

Effect of annealing on the properties of SnSe film prepared by thermal vacuum evaporation in the presence of argon gas

Nordin Sabli^{1,a}, Zainal Abidin Talib^{1,b}, Wan Mahmood Mat Yunus^{1,c},
Zulkarnain Zainal^{2,d}, Hikmat S. Hilal^{3,e}, Mohd Shahril Husin^{1,f}

¹ Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

² Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

³ Department of Chemistry, An-Najah National University, PO Box 7, Nablus, West Bank, Palestine

^anordin74@gmail.com, ^bzainalat@science.upm.edu.my, ^cmahmood@science.upm.edu.my,
^dzulkar@putra.upm.edu.my, ^ehshilal@najah.edu, ^fshahril@science.upm.edu.my

Keywords: thermal vacuum evaporation, argon gas, photoelectrochemical, SnSe, thin film

Abstract. The differences in structural, compositional and photoelectrochemical properties for SnSe films annealed at different temperatures, under nitrogen atmosphere, were studied. Annealing the film electrode significantly improved its crystallinity but lowered its photoresponse. The photoresponse lowering was thus attributed to lowering in the defect concentrations.

Introduction

Tin selenide (SnSe), with a band gap ~ 1.0 eV, is a semiconductor with layer-type character having orthorhombic structure. SnSe films received increasing interest because they offer a range of optical band gaps values suitable for various optical, optoelectronic and photoelectrochemical (PEC) solar cell applications [1-5]. Considerable attention has been devoted [6, 7] to prepare SnSe thin films by different methods, and to study annealing effect on their optical and electrical properties. Treatment of different semiconductor thin films by annealing, to improve their structures and morphologies, is a widely practiced technique. To the best of our knowledge, the preparation of SnSe thin film by thermal vacuum evaporation in the presence of argon gas, followed by annealing to study its PEC properties, has not been reported.

The film structure, chemical composition, morphology and crystallinity, which strongly influence film electrode PEC characteristics, are highly dependent on the deposition conditions and the preparation technique employed. In view of this, we have studied the structural, compositional and photoresponse properties of SnSe films, taking into consideration the effect of film annealing temperature on such properties. The results are discussed here.

Experimental

Chemicals. $K_3[Fe(CN)_6]$ and $K_4[(Fe(CN)_6)].H_2O$ were purchased from Sigma Aldrich. HCl was purchased from Friendmann Schmidt Chemical. Organic solvents, methanol and 2-propanol, were purchased from Merck KGaA and HmbG Chemicals respectively. Starting materials tin and selenium were purchased from Alfa Aesar with nominal purity 99.8% and 99.5% respectively.

Film electrode preparation and characterization. The SnSe alloy source material was prepared using the melt-quenching method [8] according to stoichiometric 1:1 nominal molar ratios. The SnSe compound was taken out from the ampoules and was ground into fine powder. After confirming their structures by XRD, the prepared compounds were then used as source materials. The prepared SnSe powder (0.10 g) was placed in a molybdenum evaporation boat. Film electrode preparation followed same procedure for film electrodes deposited as reported earlier [8]. The argon gas was introduced into the vacuum chamber via an inlet tube having a nozzle 0.5 mm in diameter at flow rate $V_A = 5$ cm³/min. To improve film adhesion, increase surface mobility of condensing atoms and enhance crystallinity, the substrate was heated and kept at 100°C during the evaporation

process [9]. The as-deposited films were heated to desired temperature ($T_A = 150, 250, 350$ and 450 °C) for 30 minutes under nitrogen gas atmosphere at ramp-up and ramp-down rate 5 °C/min. The atomic compositions of the films were investigated by EDX (Oxford Instruments model 7353) attached to a Nova NanoSEM 230 field emission scanning electron microscope (FESEM). PEC experiments were performed using $[\text{Fe}(\text{CN})_6]^{-3}/[\text{Fe}(\text{CN})_6]^{-4}$ redox system, by running linear sweep voltammetry between $+1.0$ V and -1.0 V with a scan speed of 20 mV/s using a PGSTAT 101 Potentiostat. A conventional three-electrode cell, equipped with a platinum counter electrode and an Ag/AgCl reference electrode, was used. An Osram halogen lamp was used as a light source. The light intensity at the working electrode was controlled at 0.1 W/cm² using a pyranometer (LI-200; Li-Cor, USA). The light was intermittently chopped up and down by a thick black cardboard at 0.5 cycles per second to give the effect of photocurrent and dark current.

Results and Discussion

Structural study on un-annealed and annealed films, was performed using XRD. Figure 1 shows XRD diffraction patterns for JCPDS reference, ITO substrate, and SnSe films annealed at different temperatures. The XRD results confirmed the formation of polycrystalline SnSe with the plane (111) as the strongest orientation, in agreement with earlier reports [2]. The XRD pattern recorded for un-annealed and annealed films, prepared from synthesized SnSe powder, are shown in Figures 1c-g. The prominent Bragg reflection occurred at $2\theta = \sim 30^\circ$ corresponding to (111) diffraction. Based on the XRD spectra shown in Figures 1c-g, the films are SnSe. Film crystallinity was studied using ITO (004) as a reference and SnSe films (411) as signal. The same technique was also used by Zyoud et al. [10]. The higher ratio between signal intensities of the SnSe (411) and ITO (004) indicates higher crystallinity for SnSe. Table 1 summarizes values of signal intensity ratio for all samples. Higher ratio for all annealed films indicates that the films have higher crystallinity compared with un-annealed counterpart. Crystallinity improvement could be observed by film annealing.

Energy dispersive X-Ray analysis (EDX) spectra were measured for all films. Values of the Sn/Se ratios for different films are shown in Table 2. For the un-annealed film, the Sn/Se ratio 0.72 indicates an excess of selenium content. The Table shows a general trend in which Sn/Se ratio increased with higher annealing temperature due to Se evaporation. This was more apparent at 350°C and higher temperatures. Therefore, higher temperatures increased the Sn/Se ratio, and consequently affected the number of identifiable XRD peaks for SnSe.

Figure 2 shows PEC photoresponse with chopped light illumination under a linearly increased bias. Current changed when the light was intermittently chopped up and down under cathodic and anodic bias. Carriers are excited in the illumination region in the thin film and the excited minority carriers diffuse to the surface during their lifetime to participate in an electrochemical

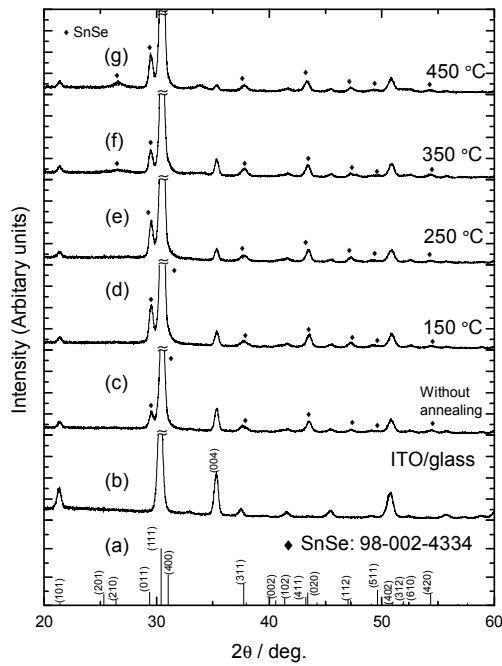


Figure 1: X-Ray diffraction spectra of JCPDS reference (a), ITO substrate (b), un-annealed (c) and films annealed at different temperatures (T_A): (d) 150, (e) 250, (f) 350 and (g) 450 °C

Table 1: Values of XRD signal intensity ratio SnSe (411) /ITO (004)

Annealing temperature (°C)	Value of ratio
Unannealed	0.53
150	0.80
250	0.83
350	0.84
450	1.29

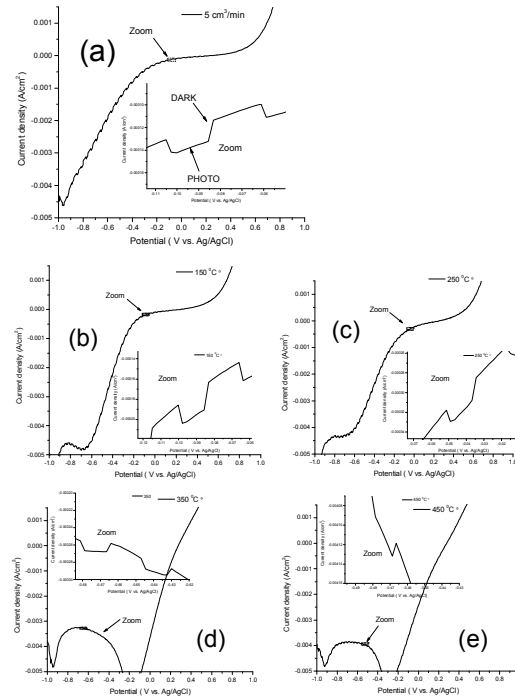


Figure 2: PEC characteristics measured for films deposited from $S_M = \text{SnSe}$ annealed at different temperatures (a) un-annealed, (b) 150, (c) 250, (d) 350 and (e) 450 °C

Table 2: Values of Sn/Se ratio

Annealing temperature (°C)	[Sn/Se]
Unannealed	0.72
150 °C	0.73
250 °C	0.74
350 °C	0.79
450 °C	0.82

reaction at the film/electrolyte interface. Figure 2 shows that the film electrode exhibited negative photocurrent when illuminated by light indicating that the un-annealed and annealed films exhibited p-type conductivity. Photoactivity was calculated from the experimental value of photo current density (J_P) and dark current density (J_D) using the formula $p\% = [(J_P - J_D)/J_D] \times 100\%$. Photo and dark current density values at -0.5 V for all samples were used to represent electrode photoactivity. The results show that annealing at 350 and 450 °C ($p\% = 0.2 \sim 0.7$) significantly lowered photoresponse compared with that of un-annealed film ($p\% = 8.3$). The results are consistent with values of Sn/Se ratio for the films. Annealing at 150 and 250 °C ($p\% = 1.2 \sim 1.5$) slightly increased Sn/Se ratios, in the films, and caused slight decrease in photoresponse. Annealing at 350 °C and higher temperatures significantly increased Sn/Se ratio and significantly lowered photoresponse. All annealed films exhibited higher crystallinity compared to the un-annealed film as signal intensity

ratios for all annealed films were higher (0.80 ~ 1.29) than the un-annealed counterpart (0.53), as summarized in Table 1. The fact that crystallinity was improved and photoresponse was lowered for films after annealing indicates that the defect formation in the films had been reduced and consequently lowered the film carrier concentration.

Conclusions

Annealing SnSe thin film electrodes, deposited by thermal vacuum evaporation under argon gas enhanced their crystallinity but lowered their PEC photoresponse. Higher crystallinity for annealed films indicates lower defect concentration in the film, which explains lower photoresponse. Higher photoresponse and lower crystallinity for un-annealed film suggest that, in addition to electron excitation from valence band to conduction band, electron excitation also occurred from defect level to conduction band in the un-annealed film. Higher photoresponse is attributed to higher carrier concentrations. Annealing SnSe films prepared by this method is thus not advisable to obtain films with higher photoresponse

Acknowledgments

The support of this research by Ministry of Higher Education of Exploratory Research Grant Scheme Grant no. 5527051 and UPM research university grant scheme is gratefully acknowledged.

References

- [1] N. Kumar, U. Parihar, R. Kumar, K. J. Patel, C. J. Panchal, N. Padha, *American Journal of Materials Science* 2(2012) 41-45
- [2] Z. Zainal, S. Nagalingam, A. Kassim, M. Z. Hussein, W. M. M. Yunus, *Solar Energy Materials & Solar Cells* 81 (2004) 261-268
- [3] B. Subramanian, T. Mahalingam, C. SAnjeeviraja, M. Jayachandran, M. J. Chockalingam, *Thin Soid Films* 357 (1999) 119-124
- [4] N. Kumar, V. Sharma, N. Padha, N. M. Sha, M.S. Desai, C. J. Pachal, I. Y. Protsenko, *Crystal Research and Technology* 45 (2010) 53-58
- [5] M. Sharon, K. Basavaswaran, *Solar Cells* 20 (1987) 323-332
- [6] N. R. Mathews, *Solar Energy* 86 (2012) 1010-1016
- [7] Z. Zainal, A. J. Ali, A. Kassim, M. Z. Hussein, *Solar Energy & Solar Cells* 79 (2003) 125-132
- [8] N. Sabli, Z. A. Talib, W. M. M. Yunus, Z. Zainal, H.S. Hilal, M. Fujii, *Materials Science Forum* 756 (2013) 273-280
- [9] K. S. V. Santhanam, M. Sharon, *Photoelectrochemical Solar Cells*, Elsevier Science, Inc, New York, NY, 1988, 156-177
- [10] A. Zyoud, I. Saa'deddin, S. Khudruj, Z. M. Hawash, D.-H Park, G. Campet, H. S. Hilal, *Solid State Sciences*, 18 (2013) 83-90.