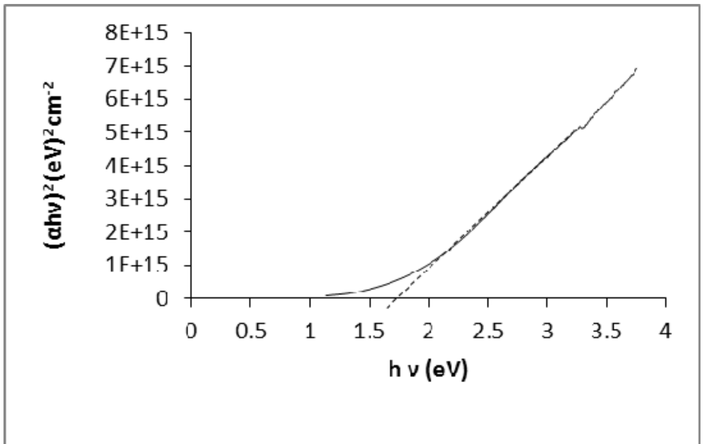

Fig. 3 $(\alpha h\nu)^2$ vs. hν plot of Bi_2S_3 thin film

3.4 Capacitance-Voltage measurement

The measurement of capacitance as a function of applied voltage provides useful information about photoelectrode such as type of conductivity and flat band potential (V_{fb}). The flat potential is an important factor in explaining charge transfer process across the semiconductor-electrolyte junction of the Photoelectrochemical cell. The value of V_{fb} can be obtained by using Mott-Schottky relation [8],

$$C^2 = \frac{2}{q\varepsilon\varepsilon_0 N_d}\left(V - V_{fb} - \frac{kT}{q}\right) \quad (1)$$

where C is the space charge capacitance, ε is the dielectric constant of the semiconductor, ε_0 is the permittivity of the free space, N_d is the donor density and V, V_{fb} are applied , flat band potentials respectively. In the present study C-V measurement is carried out by forming a three electrode electrochemical cell with the configuration Bi_2S_3/1M NaOH-1M Na_2S-1M S/C in which calomel electrode and platinum electrode served as the reference and counter electrode respectively. The space charge layer capacitance of the junction as function of applied potential is recorded using an LCR meter. The space charge layer capacitance is found to decrease with applied potential. The Mott-Schottky plot of the sample is linear and has negative slope there by indicating the n-type conductivity of the film. Flat band potential is determined by extrapolating Mott-Schottky plot to C=0 (Figure 4). Flat band potential of ECPV cell formed with $Bi_2 S_3$ thin film deposited at a substrate temperature of 573 K is 0.590V (V_{SCE}).

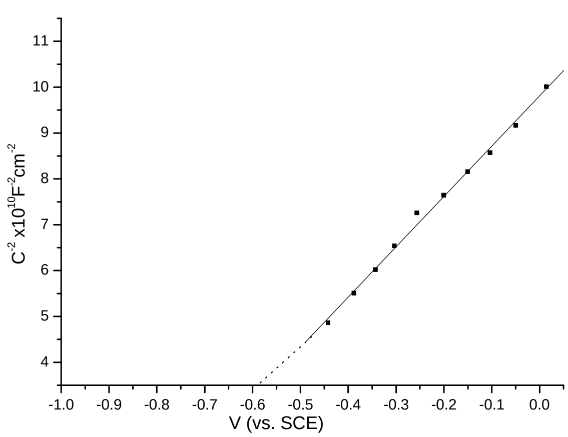

Fig. 4 Mott Schottky plot of Bismuth sulphide thin film deposited at 573K

3.5 Power Output Characteristics

The Bi_2S_3 thin films deposited by nebulised spray pyrolysis are used as photoanodes in a conventional two electrode electrochemical cell consisting of polysulphide as the redox electrolyte and platinum as the counter electrode. The current and voltage generated in the cell under illumination at different intensities of illumination (100,80,60,40,20 mW/cm^2) are recorded. The current and voltage are noted by varying the load on the cell from zero to very high value. The power output characteristics of the Bi_2S_3 based photoelectrochemical cell is shown in figure 5. The maximum power point is extracted from the power output characteristics and cell parameters such as fill factor and conversion efficiency are calculated from the equations given below.

$$\text{Fill Factor (FF)} = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \quad (2)$$

$$\text{Conversion efficiency } (\eta) = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \quad (3)$$

where V_m and I_m are the current and voltage obtained at maximum power point, V_{oc} is the open circuit voltage and I_{sc} is the short circuit current. Series resistance (R_s) and Shunt resistance (R_{sh}) of the cell are calculated from the slope of the power output characteristics using the relations given below.

$$\left(\frac{dI}{dV}\right)_{I=0} = \left(\frac{1}{R_s}\right) \quad (4)$$

$$\left(\frac{dI}{dV}\right)_{V=0} = \left(\frac{1}{R_{sh}}\right) \quad (5)$$

The cell exhibited a conversion efficiency and a fill factor of 0.009% and 0.72 respectively at an illumination intensity of 60mW/cm^2. The efficiency of the cell decreased slightly at higher illumination intensities which may be attributed to the pronounced effect of series and shunt resistances of the cell. The variation of efficiency of the cell with intensity of illumination is shown in figure 6. The dependence of V_{oc} and I_{sc} on the intensity of illumination is shown in figure 7. The plot of V_{oc} against ln I_{sc} is a straight line (figure 8) and junction ideality factor is calculated

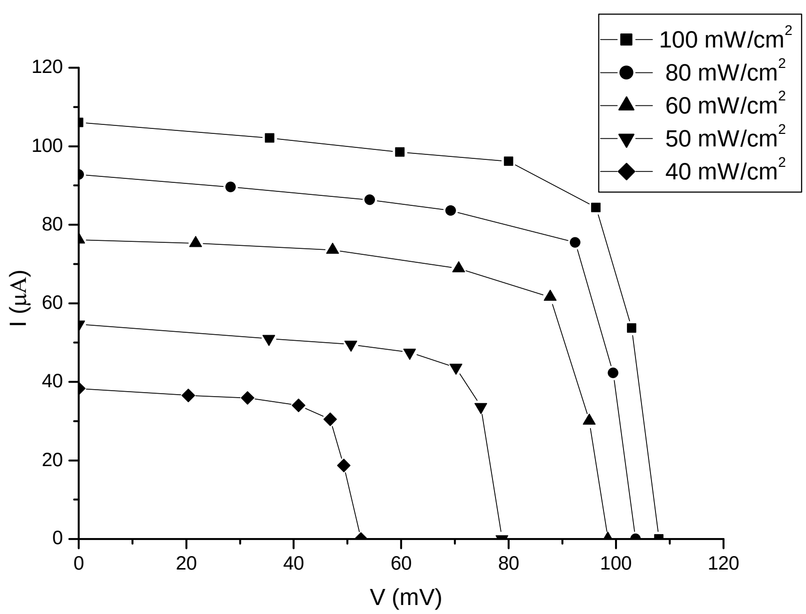

Fig. 5 Power output characteristics of Bi_2S_3 photoanode based PEC cell

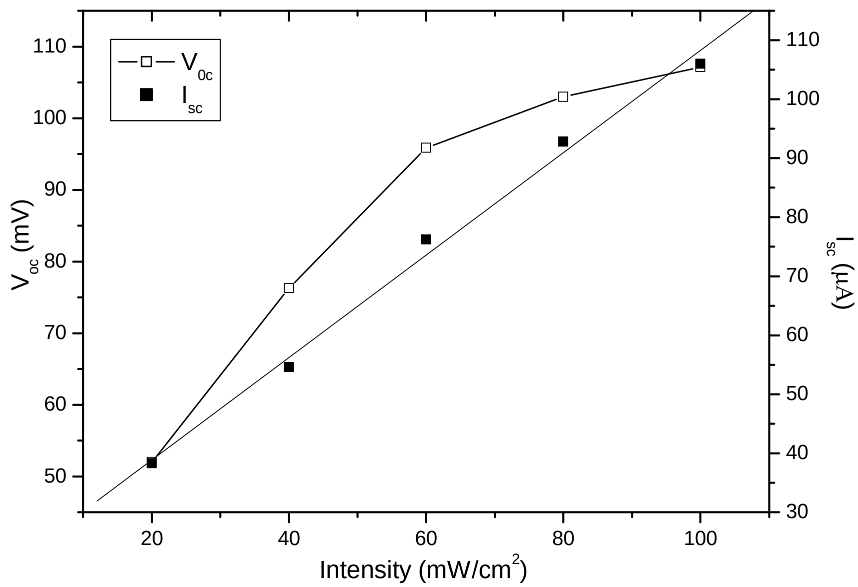

Fig. 6 Dependence of V_{oc} and I_{sc} on the illumination intensity .

from the slope of the plot. The junction ideality factor of the cell is 1.544. The lower conversion efficiency of the cell may be attributed to the high resistivity of the material of the photoanode which is of the order of 10^6 in the present case. An improvement in increasing the conductivity of the material may lead to higher conversion efficiency.

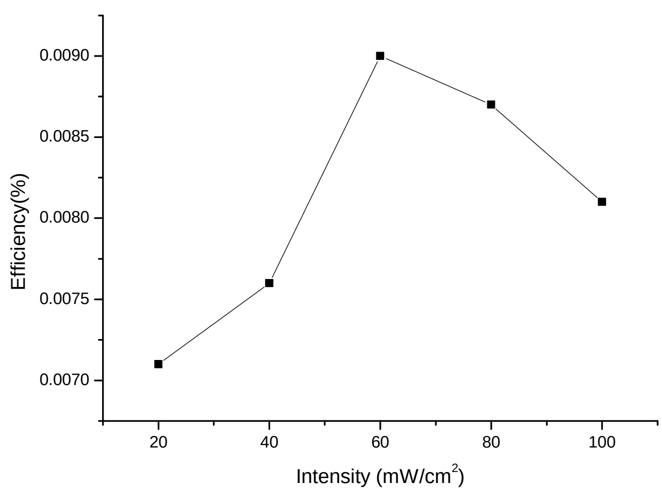

Fig. 7 Variation of efficiency with intensity

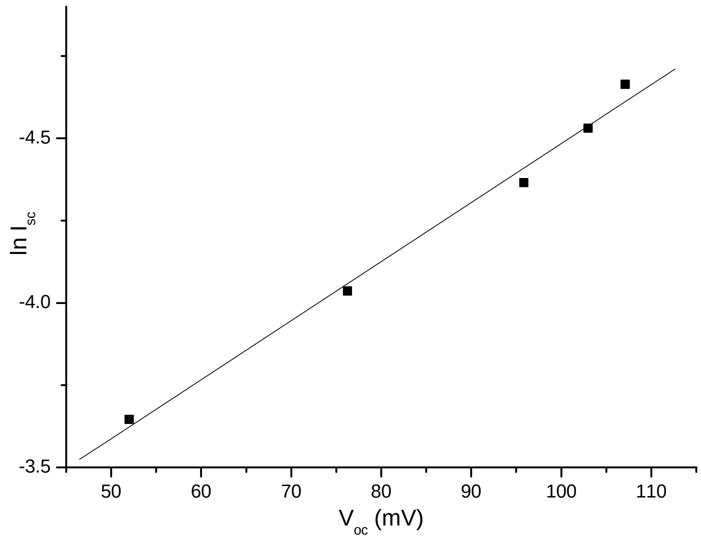

Fig. 8 The plot of V_{oc} vs. ln I_{sc}

4. Conclusions

The polycrystalline nature of the Bi_2S_3 thin films deposited by nebulised spray pyrolysis is confirmed by X-ray diffraction and the analysis of the surface morphology of the films indicated presence of uniform microcube like structures in the film. Bi2S3 thin films deposited by nebulised spray pyrolysis are used as photoanodes in Photoelectrochemical cells. The flat band potential of the junction is found to be 0.59 V (V_{SCE}) through C-V measurement. The conversion efficiency and fill factor of the cell at an illumination intensity of 60 mW/cm^2 is 0.009% and 0.72 respectively. It is concluded from the present study that it is essential to improve the optical, structural and electrical characteristics of the Bi2S3 thin film to realise higher conversion efficiencies.

Acknowledgement

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