

# Effect of Time on Electrodeposition of Tin Selenide Thin Films from Aqueous Solution

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## ABSTRACT

SnSe films were prepared by electrodeposition on indium doped tin oxide coated glass substrate, with deposition times ranging between 15-75 minutes. X-ray diffraction data showed that the intensity of major peaks at 2.92 Å, which belongs to (111) plane of SnSe, increased with deposition time. Films prepared at longer deposition times showed better surface coverage and better photoresponse. The thickness of the samples increased as the deposition time was increased. Deposition at 60 minutes is sufficient to produce films with stoichiometry composition and the highest photoresponse activity.

(Key words: photoactivity, solar cells, photoresponse, thin films, semiconductor, x-ray diffraction)

## INTRODUCTION

In the search for new semiconductor materials for efficient solar energy conversion through photo-electrochemical solar cells, metal chalcogenides with layered structure are increasingly being studied (Subramanian et al., 1999). These materials have been known to be potential candidates for photo-electrochemical solar cells. Tin selenide (SnSe) is a semiconductor with layer type character and orthorhombic structure (John et al., 1994). It has also been known to be used in memory switching devices (Subramanian et al., 1999). SnSe has an energy gap of about 1.0 eV, which might prove to be an efficient material for solar energy conversion.

Considerable attention has been given by various authors to preparation techniques for tin selenide thin films. Among the methods used are chemical bath deposition (Pramanik and Bhattacharya, 1988), vacuum evaporation, chemical vapor deposition (John et al., 1994, Bennouna et al, 1983, Dang Tran, 1984, Rao et al, 1985, 1986, Quan, 1987, Sharon et al, 1987, Singh et al, 1991, 1990, Suguna et al, 1996) and electrodeposition (Subramanian et al, 1999, Engelken et al, 1986). Electrodeposition is a simple and low cost thin film deposition method with many advantages including flexibility in substrate sizes and shapes. It can also afford precise control of the deposition process. Furthermore, the reactions involved are closer to equilibrium than in many gas-phase methods. Unlike chemical gas-phase methods, electrochemical deposition does not involve the use of toxic gaseous precursors (Rajeshwar, 1992). In comparison with chemical bath deposition, the preparation of the deposition solution for the electrochemical method is simpler, since no strict control of the oxidation state of the selenium precursor is required (Saloniemi et al, 1998).

## MATERIALS AND METHODS

Electrodeposition was performed in a conventional three-electrode cell. Ag/AgCl was used as the reference electrode to which all potentials were quoted. The working and counter electrodes were made from indium tin oxide (ITO) glass substrate and platinum, respectively. The ITO glass substrates were cleaned ultrasonically in ethanol and distilled water before the deposition process. The counter electrode was polished prior to the insertion into the electrolyte cell. An EG&G Princeton Applied Research potentiostat, driven by a software model 270 Electrochemical Analysis System, was used to control the electrodeposition process and to monitor the current and voltage profiles.

The electrolytes were prepared using analytical grade reagents and deionized distilled water. Ethylenediaminetetraacetate (EDTA) was used to chelate with  $\text{Sn}^{2+}$  to obtain Sn-EDTA complex. The presence of EDTA in aqueous solution was found to improve the lifetime of the deposition bath as well as the adhesion of the deposited film on the ITO glass substrate (Ghazali et al, 1998). The experiment was carried out using a constant concentration of Sn-EDTA complex (0.02 M, 40 ml) and  $\text{Na}_2\text{SeO}_3$  (0.005 M, 40 ml) solutions. The mixture solution temperature was maintained at 55° C. Nitrogen gas was flowed into the solutions prior to mixing to remove any dissolved  $\text{O}_2$ . The films were deposited at -0.800 V (vs. Ag/AgCl) at various time intervals (15 - 75 minutes).

Immediately after deposition, the deposits were tested for durability by subjecting them to a steady stream of distilled water. The deposited films were kept for further comparison and analysis. X-ray diffraction (XRD) analysis was carried out using a Siemens D-5000 Diffractometer for the  $2\theta$  ranging from 2 °-60 ° with  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. Scanning electron microscopy (SEM) and energy dispersive analysis of x-ray (EDX) was performed on a LEO VP 1455 Variable Pressure Scanning Microscope. The thickness of the films was also estimated from SEM. The films were tilted at 90 ° in order to determine the thickness. Photoelectrochemical (PEC) experiments were performed in  $\text{Na}_2\text{S}_2\text{O}_3$  (0.01 M) solution by running linear sweep voltammetry (LSV) between two potentials limits (-0.350 to -1.00 V). A tungsten-halogen lamp (300 W) was used for illuminating the electrode. The effect of photocurrent and darkcurrent towards the samples were studied.

## RESULTS AND DISCUSSION

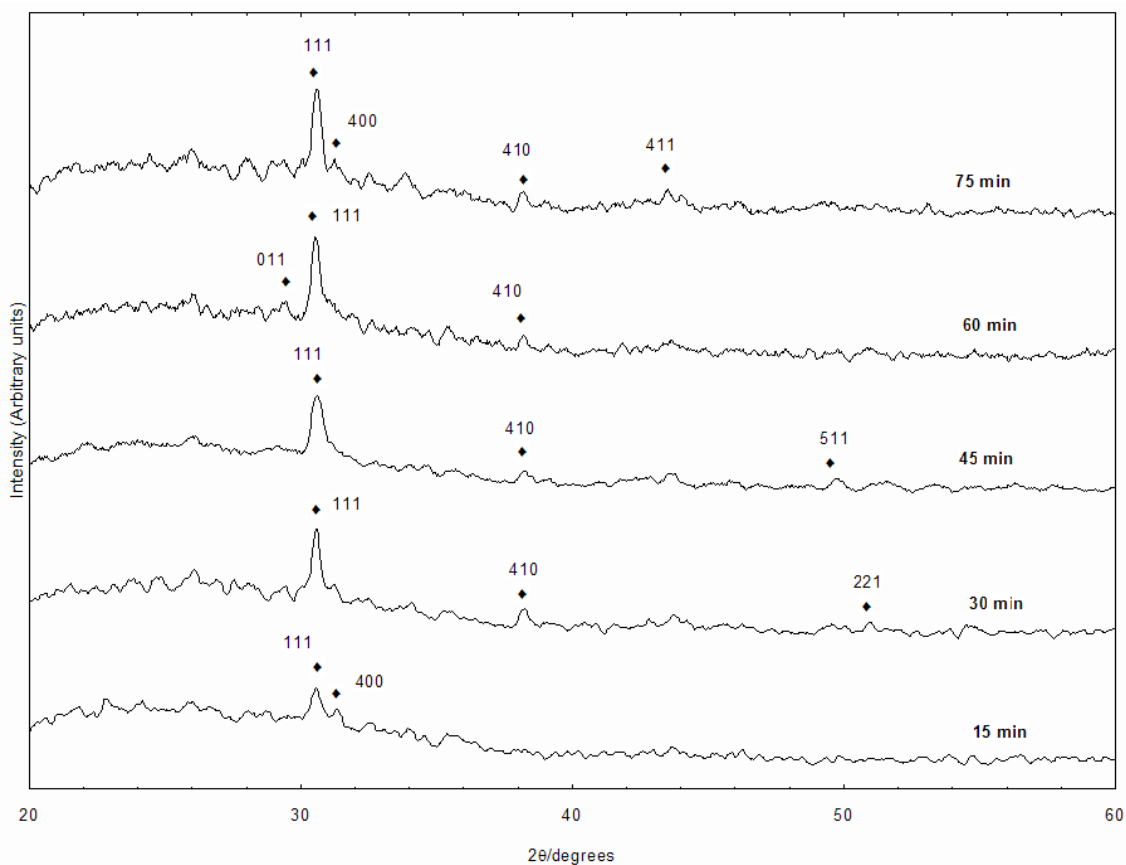
The film deposited for 15 minutes shows only two peaks at  $2\theta = 30.5$  and  $31.3^\circ$ , corresponding to interplanar distances of 2.92 and 2.85 Å (Figure 1). These peaks are in agreement to the JCPDS data for SnSe (File No.32-1382) (Table 1). As the deposition time was increased from 15 to 75 minutes, the intensity of the peak 2.92 Å that correspond to (111) plane increased. This is accompanied by the appearance of four other peaks of SnSe at  $2\theta = 30.6, 31.3, 38.2$  and  $43.5^\circ$  with interplanar distances of 2.92, 2.85, 2.35 and 2.08 Å. The increase in deposition time allows more material to be deposited onto the substrate and thicker films to be formed.

**Table 1.** XRD Data of the Samples Prepared.

Time (min)	2 $\theta$	<i>d</i> values	JCPDS* <i>d</i> values
15	30.5	2.92	2.94
	31.3	2.85	2.85
30	30.5	2.92	2.94
	38.1	2.36	2.36
	50.9	1.79	1.79
45	30.6	2.92	2.94
	38.2	2.35	2.36
	49.7	1.83	1.83
60	29.4	3.03	3.05
	30.6	2.92	2.94
	38.2	2.35	2.36
75	30.6	2.92	2.94
	31.3	2.85	2.85
	38.2	2.35	2.36
	43.5	2.08	2.08

\* File no. 32-1382

**Figure 1.** XRD Data of Samples Prepared at Various Time Intervals.



The scanning electron micrographs show the morphology of the deposits for the films prepared at 15, 30 and 60 minutes using 0.02 M Sn-EDTA and 0.005 M  $\text{Na}_2\text{SeO}_3$  (Figure 2). Films prepared at 15 minutes (Figure 2a) show incomplete coverage of material over the surface of the substrate. Films prepared at 30 minutes of deposition time (Figure 2b) show almost complete coverage of SnSe material over the substrate compared to the film prepared at shorter time. As the deposition time was increased films starts to grow thicker as can be seen in the micrographs of the film deposited at 60 minutes (Figure 2c).

**Figure 2.** SEM Micrographs of Samples Prepared at 15 minutes (a), 30 minutes (b) and 60 minutes (c); Sn-EDTA complex = 0.02 M,  $\text{Na}_2\text{SeO}_3$  = 0.005 M

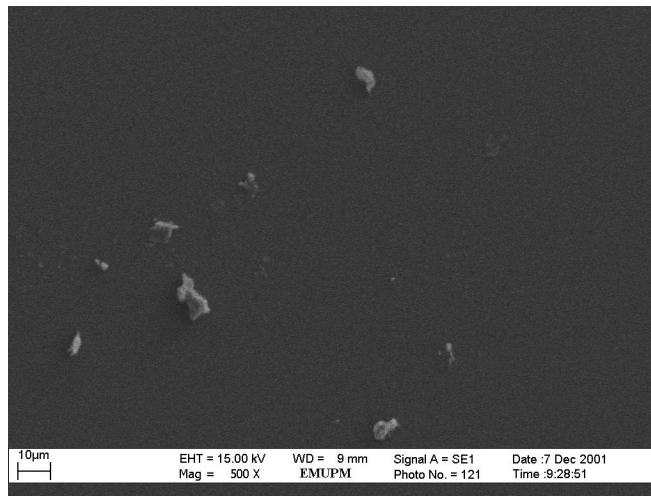


Figure 2a.

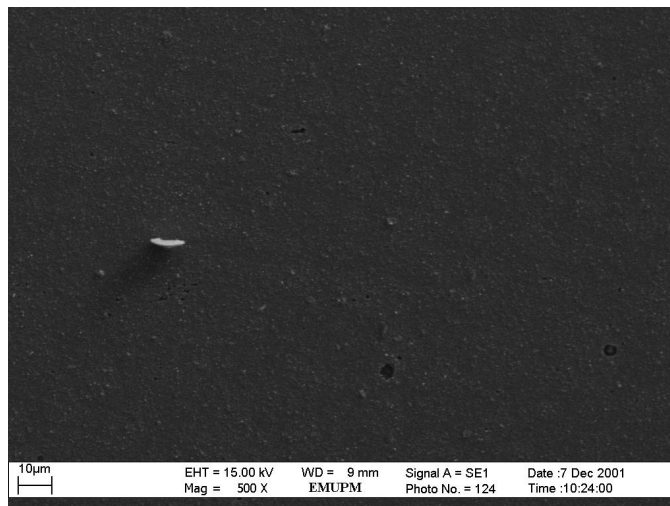


Figure 2b.

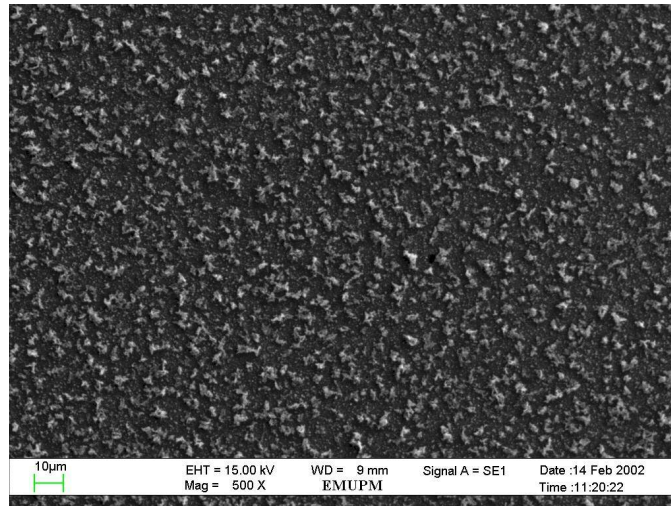


Figure 2c.

Figure 3 indicates the variation of estimated thickness of the films observed by SEM. The thickness of the sample prepared at 15 minutes deposition time could not be observed by this method. The thickness of the film increases as the deposition time was increased. The thickness for the film deposited at 30 minutes was observed to about  $3.67 \mu\text{m}$  and the rate increased slowly beyond this point. After 45 minutes the rate of deposition increased to  $1.41 \mu\text{m min}^{-1}$  showing a linear response. The thickness increased to  $52.8 \mu\text{m}$  for the film deposited at 75 minutes.

**Figure 3.** Thickness Variation vs. Deposition Time of the Samples.

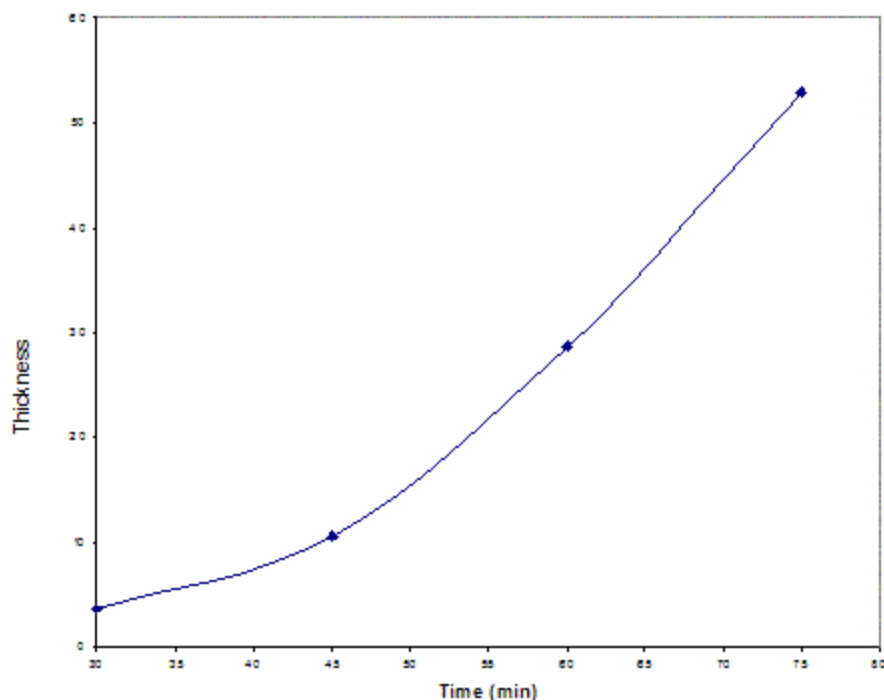


Table 2 shows the ratio of Sn to Se from the EDX spectrum. The EDX spectrum of the film prepared at 15 minutes of deposition time indicates that the Se concentration is well below the limit of detectability. The films prepared at 30 and 45 minutes showed ratio values of 0.90 and 0.87, which is almost to stoichiometry with SnSe deposit. The film prepared at 60 min deposition indicates the formation of a stoichiometry in SnSe deposit (Figure 4). Further increase in the deposition time to 75 minutes shows an increase in Se concentration.

**Table 2.** The Ratio of Sn to Se for the Samples Prepared.

Deposition time (min)	Sn:Se ratio
30	0.90
45	0.87
60	1.00
75	0.73

**Figure 4.** EDX Spectrum for the Film Prepared at 60 minutes.

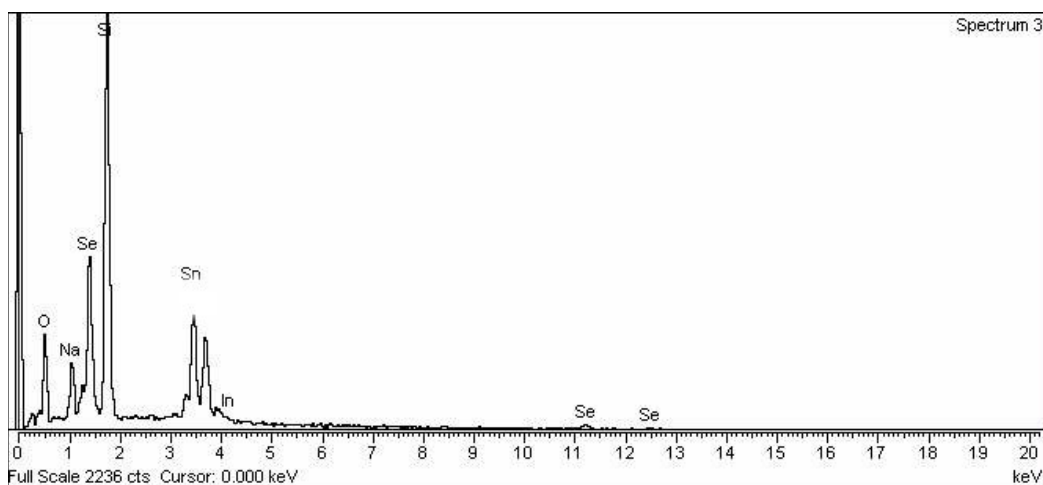
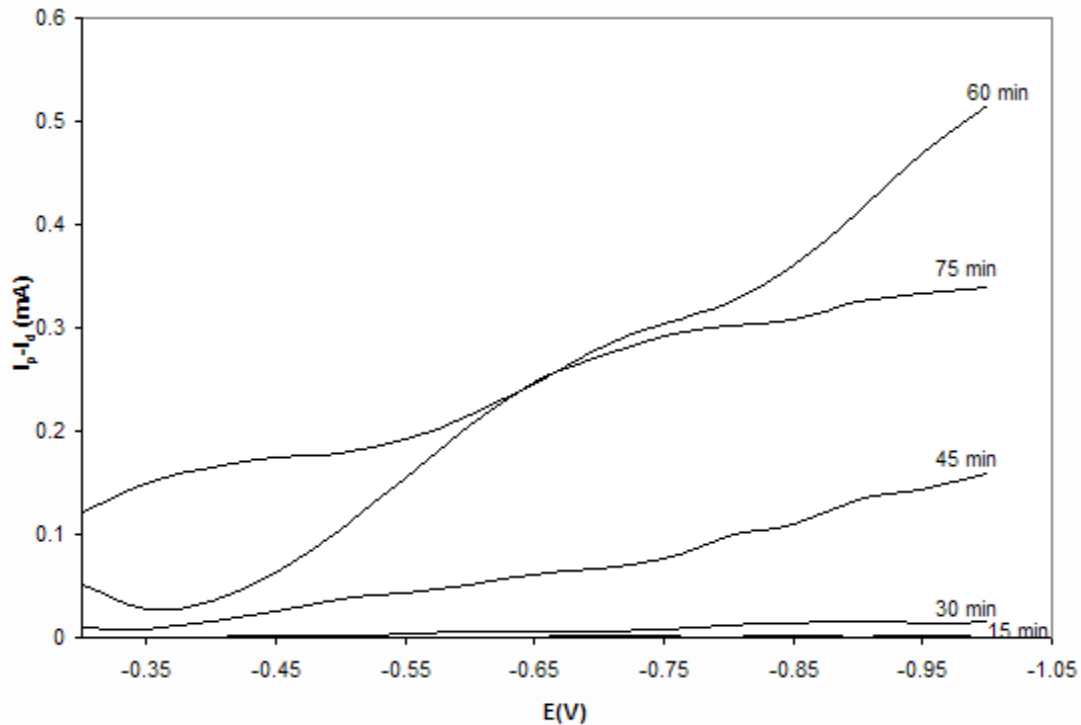


Figure 5 shows the difference between the photocurrent and darkcurrent vs. potential for the deposited films in contact with 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The graph shows the resulting difference in the current for the samples, which were employed as a cathode in the electrochemical cell. This current change with illumination confirms that the films possess semiconducting properties. The fact that the photocurrent occurs on the negative (cathode) potential indicates that the films prepared are of p-type (positive) and they can be deployed as photo cathode in the PECs application to facilitate a reduction reaction of the electro-active species in the solution. After carrying out the experiment, the films were tested for durability by subjecting it to a steady stream of distilled water.

**Figure 5.** Comparison of Photosensitivity of the Samples Prepared at Different Deposition Times





## CONCLUSIONS

The film prepared at a deposition time of 15 minutes does not respond well when there is any change in the intensity of light showing almost zero photocurrent difference throughout the potential sweep. This could be due to insufficient semiconductor material deposited onto the surface of the substrate. The films deposited at 15 and 30 minutes peeled off the surface of the substrate upon treatment with a steady stream of distilled water after the experiment.

When the deposition time was increased, the photoresponse behaviour of the films increased. The film prepared at 60 minutes showed the highest photoresponse activity. However, as the deposition time was increased to 75 minutes, the photoresponse activity of the film didn't show any significant increase. A deposition time of 60 minutes was sufficient to produce SnSe film with good photoresponse. The films deposited at this period (45, 60 and 75 minutes) showed good adherence towards the substrate upon washing with distilled water.

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