$Cu_2ZnSnSe_4$ Thin Films Prepared by Chemical Method with Different Heating Technologies

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Abstract. $Cu_2ZnSnSe_4$ thin films were prepared by spin-coating and chemical co-reduction with different heating modes. The phases of obtained samples were characterized by X-ray diffraction (XRD). The size and morphology of the products were observed by scanning electron microscope (SEM). Experimental results show that, the intensity of the XRD peaks of the samples was not significantly enhanced by segmented heating, but the XRD peak for (200) crystal plane appeared. The change of the reaction process in the tube furnace did not significantly improve crystallization and phase of the films. The technology with heating the precursor failed to significantly improve the film crystallinity while the effects of reaction conditions affect the morphology significantly.

Introduction

$Cu_2ZnSnSe_4$ (CZTSe) and Cu (In,Ga)Se_2 (CIGS) have similar crystal structure and photoelectric properties, it has better prospects than CIGS since Zn and Sn elements are abundant, non-toxic and environmentally friendly. The photoelectric conversion efficiency of $Cu_2ZnSn(SeS)_4$ solar cells has exceeded 10% reported currently [1], Although which is much smaller than the theoretical value, but it has been greatly improved than the original data that less than 1 percent. $Cu_2ZnSnSe_4$ as I_2-II-IV-VI_4 quaternary compound has custerite crystal structure with lattice parameters of a=0.56882 nm, c=1.13378 nm. CZTSe is a P-type direct band gap semiconductor with band gap Eg about 1.5 eV and absorption coefficient α greater than 10^4 cm^{-1}. Its thickness less than 2 μm can meet the application requirements of the solar battery. Therefore CZTSe is very suitable as the solar cell absorption layer material [2-4]。

There are many methods to prepare CZTSe thin films at present, including one-step and two-step methods according to the processes. One-step methods include evaporation, solvothermal, powder and sputtering etc. Two-step method includes preparing preset alloy layer and selenizing in a certain atmosphere, the former process may be sputtering, atomic beam sputtering, reactive magnetron sputtering, thermal evaporation, photochemical deposition, spray, sol gel or electrodeposition method [5-8]. For example, M.Ganchev et al obtained the CZTSe film by presetting two base layers of brass and bronze and selenizing [9]. Some university researchers have also provided many new ideas and methods for preparing CZTSe compounds with low cost and simple process. $Cu_2ZnSnSe_4$ thin films were prepared by spin coating and chemical reduction, the effects of heating methods on phase, crystallization and morphology of the product films were investigated in this work.

Experimental details

The substrates were washed in hot sulfuric acid for 30 min, and then put into acetone, ethanol respectively for ultrasonic cleaning 20 min, at last were kept in ethanol before using. The precursor solutions were prepared by dissolving raw material powders of $CuCl_2·2H_2O$, $SnCl_2·2H_2O$, $ZnCl_2$

and SeO_2 in stoichiometric proportions of $Cu_2ZnSnSe_4$ into a certain amount of solvent, such as water, alcohol. And then the precursor films with certain thickness were obtained by repeated spin coating, drying 4~8 times, and then were put into the reactor filled with 1 mL reducing agent hydrazine hydrate and heated by different technologies. The product films can be obtained after natural cooling to room temperature and the product sample was taken out and dried. The phases of product samples were characterized by X-ray diffraction (XRD) on a model of Bruker D8. The size and morphology of the products were observed by JSM6380LA electron microscope (SEM).

Results and analysis

Preparing CZTSe films by segmented heating

(1) Heating in oven: According to segmented heating method in the reference [10], CZTSe films were prepared by segmented experiments. Fig.1 shows the XRD pattern of CZTSe film on the glass substrate. The sample was first heated at 120 ^oC for 12 h and then at 200 ^oC for 12h. According to the standard PDF card (No.52-0868) of $Cu_2ZnSnSe_4$, the XRD peaks at 2θ angles of 27.1^o and 31.1^o are corresponding to (112) and (200) crystal planes respectively. Compared with previous works, the XRD peak intensity of the samples prepared by segmented heating was not significantly enhanced. However, it appeared (200) crystal plane which almost was not found in CZTSe film samples except in the powder sample with good crystallinity. So the heating process does not obviously affect CZTSe film crystallization.

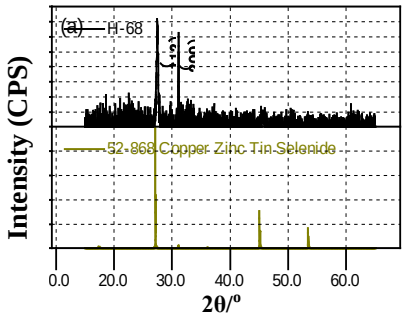

Fig.1 The XRD pattern of CZTSe film on the glass substrate

(2) Heating in in tube furnace: Fig.2 shows the XRD patterns of product films prepared by segmented heating in tube furnace. The reaction processes of two samples were as follows:

a) $100^oC \xrightarrow{30min} 120^oC \xrightarrow{120min} 120^oC \xrightarrow{80min} 200^oC \xrightarrow{30min} 200^oC \xrightarrow{60min} 260^oC \xrightarrow{1200min} 260^oC$

b) $100^oC \xrightarrow{30min} 120^oC \xrightarrow{120min} 120^oC \xrightarrow{80min} 200^oC \xrightarrow{30min} 200^oC \xrightarrow{80min} 280^oC \xrightarrow{1200min} 280^oC$

Compared with the standard PDF card (No.52-0868), the XRD peaks at 2θ angles of 27.1^o and 45.1^o are corresponding to (112) and (204) crystal planes. The XRD peak intensity of the samples shows not very high. Compared with previous experimental results, the change of the reaction process in the tube furnace has not significantly improved crystallization and phase of the product films.

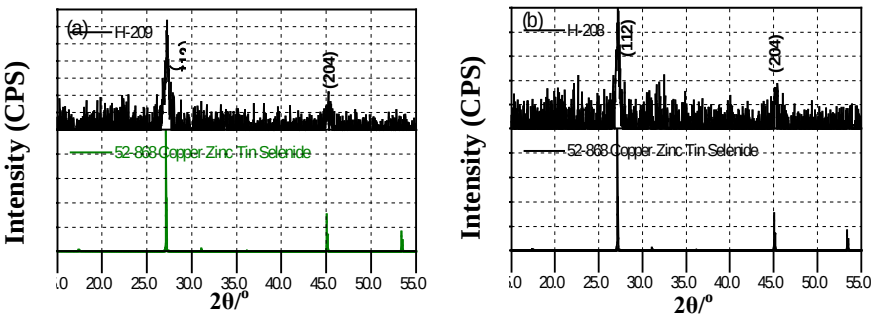

Fig.2 XRD patterns of CZTSe films prepared by segmented heating in tube furnace

Fig.3 shows the SEM images of CZTSe film sample a refered in Fig.2. Fig.3a indicates that the film surface is composed of strip sheets and small amount of polyhedral particles which may be NaCl impurities. From the scratch on the product film in Fig.3b it can be seen that it mainly consists of small particles and has about 0.7 ~ 1 μm thickness.

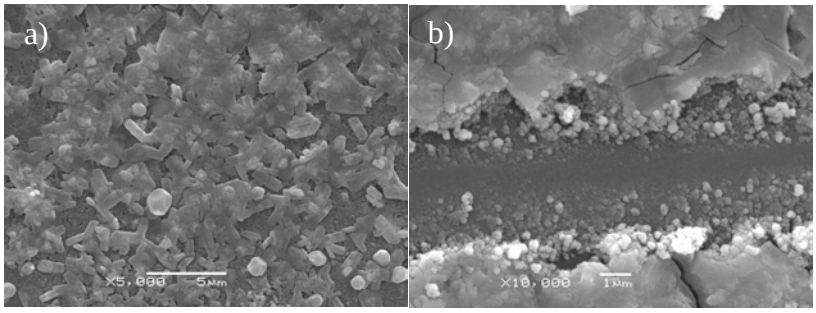

Fig.3 SEM images of CZTSe film prepared by segmented heating in tube furnace

The product films prepared by heating precursor before reaction

Fig.4 gives the XRD patterns of CZTSe films on the glass substrate prepared by different technologies with the heating precursor process at 100 ^{o}C for 20 min before reaction. The reaction conditions for each sample are as follows: a) reacting at 120 ^{o}C for 10 h, b), c) and d reacting at 200 ^{o}C for 10 h, 40 h, 60 h respectively, e) reacting at 200 ^{o}C for 60 h and the precursor without heating. The XRD peaks at 2θ angles of 27.1^{o} and 45.1^{o} are corresponding to (112) and (204) crystal planes respectively. There are only two weak XRD peaks appeared, it indicates that the crystallinity of the product compound was not good, so heating the precursor is not obvious to improve the film crystallinity significantly.

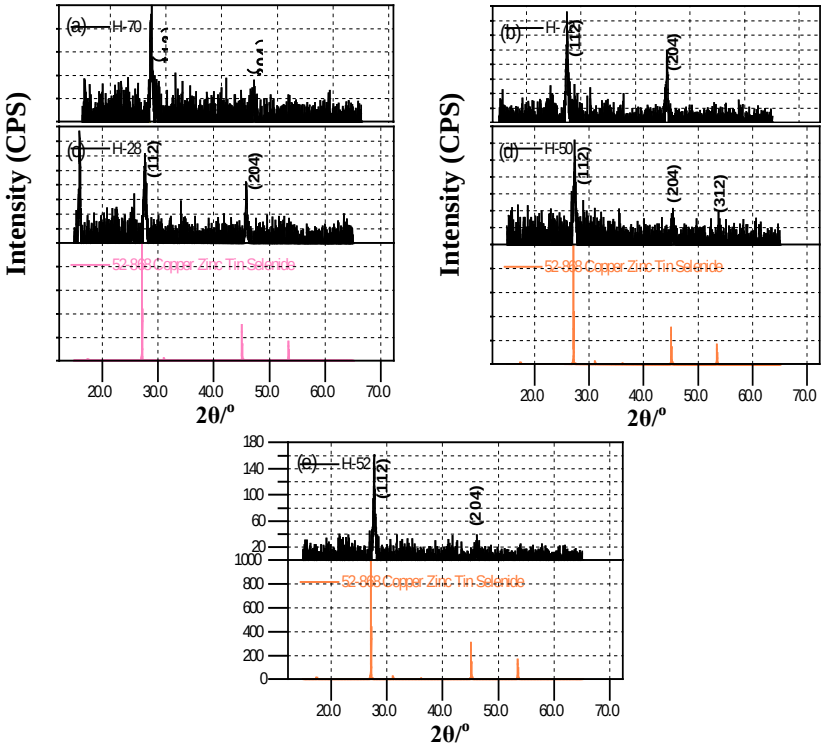

Fig.4 XRD patterns of CZTSe films prepared by different technologies

Fig.5 shows the SEM images of CZTSe film sample b in Fig.4, which was prepared by heating the precursor film. Fig.5a indicates that a lot of staggered arrangement strip products exist on the film surface embedded with some slices, it can be clearly seen that many particles adhered to blocky bar products.

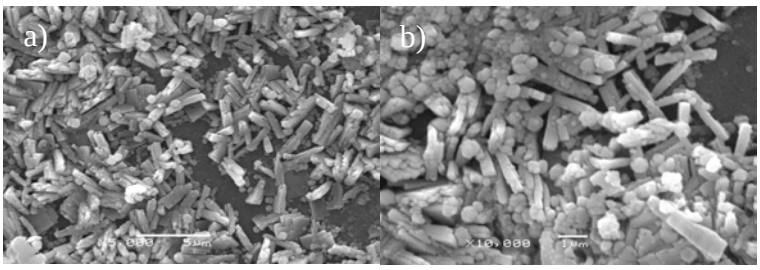

Fig.5 SEM images of CZTSe film prepared by heating the precursor film

Summary

$Cu_2ZnSnSe_4$ thin films were prepared by spin coating and chemical co-reduction by using different heating methods, such as segmented heating, heating the precursor. The intensity of the diffraction peaks of the samples was not significantly enhanced by segmented heating, but the XRD peak for (200) crystal plane appeared. The change of the reaction process in the tube furnace did not significantly improve crystallization and phase of the films. The technology with heating the precursor failed to significantly improve the film crystallinity, a lot of staggered arrangement strips exist on the thin film surface, some strips embedded in the film, some slices are adhered to many particles, the effects of reaction conditions affect the morphology significantly.

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References

[1] D. Aaron R. Barkhouse, Oki Gunawan, et al, Device characteristics of a 10.1 % hydrazine processed $Cu_2ZnSn\ (Se,S)_4$ solar cell, Prog. Photovoit, 20(1) (2012) 6-1.

[2] H. Matsushita, T. Maeda, A.Katsui, et al, Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu-III-IV-VI_4 and Cu_2-III-IV-VI_4 (II-Zn, Cd; III-Ga, In; IV-Ge, Sn; VI-Se), Journal of Crystal Growth 208 (2000) 416-422.

[3] S. Nakamura, T.Maeda, T.Wada, Electronic structure of stannite-type $Cu_2ZnSnSe_4$ by first principles calculations, Phys. Status Solidi C, 6 (5) (2009) 1261-1265.

[4] T. Maeda, S. Nakamura, T. Wada, First principles calculations of vacancy formation in In-free photovoltaic semiconductor $Cu_2ZnSnSe_4$, Thin Solid Films 519 (21) (2011) 7513-7516.

[5] A. Redinger, D. M.Berg, P.J. Dale, Route Toward high-efficiency single-phase $Cu_2ZnSn(S,Se)_4$ thin-film Solar Cells: Model Experiments and Literature Review, Journal of photovoltaics 11(2) (2011) 201-206.

[6] Ji Li, T.T. Ma, M. Wei, W.F. Liu, et al, The $Cu_2ZnSnSe_4$ thin films solar cells synthesized by electrodeposition route, Applied Surface Science, 258 (17) (2012) 6261-6265.

[7] O. Volobujeva, J. Raudoja, E. Mellikov, $Cu_2ZnSnSe_4$ films by selenization of Sn-Zn-Cu sequential films, Journal of Physics and Chemistry of Solids 70 (3-4) (2009) 567-570.

[8] P.M.P. Salomé, P.A.Fernandes, A.F.da Cunha, Morphological and structural characterization of $Cu_2ZnSnSe_4$ thin films grown by selenization of elemental precursor layers, Thin Solid Films, 517 (7) (2009) 2531-2534.

[9] M. Ganchev, L. Kaupmees, J. Iliyna, Formation of $Cu_2ZnSnSe_4$ thin films by selenization of electro-deposited stacked binary alloy layers, Energy Procedia, 2 (1) (2010) 65-70.

[10] Y. Zhao, Research on the preparation of nano-thin film by chemical method, Doctor thesis of Shandong University, 2010.12.