Synthesis and characterization of Tin Selenide thin films

KEGAO LIU[a*], NIANJING JI[b], YONG XU[a], JIYANG WANG[b]
[a]*School of Materials Science and Engineering, Shandong Jianzhu University, Fengming Road, Jinan 250101,China*
[b]*State Key Laboratory of Crystal Materials, Shandong University, 27 Shandanan Road, Jinan 250100, China*

Tin Selenide thin films were synthesized by spin coating and co-reduction from raw materials of $SnCl_2 \cdot 2H_2O$ and SeO_2. The phase and morphology of the film products were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM) respectively. XRD results show that, the obtained $SnSe_2$ thin film shows preferred growth trend along Z axis with crystal planes of (001), (002), (003) and (004); The crystallinity of film samples prepared at 160 °C, 170 °C and 180 °C increases with temperature rising. Relative pure $SnSe_2$ phase with good crystallinity can be obtained in the film sample prepared at 180 °C while impurity phase SnSe appeared in the samples obtained at 200 °C. SEM and AFM results show that, the sample obtained by reacting twice at 180 °C for 10 h shows relatively dense and continuous film with rough surface and consists of most particles with diameters of about 0.1~0.5 μm and a few larger particles. There are some few particles and many vertical nanoflakes or micropores in the film samples obtained at 200 °C.

(Received August 13, 2014; accepted November 13, 2014)

Keywords: Chemical synthesis, Semiconductors, Thin film, $SnSe_2$

1. Introduction

Metal chalcogenides with suitable band gaps can be widely applied in optical electronic field such as optical recording materials, solar cell materials and laser materials. IV-VI group semiconductor tin selenides such as SnSe, $SnSe_2$ are considered to be good materials for solar cells [1,2]. Orthorhombic SnSe about 1.0 eV band gap is P-type semiconductor used in converting solar energy [3]. While $SnSe_2$ is N-type semiconductor with hexagonal crystal system and about 0.9 eV band gap, it was often described as a Se-Sn-Se sandwiches structure bounded by Van der Waals' force [4].

Recently SnSe thin film was synthesized by thermal evaporation technology at 100 °C from $SnCl_2 \cdot 2H_2O$ and Se by R. Indirajith etc. through simple chemical reactions. They have researched the effect of different substrate temperatures on transmittance and band gap [5]. Tin selenides (pure phase SnSe, $SnSe_2$ and their mixtures) were deposited on glass by chemical vapor deposition by Nicolas D. Boscher etc. The ratio of Sn/Se varies between 1~2 according to the experimental conditions [4]. Tin selenide films were prepared by heating Sn layer deposited and Se layer made by chemical deposition in vacuum by Bindu and Nair. $SnSe_2$ and SnSe mixture film with good properties that can be used in photovoltaic devices were obtained by controlling the film thickness and heating temperature [6]. When SnSe and $SnSe_2$ nano-sheets were synthesized by solvent-thermal method, Jing Huang found that the extent of reaction can influence the product's phase, the more fully reaction the easier to form good crystallization SnSe [7]. D. Martínez-Escobar et al investigated the optical and electrical properties of $SnSe_2$ and SnSe thin films prepared by spray pyrolysis [8]. Like many reports, Tin selenide films were prepared by spin coating and co-reduction method and their phase formation was discussed in this work.

2. Experimental details

First, the substrates were cleaned in sulfuric for 20 min, and then washed in acetone and ethanol for 20 min respectively with ultrasonic vibration. After that keep the cleaned substrates in ethanol, they must be dried before using. Orange-red precursor solutions were gotten by dissolving $SnCl_2 \cdot 2H_2O$ and SeO_2 solid powders with a certain proportion into a proper quantity of different solvents such as deionized water, ethanol and hydrochloric acid respectively. They were used to prepare precursor films with certain thickness by spin coating and drying repeatedly for 4~8 times. The precursor film samples and 1 mL hydrazine hydrate were put into the reaction autoclave which will be heated in an oven at 180~200 °C and keep for 10~20 h. The reaction process may be carried out 1~2 times and the black film samples were obtained. The film products after immersion and drying naturally were analyzed by X-ray diffraction (XRD) with a model of Bruker D8 Advance, Ni-filtered CuKα ($\lambda = 1.54056$Å). The size and morphology of the products were observed by JSM6380LA scanning electron microscope (SEM) and Multimode 3DAFM atomic force microscope (AFM).

3. Results and discussion

3.1 Synthesis of $SnSe_2$ films by reacting twice at different temperatures

Fig. 1 shows XRD patterns of $SnSe_2$ thin film samples synthesized on the glass substrates. These samples were prepared by reacting twice at 160 °C, 170 °C and 180 °C respectively with ethanol as solvent in precursor solution. Compared with the standard pdf card of $SnSe_2$ (No. 89-2939), the most XRD peaks are corresponding to the crystal planes of (001), (002), (003) and (004). It indicates that $SnSe_2$ phase grows along Z axis preferentially. The XRD peak of impurity Se can be found in the sample obtained at 170 °C. The intensity of the most XRD peaks increases with temperature rising, which demonstrates the crystallinity of film samples increases. The film sample with relative pure $SnSe_2$ phase can be obtained at 180 °C. The reaction mechanism is proposed as follows: When the precursor sample film and the reducing agent are put into the autoclave and heated, the positive metal ions Sn^{2+} and Se^{4+} are easily reduced to Se and Sn by reducing agent $N_2H_4 \cdot H_2O$. The Sn atoms and Se atoms are very active and can easily combine to be $SnSe_2$ molecules. The reacting processes are as follows [9-11]:

$$SeO_2+H_2O \rightarrow H_2SeO_3$$
$$H_2SeO_3+N_2H_4 \cdot H_2O \rightarrow Se+N_2\uparrow+4H_2O$$
$$2SnCl_2 \cdot 2H_2O+N_2H_4 \cdot H_2O \rightarrow 2Sn+N_2\uparrow+4HCl+5H_2O$$
$$Sn+2Se \rightarrow SnSe_2$$

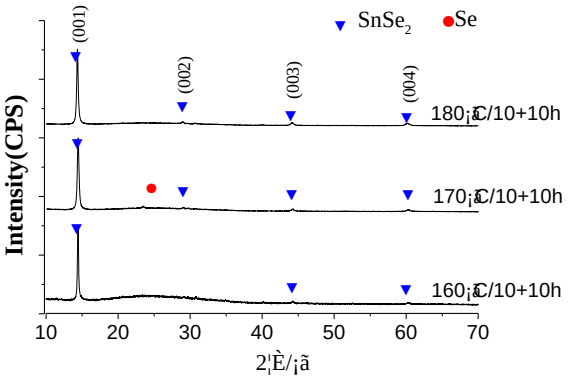

Fig. 1. XRD patterns of $SnSe_2$ thin films synthesized on the glass substrates.

3.2 The Sn-2Se film sample prepared by reacting once at 180 °C

Fig. 2 shows the XRD pattern of Sn-2Se thin film synthesized with ethanol as solvent on the glass substrate and the reaction was carried out at 180 °C for continuous 20 h. According to the standard pdf card of $SnSe_2$ (No. 89-2939), the XRD peaks at 2θ of 14.4°, 29.1°, 30.7°, 44.3° and 60.3° in Fig. 2 are corresponding to (001), (002), (011), (003) and (004) crystal planes respectively. It also gets $SnSe_2$ film sample which grows along Z axis preferentially with good crystallinity.

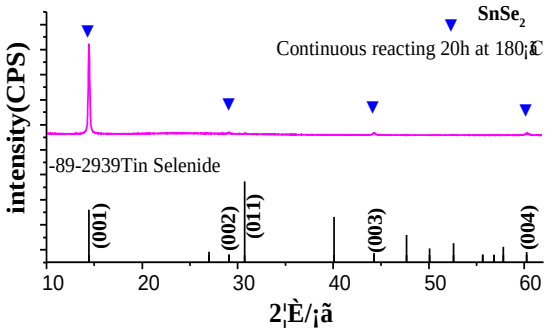

Fig. 2. The XRD pattern of $SnSe_2$ thin film synthesized on the glass substrate.

3.3 The phases in Sn-2Se thin film samples prepared at 200 °C

Fig. 3 shows XRD patterns of Sn-2Se thin film samples synthesized on silicon substrates at 200 °C with different time 10 h and 20 h respectively. Ethanol was used as solvent in the red dark precursor solution. It also indicates that these two examples consist of major phase $SnSe_2$ and minor phase SnSe. The XRD peaks belong to $SnSe_2$ at 2θ of 14.4°, 29.1°, 44.3° and 60.3° in Fig. 3a are corresponding to the crystal planes of (001), (002), (003) and (004) respectively, so $SnSe_2$ phase also grows along Z axis preferentially. The longer reacting time 20 h is beneficial to crystallization of $SnSe_2$ in sample a with sharper XRD peaks. It can be found that the XRD peaks at 2θ of 15.4° and 31.2° correspond with the standard pdf card of SnSe (No 53-0527). The reason that two tin selenides appear at the same time may be that an equilibrium reaction $SnSe_2 \leftrightarrow$ SnSe+Se exists at 200 °C [9].

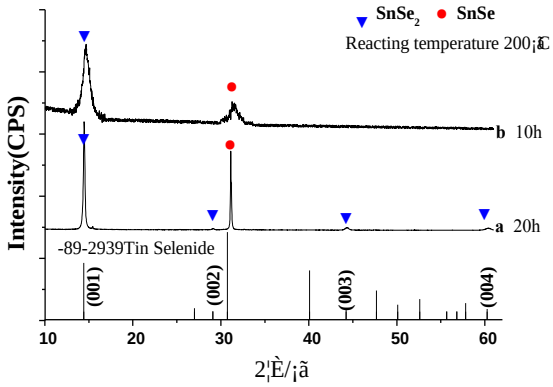

Fig. 3. XRD patterns of Sn-2Se thin films synthesized on silicon substrates Reacting time: a) 10h, b) 20h.

3.4 The morphology of film samples

Fig. 4 shows the SEM images of $SnSe_2$ thin film synthesized on glass substrates at 180 °C. It can be seen that dense and continuous film can be formed locally although it looks very rough. Fig. 4c reveals that the film sample consists of most particles with diameters of about 0.1~0.5 μm and a few larger particles. Fig. 5 is the AFM image of the sample synthesized under conditions of 180 °C+20 h on the glass substrate. Similarly it can be seen from that the surface roughness is very high, so the surface quality of film products needs to be improved by adjusting technologies.

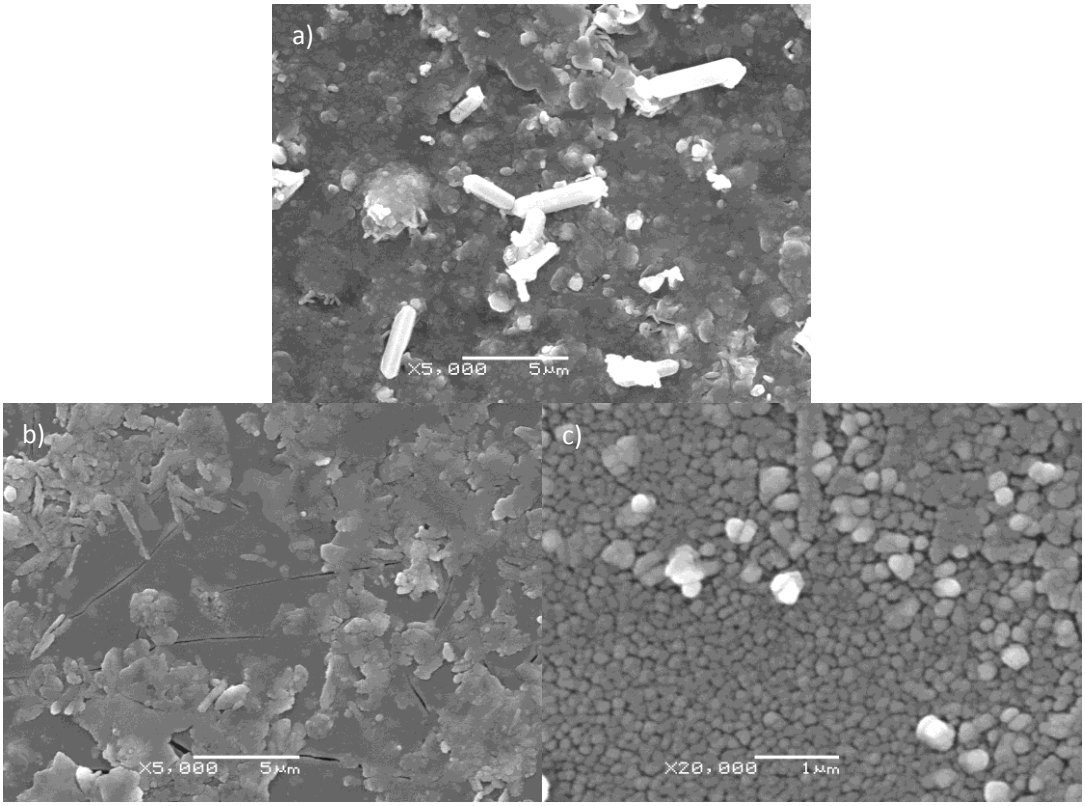

Fig. 4. SEM images of $SnSe_2$ thin films synthesized on glass substrates at 180 ºC; a) 10 h, reacting twice; b and c) 20 h, reacting once.

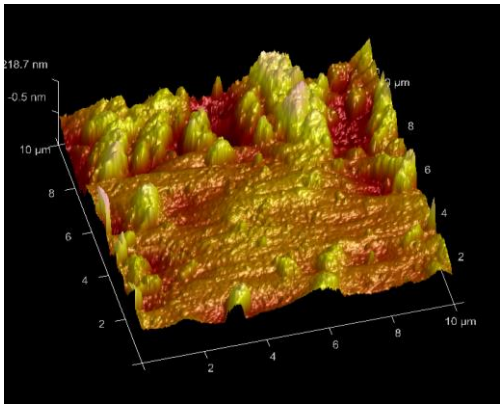

Fig. 5. The AFM image of $SnSe_2$ thin film synthesized under conditions of 180 °C+20 h on the glass substrate.

Fig. 6 shows the SEM images of thin film samples mentioned in Fig. 3. Some few particles and more vertical nanoflakes can be found in the film sample obtained by reacting at 200 °C for 10 h as shown in Fig. 6a and b. The morphology of these flakes is similar to the $SnSe_2$ nanoflakes with thick regular blade shape prepared by Peng Hongrui with solvothermal method [12]. Many micropores as shown in Fig. 6c and d appeared on the surface of the relative dense and continuous film sample synthesized at 200 °C for 20 h. These micropores may be produced by volatilizing of Se generated by reaction $SnSe_2 \leftrightarrow SnSe+Se$.

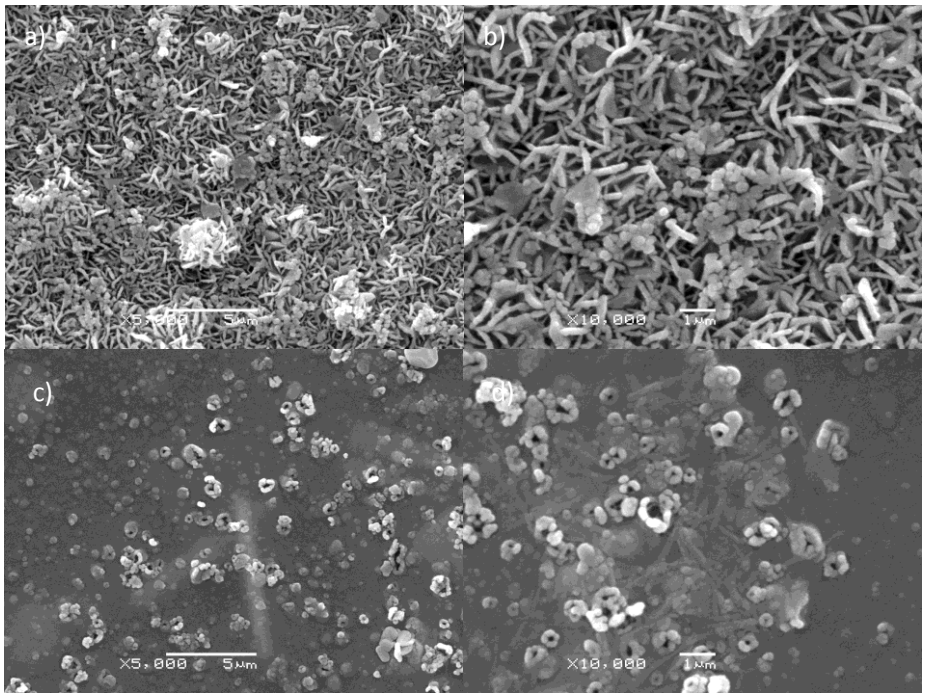

Fig. 6. The SEM images of thin film samples synthesized on silicon substrates Reacting conditions: a) and b) 200 °C+10 h, c) and d) 200 °C+20 h.

4. Conclusions

Tin Selenide thin films were synthesized by spin coating and co-reduction from raw materials of $SnCl_2 \cdot 2H_2O$ and SeO_2 on the glass or silicon substrates at 160~200 °C. The phases and morphology of the film products were investigated. The obtained $SnSe_2$ thin film shows preferred growth trend along Z axis with growth planes of (001), (002), (003) and (004); The crystallinity of film samples prepared at 160 °C, 170 °C and 180 °C increase with temperature rising. The film sample with relative pure $SnSe_2$ phase can be obtained at 180 °C with good crystallinity, impurity phase SnSe appeared in the samples obtained at 200 °C. The sample obtained by reacting twice at 180 °C for 10 h shows relatively dense and continuous film with rough surface and consists of most particles with diameters of about 0.1~0.5 μm and a few larger particles. Some few particles and more vertical nanoflakes can be found in the film sample obtained by reacting at 200 °C for 10 h. Many micropores appeared on the surface of the sample synthesized at 200 °C for 20 h.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No.51272140 and 51101093).

References

[1] Zhen Li, Zheng Jiao, Minghong Wu, et al, Colloids and Surfaces A: Physicochem. Eng. Aspects, **313-314,** 40 (2008)
[2] B. Pejova, I. Grozdanov, Thin Solid Films, **515,** 5203 (2007).
[3] B. Subramanian, T. Mahalingam, C. Sanjeeviraja, et al, Thin Solid Films, **119-124**, 357 (1999).
[4] Nicolas D. Boscher, Claire J. Carmalt, Robert G. Palgrave, et al, Thin Solid Films, **516**, 4750 (2008).
[5] R. Indirajith, T.P. Srinivasan, K. Ramamurthi, et al, Current Applied Physics, **10,** 1402 (2010).
[6] K. Bindu, P.K. Nair, Sci. Technol., **19,** 1348 (2004).
[7] Jin Huang, Solvothermal synthesis and characteristic of tin sulfide and tin selenide nanocrystals, Master degree thesis of Qingdao University of Science and Technology, Qingdao, p. 36, 06, 2006.
[8] D. Martínez-Escobar, Manoj Ramachandran, A. Sánchez-Juárez, Thin Solid Films, **535,** 390 (2013).
[9] M. Ganchev, J.lljina, L.kaupmees, et al, Thin Solid Films, **519**, 7394 (2011).
[10] Kegao Liu, Hong Liu, Jiyang Wang, et al, Journal of Alloys and Compounds, **484**, 674 (2009).
[11] Kegao Liu, Hong Liu, Jiyang Wang, et al, Materials Letters, **63,** 512 (2009).
[12] Hongrui Peng, Jin Huang, Journal of Qingdao University of Science and Technology, **27**(5), 427 (2006).

*Corresponding author: liukg163@163.com