Fabrication of CZTSe thin-film absorber of solar cell by hybrid inks

Shiang-Hua Pan*, Shih-Chang Shei

Department of Electrical Engineering, National University of Tainan

33, Sec. 2, Shu-Lin St., Tainan 700, Taiwan

*E-MAIL：s10482016@gm2.nutn.edu.tw

Abstract

The main idea of this study is to figure out the CZTSe thin-film quality by using the hybrid inks of CTSe and ZnSe under the influence of the selenization time. In this study, we provide a sample with low-cost and non-toxic method to get a uniform and good crystallinity thin film. The $Cu_2ZnSnSe_4$ (CZTSe) compound layers were grown by using the two-step technique. Firstly, we use the non-vacuum process and solvothermal refluxing method with polyetheramine (D400) as the solvent to prepare the Cu_2SnSe_3 (CTSe) and ZnSe inks, and then we mixed CTSe with ZnSe inks to turn into the CZTSe hybrid inks. Secondly, the sample was selenized in a two-temperature zone closed quartz reactor with a saturated selenium atmosphere, and then a flowing Nitrogen gas is maintained to deliver a constant supply of Se vapor during the process. After the two-step technique, the morphology, structure and optical properties of CZTSe thin films was obtained by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), Ultraviolet–visible spectroscopy (UV-vis) and Raman scattering spectrum, respectively.

Keyword：CZTSe, Hybrid inks, Solar cell absorber, Non-vacuum process, Polyetheramine, Selenization

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* Corresponding author:s10482016@gm2.nutn.edu.tw
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I. INTRODUCTION

The thin film solar cells have been attracted highly attention during the recent 20 years. CIGS and CIS are currently accepted to fabricate the efficient solar cells because their conversion efficiencies have been recording for 19.9% [1] and 14.28% [2], respectively. However, indium and gallium used for the preparation of CIGSe and CIS are somewhat rare and costly metals [3] and [4]. That must hinder cost-effective and large-scale production of CIGSe and CIS based solar cells. To decrease the price of solar cells, these elements should be replaced by another elements which are more abundant and more cost-effectively. The Cu_2–II–IV–VI_4 quaternary compound CZTSe is a very promising alternative based on CIGSe [5].

The semiconductor compound $Cu_2ZnSnSe_4$ (CZTSe) is a promising material for the absorber layer of the thin-film solar cells because CZTSe contain inexpensive and earth-crust-abundant elements [6], have the same tetragonal structure as the CIGS but having Zn and Sn substituted for In and Ga in the ratio 50:50 and have the highest reported conversion efficiencies exceeding 11% [7]. CZTSe is a p-type semiconductor with a suitable optical band gap (1.0–1.5 eV) and high absorption coefficients (105 cm^{-1}) [8], these advantages make it appropriate for the conversion of the solar energy.

The pure CZTSe thin-film solar cells are fabricated by co-evaporation deposition [9], [10] and [11], sputter deposition [12], spray pyrolysis [13], electrodeposition [14], and pulsed laser deposition [15] and [16]. Conventional approaches to the fabrication of CZTSe photovoltaic devices involve high-cost vacuum processes followed by selenization [17]. Because of that, it is necessary to develop a low-cost CZTSe film by a two-step process. To develop a two-step process, it is necessary to investigate the formation mechanisms based on the reaction solvent chemical structure, and catalytic ability. The reactive annealing is also the key point in the fabrication of high performance solar cells. The reactive annealing process in a 11.2% CZTSe solar cell, reported by IBM [18], was carried out at very high temperature (590°C) and for a 10.4% CZTSe solar cell, reported by IMEC [19].

The main idea of this study is to figure out the CZTSe thin film quality by using the hybrid inks of the CTSe and ZnSe under the influence of the selenization time. After the two-step technique, the morphology and structure of CZTSe thin films will be measured by SEM, EDS, XRD, UV-vis and Raman scattering spectrum.

II. MATERIALS AND METHODS

To synthesis the CZTSe hybrid inks, the synthesis procedure began by elemental metal sources (Kurt Lesker, purity in 99.99%) and elemental selenium (Kurt Lesker, purity in 99.99%). First, we synthesis the CTSe precursor by Solvothermal Refluxing Method. We use Cu powder 7.365 (g), Sn powder 6.88 5(g) and Se powder 16.1 (g) all were dissolved in 100 (ml) of polyetheramine (D400) in three-necked flasks. Then, the mixture stirring and heating to 210°C for 20 hr then allowed to cool to room temperature. Second, we synthesis the ZnSe precursor by Solvothermal Refluxing Method. We use Zn powder 3.8 (g) and Se powder 5.373 (g) all were dissolved in 60(ml) of polyetheramine (D400) in three-necked flasks. Then, the mixture stirring and heating to 230 °C for 20hr then allowed to cool to room temperature. Third, we mix the CTSe precursor with the ZnSe precursor by the magnetic stirrer to turn into the CZTSe hybrid inks.

To get the CZTSe powder, the CZTSe hybrid inks were made centrifugation by the centrifuge and we use methanol and n-hexane to remove the polyetheramine (D400). Then, we take CZTSe powder 2 (g) dissolved in 10(ml) of $C_6H_{14}S$ and 0.06 (g) of C_3H_4O. The final mixture was coated at soda lime glass dimensions 2.5×2.5 cm^2 and dried in a vacuum.

The sample was selenized in a two-temperature zone closed quartz reactor with a saturated selenium atmosphere and then a flowing Nitrogen gas is maintained to deliver a constant supply of Se vapor during the process. The Se elemental sources are placed in the left zone for 500°C and the samples are placed in the right zone for 550°C, kept 15, 45, 60, 75, 90 and 105 min, respectively.

The CZTSe thin film's structural quality was characterized by X-ray diffraction (XRD). The formation of CZTS phase was further confirmed by Raman measurement at 633 nm. The CZTSe layer surface was characterized by scanning electron microscopy (SEM). The purity and the chemical composition were analyzed by Energy Dispersive Spectrometry (EDS). The ultraviolet–visible spectroscopy (UV-vis) absorption spectra were measured to evaluate the optical properties of the CZTSe absorber thin films of solar cell.

III. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) results are show in Fig.1 and Fig.2. The Fig.1 shows the XRD patterns for (a) ZnSe precursor and (b) CTSe precursor and (c) mixed with (a) and (b). We can realize that the pure CTSe precursor can be synthesized by Cu powder 7.365 (g), Sn powder 6.885 (g) and Se powder 16.1 (g) and all dissolved in 100(ml) of D400 then heating to 210 °C for 20 hr. Similarly, we can realize that the pure ZnSe precursor can be synthesized by Zn powder 3.8 (g) and Se powder 5.373 (g) and all dissolved in 60 (ml) of D400 then heating to 230 °C for 20 hr. Because the chemical activity of Cu to Se is higher than Zn to Se, the synthesis temperature of ZnSe is higher than the synthesis temperature of CTSe. After mix the CTSe precursor with the ZnSe precursor, the XRD pattern is shows in the Figure1. (c), we can realize that the CZTSe hybrid inks contain the CTSe and ZnSe by the enlarge image which has two peaks to represent the CTSe and ZnSe, respectively. Fig.2 (a) shows the X-ray

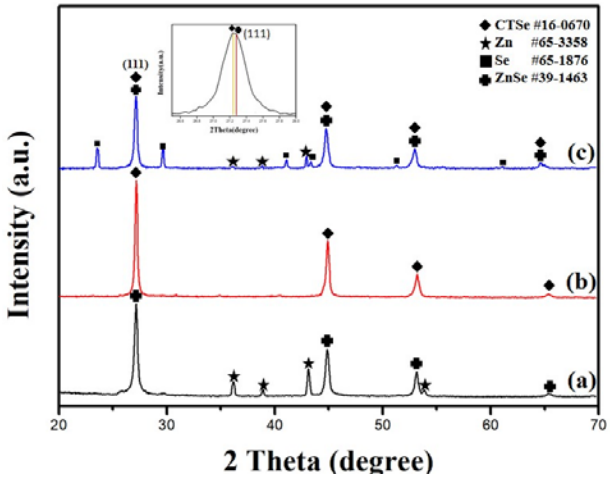

Fig.1 XRD patterns of precursors (a) ZnSe, (b) CTSe and (c) mixed with (a) and (b).

diffraction patterns of the selenization of the same reaction temperature for 550 ℃ but different reaction time for (a) 15 min (b) 45 min (c) 60 min (d) 75 min (e) 90 min (f) 105 min. By the Figure 2(a), we can realized that the increase of the selenization time with the increase of the purity of the CZTSe thin film. The Fig.2 (b) shows the extended XRD patterns in the range of 25-30 degree. We can see that the reaction time for 15 min and 45 min, the peaks are observed in Se with kesterite structure (JCPDS#24-0714), Cu_2SnSe_3 with kesterite structure (JCPDS#16-0670) and $Cu_2ZnSnSe_4$ with kesterite structure (JCPDS#52-0868) indicate that the thin film have Se, CTSe and CZTSe phase because the selenization time is too short to become the single CZTSe phase. The reaction time for 60 min, 75 min, 90 min and 105 min, the peaks are observed in $Cu_2ZnSnSe_4$ with kesterite structure (JCPDS#52-0868) indicate that the thin film are completely single CZTSe phase without any other secondary phase existed. Besides, from the Fig.2 (b), we can realized the increase of the selenization time with the decrease of the CTSe amount and the increase of the CZTSe amount. To find out more information of the XRD, Table 1 show the information of the FWHM and the Grain size. We can find that growth the grain by increasing the selenization time but decreasing when the selenization time exceed 75 min.

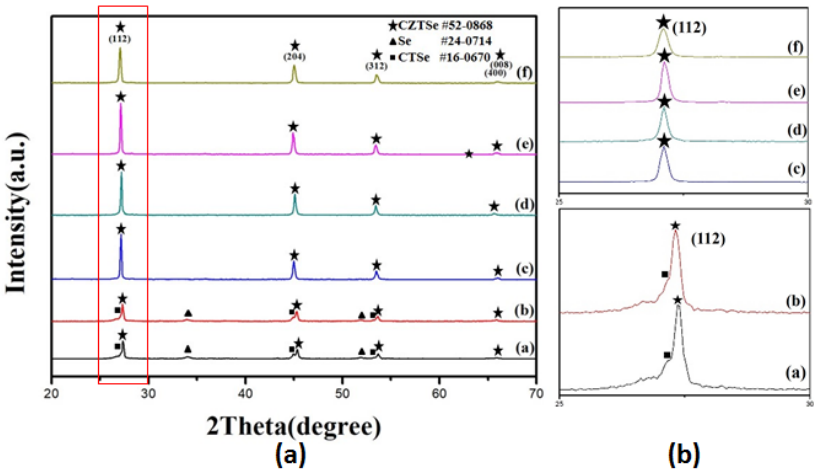

Fig.2 (a) XRD patterns of post-selenization of hybrid inks at 550℃ for (a) 15 min (b) 45 min (c) 60 min (d) 75 min (e) 90 min (f) 105 min. (b) Extended XRD patterns in the range of 25-30 degree.

Plane	Time (min)	2 Theta	FWHM (degree)	Grain size (nm)	D-spacing (μm)
(111)	15	27.317	0.284	28.489	3.2621
	45	27.317	0.270	29.966	3.2620
(112)	60	27.230	0.168	48.151	3.2722
	75	27.208	0.150	53.927	3.2749
	90	27.202	0.165	49.024	3.2756
	105	26.947	0.213	37.956	3.3059

Table 1 FWHM and the Grain size.

The crystalline phases of the fully crystallized CZTSe thin film were further investigated by Raman spectroscopy. Fig.3 shows the Raman patterns of post-selenization of hybrid inks at 550℃ for (a) 15 min (b) 45 min (c) 60 min (d) 75 min (e) 90 min (f) 105 min. We can see the CZTSe peaks with Raman shift at 190cm^{-1} and 240-250cm^{-1}[20]. All these values are in good agreement with the XRD results.

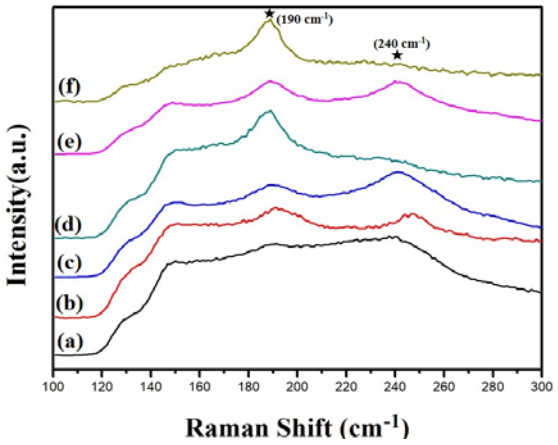

Fig.3 Raman patterns of post-selenization of hybrid inks at 550℃ for (a) 15 min (b) 45 min (c) 60 min (d) 75 min (e) 90 min (f) 105 min.

Fig.4 shows the top-view SEM micrographs of the same selenization temperature but the different selenization time for (a) 60 min (b) 75 min (c) 90 min and (d) 105 min. The Fig.4 (b) shows in the CZTSe thin film with high density, well homogeneity and large grains, is compact and the crystals are in the size of micrometer order. The SEM results are in good agreement with the Table 1.

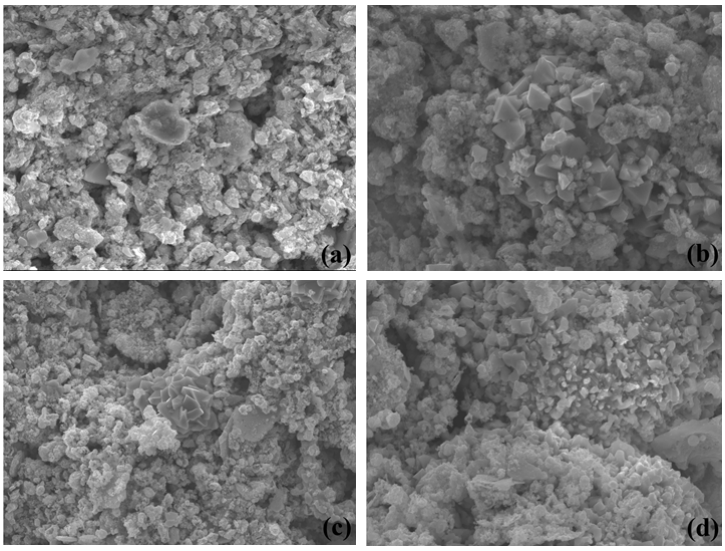

Fig.4 Top-view SEM micrographs of selenization at 550 C for (a) 60 min (b) 75 min (c) 90 min and (d) 105 min.

The Table 2 shows the EDS measurement for selenization temperature at 550 ℃ for 60-105 min. We can see the selenization temperature at 550 ℃ for 75 min film, were measured to be Cu:Zn:Sn:Se =26.93:18.14:10.56:44.36. The elemental ratio of Cu/(Zn+Sn) = 0.938 and Zn/Sn= 1.717 is Cu poor Zn rich absorber [21].

Time (min)	Atomic ratio(%)				Compositional ratio	
	Cu	Zn	Sn	Se	Cu/(Zn+Sn)	Zn/Sn
60	24.48	10.95	11.76	52.81	1.077	0.931
75	26.93	18.14	10.56	44.36	0.938	1.717
90	28.16	15.61	14.42	41.82	0.937	1.082
105	14.21	33.42	7.49	44.89	0.347	4.461

Table 2 EDS measurement for selenization temperature at 550℃ for 60-105 min.

UV-vis measurements of post-selenization of hybrid inks at 550℃ for (a) 15 min (b) 45 min (c) 60 min (d) 75 min (e) 90 min (f) 105 min are shown in Fig.5. We can realize that the band gap was decreasing when increasing the selenization time, but increasing when the selenization time exceed 75 min because the secondary phases and the CZTSe thin film quality will influence the optical band gap energy. The Fig.5 (d) has the lowest band gap of 1.26eV because it is without any other binary phase.

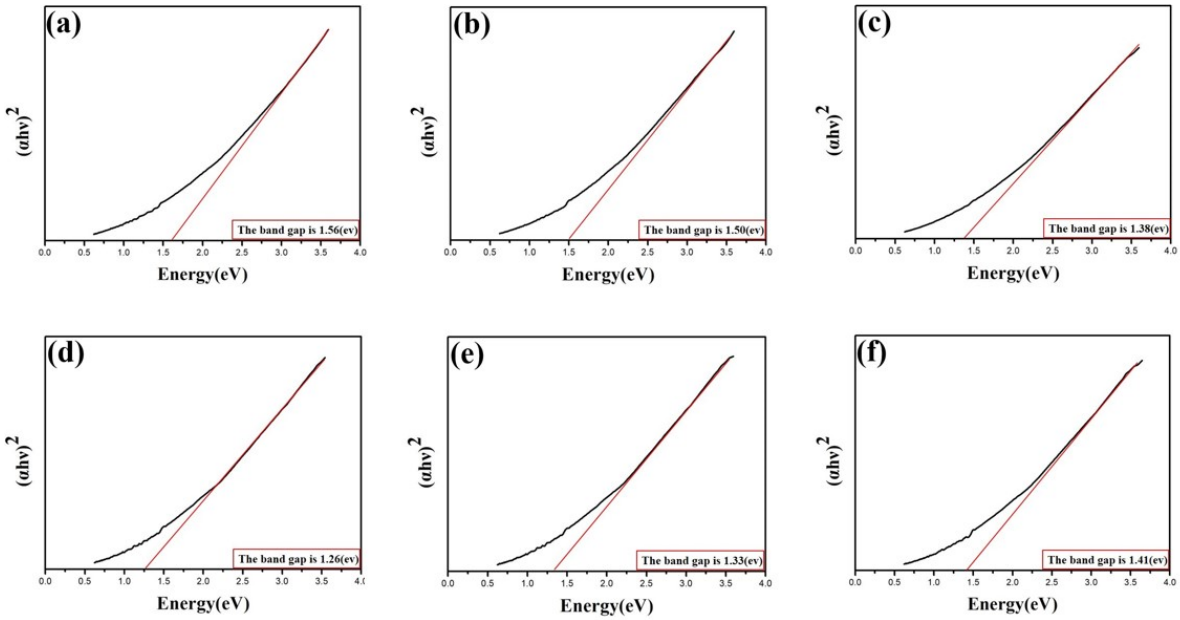

Fig.5 UV-vis measurements of post-selenization of hybrid inks at 550℃ for (a) 15 min (b) 45 min (c) 60 min (d) 75 min (e) 90 min (f) 105 min, and calculated its band gap.

IV. CONCLUSIONS

In this study, we have prepared the CTSe and ZnSe precursor by two-step processing then mix the CTSe with ZnSe to turn into the CZTSe hybrid inks. After coating, the thin films annealing at Se powder temperature at 500°C and Sub temperature at 550°C for 15min, 45min, 60min, 75min, 90min and 105 min. From the XRD, FWHM and Raman, it can be concluded that the selenization time for 75 min is the optimal reaction condition for the CZTSe hybrid inks because the sample consist of the pure CZTSe phase and have the largest grain size. SEM micrograph shows the selenization time for 75 min has a dense and homogeneous CZTSe thin film with the large grains, is compact and the crystals are in the size of micrometer order. The EDS shows the CZTSe thin films after selenization for 75min are Cu-poor, and Zn-rich. The UV-vis shows the selenization time for 75 min have the lowest band gap of 1.26eV which is suitable for the fabrication of CZTSe thin-film solar cells. From above results by XRD, Raman, SEM, EDS, and UV-vis, we conclude that the optimal selenization time to obtain the CZTSe thin films from hybrid inks of Cu_2SnSe_3 and ZnSe was 75 min.

V. ACKNOWLEDGMENT

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