ELSEVIER

Solar Energy Materials & Solar Cells 79 (2003) 57–65

Solar Energy Materials & Solar Cells

www.elsevier.com/locate/solmat

Photoelectrochemical characteristics of brush plated tin sulfide thin films

B. Subramanian[a,*], C. Sanjeeviraja[b], M. Jayachandran[a]

[a] *Central Electrochemical Research Institute, Karaikudi 630 006, India*
[b] *Department of Physics, Alagappa University, Karaikudi 630 006, India*

Received 8 August 2002; accepted 2 September 2002

Abstract

Thin films of tin sulfide find wide applications in optoelectronic devices and window materials for heterojunction solar cells. Thin films of p-SnS were brush plated onto tin oxide coated glass substrates from aqueous solution containing $SnCl_2$ and $Na_2S_2O_3$. Deposits have been characterized with XRD and SEM for structural analysis. Hot probe method showed invariably p-type nature for all the brush plated SnS films. The variation of space charge capacitance, C_{sc}, with applied potential, V, was recorded for the PEC cell with p-SnS/Fe^{3+}, Fe^{2+}/Pt system. The spectral response of the PEC cell formed with SnS photoelectrode was studied and reported.

Keywords: Thin films; Brush plating; Tin sulfide

1. Introduction

Research on photovoltaics and photoelectrochemical (PEC) cells has been focused on the development of new materials with properties specially suited to solar cell applications. Tin sulfide (SnS) a IV–VI semiconductor compound with a band gap of 1.10 eV is an interesting layered semiconductor material that finds application in different fields of technological importance and in solar energy conversion [1]. The layered semiconductors are of interest in solar energy conversion due to the ingenious arrangement of the structural lattice with cations and anions. The layers of cations are separated by Van der Waals forces alone [2], which provides intrinsically a chemically inert surface with no dangling bonds, no surface density of states and

*Corresponding author.
E-mail address: tspsenthil@yahoo.com (B. Subramanian).

0927-0248/02/$ - see front matter
PII: S0927-0248(02)00366-5

therefore no Fermi level pinning at the surface. This fact leads to considerably higher chemical stability avoiding photocorrosion in PEC cells and to the fabrication of highly mismatched solid state junction without interface states. Brush plating technique has been adopted for the first time to coat SnS films on conducting tin oxide (CTO) substrates. Brush plating or selective plating differs from traditional tank or bath plating in that the work piece is not immersed in a plating solution (electrolyte). Instead, the electrolyte is brought out to the part to be plated and applied by a hand held anode or stylus, which incorporates an absorbent wrapping for applying the solution to the cathode (work-piece). A DC power pack drives the electrochemical solution, depositing the desired material on the substrate. A schematic of the brush plating process is presented elsewhere [3] by the authors. The key advantage of this process is portability. Also it is a simple and low cost electrochemical method for obtaining large area thin films, which has been increasingly used for developing metal and alloy coatings [4]. This note presents the results related to the brush plated SnS films and the SnS/electrolyte interface in PEC cells.

2. Experimental

Tin sulfide thin films were brush plated on CTO substrates (sheet resistance 20 Ω per square which is acting as the negative electrode). The stylus, consisting of a carbon rod wrapped with cotton wool served as the anode and typical deposition condition which gave SnS films [3], consists of the following: electrolyte bath contained 5.0 mM of $SnCl_2$ and 2.5 mM $Na_2S_2O_3$, pH 1.5, temperature 60°C and a plating time of 5 min. Prior to plating, the electrodes were connected to the power supply. The stylus was then brought into contact with the substrate and moved back and forth at uniform speed. The thickness of the SnS films were found to be in the range of 1.0–2.5 μm. The films were annealed in vacuum at 250°C for 30 min. Hot probe method was used to find the semiconducting nature which showed p-type conducting nature for all the SnS films. Structural characterization of the films was carried out by XRD using JEOL JDX 803a diffractometer. Surface morphological examinations were carried out by employing JSM 6400 JEOL scanning electron microscope to measure the grain size. A three electrode configuration was used for all PEC measurements. The counter electrode was platinum, the reference electrode was a saturated calomel electrode (SCE) placed very close to the SnS electrode surface during the measurements. The redox electrolyte was an aqueous solution of 0.1 M $FeCl_3/FeCl_2$ (0.05 M H_2SO_4). SUNLUX 500/250 V tungsten filament—halogen lamp was used for illuminating the electrode with a light intensity of 100 mW/cm^2. Monochromatic light was selected using ORIEL grating monochromator (USA) to study the spectral response behavior of the PEC cells. Oriel thermopile detector was used to measure the light intensities. A Vasavi VCLR7 LCR bridge with an inbuilt function generator at a frequency of 1 kHz was used for the measurement of space charge capacitance to obtain Mott-Schottky plot.

3. Results and discussion

3.1. Structural properties

In order to optimize the plating parameters for the preparation of SnS films, their colors have been observed as a first hand information at different plating parameters like concentration of S_2O_3, plating potential and plating time.

Initially 5 mM of $SnCl_2$ is taken in the plating bath. When a low concentration of 1 mM of $Na_2S_2O_3$ is added to this, a pale colored film showing the sulfur rich in the film. For the addition of 2.5mM of S_2O_3, a gray black film is obtained which is the typical color of tin sulfide film. At higher concentrations, tin-rich films are observed. These observations are shown in Fig. 1a. The effect of plating potential is studied by varying between 2 and 8 V. The optimum potential for which the characteristic black gray color of tin sulfide is obtained at 4 V as shown in Fig. 1b. Plating time is varied between 2 and 8 min. The gray black color of SnS film is obtained when plating time is 5 min, which is shown in Fig. 1c.

XRD studies revealed the polycrystalline nature of all the SnS films with the orientations corresponding to orthorhombic structure. The peaks at 26.8°, 30.1°, 33.9°, 37.8° indicate the (1 2 0), (1 0 1), (0 4 0) and (1 3 1) planes of SnS.

Fig. 2 shows the surface morphology of the brush plated SnS film. Uniform film surface without cracks and pinholes is observed. Grain size measurements were done using intercept method [5]. The grains exhibit an average size of 0.3 μm. The closely packed grains provide a pin hole free morphology leading to better spatial contact between the grains which is desirable for use in photoelectrochemical cells.

3.2. Photoelectrochemical characterization

The brush plated SnS electrodes were immersed in different electrolytes like 0.1 M (Na_2S–S–NaOH); 0.1 M [$K_3Fe(CN)_6$–$K_4Fe(CN)_6$]; 0.1 M (KI–I_2) and 0.1 M ($FeCl_2$–$FeCl_3$), 0.05 M H_2SO_4. Preliminary PEC studies are carried out for these electrolytes to choose the most suitable electrolyte for best conversion efficiency and stability. It is found that 0.1 M ($FeCl_2$–$FeCl_3$), 0.05 M H_2SO_4 is the most suitable electrolyte which shows photoactivity and the layers are very stable in this electrolyte.

To investigate the nature of the junction formed with SnS and the electrolyte, dynamic current–voltage ($I-V$) characteristics of the PEC cell are studied. The potentiostatic current–voltage ($I-V$) curve of the semiconductor electrode, usually obtained by impressing varying voltages on the semiconductor and measuring the current both in dark (I_d) and under illumination (I_{ph}) provides important informations. It is observed from Fig. 3 that the curves obtained for the film under illumination are shifted to higher current region. It indicates that the films prepared by the brush plating technique have high photosensitivity.

The linear plot of I^2ph versus potential V(SCE) is extrapolated to intercept the x-axis. The flat band potential value of 0.52 V(SCE) for electrodeposited SnS film and 0.46 V(SCE) for brush plated SnS film have been obtained. This is

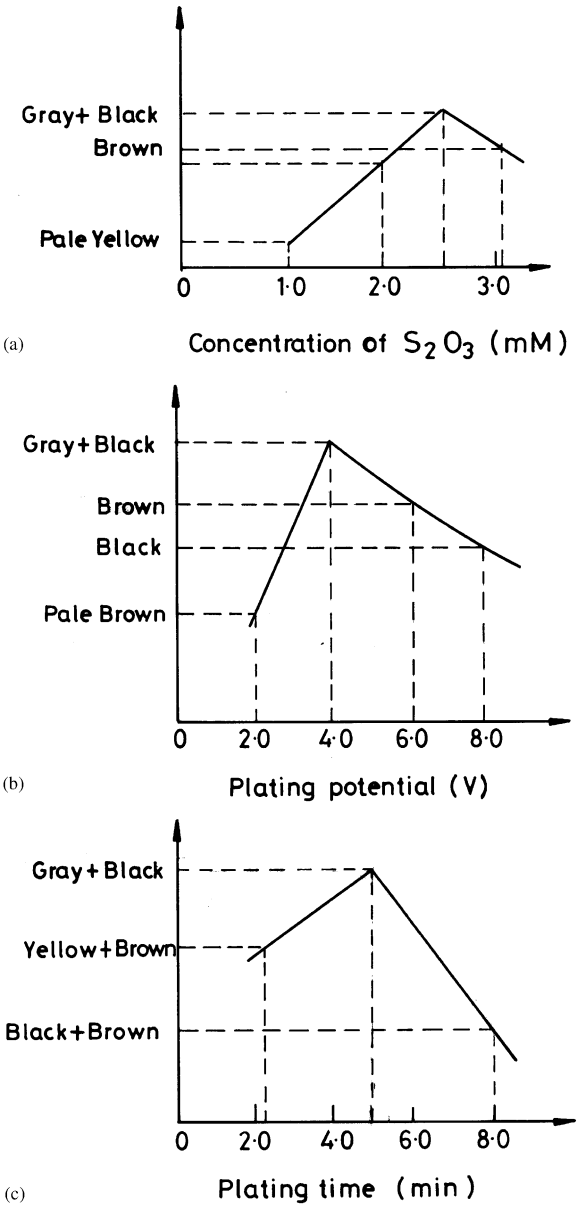

Fig. 1. Primary color observations for different plating parameters on brush plated SnS films (a) concentration of S_2O_3, (b) plating potential, (c) plating time

good agreement with the values of 0.48 V(SCE) and 0.42 V(SCE) obtained for electrodeposited and brush plated SnS films, respectively.

The variation of space charge capacitance, C_{sc} with applied potential, V was recorded [6] for the PEC cell with p-SnS/Fe^{3+}, Fe^{2+}/Pt system in dark at a

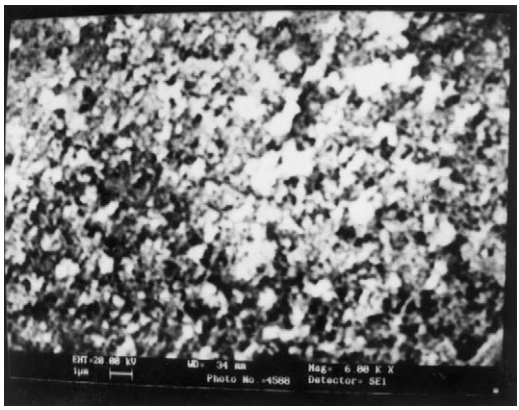

Fig. 2. Surface morphology of the brush plated SnS film.

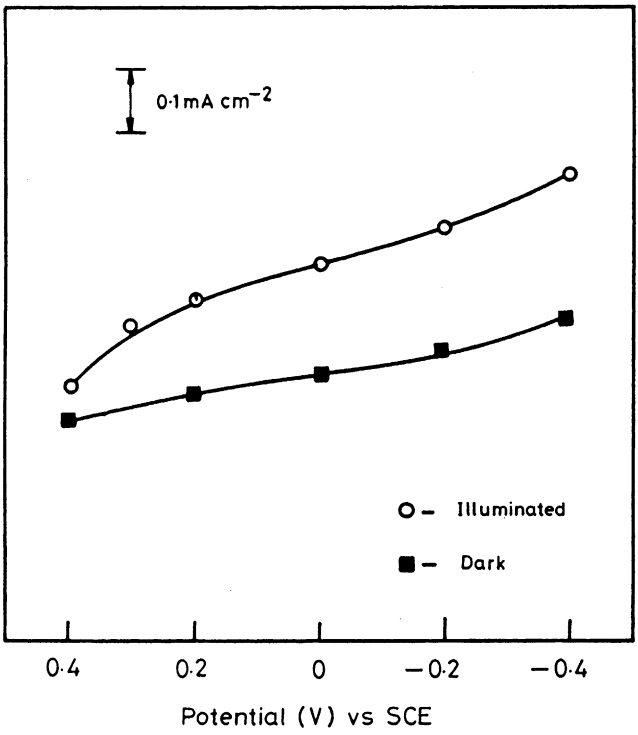

Fig. 3. Current–voltage (I-V) characteristics of the brush plated SnS film.

frequency of 1 kHz. Mott-Schottky plot drawn between C_{sc}^{-2} and V is shown in Fig. 4 whose slope confirms the p-type conductivity of the brush plated SnS films. The intercept of the linear plot at $C_{sc}^{-2} = 0$ gives the flat band potential and the other

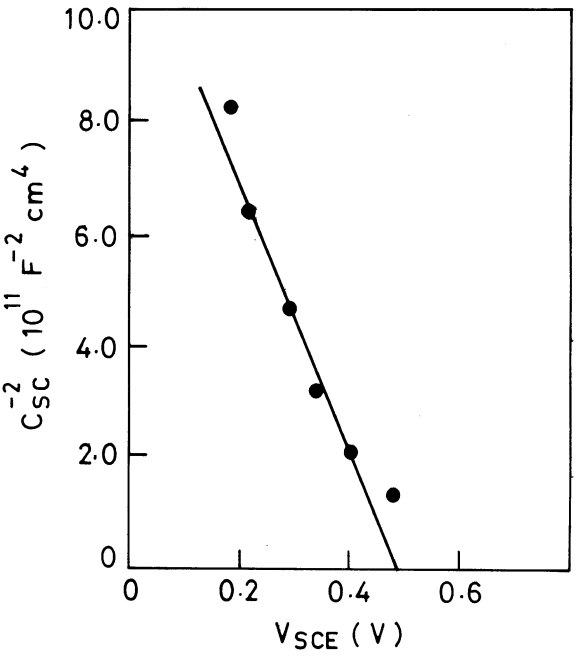

Fig. 4. Mott-Schottky plot for a brush plated SnS film.

Table 1
Summary of results obtained from Mott-Schottky plot

Sl. No.	Physical parameter	Value obtained
1	Electrolyte used	Fe^{3+}/Fe^{2+}
2	Flat band potential, V_{fb}	$0.49V$(SCE)
3	Acceptor concentration, N_A	$3.1 \times 10^{16}\,cm^{-3}$
4	Density of states in valance band, N_V	$4.1 \times 10^{19}\,cm^{-3}$
5	Built in voltage (band boundary), V_b	0.04 V
6	Depletion layer width, w	4.9×10^{-5} cm
7	Conductivity	p-type

important physical parameters pertaining to the semiconductor properties of SnS films, calculated using the Mott-Schottky plot, are presented in Table. 1.

Spectral response study is important in the sense that it enables to identify the recombination centers and consequently in diagnosing the problems that have influence on the conversion efficiency [7]. Ideally, the normalized spectral response is flat at wavelengths below the edge limit and is independent of the irradiance. In order to study the PEC reaction under illumination in a PEC cell fabricated with a given semiconductor film, it is quite obvious to measure the wavelength dependence of its photocurrent. The profile of a photocurrent to the wavelength of the incident light is the action spectrum of photocurrent [8].

The spectral response of the PEC cell formed with SnS photoelectrode was studied by recording the short circuit photocurrent (I_{sc}) as a function of wavelength (λ) of the illumination light and is shown in Fig. 5. The I_{sc} value is increasing up to the spectral region of 1030–1070 nm and then decreases. A peak in the photocurrent spectrum is observed at 1050 nm, which corresponds to the maximum absorption behavior of the SnS film. The band gap calculated from this peak is equal to 1.18 eV, which is in good agreement with the literature value of 1.10 eV [1].

The decay of the photocurrent towards the shorter wavelength side may be due to the absorption of the incident light by the electrolyte or due to large amount of the surface recombination of the photo-generated minority carriers. Similarly, the sharp decay of photocurrent towards the longer wavelength side is attributed to the poor absorption of light of short wavelength by the photoelectrode [7].

PEC cells were fabricated using as-deposited and vacuum annealed p-SnS films. The area of the electrode exposed to the electrolyte was kept constant as 0.25 cm^2. The photocurrent versus photovoltage (power out put) out put curves under 100 mW/cm^2 illumination for these cells are shown in Fig. 6. The PEC device parameters like short circuit current (I_{sc}), open circuit voltage (V_{oc}), series resistance (R_s), shunt resistance (R_{sh}), fill factor (FF) and conversion efficiency (η) have been extracted from these power out put curves and are presented in Table 2. The values of series resistance (R_s) and shunt resistance (R_{sh}) were evaluated from the slopes of the power output plots using the relation [9]

$$(dI/dV)_{I=0} \sim 1/Rs, \tag{1}$$

$$(dI/dV)_{V=0} \sim 1/R_{sh}. \tag{2}$$

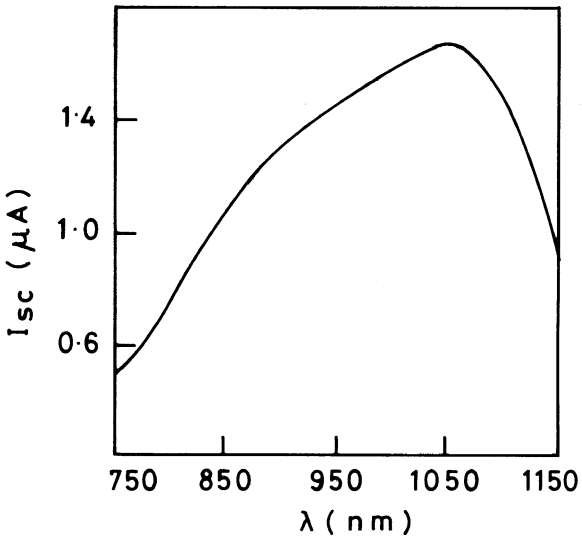

Fig. 5. Spectral response of SnS photoelectrode.

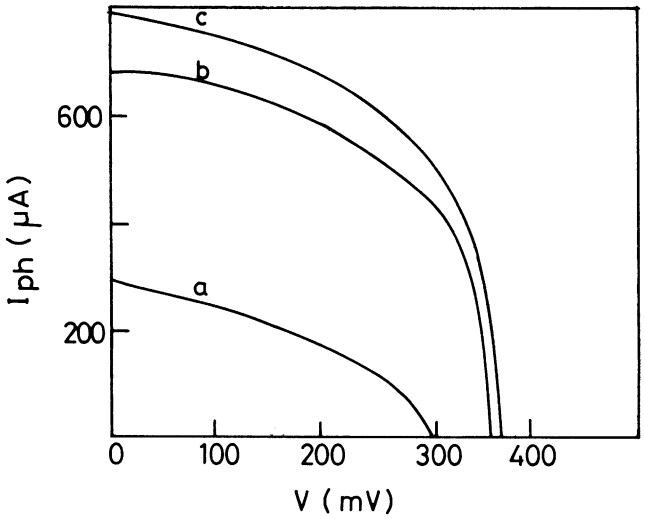

Fig. 6. Plot of power output characteristics for a typical p-SnS/Fe^{3+}, Fe^{2+}/Pt PEC solar cell.

Table 2
Parameters obtained from power output plot

Sl. No.	Condition of SnS film	I_{sc} (μm)	V_{oc} (mV)	FF(%)	η (%)	R_s (Ω)	R_{sh} (Ω)
1	As-deposited	300	310	41	0.21	200	1900
2	Vacuum annealed	690	360	52	0.51	45	4000
3	Photoetching	780	370	55	0.63	50	5000

The conversion efficiency of the PEC cell with as-deposited SnS film as shown in Fig. 6a is very low of about 0.21%. This may be due to the high series resistance of 200 Ω and low shunt resistance which reflects the quality of the as-deposited SnS films. To improve the film quality, vacuum annealing was carried out which increased the packing density of the grains and the grain size as well. Further, vacuum annealing might have improved the adhesion of the substrate thereby increasing the contact area to a larger extend. Consequently, this annealing step has increased the PEC conversion efficiency to about 0.51% as seen from Table 2 and Fig. 6b. This improved efficiency for the vacuum annealed films may be attributed to the decrease in R_s and to the substantial increase in R_{sh} value.

In order to improve the conversion efficiency further, photoetching was carried out for the vacuum annealed p-SnS films in 0.1 M $FeCl_3$–$FeCl_2$, 0.05 M H_2SO_4 solution for 30 s and illuminating the electrode with of 50 mW/cm^2 white light. The power out put curve of the PEC cell with photoetched p-SnS film is shown in Fig. 6c and the cell parameters are given in Table 2. Photoetching is found to increase the I_{sc} to a greater extend while the photovoltage is marginally increased by 10 mV. Though R_s value is slightly increased, R_{sh} value is largely increased to 5000 Ω which has improved the conversion efficiency to 0.63%. This increase may be due to the

removal of unwanted material over the film surface as well as in the grain boundaries by the etching process which might have exposed layer surface of the SnS films to make contact with the electrolyte. Consequently, more electron–hole pairs might have been produced leading to an increase in photovoltage and photocurrent.

But the overall efficiency of the PEC cells is lower than 1% which may be due to the low diffusion length of the carriers in the SnS layer, high superficial recombination in the interface and a low electric field in the p-SnS/electrolyte interface.

4. Conclusions

The brush plating technique can be successfully employed for the preparation of device quality SnS films. Vacuum annealing improves the film quality and the surface morphology leading to an increase in the PEC conversion efficiency. Photoetching further increases the conversion efficiency of the PEC cell. Further, it is an interesting observation to note that the output of the PEC cells with brush plated p-SnS films was constant for more than 3 months which indicates that the SnS film is highly stable both in chemical as well as photochemical conditions.

References

[1] M. Parenteau, C. Carlone, Phys. Rev. B 41 (1990) 5227.
[2] F. Huiller, in: F. Ley (Ed.), Structural Chemistry of Layered Type Phases, D. Reidel, Dodrecht, Holland/Boston, 1976.
[3] M. Jayachandran, S. Mohan, B. Subramanian, C. Sanjeeviraja, V. Ganesan, J. Mater. Sci. Lett. 20 (2000) 381–383.
[4] J.C. Norris, Metal Finishing 86 (1988) 45.
[5] A. Cottrell, Introduction to Metallurgy, Arnold, London, 1975, p.173.
[6] V. Damodara Das, L. Damodare, Solid State Commun. 99 (1996) 723.
[7] M. Sharon, B.M. Prasad, K. Basavaswaran, Ind. J. Chem. 28 (1989) 935.
[8] A. Fujishima, M. Aizawa, T. Inove, Electrochemical Methods, Giho-do Tokyo, 1984.
[9] T.J. Coutts, Sol. Energy Mater. 50 (1978) 99.