Fabrication of single-phase CZTSe thin film by Solvothermal Refluxing Method

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Abstract

The purpose of this study is to investigate the effect of the quality of $Cu_2ZnSnSe_4$ (CZTSe) thin film with the variation at different synthesis process, selenization reaction time. To improve the quality of CZTSe thin film, this study will find the optimal synthesis method, selenization reaction time for the growth of CZTSe nanocrystals. In the non-vacuum environment, we used the Solvothermal Refluxing Method to synthesize $Cu_2ZnSnSe_4$ (CZTSe) nano-ink by using metal powder as the raw materials directly. Lastly, CZTSe thin film will be deposited on the glass substrate through the blade method. Then we placed the CZTSe thin film into an open selenization furnace which has two temperature zones, and further aerate nitrogen gas to proceed pressurize enclosure selenization process at different temperatures and time. We will attempt 550℃ and the selenium powder will be heated to provide the selenium compensation. From X-ray diffraction and Raman scattering measurements, we can observe the formation process of $Cu_2ZnSnSe_4$. After selenization, it has good crystallinity and morphology observed by SEM. And the elemental compositions are measured by EDS. And the optical properties are measured by UV–Vis absorption spectrum. According to the material properties measurements, the CZTSe thin film for 550℃ and 75 minutes selenization condition has a good crystallinity.

Keywords **-- $Cu_2ZnSnSe_4$, solar cell, selenization, polyetheramine, Solvothermal Refluxing Method**

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I. INTRODUCTION

Up till the present moment, the main energy resources around the world are petroleum oil, natural gas, coal and nuclear power[1]. However, these are limited instead of exhaustible. In addition, carbon dioxide, nitrides and sulfides are produced when using them, and it may cause a great damage to the global environment. Therefore, there are more and more countries in recent have begun to pay highly attention to these serious problems and invested in researching renewable energy, striving to find the solutions[2]. As shown in Fig. 1, the common-used renewable energy resources include solar energy, wind power, hydropower, tidal, geothermal and biomass energy[3]. According to the research, the energy emitted from the sun is about 1.2 x 10^{14} (kW), and the energy irradiated on earth sustained for one hour is equivalent to the human needs[4]. Besides, solar energy is a clean renewable energy, so it won't produce harmful substances such as CO_2 etc. and doesn't cause global warming[5]. Taiwan is a subtropical climate environment, it has good sunshine conditions and is very suitable for developing solar energy. Therefore, the key to develop it is how to reduce the manufacturing cost, including simplify the process of fabrication and easy access to raw materials.

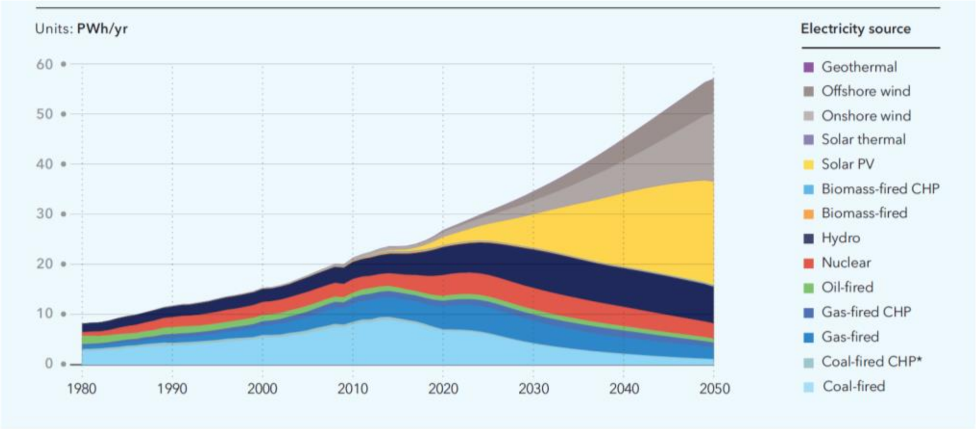

Fig. 1 Prognostic chart of future energy usage[4]

So far the development of CIGS solar cells, though its conversion efficiency is about 19.2%, the indium (In) and gallium (Ga) materials have limited earth reserves, and there is a possibility of material shortage and the price is relatively expensive[6][7]. This will not be conducive to the reduction of fabricating costs and thus the willingness to use solar energy. Therefore, considerable researches have been devoted to finding compound materials that can replace these bare elements. Copper-zinc-tin-selenide (CZTSe) replaces indium (In) and gallium (Ga) of CIGS with zinc (Zn) and tin (Sn). The compositional elements of this compound semiconductor, copper, zinc, tin and selenium, are abundant in the earth's crust, and their contents are about 50 ppm, 75 ppm, 2.2 ppm, and 0.05 ppm, respectively[8][9]. Therefore, the price of CZTSe is relatively cheaper than CIGS, and is considered to be the most potential material for thin film solar cell[10].

II. MATERIALS AND METHODS

Precursor ink was prepared with two synthesis process by Solvothermal Refluxing Method, and synthesized via combine copper (Cu), zinc (Zn), tin (Sn), and selenium (Se) powder in a four-neck flask filled with the chelating solvent polyetheramine (D400, $C_2H_5C[CH_2[OCH_2CH(CH_3)]nNH_2]_3$)[11]. As shown in Table. 1, elemental metal sources (Kurt Lesker, purity in 99.99%) were used, Cu powder 7.36 (g), Zn powder 3.8 (g), Sn powder 6.89 (g) and Se powder 19.545 (g) were all dissolved in 150 (ml) of polyetheramine in a four-neck flask. Then stirring consistently and heating to 230℃ for 20hr under nitrogen atmosphere and then cooled down to the room temperature.

In order to facilitate the subsequent coating process, we must remove the solvent D400 in the CZTSe nano-ink to obtain the powder. First, we extract CZTSe ink 5 (ml), ethanol 10 (ml), C_6H_{14} 5 (ml) and add them into the centrifuge tube. Second, stir them with the CZTSe ink thoroughly by a glass rod. Then centrifuge at 6000 rpm for 10 min and repeat 4~6 times. Afterwards, we take CZTSe powder 1(g) dissolved in $C_6H_{14}S$ 4(ml) and 0.03 (g) of C_3H_4O. In the end, as-synthesized nano-ink was deposited on glass substrates by blade method.

Selenization with Se powder was then applied to investigate how the different temperature and time influenced the reaction process and morphology of the final thin film. Before selenization, the pressure in the chamber was decreased to 5×10^{-2} torr, whereupon the temperature was increased at a rate of 10℃ per minute. The selenization process is shown in Table. 2, the temperature was held at 550℃ for 15 min to 90 min within a nitrogen atmosphere and then cooled naturally to room temperature. Finally, the prepared films were characterized by using X-ray diffraction (XRD), Raman spectroscopy (Raman), high-resolution thermal field emission scanning electron microscopy (HR-SEM), Energy Dispersive Spectrometry (EDS) and UV-vis spectroscopy[12].

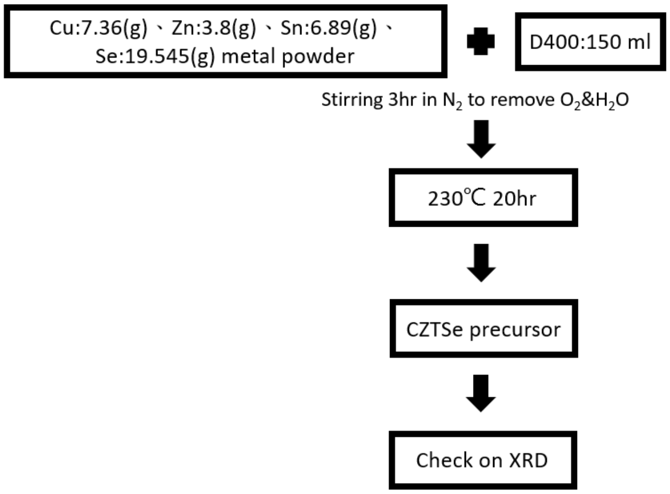

Table. 1 Process chart in fabrication of CZTSe precursor

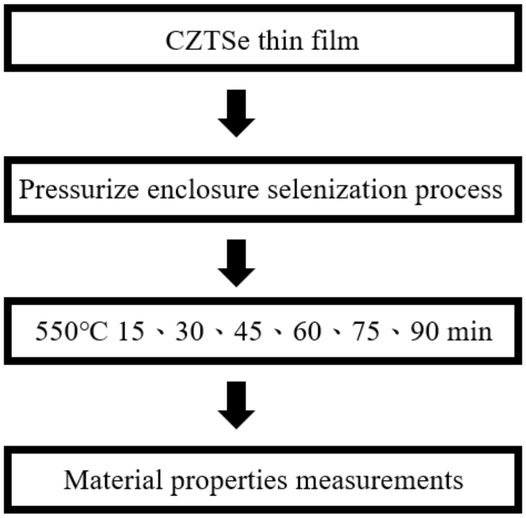

Table. 2 Process chart in selenization of CZTSe precursor

III. RESULTS AND DISCUSSION

As shown in Fig. 2, single-phase CZTSe precursor was fabricated by (a) Stir bar (b) Stirrer for 230℃ 20hr. From the XRD patterns, we can compare the results with the ICDD standard database, and we can obtain that both (a) and (b) have the same characteristic peaks and preferred phase 112 (#52-0868). Besides, the peak intensity of Se in (a) is relative weakness to (b), due to the difference of rotational speed, agitation range and thus the uniformity. Therefore, stirrer is superior to the stir bar.

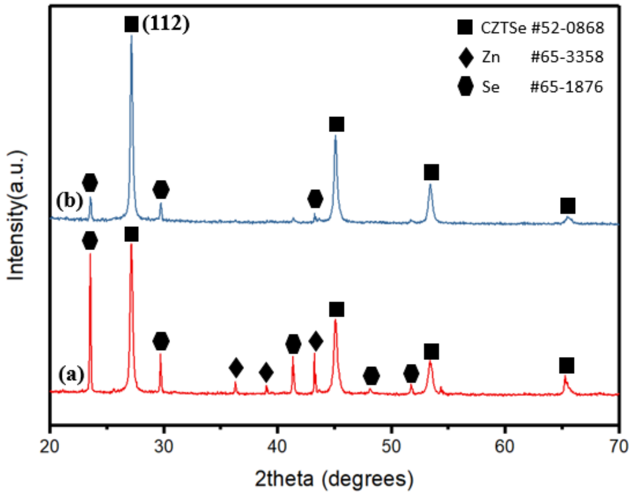

Fig. 2 XRD patterns of CZTSe precursor fabricated by (a) Stir bar (b) Stirrer

Fig. 3 shows the XRD patterns of CZTSe thin films selenized at 550℃ for different reaction time. From the XRD patterns, we can realize that all selenization time have formed quaternary single-phase CZTSe, it's because of CZTSe thin film has sufficient energy to make high bandgap compound Cu_xSe react with Zn and Sn. With the strongest diffraction peak of the 112 plane, according to Debye Scherre equation, the diameters of selenized CZTSe nanoparticles was evaluated and shown in Table. 3. For 15~60 min, we can observe that FWHM was increased with the reaction time increased. As for 60~90 min, FWHM was decreased with the reaction time increased and has the narrowest at 75 min, it's because of CTSe and ZnSe agglomerate thoroughly. Furthermore, grain size is inversely proportional to FWHM, so 75 min has the largest grain size. Besides, we find that the grain size at 90 min is smaller than 75 min because CZTSe grains are under high temperature for a long time, causing them pyrolysis.

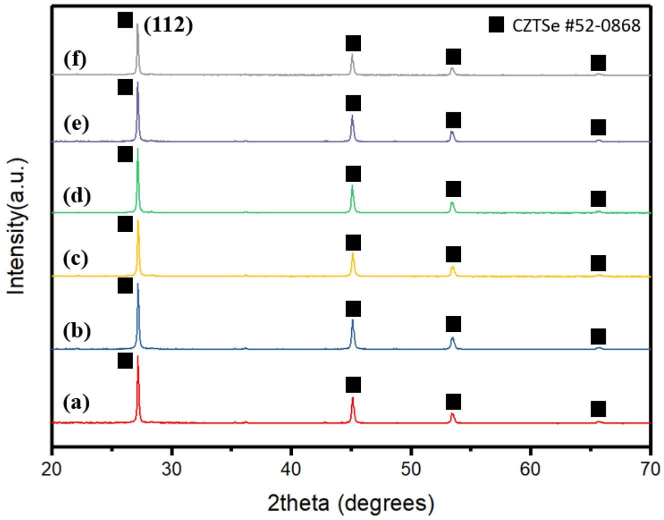

Fig. 3 XRD patterns of CZTSe thin films selenized at 550℃ for (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min (f) 90 min

	Time (min)	2 Theta	FWHM (degree)	Grain Size (nm)
Plane (112)	15	27.17	0.152	51.93
	30	27.182	0.164	48.13
	45	27.185	0.166	47.55
	60	27.167	0.162	48.72
	75	27.18	0.15	52.62
	90	27.148	0.155	50.92

Table. 3 FWHM and grain size of CZTSe thin films selenized at 550℃ for different time

According to the literature, the main characteristic peak of CZTSe is located at 190 cm^{-1} and 240~250 cm^{-1}[13]. Therefore, we can use Raman spectroscope to further investigate the phase transformation. Fig. 4 shows the Raman spectrum of CZTSe thin films selenized at 550℃ for different reaction time. From the Raman spectrum, we can compare the results based on the literature, and we can confirm that all curves have existed CZTSe after selenized at 550℃ for 15, 30, 45, 60, 75, 90 min. In addition, the peak intensity at 190 cm^{-1} is weak at 15, 30 min, due to the selenization time is too short to make CTSe and ZnSe have sufficient energy to agglomerate thoroughly. Therefore, the crystallite is under the formative stage and its grain size is small and loose structure. Lastly, the peak intensity is the strongest when the reaction time is 75 min, this phenomenon is consistent with XRD results.

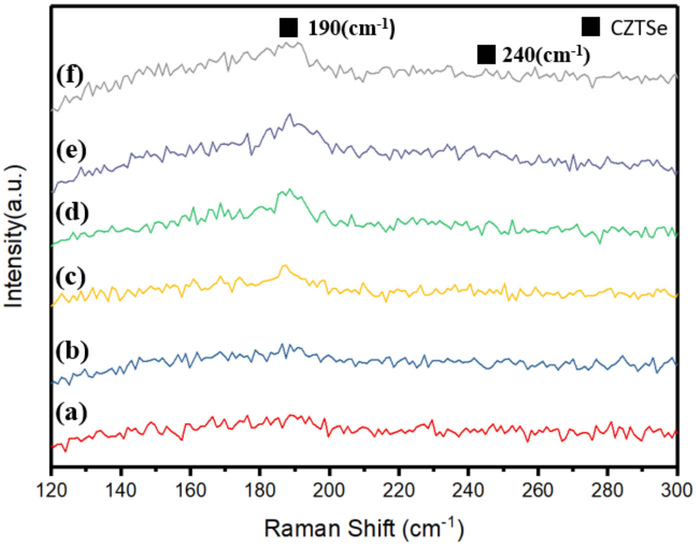

Fig. 4 Raman spectrum of CZTSe thin films selenized at 550℃ for (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min (f) 90 min

Through the SEM analysis of the quaternary single-phase CZTSe, we can observe the surface morphology and the quality of CZTSe thin film. Fig. 5 shows the top-view SEM micrographs of CZTSe thin films selenized at 550℃ for different reaction time. From (a), although CZTSe grains have been formed, the selenization time is too short so it has poor consistency, obvious pores and small grain size. From (b), CZTSe grains grow up to 1.2~1.5 μm and become sharp corner, and the consistency is apparently improved. From (c) and (d), CZTSe grains agglomerate at 45 min and disperse at 60 min, this process is called formative stage. From (e), CZTSe grains grow up to 1.8~2.1 μm, have the best consistency and the edge of grains become sharp. From (f), CZTSe grains are under high temperature for a long time, causing them pyrolysis. The SEM results are in agreement with the Table. 3.

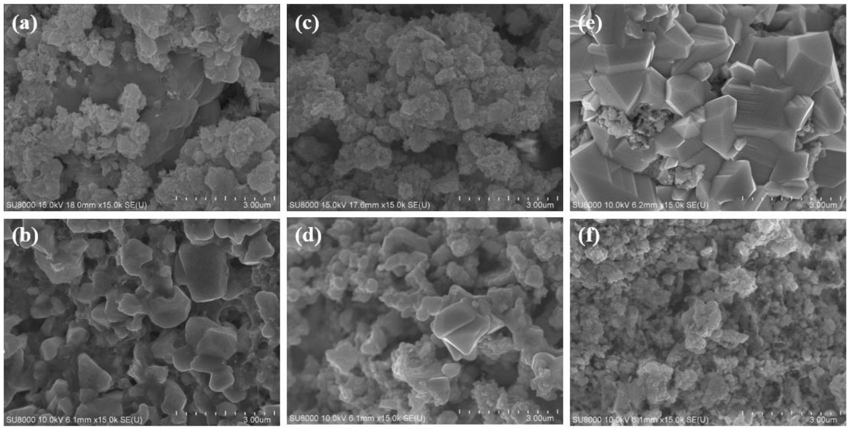

Fig. 5 SEM micrographs of CZTSe thin films selenized at 550℃ for (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min (f) 90 min

From the EDS analysis results shown in Table. 4, it can be seen that when reaction time is 15, 30, 45, 60, 75, 90 min, the actual compositional ratios are 0.85, 0.82, 0.84, 0.89, 0.95, 1.08 respectively. When reaction time is 60 min, the content of Zn is lesser than Sn, it's because of CZTSe grains agglomerate at 45 min and disperse at 60 min, causing ZnSe exposed to high temperature for a long time and thus evaporated[14]. When reaction time is 75 min, the molar ratio is the closest to 2:1:1:4, and the elemental ratio of Cu/[Zn+Sn]=0.95 and Zn/Sn=1.23 is Cu-poor, Zn-rich absorber[15].

Time (min)	**Atomic ratio(%)**				**Compositional ratio**	
	Cu	Zn	Sn	Se	Cu/(Zn+Sn)	Zn/Sn
15	22.92	8.29	18.57	50.22	0.85	0.45
30	22.18	7.52	19.67	50.63	0.82	0.38
45	22.86	9.26	18.00	49.88	0.84	0.51
60	22.87	6.22	19.54	51.37	0.89	0.32
75	23.34	13.61	11.09	51.96	0.95	1.23
90	25.23	9.84	13.45	51.48	1.08	0.73

Table. 4 EDS analysis of CZTSe thin films selenized at 550℃ for different time

The UV-vis absorption spectrum of CZTSe thin film is shown in Fig. 6. The determined optical bandgap of CZTSe thin film decreased from 1.78 eV to 1.28 eV and then increased to 1.63 eV. We find 550℃ 75 min has the lowest bandgap 1.28 eV, due to its crystallinity and consistency is the best and the particle size is the largest, prompting to enhance the quality of CZTSe thin film and lower its bandgap.

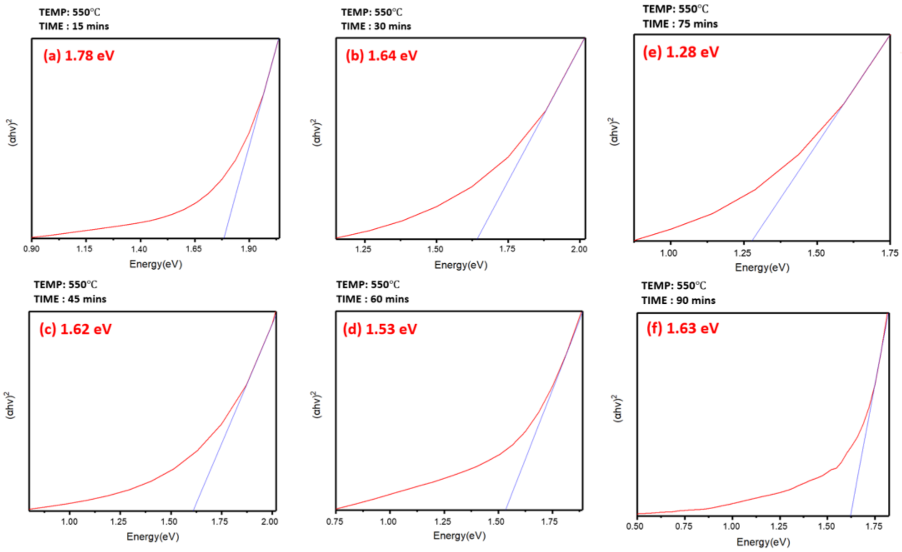

Fig. 6 UV-vis absorption spectrum of CZTSe thin films selenized at 550℃ for (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min (f) 90 min

IV. CONCLUSIONS

In this study, a non-vacuum process for nanoparticle precursors of $Cu_2ZnSnSe_4$ (CZTSe) thin film solar cells were described in this work. Quaternary kesterite-type $Cu_2ZnSnSe_4$ nanoparticle precursors were successfully synthesized by using a relatively simple and convenient Solvothermal-Refluxing Method. XRD, Raman, SEM, EDS and UV-vis confirm that the single-phase CZTSe were successfully synthesized without any other secondary phase existed. From the synthesis process, we can find that CZTSe precursor has better uniformity by stirrer instead of stir bar and the best synthesis condition is 230℃ for 20hr.

From the previous discussion of the selenization process, it can be seen that the best selenization condition is 550℃ 75 min, which has the narrowest FWHM=0.114, maximum grain size=69.24 nm, and minimum energy bandgap=1.12 eV. Therefore, when CZTSe thin film was selenized at 550℃ for 75 min, CZTSe thin film has the best consistency and uniformity.

V. ACKNOWLEDGMENT

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