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Synthesis and characteristic of $\text{Cu}_2\text{ZnSnS}_4$ thin film prepared by appropriate non-stoichiometry precursor

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Abstract. Non-stoichiometry sulphur-containing precursors were studied to picture its connection to the formation of kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) phase. The precursors were prepared from metal (Cu-Zn-Sn) chlorides with ethanol as solvent and 2-mercaptopropionic acid as capping ligand. Mol ratio of S/Cu 4.4 was observed as the limit of non-stoichiometry. Confirmed by XRD characterization, the employment of sulphur in higher concentration resulted in the formation of secondary phases with a porous morphology. Further, a modification in holding time of annealing treatment was successfully improved the crystallinity of the CZTS film. The SEM micrograph was showed the formation of well-growth CZTS grains with size $\sim 1.5 \mu\text{m}$. However, porosity was still encountered at the surface film as indication of insufficient growth processes (heat treatment). The energy band characteristic of the film is 1.4 eV, determined by extrapolating the gradient line of $(\alpha h\nu)^2$ vs $h\nu$ (photon energy). The route presented in this paper offers alternative solution to synthesize CZTS semiconductor from ethanol-based precursor.

1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has attracted much effort from scientists to develop low cost and highly efficient thin-film solar cells (TFSC) due to its internal properties: direct mechanism and wide-range absorption of sun spectra, high absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$) and tuneable band gap energy [1-3]. The latter property is potentially significance to the development of multijunction solar cells which involved certain adjustment on the band gap energy of absorber semiconductor. The energy band varies accordingly to metal composition and type of chalcogenide used in the preparation. CZTS firstly investigated as absorber semiconductor for photovoltaic by Ito and Nakazawa in 1988 and started get attention to develop TFSC in 1996 [1,2]. Further, CZTS-based solar cells intensively investigated by IBM research group led by Mitzi [1,4]. In 2014, Mitzi group has successfully attained 12.7% of energy conversion efficiency, a record in CZTS-based thin-film solar cells [5]. This efficiency is low enough compare to other active materials used in TFSC technologies such as CIGS, CIS and CdTe which have demonstrated cell efficiencies well beyond 14% for commercial module and around 20% for laboratory scale [6-8]. However, CZTS-based semiconductor has not yet reached mature production line due to shallow knowledge in this material; therefore, there seems to be still open room to improve in the direction of high-efficiency and cost-competitive way.

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The formation of chalcogenide quaternary system, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), involves complex competition between CZTS growth and secondary phases growth: binary phases (Cu_2S , SnS , ZnS , SnS_2) and ternary phases (Cu_2SnS_3) [4]. Attacking this issue remains to be the key solution to fill the performance gap between CZTS and CIGS/CIS/CdTe TF solar cells. SnS_2 is a n-type semiconductor with a band gap energy of 2.2 eV while ZnS is insulator in nature with wide band gap (3.54 eV) [1,9]. These binary phases may form a secondary diode inside absorbing semiconductor and reduce the active area to absorb sun spectra and thus generate low-density of electron-hole pairs. Cu_2S , SnS and other sulphide compounds have different electrical properties to CZTS phase. At the end, unwanted secondary phases can cause high photocarrier recombination and thus hamper solar cell performance [10-13].

In this study, we synthesized CZTS films using single-solution approach as precursor preparation and spin coating method as film deposition. Four elemental constituents, Cu-Zn-Sn-S, are directly included in the first stage by employing ethanol and 2-mercaptopropionic acid as solvent and capping ligand (stabilizer), respectively [14]. In previous research, this route has successfully been proven to fabricate CZTS phase without the use of sulfurization (annealing at sulfur-containing atmosphere) [13]. Different from common approach, 2-mercaptopropionic acid can efficiently form metal-sulfur complex ligand and induce the formation of binary sulphide phase before eventually form CZTS phase through heat treatment. These ligands mitigate the lost of elemental sulfur during high temperature annealing (± 500 °C) and thus makes sulfurization no longer necessary. Figure 1 shows the XRD peak of CZTS kesterite phase processed from sulfurization route and without sulfurization [13]. The vanishingly difference in correspondence CZTS peak between both routes showed successful employment of 2-mercaptopropionic acid to eliminate sulfurization step. In this research, the attention is given to study non-stoichiometry sulfur-containing precursor on the formation of kesterite CZTS-phase and the growth of secondary phases.

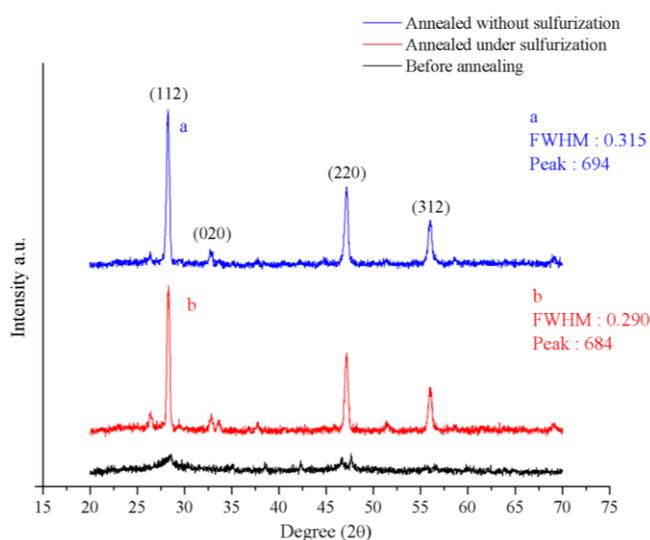


Figure 1. XRD data plot of as-deposited CZTS film, annealed with sulfurization, and annealed without sulfurization, respectively from bottom to top.

2. Experimental Setup

The synthesis of CZTS-films was carried out using chemical method followed by spin-coat deposition on top of soda lime glass substrate. The route is adapted from previous report; briefly, copper chloride (CuCl_2), zinc chloride (ZnCl_2) and tin chloride (SnCl_2) were dissolved at designed ratios [$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.8$ and $\text{Zn}/\text{Sn} = 1.2$] in ethanol and 2-mercaptopropionic acid under ambient environment and constant temperature at 80 °C [13]. After 15 minutes of agitation, thiourea was hot injected at different

mol ratio to Cu and keep under agitation for another 10 minutes. After cooling down to ambient temperature, this solution then referred as precursor.

Soda lime glass (15 mm x 15 mm) is used as substrate for deposition stage. The glass firstly soaked in distilled water before ultrasonically cleaned in acetone and ethanol for 10 minutes, respectively. The precursor then deposited onto the glass using spin coater at 2000 rpm for 20 seconds followed by drying using hot plate at 150 °C for 12 minutes. These processes were repeated five times with the fifth (final) drying conducted at 170 °C for 60 minutes. The thus-obtained film was then annealed at 520 °C with a holding period of 60 minutes. The experimental images and final film are shown in figure 2.

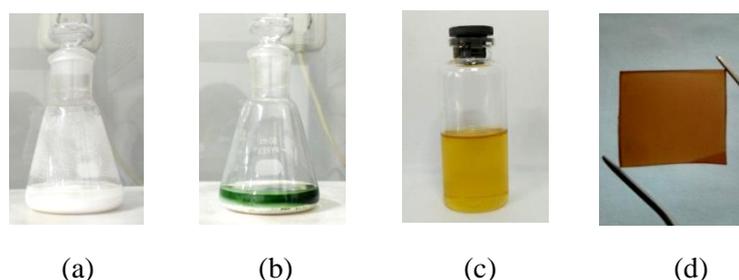


Figure 2. Experimental pictures of (a) Cu-Zn-Sn-ethanol solution, (b) addition of 2-mercaptopropionic acid, (c) addition of thiourea to form final CZTS precursor, and (d) as-deposited CZTS film.

3. Results and Discussion

Previous research, conducted by Si-Nae *et al.* (2014), has studied the use of thiourea as both stabilizer and source of sulphur [15]. Their work showed successful reaction between thiourea and metal chlorides to form complexes ligand. However, excess thiourea was required to obtain homogenous precursor solutions, and sulphurization was needed to induce CZTS phase. In this research, in favor of 2-mercaptopropionic acid, homogenous solution was obtained at stoichiometry of its constituents. Further, since the indication of unnecessary sulphurization step in our previous research, we developed precursor with excess-containing-thiourea to find optimum condition for the growth of CZTS phase in absence of sulphur atmosphere during heat treatment (annealing).

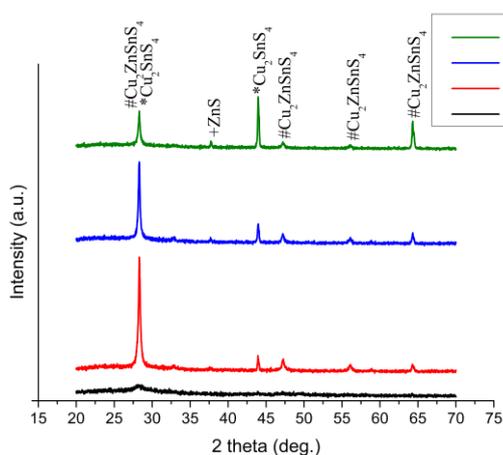


Figure 3. XRD signal of CZTS and secondary phases from the selected samples.

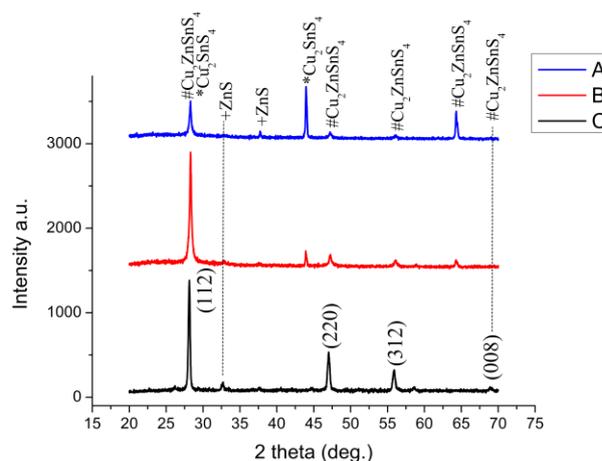


Figure 4. XRD spectra of CZTS film prepared from different condition: mol S/Cu:4.4 with annealing holding time of 30 minutes (A), 60 minutes (B), and mol S/Cu:6.4 annealed 60 minutes (C).

In order to understand the role of sulphur in the formation of CZTS phase, three samples with different mol ratio of sulphur to Cu were selected in the experiment: the ratio of 4.4, 5.4 and 6.4 were used, respectively. The crystallinity of CZTS phase, as first main consideration, is summarized in the form of XRD data plot at figure 3. The figure shows the existence of kesterite CZTS phase (JCPDS no. 26-0575) along with secondary phases, Cu_2SnS_3 (JCPDS no. 1-089-4714) and ZnS (JCPDS no. 5-0566), particularly at higher non-stoichiometry ratio of the precursor chemicals (Mol S/Cu: 6.4). The formation of secondary phases at non-stoichiometry condition is also encountered in other researches [16-18]. Although the exact reaction mechanism of secondary phases is still unclear, recent research works suggest two responsible causes: the considerable loss of Zn, Sn and S during annealing and the excess of certain element, especially sulphur [15,19,20].

From the previous discussion, it is evidence that sulphur content in the precursor strongly affects the purity of CZTS phase. To support this conclusion, we managed to slightly change the sulphur content through thermal treatment, lowering holding time of the annealing from 60 minutes to 30 minutes. XRD measurements for this experiment is shown in figure 4 line C, with the main peaks indexed to the (112), (220), (312) planes of the kesterite structure. Minor peaks at 33.3° and 69.3° could also be observed for this sample, further confirm the formation of CZTS kesterite phase. Differ from the figure 4 line B, which represents XRD spectra of similar processed-sample apart from annealing holding time, relatively clear CZTS XRD peaks of sample C was observed with an increase in the crystallinity (indicated from a sharper of the width and the height of the respective peaks).

Table 1. Chemical composition of respected CZTS film.

Ratio/ Sample	CZTS Film before annealing		Annealed CZTS Film (Mol S/Cu)			
	Pre-dried	dried	(4.4)*	(5.4)*	(6.4)*	(4.4)**
S/Metal	1,29	1,13	0,97	0,97	0,96	0,95
S/Cu	4,93	2,60	1,96	2,03	2,04	2,06
Cu/(Sn+Zn)	0,35	0,78	0,99	0,92	0,91	0,86
Zn/Sn	0,56	0,52	0,88	1,03	1,09	1,09

* annealing holding time 30 minutes.

** annealing holding time 60 minutes

Table 1 is EDS data representing the chemical composition of the CZTS films. To discuss the mechanism of changing peak intensity from the previous XRD analyses, the ratio of sulphur to metal, $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn are summarized in the table. Overall, the atomic ratio of S to metal and S to Cu share similar number for annealed CZTS film. However, the chemical composition at each certain temperature during annealing hides more significant information to picture the reaction path rather than the composition of final film. From table 1, the effect of sulphur concentration can be indirectly found by observing the ratio of $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn .

As identified by most of the reports, Cu poor (~ 0.8) and Zn rich (~ 1.2) hold the proper condition to fabricate high conductivity CZTS films, inferring the high purity of CZTS phase as secondary phases are naturally poor conductive compound [11-13,22]. In addition to final chemical ratio (Cu poor and Zn rich), the composition of the precursor also plays important role to the formation of CZTS and secondary phases during heat treatment [11]. Based on these considerations, and as suggested by EDS and XRD figures, 4.4 mol ratio of S to Cu is the limit of non-stoichiometry for CZTS ethanol-based precursor using 2-mercaptopropionic acid as capping ligand. Further, from the EDS information of 4.4* and 4.4** samples, lowering holding time of annealing treatment (from 60 minutes to 30 minutes) results in the closer composition to the desire Cu poor and Zn rich. Subsequently, confirmed by XRD spectra, 4.4** sample condition successfully formed relatively high and pure CZTS kesterite phase.

Figure 5 displays the surface micrograph of five samples, in correspond to different sulphur concentration of the precursor and holding time of the annealing treatment. Understanding the connection between preparation and final microstructure is crucial to minimize internal resistivity created by void, insulator phases, and grain boundary. Void and non-conductive compound have electrical barriers to hinder charge collection whereas grain boundary has supportive spaces for charge carriers (electron-hole pairs) to recombine [23-25]. However, specific to grain boundary, 1-2 μm is found to be the optimal size for kesterite CZTS rather than to reduce the number of grain boundary (increases grain growth). The grain boundary has previously been reported to provide a current path for minority carriers [22]. From figure 5, all of the annealed samples showed a densely packed structure except for figure 5e which showed a well-growth CZTS kesterite grains despite the porosity at the surface films. The densely packed structure of figure 5a, 5b and 5c, as confirmed from XRD spectra, might be attributed to the existence of the considerable amount of the secondary phases.

CZTS film prepare from 4.4 mol ratio of S to Cu (figure 5e), the highest crystallinity of CZTS kesterite phase, shows a uniform grain size around~ 1.5 μm . However, the growth still does not compensate the path (porosity) of gaseous phases from decomposed organic chemicals. Constraints on CZTS morphology are interestingly challenging as the kinetics of CZTS growth is affected by many condition: the chemicals, temperature and holding time of annealing as well as drying, and atmosphere during preparation and heat treatment. Another comprehensive study is needed to establish a robust environmentally-friendly route to synthesize well-characteristic of CZTS semiconductor, especially to manipulate the morphology of the film.

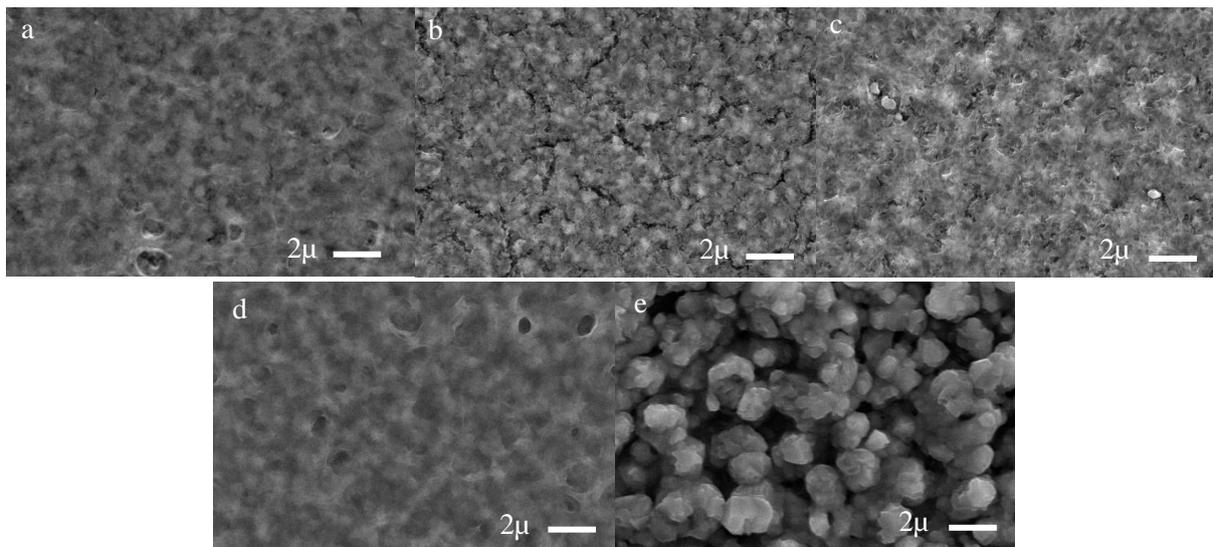


Figure 5. SEM micrographs of the surface morphology: Mol S/Cu (a) 4.4*, (b) 5.4*, (c) 6.4*, (d) as-deposited CZTS film and (e) 4.4**.

The final and main properties of semiconductor is the ability to absorb photon energy which represented by the band gap energy. The band energy was determined by extrapolating gradient line of $(\alpha h\nu)^2$ vs $h\nu$ (photon energy) curve to the based horizontal line of its axis as depicted in figure 6. It is evidence that the band energy fluctuates in correspond to chemical composition: particularly, the number of $\text{Cu}/(\text{Sn}+\text{Zn})$, Zn/Sn and the existence of secondary phases [26]. Cu_2SnS_3 (CTS), considered as secondary phase, is reported to has band gap energy in the range of 0.98 to 1.35 eV. CTS is p-type semiconductor with a similar crystal structure and band energy gap to CZTS semiconductor (~ 1.45 eV), and thus could absorb the same range of photon energy; however, it is reported to has a considerably lower efficiency than CZTS [27].

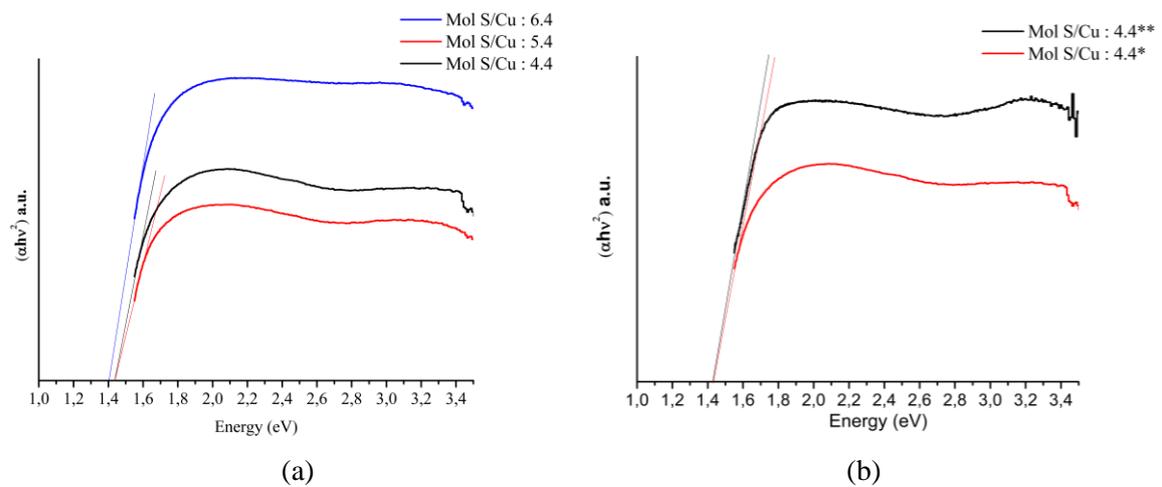


Figure 6. $(\alpha h\nu)^2$ vs $h\nu$ (photon energy) curve to determine optical properties of CZTS films.

Figure 6 shows the energy gap of CZTS films slightly ranging from 1.4 eV to 1.42 eV. The lower energy gap, 1.4 eV, was observed for the sample prepared from the highest non-stoichiometry precursor. This condition is attributable to the existence of secondary phases, as discussed from the previous section. From figure 6 (b), both samples (4.4* and 4.4**) share similar band energy at around 1.42 eV. At this level, the figure indicated the vanishingly small influences of the crystallinity of CZTS to its energy gap; the chemical composition hold more significant part to the tunable band energy properties of CZTS. The highest device efficiency of CZTS-based solar cells, however, is found with the bandgap of ~ 1.12 eV prepared by exchange some part of sulphur with selenium (doping), forming CZTSSe matrix [12,28]. Meanwhile, other researches successfully tune the energy gap by modifying the cation matrix [4,5,12]

4. Conclusion

Non-stoichiometry sulphur-containing precursor has been observed to develop single solution approach to synthesize CZTS film. Atomic ratio of S to Cu 4.4 is found to be the limit of excess sulphur in the precursor. From this sample, kesterite CZTS phase has confirmed by XRD measurements with band gap energy ~ 1.42 eV. Further, technical modifications on the annealing treatment successfully reduce the existence of secondary phases and formed well-growth CZTS grains with size ~ 1.5 μm . Meanwhile, non-stoichiometry precursor with S/Cu higher than 4.4 demonstrated CZTS phase along with high concentration of secondary phases, particularly Cu_2SnS_3 and ZnS. All of the CZTS film prepared without the use of sulphur atmosphere during annealing treatment (sulfurization). This route offers the solution to fabricate CZTS semiconductor as low-cost and environmentally-friendly solar cells.

5. Acknowledgement

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