



Materials properties of electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ films and characterization of photoelectrochemical solar cells

B. Subramanian^{a,*}, C. Sanjeeviraja^b, M. Jayachandran^a

^aCentral Electrochemical Research Institute, Karaikudi 630 006, India

^bDepartment of Physics, Alagappa University, Karaikudi 630 003, India

Received 23 August 2002; received in revised form 6 January 2003; accepted 6 January 2003

Abstract

Thin films of tin sulfoselenide ($\text{SnS}_{0.5}\text{Se}_{0.5}$) have been electrodeposited from an aqueous solution on tin oxide coated glass substrates by potentiostatic technique. XRD pattern of $\text{SnS}_{0.5}\text{Se}_{0.5}$ films showed polycrystalline nature and orthorhombic structure. The presence of Sn, S, and Se of the films were confirmed by XPS analysis. All films showed an indirect band gap. Surface morphological studies were carried out using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) analyses. Mott–Schottky plots have been drawn (in the dark condition) to evaluate the semiconductor parameters which confirmed the p-type nature of the films. The photoelectrochemical behavior of the $\text{SnS}_{0.5}\text{Se}_{0.5}$ films was studied in the electrolyte containing 0.1 M ($\text{FeCl}_2/\text{FeCl}_3$) + 0.05 M H_2SO_4 and the results are reported.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: A. Thin Films; B. Chemical synthesis

1. Introduction

This ternary compound has recently attracted much interest in solar energy conversion because of the bandgap tailoring effected by the incorporation of sulfur (S) in tin selenide (SnSe). Structural properties of the material play a dominant role in the performance of the devices and a knowledge of the influence of various deposition parameters on the structural properties of thin films is essential before the application of this materials in devices [1–3].

Literature shows very few reports on SnSSe in their thin film form. The two compounds SnSe and tin sulfide (SnS) form a continuous series of mixed crystals with a minimum melting point of 853 °C at the

* Corresponding author. Tel.: +91-4565-427-555; fax: +91-4565-427-713.

E-mail address: tpsenthil@yahoo.com (B. Subramanian).

composition $\text{SnS}_{0.5}\text{Se}_{0.5}$. The crystals are all p-type with hole concentration of about 10^{18} cm^{-3} . The band edge absorption is found to be allowed indirect transition. The band gap of SnS and SnSe at 300 K was 1.30 and 0.90 eV, respectively [4].

The mixed crystals of composition $\text{SnS}_{0.5}\text{Se}_{0.5}$ have the same crystal structure as SnS and SnSe. No superstructure was observed [5]. The unit cell contains eight atoms which are arranged in two adjacent double layers orthogonal to the largest cell dimensions [6]. Within either double layer, each atom has three nearest neighbors and two next nearest neighbors. A sixth nearest neighboring atom lies in the other double layer and provides the bond between double layers. The resulting highly layered structure, typical of all orthorhombic chalcogenide crystals, causes a strong anisotropy of the physical properties of these compounds [6]. An elaborate research is carried out on the structural, optical, electrical, and photoelectrochemical properties of electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ with composition varied from $x = 0, 0.5$, and 1. The material properties of SnSe ($x = 0$) and SnS ($x = 1$) are published elsewhere by the authors [6,10] and the results presented in this article refers only to $x = 0.5$.

2. Experimental

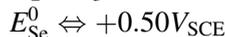
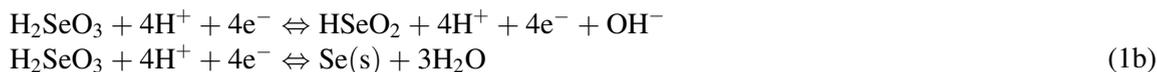
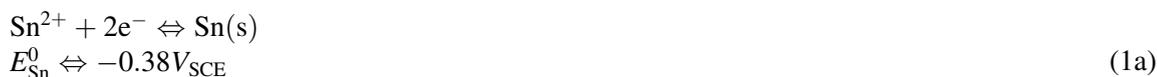
The $\text{SnS}_x\text{Se}_{1-x}$ films were cathodically electrodeposited on tin oxide coated glass substrates. The deposition bath has been chosen to have x value of 0.5 in the deposits. The deposition bath contained 5.0 mM of SnCl_2 , 2.5 mM of $\text{Na}_2\text{S}_2\text{O}_3$ and 2.5 mM of SeO_2 . The pH of the bath was adjusted to 1.5. An EG&G PAR potentiostat Model 270 was employed in performing cyclic voltammetry experiments. The films were characterized by X-ray diffraction for structural analysis using JEOL JDX 803a X-ray diffractometer. A carry 5E spectrophotometer was used to carry out the optical studies in the range 400–1500 nm. Morphological studies were carried out by employing JSM 6400 JEOL scanning electron microscope and Nanoscope E scanning probe microscopy 3138 J. The X-ray photoelectron spectroscopy (XPS) spectrum was taken using VG MKII ESCA spectrometer. A three electrode configuration was used for the photoelectrochemical measurements. Platinum was used as a counter electrode and the reference electrode was a saturated calomel electrode (SCE) placed very near to the thin film photoelectrode during the measurement of cell output. The distance between the semiconductor photoelectrode and counter electrode was kept constant at 1.0 cm. The redox electrolyte, (aq) 0.1 M $\text{FeCl}_3/\text{FeCl}_2$ (0.05 M H_2SO_4), was prepared using analytical reagent (AR) grade chemicals. SUNLUX 500 W/250 V tungsten filament halogen lamp was used for white light illumination at 100 mW/cm^2 . The illumination intensity was measured by CEL suryamapi instrument. A Vasavi LCR bridge with in-built 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

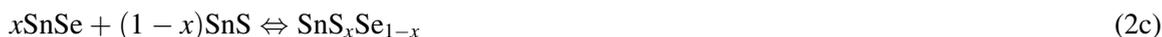
3.1. Electrodeposition of $\text{SnS}_{0.5}\text{Se}_{0.5}$

Tin selenide, tin sulfide, and tin sulfoselenide have been electrodeposited on tin oxide coated glass substrate by potentiostatic technique. The primary electrochemical reactions for the deposition of films

and their respective Nernst equilibrium potentials are



When the required potential is applied, the ions undergo the discharge process and the deposit of $\text{SnS}_x\text{Se}_{1-x}$ is formed by the solid state reaction plated species as



To deposit $\text{SnS}_{0.5}\text{Se}_{0.5}$ solid solution, the different sulfur and selenium ion concentrations are used. Fig. 1 shows the curves obtained for 5 mM SnCl_2 + 2.5 mM $\text{Na}_2\text{S}_2\text{O}_3$ + 2.5 mM SeO_2 solution keeping pH at 1.5. During the cathodic scan the current starts increasing first at about -0.4 V and then a peak is observed at about -0.75 V. The broad peak may be due to the deposition of tin sulfoselenide compound. When the scan reverses, no anodic peak is observed. This confirms the formation of stable $\text{SnS}_{0.5}\text{Se}_{0.5}$ compound alone without any individual species deposited along with the compound. The compound is highly stable and it does not dissolve in the potential range engaged for the scan.

It is observed that when the scan rate increases, the cathodic peak height increases. However, there is no dissolution peak observed for all the scan rates. This confirms the stable compound formation and the irreversible nature of $\text{SnS}_{0.5}\text{Se}_{0.5}$ formed.

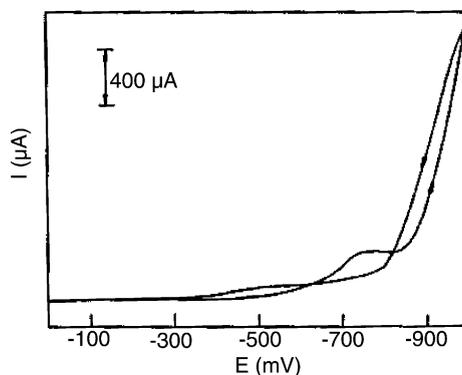


Fig. 1. Cyclic voltammogram pattern obtained for 5.0 mM SnCl_2 + 2.5 mM $\text{Na}_2\text{S}_2\text{O}_3$ + 2.5 mM SeO_2 at the scan rate of 20 mV/s.

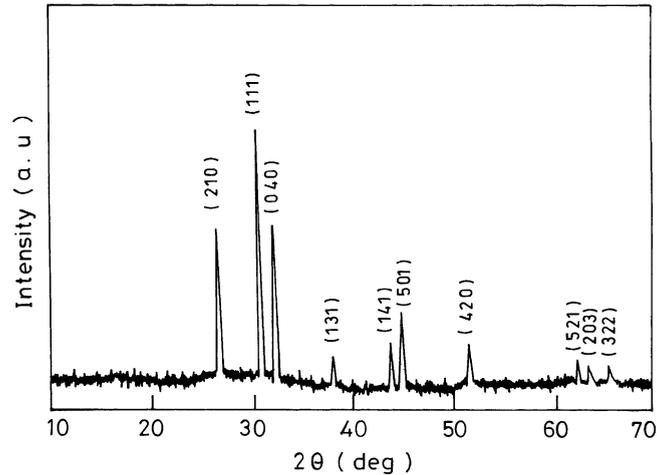


Fig. 2. XRD pattern obtained for electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ films.

3.2. Materials properties of $\text{SnS}_{0.5}\text{Se}_{0.5}$ films

XRD patterns for the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ film prepared under the optimized conditions are as shown in Fig. 2. The XRD peaks are corresponding to orthorhombic structure [5]. The lattice parameter values for the dominant orthorhombic structure are $a = 1.135$, $b = 0.404$, and $c = 0.437$ nm. The presence of monophase confirms the fact that SnSe and SnS form good solid solutions.

An XPS spectrum obtained for a typical $\text{SnS}_{0.5}\text{Se}_{0.5}$ film electrosynthesized at optimized conditions is shown in Fig. 3. A relative atomic concentration of 41.4% of Sn, 18.8% of Se, 19.5% of S, 10.5% of O and 8.8% of carbon is noticed. After argon ion sputtering for 4 min, a slight change is only observed

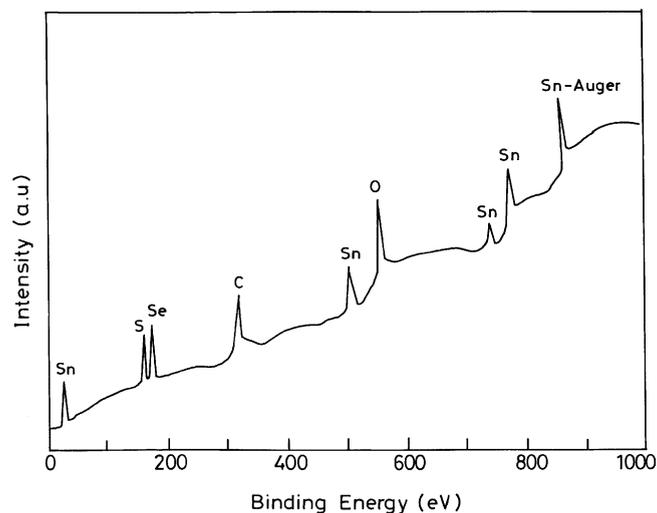


Fig. 3. Survey XPS data for the as prepared and sputtered $\text{SnS}_{0.5}\text{Se}_{0.5}$ films.

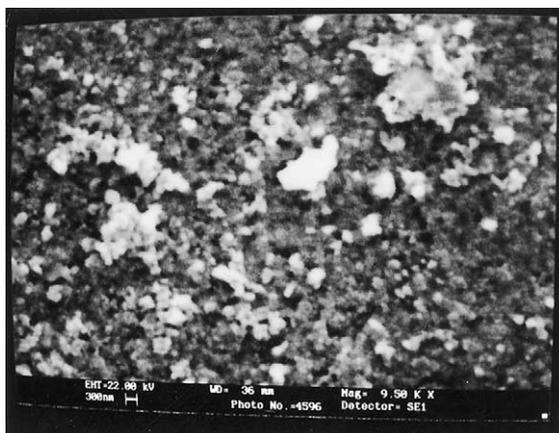


Fig. 4. Scanning electron micrograph of the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ films.

in the atomic concentration. The significant level of ‘O’ may be due to incipient corrosion process during the synthesis of films [7]. XPS data unequivocally rule out the presence of any SnS_2 or SnSe_2 in all the samples.

Using the hot probe method, it was observed that all the samples have p-type conductivity. Thickness of the films was measured from weight difference method and found to be 1.0–1.1 μm .

The surface morphological examination of $\text{SnS}_{0.5}\text{Se}_{0.5}$ deposited onto tin oxide coated glass substrates is as shown in Fig. 4. The deposit distribution is almost homogeneous, adherent, and in spherical granular shape. Grain size is determined from the intercept method [8,9]

$$\text{Grain size} = 1.5 \times l / (nm)$$

Where m is the micrograph magnification, l the length of the line drawn on the micrograph, n the number of grains crossed by the line, and 1.5 is the parameter assuming spherical grains. The grain size and grain density as determined from intercept method are found to be 0.6 μm and $4.42 \times 10^{12} \text{ cm}^{-3}$, respectively.

AFM images reveal that these films have a granular morphology. Irregular shaped grains are also seen. The AFM data are analyzed by averaging the roughness of an area of $5 \mu\text{m} \times 5 \mu\text{m}$ for different random positions on the sample surface in order to minimize the influence of local topography variations. Fig. 5 shows three-dimensional AFM images for an area of $5 \mu\text{m} \times 5 \mu\text{m}$ for $\text{SnS}_{0.5}\text{Se}_{0.5}$ with thickness of 1.0 μm . It shows the presence of high hills on top of a homogeneous granular background surface. The density and the height of the hills increase with the thickness of the deposit. The growth of the tin chalcogenide film on tin oxide substrates by electrodeposition is associated with the formation of three-dimensional grains in the perpendicular direction without lateral diffusion of ad-atoms on the surface parallel to the substrate. This is attributed to the preferentially oriented crystalline nature of the tin oxide substrate over which the film is deposited [10].

The absorption spectrum for the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ film is shown in Fig. 6. Since the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ are linear, the indirect nature of the optical transition is observed. The bandgap values calculated is 1.1 eV which is the first ever reported value for $\text{SnS}_{0.5}\text{Se}_{0.5}$ thin films. A linear variation of the band gap E_g with the composition ‘x’ was observed [6,10]. The continuous differential

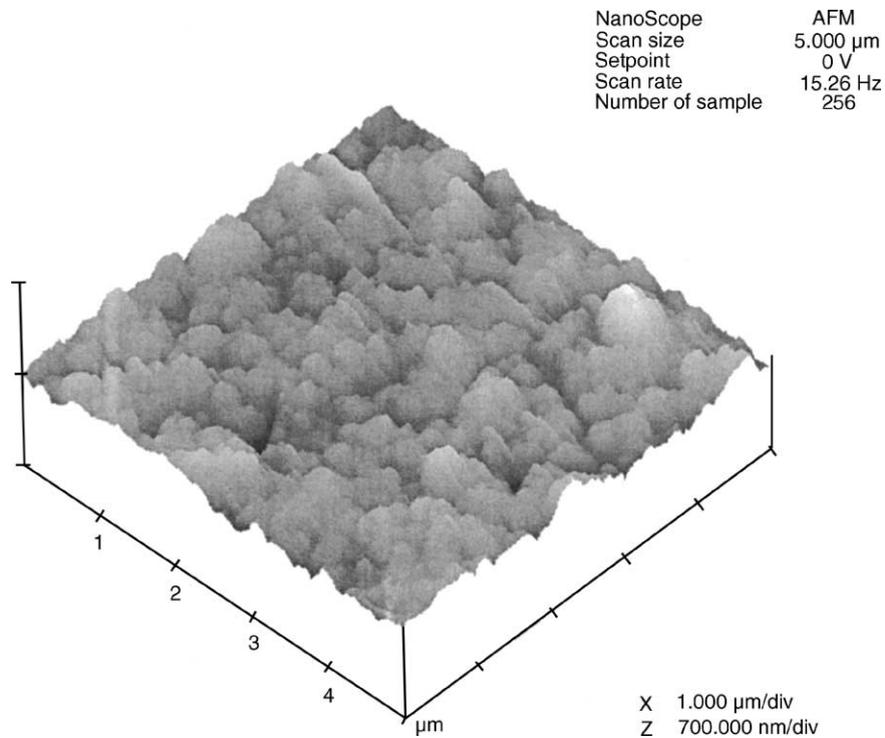


Fig. 5. AFM image of the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ films.

descent (CDD) method [11] was used to determine the optical constants, the refractive index (n) and the extinction co-efficient (k). The variation of the values of ' n ' and ' k ' for the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ film is shown in Fig. 7. The ' n ' values vary in the range of 2.5–3.5 which shows the same trend as the end members (i.e. SnS and SnSe). The k values are very low in the order of 0.1.

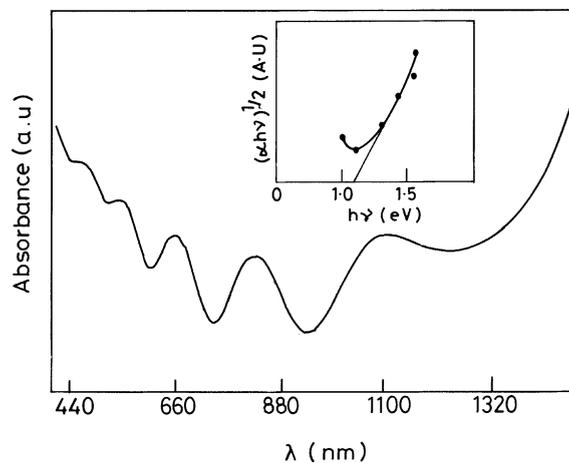


Fig. 6. Variation of optical absorption with wavelength for the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ films.

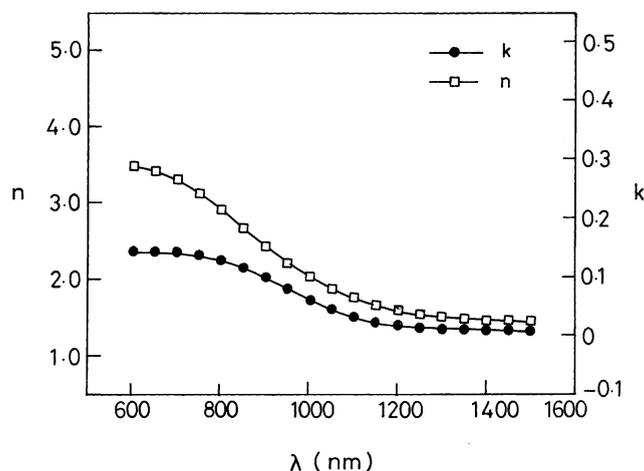


Fig. 7. Variation of refractive index (n) and the extinction coefficient (k) with wavelength for the $\text{SnS}_{0.5}\text{Se}_{0.5}$ thin films.

3.3. Photoelectrochemical studies

The $\text{SnS}_{0.5}\text{Se}_{0.5}$ thin film samples were kept in 0.05 M H_2SO_4 for a period of 3 weeks, and the filtered solution was analyzed by atomic absorption spectrometry (AAS) for any possible presence of Sn and Se. The resulting solution contained no tin or selenium, confirming the stability of the films in 0.05 M H_2SO_4 . The PEC cells formed with this samples were subjected to constant illumination using tungsten–halogen lamp at an intensity of $100 \text{ mW}/\text{cm}^2$ for 24 h. The redox electrolyte was analyzed by AAS for tin and selenium, and was found to contain very small traces of Sn^{2+} ions. This suggests that the compound is photochemical stable.

Fig. 8 shows the Mott–Schottky plot [12,13] for the typical $\text{SnS}_{0.5}\text{Se}_{0.5}$ film in 0.1 M ($\text{FeCl}_2/\text{FeCl}_3$) + 0.05 M H_2SO_4 redox electrolyte solution. The nature of the Mott–Schottky plot shows that the films are p-type. The intercept on the voltage axis yields the value of flat band potential, V_{FW} as $0.57V_{\text{SCE}}$. Using Mott–Schottky plots, the important semiconductor parameters such as acceptor concentration, density of states in the valance band and depletion layer width (W) are estimated and presented in Table 1.

The spectral response of the PEC cell formed with $\text{SnS}_{0.5}\text{Se}_{0.5}$ photoelectrons was studied by recording the short circuit photocurrent as a function of wavelength (λ) of the illumination light and is illustrated in Fig. 9. The I_{sc} values are found to increase with increase in wavelength upto 1100 nm and

Table 1
Semiconductor parameters derived from Mott–Schottky plot

Physical parameter	Results
Electrolyte used	$\text{Fe}^{3+}/\text{Fe}^{2+}$
Acceptor concentration, (N_A) (cm^{-3})	4.5×10^{16}
Density of states in the valance band, (N_V) (cm^{-3})	4.02×10^{19}
Depletion width (W) (cm)	4.4×10^{-5}
Carrier type	p

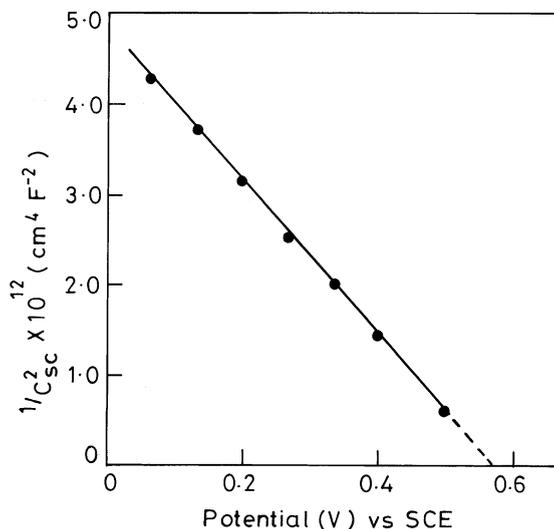


Fig. 8. Mott-Schottky plot for the p-SnS_{0.5}Se_{0.5}/Fe³⁺, Fe²⁺/Pt systems at a frequency of 1 kHz.

then decreased. It is seen that the PEC cell with electrodeposited SnS_{0.5}Se_{0.5} photoelectrode exhibits a peak photocurrent which corresponds to a bandgap value of 1.12 eV. The results obtained are in good agreement with the results from optical absorption studies. The steep rise in photocurrent towards the higher energy (shorter wavelength) side may be due to absorption of incident light by the electrolyte and the sharp fall in the photocurrent towards the longer wavelength can be attributed to the poor photoresponse of the electrode.

For photoelectrochemical solar cell applications, a chemical etching is usually beneficial to remove damaged surface layers. The vacuum annealed SnS_{0.5}Se_{0.5} films were etched chemically at 50 °C for 15 s in a dilute acid mixture containing HCl, HNO₃, H₂SO₄, and CH₃COOH in the ratio 4:1:0.2:0.1 (by volume) and rinsed in triple distilled water.

The performance of the photoelectrodes depends strongly on the etching treatment used. In Fig. 10 curve (a) shows the *I*–*V* behaviour of unetched photocathode which exhibit poor performance due to

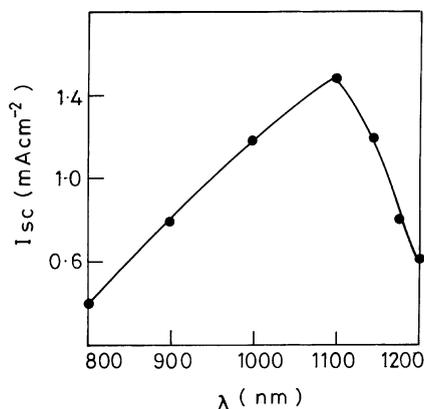


Fig. 9. Variation of photocurrent (*I*) with wavelength (λ) for the PEC cell formed using p-SnS_{0.5}Se_{0.5} thin film photoelectrode.

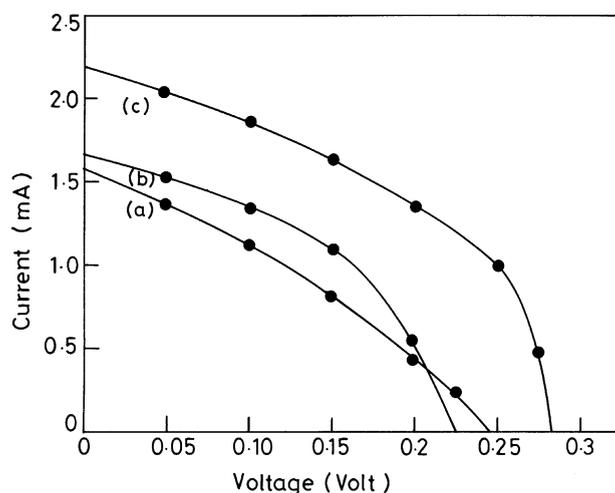


Fig. 10. Power output characteristics of PEC cells using $\text{SnS}_{0.5}\text{Se}_{0.5}$ thin film photoelectrode.

irregular morphology and damage. V_{oc} value of 0.24 V and I_{sc} value of 1.55 mA is found. Chemical etching yields an open circuit voltage (V_{oc}) of 0.23 V and short circuit current (I_{sc}) of 1.63 mA as shown in curve (b). An appreciable increase in efficiency is observed by a subsequent photoetch as observed from curve (c). Etching (chemical and photo) removes the top most surface layer resulting in selenium and sulfur vacancies [4]. The overall efficiency of the PEC cells formed with the $\text{SnS}_{0.5}\text{Se}_{0.5}$ as photoelectrodes is less than 1% which is attributed to the low diffusion length of the carriers, high superficial recombination in the interface and a low electric field in the p- $\text{SnS}_{0.5}\text{Se}_{0.5}$ electrolyte interface.

4. Conclusions

Tin sulfoselenide films have been electrodeposited from an aqueous solution on SnO_2 coated glass substrates. The $\text{SnS}_{0.5}\text{Se}_{0.5}$ films have orthorhombic structure. The voltammogram confirms the codeposition process of $\text{SnS}_{0.5}\text{Se}_{0.5}$.

The deposit distribution is almost homogeneous and adherent as observed from scanning electron micrographs. Optical studies revealed the indirect nature of the films. Using Mott–Schottky plots, the important semiconductor parameters are estimated and presented. The effect of chemical and photoetching on vacuum annealed photoelectrodes is studied. Since the semiconductor films were found to be stable chemically as well as photochemically, it could be a promising candidate for photoelectrochemical solar cell if the efficiency is improved.

References

- [1] D. Bhattacharya, S. Chaudhuri, A.K. Pal, S.K. Bhattacharya, *Vacuum* 42 (1991) 1113.
- [2] R.D. Englken, A.K. Berry, T.P. Van Doren, J. Boone, A. Shahnazary, *J. Electrochem. Soc.* 133 (1985) 581.

- [3] M.F. Ladd, R.A. Palmer, *Structural Determination by X-ray Crystallography*, Plenum Press, New York, 1964, p. 71.
- [4] F. Huiller, *Structural chemistry of layer type phases*, in: F. Ley, D. Reifel (Eds.), Dordrecht-Holland, Boston, 1976.
- [5] W. Albers, C. Hass, H. Oar, G.R. Schodder, J.D. Wascher, *J. Phys. Chem. Solids* 23 (1962) 215.
- [6] B. Subramanian, T. Mahalingam, C. Sanjeeviraja, M. Jayachandran, M.J. Chockalingam, *Thin Solid Films* 357 (1999) 119.
- [7] Z. Zainal, M.Z. Hussein, A. Ghazali, *Sol. Energy Mat. Sol. Cells* 40 (1996) 347.
- [8] Y. Wada, S. Nishimatsu, *J. Electrochem. Soc.* 125 (1978) 1499.
- [9] F.C. Hall, W.J. Howk, *J. Met.* 5 (1953) 565.
- [10] B. Subramanian, C. Sanjeeviraja, M. Jayachandran, *Mat. Chem. Phys.* 71 (2001) 40.
- [11] F.A. Bondar, Y.A. Kulypin, Y.M. Poporich, *Thin Solid Films* 55 (1970) 255.
- [12] N.F. Mott, *Proc. R. Soc. Lond. Ser. A* 171 (1939) 27.
- [13] W.Z. Schottky, *Z. Phys.* 118 (1942) 539.