Brush plating of tin(II) selenide thin films

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

[a] *Department of Physics, Alagappa University, Karaikudi 630 003 India*
[b] *Central Electrochemical Research Institute, Karaikudi 630 006 India*

Abstract

Brush plating technique has been adopted for the first time to coat tin selenide thin film on tin oxide coated conducting substrates at room temperature, 50°C and 60°C. Uniform and pinhole free films were deposited at potentials 5.0 V. XRD analyses show the polycrystalline nature of the films with orthorhombic structure. Optical studies show the indirect nature with a bandgap of 1.0 eV. SEM pictures show smooth and uniform surface morphology with a grain size of about 0.3 μm. Film roughness was characterized by atomic force microscopy. Mott–Schottky plot has been drawn to evaluate the semiconductor parameters. © 2002 Published by Elsevier Science B.V.

1. Introduction

Tin selenide films have great potential in photovoltaic systems [1] as well as their applications as memory switching devices. Because of their anisotropic character, the tin chalcogenides are attractive layered compounds, and can be used as cathode materials in lithium intercalation batteries [2]. The indirect character of the bandgap of SnSe (~ 0.9 eV) is a common property of orthorhombic IV–VI compounds [3,4] and has been confirmed by band structure calculations for

SnSe [5]. X-ray photoemission studies of valence band of tin selenide (SnSe) films were performed by Shalvoy et al. [6]. Engelken et al. [7] have deposited these films by electrodeposition and analysed their optical properties and photoconductance. Pramanik et al. [8] have also exploited a chemical method for deposition of SnSe films. The structure, composition, dielectric and AC conduction studies on thermal evaporated SnSe films have been reported [9].

Brush plating is an electroplating process which is similar to a painting operation. The equipment is compact and easy to operate. It is used to coat metal and alloy coatings on surfaces of varying size and shape. To the author's knowledge it is the first time this technique is used to prepare SnSe semiconductor film. The structural and

*Corresponding author. Tel.: +91-4565-425205; fax: +91-4565-425202.

E-mail address: alagappa@md3.vsnl.net.in, sanjeeviraja@rediff.com (C. Sanjeeviraja).

optical properties are presented in this communication.

2. Experimental details

Brush plating was carried out using Selectron Power Pack MODEL 150A-40 V. Layers were brush plated on tin oxide coated conducting substrates of about $50 \, cm^2$ which is the negative electrode. The stylus, consisting of a carbon rod wrapped in cotton wool served as the anode. The cotton wool was held in position by a porous sleeve. A sketch of the system is shown in Fig. 1. Prior to plating, the stylus was wired to the power supply and the cotton wool was soaked in the electrolyte. The stylus was then brought into contact with the tin oxide substrate and moved at uniform speed. An electrical current was found passing whenever the stylus was in contact with the substrate. This is associated with the acceleration of the ions in the electrolyte trapped within the cotton wool which were subsequently reduced at the substrate to form the SnSe layer. The bath contained $5.0 \, mM$ of $SnCl_2$ and $2.0 \, mM$ of SeO_2 and the pH was maintained at 1.5 throughout the experiment. In each case, the power unit was preset at voltage values between 2.0 and 8.0 V and the electrolyte temperature was at room temperature (RT), 50°C and 60°C. The SnSe films were characterized by X-ray diffraction for structural analysis using JEOL JDX 803a X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418 \, \text{Å}$). A cary-5E UV-VIS-NIR spectrophotometer was used to carry out the optical studies in the range 400–1500 nm for the determination of the optical bandgap. The surface morphology was studied using the JSM 35CF JEOL scanning electron microscope (SEM). A Nanoscope E scanning probe microscopy 3138 J was used for AFM analysis to observe fine structure.

3. Results and discussion

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

A low concentration of $5.0 \, mM$ of $SnCl_2$ is taken in the electrolyte bath. When deposition is performed with addition of $1.0 \, mM$ of SeO_2, a pale red colored film is obtained. Addition of $2.0 \, mM$ of SeO_2 yielded a steel gray film, the typical color of tin selenide thin films. When concentration is increased to $3.0 \, mM$ of SeO_2, a reddish colored film is formed. These are indicated in Fig. 2a. The plating potential is varied between 2.0 and 8.0 V. The optimum plating potential is found to be 5.0 V at which the steel gray colored film is obtained as shown in Fig. 2b. A thick gray color film obtained at higher potentials indicates the formation of tin rich film. The effect of plating time is studied by varying the plating time from 2 to 8 min. The typical color of SnSe thin films the steel gray is obtained at 4 min as shown in Fig. 2c. The results of XRD analysis show good agreement with these initial observations. Fig. 3 shows the typical X-ray diffractogram of SnSe thin films deposited at plating potential of 5.0 V, 4 min of deposition time and the temperature of the electrolyte was 50°C. The diffractogram indicates the polycrystalline nature of the film with all the major peaks corresponding to the orthorhombic structure. The lattice parameter values are $a = 0.445 \, nm$, $b = 0.417 \, nm$ and $c = 1.144 \, nm$ which are in good agreement with the reported value for the SnSe films prepared by molecular—beam method [10]. The calculated inter-planar spacing (d values) from these patterns was found to agree well with the ASTM data. A high intensity preferentially oriented $(1\,1\,1)$ plane is observed for the films
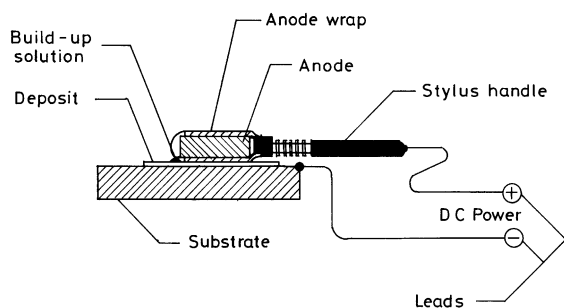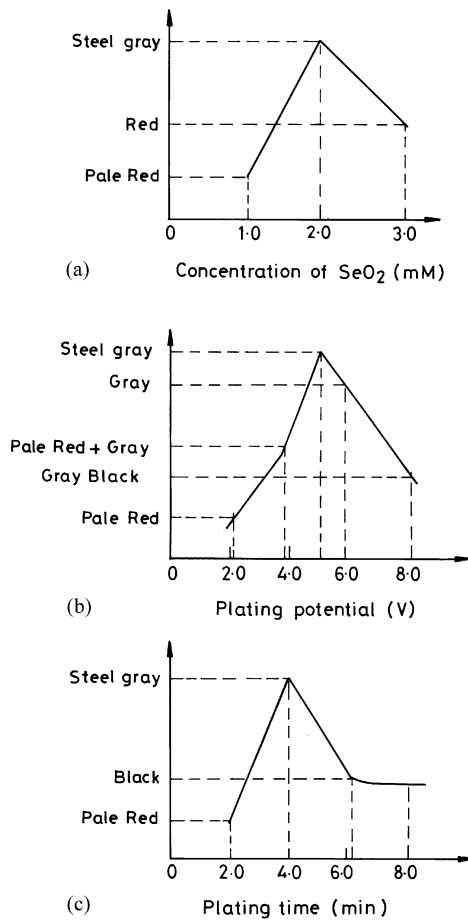

Fig. 1. Schematic diagram of brush plating.

(a) Concentration of SeO₂ (mM)

(b) Plating potential (V)

(c) Plating time (min)

Fig. 2. Variation of color with the plating parameters: (a) concentration of SeO_2; (b) potential; (c) time.
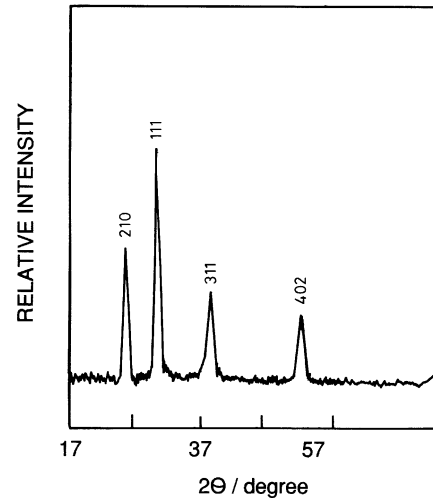

Fig. 3. X-ray diffraction spectra of the brush plated SnSe thin film.
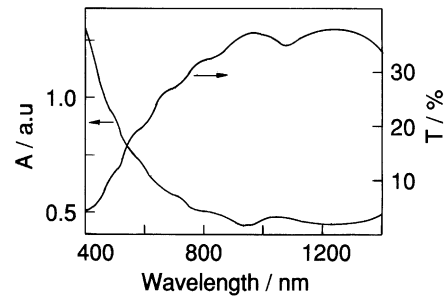
Fig. 4. Optical absorbance and transmittance spectra for brush plated SnSe film.

deposited at 5.0 V. A similar (1 1 1) orientation of the diffraction peak is observed for the SnSe films obtained by hot wall epitaxy on the glass substrates [11]. At higher potentials the film gets peeled off. A bath temperature of $50°C$ is fixed as the films obtained at this temperature are smooth, uniform and having better crystallinity. Above $50°C$, a suspension of selenium particles with orange brown in colour is observed at the bottom of the cell. A tin rich SnSe compound formation is indicated in the XRD pattern. Near stoichiometric films of SnSe as evidenced by XRD and ESCA studies are obtained for a plating time of 4.0 min. ESCA studies revealed the presence of Sn and Se on the gray brown sample as observed in the

electrodeposited SnSe thin films [12]. By the hot-probe method it was observed that all the plated films are p-type. Optical absorbance and transmittance spectra in the wavelength region of 400–1500 nm are shown in Fig. 4. The films show good absorption in the visible region. The optical data were analyzed at the near-absorption edge using the equation

$$A = K(hv - E_g)^{n/2}/hv,$$

where K and n are constants and E_g is the bandgap of the semiconductors. The value of n is equal to 4 for a direct bandgap material and 1 for indirect gap. Apparently the plot of $(\alpha hv)^{1/2}$ versus hv yields a straight line which indicates the indirect
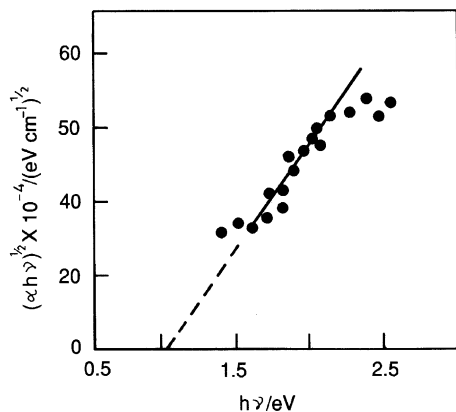
Fig. 5. A plot between $(\alpha h v)^{1/2}$ and hv for SnSe thin film.

Fig. 6. Scanning electron micrograph of orthorhombic SnSe film.

optical transition near the absorption edge, the bandgap value, estimated by extrapolating the plot to the hv axis was $1.0\,\mathrm{eV}$ (Fig. 5). This is in good agreement with the reported bandgap of $0.95\,\mathrm{eV}$ for the SnSe films prepared by chemical method [8]. The average thickness of the synthesized films was calculated from the successive maximum of the interference pattern observed in the transmittance curves as $1.2\,\mu\mathrm{m}$. The continuous differential descent (CDD) method [13] was used to determine the optical constants, the refractive index (n) and the extinction co-efficient (k). The film exhibited a continuous variation of refractive index values from 5.1 to 2.1 in the wavelength region of 400 to $1500\,\mathrm{nm}$ [14]. The extinction co-efficient for the films were observed to be very low of the order of 0.003.

As the thermal, electrical, and thermoelectric properties depend to a greater extend on thin film microstructure which in turn incorporates the important aspects like porosity, number of phases, grain size of the crystallites, the boundaries between them and texture. SEM and AFM studies were carried out in detail on these films. Further, in photoelectrochemical solar cells the series and shunt resistance mainly arises from the semiconductor films used, a knowledge of the grain size and their distribution over the surface constitutes an important study. The average size of the microcrystallites (grain size) was calculated from the extercept method using SEM pictures (Fig. 6) [15].
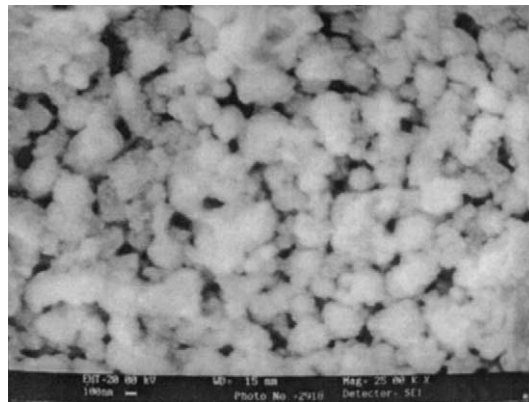
Average grain size $= 1.5\,(l/mn)$,

where m is the magnification of the micrograph, l is the length of the line drawn on the micrograph, n is the number of grains crossed by the line and 1.5 is the parameter assuming spherical grains. It is seen that the grains exhibit an average size of $0.3\,\mu\mathrm{m}$ with grain density of about $7 \times 10^{13}\,\mathrm{cm}^{-3}$. This reveals that the closely packed grains provide a pin hole free morphology leading to better spatial contact between the grains. It shows that the brush plating technique can provide device quality SnSe films with better qualities for use in photoelectrochemical cells. Fig. 7 shows an atomic force microgragh of the brush-plated SnSe film. The device quality of the film is confirmed by the smoothness of the surfaces observed from the z-axis of the three-dimensional representation. The surface is more uniform without any unwanted projections of the grains above the average surface, which renders these SnSe films more useful for photovoltaic applications. A similar observation is reported for the brush plated SnS films [16]. The well known Mott–Schottky relation in the dark gives the variation of space charge capacitance with electrode potential as

$$1/C_{\mathrm{sc}}^2 = 2/q\varepsilon_0\varepsilon_{\mathrm{s}}N_{\mathrm{A}}[V - (V_{\mathrm{FB}}k_{\mathrm{B}}T/q)],$$

where q is the electronic charge, k_{B} is the Boltzmann constant, T is the absolute temperature, V is the electrode potential, V_{FB} is the flat band potential, N_{A} is the acceptor concentration,
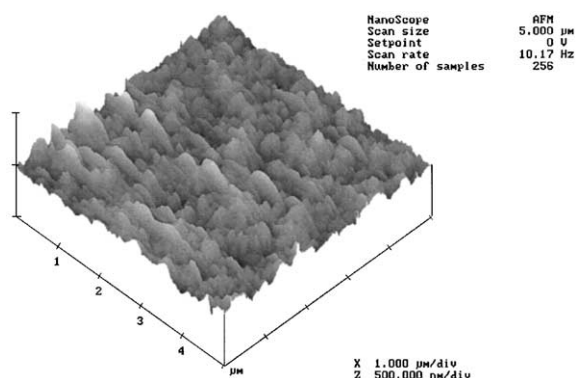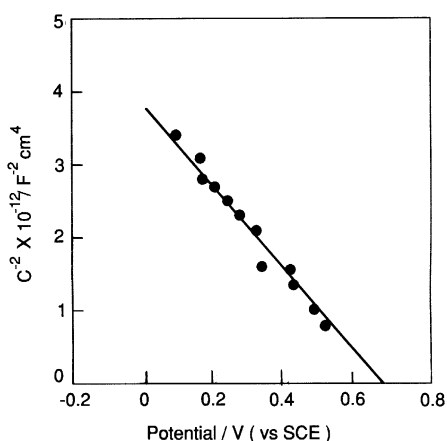
Fig. 7. AFM surface plot of brush plated SnSe film.

Table 1
Material parameters of p-SnSe thin film

Physical parameter	Value optained
Electrolyte	Fe^{3+}/Fe^{2+}
Nature	p-type
Redox Fermi level of the electrolyte (E_F redox)	$0.53\ V_{SCE}$
Flat band potential (V_{FB})	$0.68\ V_{SCE}$
Acceptor concentration (N_A)	$7.711 \times 10^{16}\ cm^{-3}$
Density of states in the valance band (N_V)	$4.144 \times 10^{19}\ cm^{-3}$

agreement with the reported value [17]. The materials parameters of the p-SnSe thin films obtained from Mott–Schottky plot are given in Table 1.

4. Conclusions

SnSe semiconductor films were deposited for the first time by the brush plating technique. The films are polycrystalline in nature and show p-type semiconducting nature. The structural, surface morphology and optical studies reveal that device quality semiconductor films can be prepared by the brush plating technique. The brush plated SnSe electrode is found stable chemically as well as photochemically making it a promising candidate for photoelectrochemical (PEC) solar cells.

Fig. 8. Mott–Schottky plot for a p-SnSe $|Fe^{3+},\ Fe^{2+}|$ Pt system.

ε_s is the static permittivity of SnSe and ε_0 is permittivity of the free space. The flat band potential was determined for the system p-SnSe $|Fe^{3+},\ Fe^{2+}|$ Pt, by plotting the reciprocal of the square of the capacitance value for the semiconductor film measured against the SCE at 1 kHz frequency. The intercept of linear plot at $1/C_{sc}^2 = 0$ gives a value of 0.68 V_{SCE} as the flat band potential at which the band bending is zero as shown in Fig. 8. The negative slope of the Mott–Schottky plot confirms p-type conductivity of the SnSe films. The acceptor concentration N_A was calculated as $7.71 \times 10^{16}\ cm^{-3}$ which is in good

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