Effects of Annealing Time on the Properties of SnSe Coatings

Zulkarnain Zainal* (a), Saravanan Nagalingam (a), Anuar Kassim (a), Mohd Z. Hussein (a) and Wan M.M. Yunus (b)

(a) Department of Chemistry, Universiti Putra Malaysia, Selangor, Malaysia
(b) Department of Physics, Universiti Putra Malaysia, Selangor, Malaysia
*Author for correspondence, e-mail: zulkar@fsas.upm.edu.my

ABSTRACT

Tin selenide powder was prepared using chemical precipitation method in alkaline aqueous medium. The crystalline powder was coated onto indium doped tin oxide glass substrates using polyvinyl alcohol solution. The coatings were subjected to annealing at various times to study the effect towards the structure and morphology of the materials. The product prepared was characterised using various techniques. The photoresponses for the samples were also studied. Annealing for 1 h was found optimum for the coatings prepared.

1. INTRODUCTION

The synthesis and characterisation of metal chalcogenides of different groups have attracted considerable attention due to their brilliant application prospects. These compounds are reported to be used as sensor and laser materials, thin films polarizers and thermoelectric cooling materials [1]. They also possess certain criteria to make them potential candidates in photoelectrochemical (PEC) solar cells. These materials are usually prepared through various techniques such as electrochemical and chemical deposition method and are quite attractive for designing systems for electro-optics and PEC solar cells. The preparation technique plays an important role in this field of research.

Considerable attention has been given by various authors in the preparation techniques of tin selenide (SnSe) films. Among the methods used are chemical bath deposition [2], vacuum evaporation, chemical vapour deposition [3-11] electrodeposition [12-14]

and brush plating [15]. SnSe is a narrow band gap binary IV-VI semiconductor displaying a variety of applications as essential material in photoelectrochemical solar cells to suppress the photocorrosion and to enhance the fill factor in electrical switches and in junction devices [11]. Because of their anisotropic character, the tin chalcogenides are attractive layered compounds, and can be used as cathode materials in lithium intercalation batteries. Thin films of tin selenide (SnSe) are also used in infrared optoelectronic devices and memory switching devices [12]. The indirect character of the bandgap of SnSe is a common property of orthorhombic IV-VI compounds and has been confirmed by band structure calculations for SnSe [15]. Its orthorhombic crystal structure with layers are stacked along the c axis with a = 4.30 Å, b = 4.05 Å and c = 11.62 Å [17]. Motivated by the potential applications of tin chalcogenides, investigations of these compounds are becoming particularly active in the field of materials

chemistry. The studies comprise spectroscopy, sensing properties and electronic structure of SnSe compounds [18]. In this paper, the properties of SnSe prepared by chemical precipitation followed by brush coating using polyvinyl alcohol solution as a binder was studied.

2. MATERIALS AND METHODS

All the reagents were of analytical grade and used without further purification. Tin selenide precipitation was carried out by mixing alkaline solutions of Sn-EDTA and elemental selenium. Sn-EDTA solution was prepared from $Na_2EDTA.2H_2O$ and $SnCl_2$. $2H_2O$. Sn-EDTA stabilised Sn2+ from further oxidation and ensure slow release of Sn2+ ions into the reaction bath [14]. The alkaline selenium solution was prepared by mixing elemental Se with excess NaOH solution (10 M). The addition of NaOH initiated the dissolution of elemental Se. The mixture was stirred rapidly to ensure complete Se dissolution. The mixture was stirred rapidly for 20 min. Upon complete dissolution of elemental Se, Sn solution complexed with EDTA was added and the stirring process was maintained for almost 15 min. Black precipitate (SnSe) obtained was centrifuged, washed with distilled water and dried in oven for 2 h.

The powder obtained was mixed together with polyvinyl alcohol solution (PVA) 10 % w/w, to form SnSe-PVA mixture. The mixture was later brush coated onto indium dopes tin oxide (ITO) glass substrate and dried for 12 h. The ITO slides was cleaned in ultrasonic bath containing ethanol and distilled water prior to use. Effects of annealing were carried out for at different time (30, 60 and 180 min) in nitrogen atmosphere at 150 °C.

X-ray diffraction (XRD) analysis was carried out using a Siemens D-5000 Diffractometer for the 2q ranging from 2 ° - 60 ° with CuKa (l = 1.5418 Å) radiation. Scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDX) was performed on a JEOL JSM 6400 Scanning Microscope. Photo responsiveness of the samples were

tested in $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system, by running linear sweep voltammetry (LSV) between -0.40 to −1.00 V. An EG & G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used to control the LSV process and to monitor the current and voltage profiles. The system consists of SnSe-PVA coatings on indium doped tin oxide glass as a working electrode, platinum and Ag/AgCl as the counter and reference electrodes. The photocurrent (I_p) and darkcurrent (I_d) of the PEC cells were recorded under dark and light illumination using a tungsten-halogen lamp (100 W).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the SnSe crystalline powder obtained. The peaks in the pattern indicate the formation of orthorhombic phase of SnSe. The results are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS) values (File No. 32-1382) for SnSe (Table 1). $Na_2EDTA·2H_2O$ was used to complex tin ions, in order to ensure slow release of Sn^{2+} ions into the reaction bath, leading to the formation of tin selenide. If $SnCl_2·2H_2O$ was directly used, it would hydrolyse in aqueous solution and produce a precipitate of Sn(OH)Cl. In the meantime it would also produce tin oxides in alkaline solutions. The formation of tin complex avoids the occurrence of these impurities. From the XRD pattern, no peaks corresponding to Se could be seen. This indicates that the sample powder contains no elemental Se.

Figure 2 shows the XRD patterns of the SnSe-PVA coatings annealed at different period. The results are well matched with the JCPDS values (File No. 32-1382) for SnSe (Table 2). The crystalline phase of the peaks due to SnSe improved as the annealing time was increased from 30 to 180 min. This could be clearly seen in the higher intensity peak for the (111) plane in the coating annealed at 60 min. The total peaks due to SnSe also increased for the coating annealed at 60 min
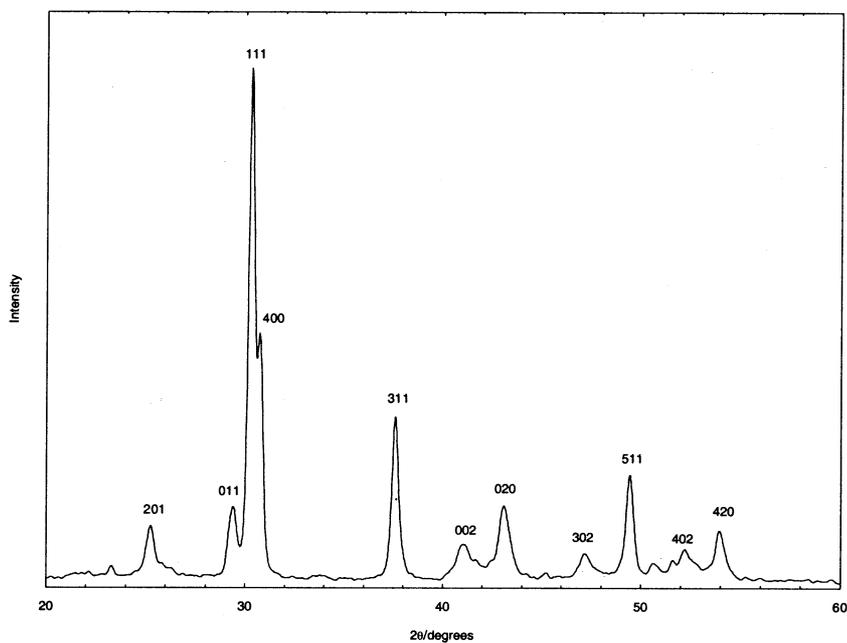
Figure 1. XRD pattern of SnSe powder.

Table 1. Comparison between d values of SnSe powder and JCPDS data (File no. 32-1382).

2θ (°)	d (Å)	d (Å)	hkl
	Obtained values	JCPDS values	
25.2	3.53	3.52	201
29.3	3.04	3.05	011
30.2	2.94	2.94	111
31.0	2.90	2.90	400
37.5	2.39	2.38	311
40.8	2.22	2.21	002
43.0	2.09	2.09	020
47.1	1.93	1.92	302
49.3	1.84	1.83	511
52.2	1.75	1.75	402
53.9	1.69	1.68	420
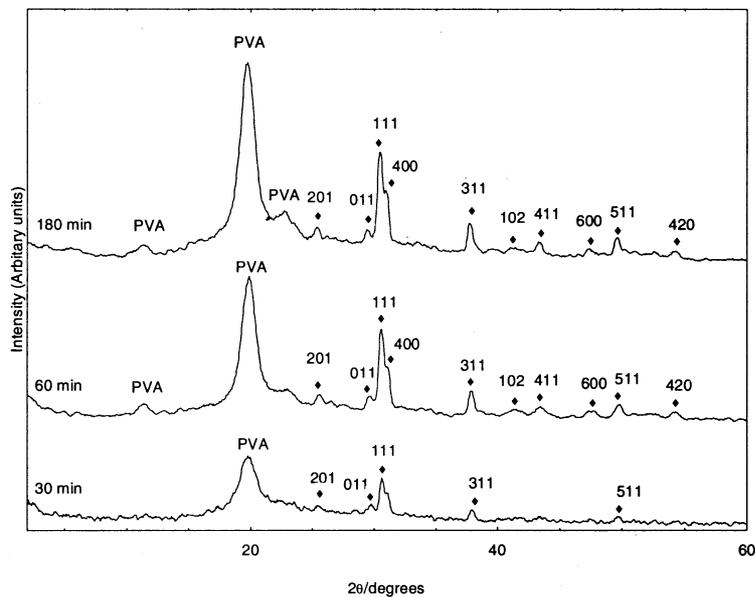
Figure 2. XRD patterns of coatings annealed at different times. Polyvinyl alcohol (PVA); SnSe (♦).

Table 2. Comparison between d values of SnSe coatings annealed at different times and JCPDS data (File no. 32-1382).

Annealing time (min)	2θ (°)	d (Å) Obtained values	d (Å) JCPDS values	hkl
30	25.5	3.5	3.5	201
	29.5	3.0	3.0	011
	30.5	2.9	2.9	111
	37.8	2.4	2.4	311
	49.7	1.8	1.8	511
60	25.5	3.5	3.5	201
	29.6	3.0	3.0	011
	30.6	2.9	2.9	111
	31.1	2.9	2.9	400
	37.9	2.4	2.4	311
	41.3	2.2	2.2	102
	43.3	2.1	2.1	411
	47.6	1.9	1.9	600
	49.8	1.8	1.8	511
	54.3	1.7	1.7	420
180	25.5	3.5	3.5	201
	29.6	3.0	3.0	011
	30.6	2.9	2.9	111
	31.1	2.9	2.9	400
	37.9	2.4	2.4	311
	41.3	2.2	2.2	102
	43.3	2.1	2.1	411
	47.6	1.9	1.9	600
	49.8	1.8	1.8	511
	54.3	1.7	1.7	420

compared to 30 min. As the annealing time was increased to 60 min and above the crystalline phase of PVA also improved. However, the crystalline phase of the SnSe material remains almost the same. Increasing the annealing time improved the crystalline phase of PVA but did not induce any structural changes in SnSe beyond 60 min.

Figure 3 shows the SEM micrographs of the SnSe-PVA coatings that underwent heat treatment at different time. Fewer grains are visible in the SnSe-PVA mixture for the sample annealed at 30 min. The grains are distributed randomly over the substrate surface. The size of the grains varies from one to another. As the annealing time was increased to 60 min, the surface of the coating exposed more SnSe materials, which could be seen in the micrographs as the white grains. As the annealing time was increased, decreasing in the number of the grains could

be observed. Table 3 shows the ratio of Sn to Se obtained from the EDX analysis. The results indicate that the composition of Sn to Se is almost stoichiometric for the coating treated for 30 min. However, the ratio reached a stoichiometric value as the annealing time was increased to 60 min.

Figure 4 indicates the difference between the photocurrent and darkcurrent response for the coatings in $[Fe(CN)_6]3-/Fe(CN)_6]4-$ redox system. As the annealing time was increased from 30 to 60 min, the difference in the photoactivity increased. The increase in the photoresponse for the coatings could be explained as seen from the SEM micrographs. More SnSe grains are exposed towards the redox system for the coatings that are annealed at 60 min compared 30 min. An increase in the point of contact between the redox system and the semiconducting material (SnSe) increases the photocurrent of the
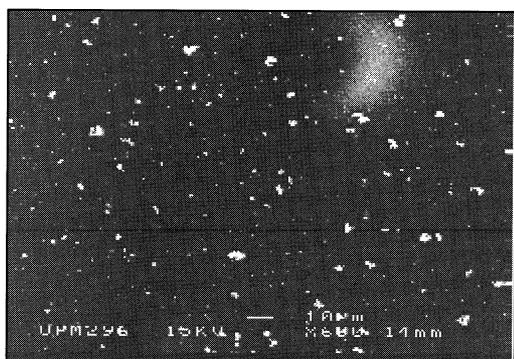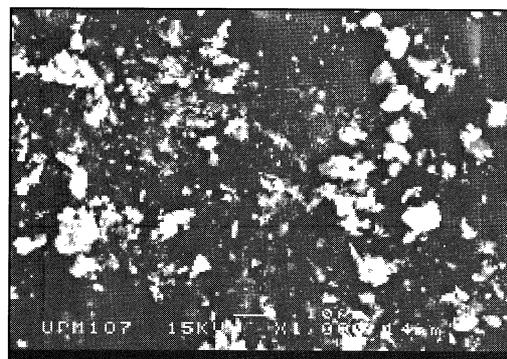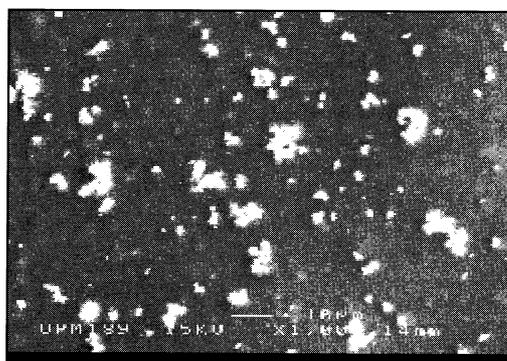
Figure 3. SEM micrographs of SnSe coatings annealed at different time; 30 min (a), 60 min (b) and 180 min (c).

Table 3. Sn to Se ratio of the coatings

Annealing Time (min)	Sn/Se ratio
30	0.9
60	1.0
180	0.7
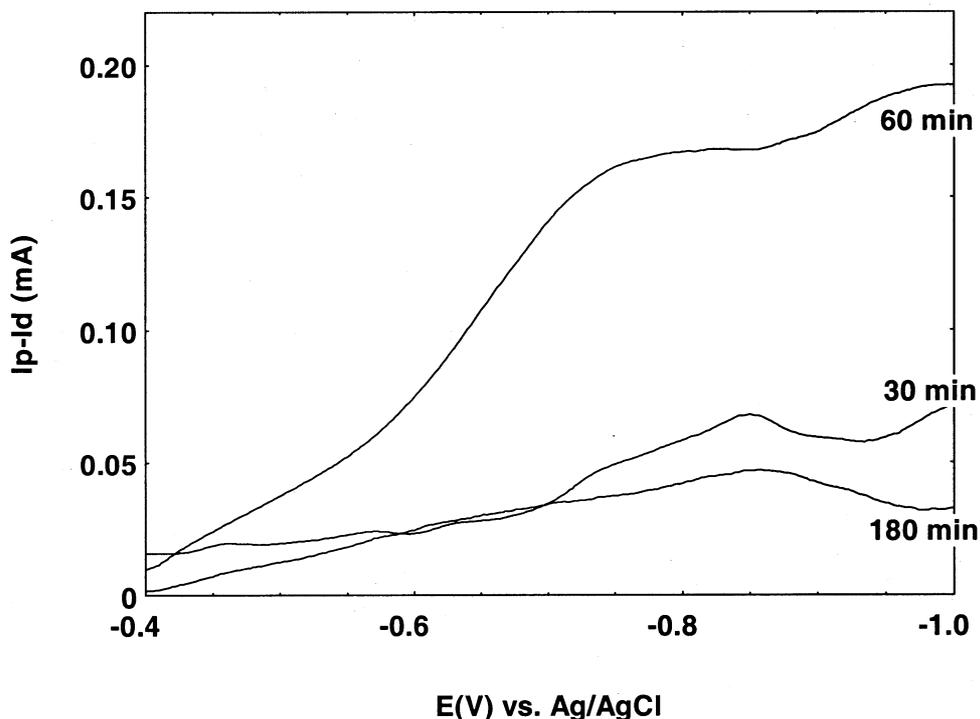
Figure 4. Difference between photocurrent (Ip) and darkcurrent (Id) for the samples annealed at different time.

system. The reduce in the difference between the photocurrent and darkcurrent as the annealing time was increased to 180 min could be due to the damaging effect towards the PVA coating itself. Extreme exposure of the coating at high temperature (150 °C) causes physical changes on the surface of the coating that effects the binding properties of SnSe-PVA mixture and finally disrupts the photoresponse on the SnSe material. A steady increase in the current could be observed for the samples, which was employed as a cathode in the electrochemical cell as the potential is swept to more negative region. This indicates that the annealing process promotes incipient fusion of small crystallites and thereby reduces the number of grain boundaries, which are known to act as recombination centres for minority carriers and trapping centres for majority carriers, thereby reducing the carrier lifetime of a semiconductor.

This current change with the illumination confirms that the films posses semiconducting behaviour. The fact that the photocurrent occur on the negative (cathode) potential indicates that the films prepared are of p-type (positive) and they can be employed as photo cathode in the PECs application to facilitate a reduction reaction of the electroactive species in the solution.

4. Conclusions

SnSe coatings to be used in electronic and optoelectronic devices could be obtained through the method discussed. Annealing the coating at 150 °C for 60 min was sufficient to improve the photoresponse of the coatings. Prolonged exposure to heat proved destructive towards the coating, which reduced the photoresponse.

Acknowledgements

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