



Improved photoelectrochemical performance of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ photoanodes

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ABSTRACT

$(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ ($0 \leq x \leq 0.10$) thin films deposited by nebulised spray pyrolysis technique are employed as photoanodes in electrochemical photovoltaic cells. Photoelectrochemical and power output characteristics of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ photoanodes are analysed. Photovoltaic parameters such as open circuit voltage, short circuit current, fill factor and efficiency of the photoelectrochemical cells employing n- $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ photoelectrodes are determined. Composition of the photoanode is found to have significant effect on the performance of the cell. The photoanode of composition $(\text{Bi}_{0.95}\text{Sb}_{0.05})_2\text{S}_3$ is found to exhibit superior performance. The conversion efficiency and fill factor of the cell employing $(\text{Bi}_{0.95}\text{Sb}_{0.05})_2\text{S}_3$ electrode are 0.3% and 0.77 respectively.

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1. Introduction

Escalating fuel prices and fast depleting conventional energy sources indicate the necessity and drive the search for alternate sources of energy which are economically and environmentally acceptable for sustainable development. Presently, the world energy consumption is 10 terawatts (TW) per year and by 2050, it is projected to be about 30 TW [1]. 120,000 TW of solar energy strikes the surface of the earth at any given moment [2]. Effective capture and conversion of solar energy into other forms of energy is a viable approach for solving the problem of energy crisis. The solid state solar cells are advanced, efficient and reliable devices with better conversion efficiency when compared to Schottky barrier and photoelectrochemical solar cells. Since p–n junction solar cells require high quality material for efficient operation and employ sophisticated technology for their production, overall cost of such systems remains high which restricts their widespread commercialisation. In contrast to solid state photovoltaic devices, semiconductor–liquid junction based electrochemical photovoltaic (ECPV) cells are relatively inexpensive. In spite of being relatively cheaper when compared to p–n junction solar cells, ECPV systems suffer from lower conversion efficiency and shorter life time. The conversion efficiency of the ECPV cells can be enhanced by improving the characteristics of the semiconductor material which is used as photoelectrode. The identification of an appropriate

material which can be used as an efficient photoelectrode for ECPV cell is a challenging task.

Metal chalcogenides are important class of solar energy materials and have suitable optical and electrical properties for photovoltaic application. Number of binary and ternary chalcogenide materials such as CdS [3], CdSe [4], $\text{CdS}_{1-x}\text{Se}_x$ [5], ZnS [6], ZnSe [7], $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ [8], $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ [9], Sb_2Se_3 [10], Sb_2S_3 [11], Bi_2Se_3 [12] and Bi_2S_3 [13,14] have been used as semiconductor electrodes in ECPV cells. In particular bismuth trisulphide (Bi_2S_3) is a potential material because of its band gap and high absorption coefficient in visible region [15]. An important aspect of Bi_2S_3 as regards to ECPV application is that it belongs to the class of layered semiconductors which are stable against photocorrosion [16]. Reports are available on the properties of Bi_2S_3 thin films deposited by conventional methods and also on characteristics of ECPV cells formed with Bi_2S_3 photoelectrode. The performance of ECPV cells formed with Bi_2S_3 photoanodes has not been found satisfactory and the efficiency of the cells was very low [15].

The performance of Bi_2S_3 photoelectrodes can be improved by tailoring the characteristics of the material as required for more efficient conversion of solar radiation. To achieve desired structural, optical and electrical properties, it is necessary to synthesize multi component alloys of variable and well controlled composition. It is possible to improve the characteristics of the binary semiconductor material by forming an isostructural and isovalent solid solution. Antimony (Sb), the element which belongs to group-V and which forms binary sulphide known as antimony trisulphide (Sb_2S_3) having orthorhombic crystal structure is a suitable choice for the formation of isostructural and isovalent ternary semiconductor based on Bi_2S_3 . The potential of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ semiconductor as a prospective material for the preparation of photoelectrode for ECPV cells has not been examined so far. And

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hence in the present work an attempt has been made to investigate the performance of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ electrodes in an electrochemical photovoltaic cell. The paper reports the deposition of Bi_2S_3 and $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ thin films by nebulised spray pyrolysis and photoelectrochemical and power output characteristics of the electrochemical cell formed with $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ photoanodes.

2. Experimental details

2.1. Preparation of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ ($0 \leq x \leq 0.10$) Photoelectrodes

Bi_2S_3 and $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ thin films are deposited on FTO (fluorine doped tin oxide) coated glass substrates (Pilkington, Resistivity: $9 \Omega/\text{sq.}$) by nebulised spray pyrolysis technique under optimised deposition conditions (Table 1). Analytical grade bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), antimony chloride (SbCl_3) and thiourea ($\text{CS}(\text{NH}_2)_2$) are used as precursors for bismuth, antimony and sulphur ions respectively. Equimolar solutions (0.2 M) of the precursors are mixed in appropriate volumes to obtain required Bi:Sb:S ratio in the solution and hence in the film. Compressed air is used to nebulise the spray solution. $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ ($0 \leq x \leq 0.10$) thin films are deposited by varying the composition of the spray solution in such a way that 'x' increases from 0 to 0.10. Spray parameters are maintained at optimised conditions (Table 1). Thickness of the films is in the range of 1.3–1.5 μm . The as-deposited $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ films are annealed at 200 $^\circ\text{C}$ for an hour (in air).

2.2. Formation and characterisation of ECPV cells

Bi_2S_3 and $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ thin films deposited by nebulised spray pyrolysis technique are employed as photoanodes in electrochemical photovoltaic cells of configurations FTO/ Bi_2S_3 / Na_2S – S – NaOH /Pt and FTO/ $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ / Na_2S – S – NaOH /Pt. 1 M polysulphide is used as the redox electrolyte. Concentrated electrolyte is used in order to minimise the internal resistance of the cell [17]. A Keithley LCZ meter (3330) is used for capacitance–voltage (C–V) measurement. The measurement is carried out at a frequency of 1 kHz. Conventional three electrode electrochemical cell is used for C–V measurement. The potential (V) is applied to the cell using APLAB high voltage power supply. The photoactive area of electrode is 5 mm $\times$ 5 mm and the surface of photoelectrode excluding the photoactive area is sealed with Araldite (Sigma) epoxy resin. A Tungsten-halogen lamp is used as light source. At a particular intensity of illumination, the current and voltage produced in the cell are measured by successively increasing the load resistance. The current and voltage produced in the cell under short circuit and open circuit conditions are noted.

3. Results and discussion

$(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ thin films annealed at 200 $^\circ\text{C}$ are polycrystalline. The crystalline phase of the deposited material is identified as bismuthinite (JCPDS card no. 75-1306) by X-ray diffraction analysis (Panalytical, X-Pert Pro, $\text{Cu K}\alpha$, Bragg–Brentano configuration) and energy dispersive X-ray analysis (Quanta 200 FEG scanning electron microscope with EDS attachment, operating voltage 30 kV) revealed no remarkable deviation

from the nominal composition of the films. Optical band gap of the films is determined from optical transmission measurement and the values are listed in Table 2.

3.1. C–V characteristics

Space charge capacitance (C_{sc}) is the most important parameter characterising a semiconductor–electrolyte interface. The measurement of space charge capacitance is of paramount importance for understanding the nature of semiconductor–electrolyte interface. Space charge layer capacitance is obtained by measuring the capacity of the semiconductor–electrolyte junction. The measurement of space charge layer capacitance as a function of applied potential under depletion condition is based on the Mott–Schottky relationship:

$$\frac{1}{C_{sc}^2} = \frac{2}{2\epsilon\epsilon_0 N} \left(V - V_{fb} - \frac{kT}{e} \right) \quad (1)$$

where C_{sc} is the capacitance of the space charge region, ϵ and ϵ_0 are the dielectric constant of semiconductor and permittivity of free space respectively, N is the donor density and V , V_{fb} are the applied and flat band potentials, respectively. The quantity $(V - V_{fb})$ is the potential drop in the space charge region. A plot of $\frac{1}{C_{sc}^2}$ vs. applied voltage (V) gives a straight line and an extrapolation of the line to x-axis ($\frac{1}{C_{sc}^2} = 0$), gives the flat band potential. The Mott–Schottky plots (Fig. 1) of Bi_2S_3 and $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ thin films have positive slope thereby indicating the n-type conductivity of the material. The flat band potential of the cells employing $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ photoanodes are given in Table 2. Flat band potential of the ECPV cells employing Bi_2S_3 photoanodes is -0.59 V (vs. SCE). Flat band potential of 0.55 V (vs. SCE) was reported by Ahire and Sharma [18] for chemical bath deposited Bi_2S_3 thin films. The flat band potential of ECPV cell employing $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ photoanodes is more negative than the cell employing binary material. V_{fb} of the cell is dependent on the electrode composition (Fig. 2). Initially, flat band potential is found to increase with the value of 'x' and reaches a maximum value at $x = 0.05$ and then decreases. The increase in the flat band potential for the values of $x < 0.06$ may be attributed to the following factors:

- > Decreased electron affinity of the material (Bi_2S_3) as a result of introduction of 'Sb'.
- > Creation of donor levels in the band gap of the material which effectively shifts the Fermi level in upward direction and hence an increase in the band bending at the interface [19,20].

For n-type photoanode, the larger the value of flat band potential, more negative is the photoelectrode and greater is the possible photovoltage. The flat band potential decreases at higher values of 'x', which may be attributed to the pinning of Fermi level [6].

Table 2

Photovoltaic parameters of ECPV cells employing n- $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{S}_3$ ($x = 0-0.10$) photoanodes. Intensity of illumination: 60 mW/cm².

x	Electrode composition	V_{oc} (mV)	I_{sc} (μA)	η (%)	FF	R_s (Ω)	R_{sh} (Ω)	n	V_{fb} (V)	E_g (eV)
0	Bi_2S_3	85	66	0.02	0.71	469	1381	4.16	0.590	1.71
0.01	$(\text{Bi}_{0.99}\text{Sb}_{0.01})_2\text{S}_3$	98	76	0.03	0.71	273	1789	3.08	0.649	1.65
0.02	$(\text{Bi}_{0.98}\text{Sb}_{0.02})_2\text{S}_3$	126	90	0.04	0.74	229	1917	5.05	0.663	1.63
0.03	$(\text{Bi}_{0.97}\text{Sb}_{0.03})_2\text{S}_3$	193	104	0.07	0.62	217	2802	2.50	0.757	1.56
0.04	$(\text{Bi}_{0.96}\text{Sb}_{0.04})_2\text{S}_3$	324	140	0.21	0.68	195	2894	2.35	0.895	1.51
0.05	$(\text{Bi}_{0.95}\text{Sb}_{0.05})_2\text{S}_3$	332	182	0.30	0.77	139	3379	1.15	0.930	1.42
0.06	$(\text{Bi}_{0.94}\text{Sb}_{0.06})_2\text{S}_3$	277	84	0.11	0.79	220	2957	1.93	0.850	1.49
0.07	$(\text{Bi}_{0.93}\text{Sb}_{0.07})_2\text{S}_3$	241	90	0.10	0.75	249	2421	2.31	0.790	1.53
0.08	$(\text{Bi}_{0.92}\text{Sb}_{0.08})_2\text{S}_3$	144	66	0.05	0.72	280	2318	1.54	0.672	1.62
0.09	$(\text{Bi}_{0.91}\text{Sb}_{0.09})_2\text{S}_3$	104	34	0.01	0.57	386	1979	1.62	0.640	1.73
0.10	$(\text{Bi}_{0.90}\text{Sb}_{0.10})_2\text{S}_3$	97	28	0.01	0.62	475	1587	3.24	0.630	1.90

Table 1

Film deposition conditions.

Spray parameter	Condition
Substrate temperature	300 $^\circ\text{C}$
Substrate–nozzle distance	5 cm
Molar concentration of the precursors	0.2 M
Compressed air pressure	10^5 Pa
Spray rate	0.5 ml/min
Total volume of the solution sprayed for each deposition	50 ml

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