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Preparation of $\text{Cu}_2\text{ZnSnS}/\text{Se}_4$ Thin Films from Oxide Precursors and its Prospect for Other Cu_2MSnS_4 Thin Films

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/63049>

Abstract

In this chapter, the preparation of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films from oxide precursors was described. Such an oxides-based route is a low cost, facile way for the kesterites thin films. The rationality of applying oxides method into CZTSe and CZTS thin films was also clarified, including the reactive thermodynamics and annealing process. Finally, this oxide-based approach is also expected for the preparation of the other Cu_2MSnS_4 ($M = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) thin films.

Keywords: $\text{Cu}_2\text{ZnSnS}/\text{Se}_4$ thin films, oxides, annealing, oxide nanoparticles, Cu_2MSnS_4

1. Introduction

As the exponential growth of the conventional energy consumption, environmental pollution and greenhouse effect, human beings need to find and exploit renewable, clean energy e.g. solar energy. Solar cell is one of the effective routes to utilize solar energy. Such a green technology produces less effect on the environment and human health. The wide-scale use of clean, renewable solar energy requires a reduction in the manufacturing costs of solar panels. Thin film solar cells (TFSCs) can convert sunlight into electricity with much less material than conventional crystalline silicon solar cells, resulting in a potential for lower material cost. There are three main thin film photovoltaic (PV) technologies in the PV market, such as CdTe, $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS), and Si thin film. However, Si TFSC shows low efficiency and instability from the Staebler–Wronski effect. As for CdTe and CIGS TFSC, they have been considered as the most promising material for TFSC due to respectable conversion efficiency and

their outdoor stability [1]. But the above two compounds contain toxic or expensive materials such as Cd and In (Ga). These factors reduce the production capacity of the existing CdTe and CIGS technologies. Recently, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and their solid solutions $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (CZTSSe) have attracted significant attention owing to their interesting photoelectric properties [2, 3]. They have a tunable optical band gap ranging from 1.0 to 1.5 eV, a high absorption coefficient of 10^4 cm^{-1} and a suitable charge carrier concentrations ($5 \times 10^{15} \sim 6 \times 10^{16} \text{ cm}^{-3}$) [4-6]. All the constituents of CZTS-based thin films are rich on earth. The content of Zn and Sn are about 79 ppm and 2.2 ppm in the crust, which is about 1500 and 45 times the content of In respectively. As they consist of low-cost and readily available elements, they have high potential for mass production as solar absorber material [7, 8]. Because of these optimal characteristics, 32.2% power conversion efficiency is expected for CZTS thin films solar cell, according to Shockley-Queisser theory [9]. Until now, the highest efficiency, which is up to 12.6%, has been obtained by adopting mixed sulfoselenide CZTSSe thin film as absorber layers, which was prepared from hydrazine solution [10].

There are many methods to prepare CZTS-based thin films. In this chapter, we will consider a low cost, facile, and green oxides-based route for absorber thin films in three parts. The first part, we will briefly review the deposition techniques of CZTS-based thin films. The second is a review on the oxides-based method for CZTS/CZTSe TFSC. The third part is the study of the possibility of applying such an oxide precursors method to prepare the other Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) thin films. Meanwhile, the prospect for forming new type Cu_2MSnS_4 (i.e. $\text{M} = \text{Ba}, \text{Ca}, \text{Mg}$) will also be carried out.

2. Deposition techniques of CZTS thin films

To prepare absorber films for solar cell, such as CdTe and CIGS, many methods were developed. These different processes generally include evaporation, sputtering, electroplating, solution processing, and nanoparticles [11]. Due to the similar crystal structure and properties of CIGS thin films, most of the above techniques have been developed for the TFSCs-based CZTS absorber layers. The techniques for the deposition of CZTS thin films may be classified into two categories: vacuum (evaporation, sputtering) and non-vacuum based approaches (electroplating, solution processing, and nanoparticles) [12]. The development of the non-vacuum process for CZTS thin films can greatly reduce the production cost because they abandoned using expensive vacuum equipment.

2.1. Evaporation

Evaporation techniques are the most straightforward choice for preparing thin films due to the easy control of evaporation process by adjusting pressure and temperature. Meanwhile, this method has been successfully used to evaporate other absorber materials, and also provides better opportunity for fabrication of high quality thin film devices. Evaporation deposition routes can produce high uniform thin films, which also have a good reproducibility. Various evaporation technologies such as electron beam (EB), co-evaporation, fast evaporation, and thermal evaporation have been employed for the deposition of CZTS thin films [13-

15]. Recently, IBM has successfully fabricated CZTS TFSC by using the thermal evaporation method, which shows a high efficiency of 8.4% [16]. They adopted two step routes to deposit CZTS thin films. Firstly, the CZTS thin films were grown by thermal evaporation with elements Cu, Zn, Sn, and S. Secondly, the CZTS thin films were then annealed at 570°C for 5 min in air atmosphere. So far, this is the highest conversion efficiency reported for pure CZTS thin film based solar cells by using vacuum-based technique.

2.2. Sputtering

Sputtering is a conventional way for thin films 'growth in industry which have been successfully introduced in CIGS thin films. Typically, researchers used two steps to prepare high quality CZTS thin films [17]. The metallic precursors (Cu, Zn, and Sn) were firstly deposited in a stacking sequence, for example Cu–Zn–Sn/Cu–Zn–Sn–Cu or Cu–ZnS–SnS. The obtained metallic precursor was sequentially annealed under S vapor or H_2S atmosphere. The smooth CZTS thin films with high crystallinity can be achieved through the sputtering and post sulfurization method. A CZTS based TFSC with 6.7% efficiency had been fabricated by Katagiri et al using magnetron sputtered CZTS thin films, which showed Voc of 610 mV and Jsc of 17.9 mA cm^{-2} with a filling factor of 0.62 [18].

2.3. Electroplating

Electroplating appears to be a promising technique for the low-cost, non-toxic solution preparation of semiconductors and was previously used in CdTe and CIGS TFSC. Similar to sputtering method, the common process of preparing CZTS thin films is known as two steps method: single step electrodeposition of precursors, followed by annealing at high temperature [19-21]. Shafaat Ahmed et al [22] have presented a high-performance CZTS TFSC by using the electrodeposition of metal stacks and the annealing of a CuZnSn precursor in a sulfur atmosphere. In their work, a champion electroplated CZTS solar cell achieves a power conversion efficiency of 7.3%, which is a record efficiency for electrodeposited CZTS TFSC [22].

2.4. Solution processing

Solution based coating technique is a very simple and low-cost route for the preparation of many thin films. This technique contains two steps: (I) preparation of precursor solution; (II) coating the precursor solution onto substrate to obtain desired thin films by using various wet coating methods (e.g. spin coating, drop casting, and doctor blade). The true solution mix chemical species in molecular level can enhance the homogeneity of chemical compositions. So a highly homogeneous CZTS thin film can be obtained by this method. Such solution precursors can broadly be sub-categorized as being: (1) metal salt based precursors; (2) organometallic precursors; (3) hydrazine-based precursors and related approaches. Comparing with other two methods, the hydrazine-related solution contains all required elements, but not extra elements (e.g. C, O, Cl) are included. After coating the solution on substrate, the precursor thin films were heated. During this process, hydrazine decomposes cleanly into N_2 and H_2 or NH_3 and H_2 , facilitating good film morphology. By using this hydrazine-based approach, IBM have achieved a great energy conversion efficiency of CZTS TFSC (9.2%) [23].

2.5. Nanoparticles-based process

Nanoparticles-based processes use solid particles dispersed in a solvent to form an ink or slurry which can be coated onto a substrate. This offers an extremely materials-efficient method of depositing a thin-film precursor layer. Such a process is one of the successful non-vacuum approaches to formatting CIGS thin films, with variations employing particles composed of CIGS, oxides, metal, and binary selenide particulates as precursor. For example, CIGS TFSC showed an efficiency of 13.6% by using oxide nanoparticles-based process [24]. Nanosolar also reported 14% efficient cells by using mixed selenide nanoparticles and a single-stage annealing treatment [25]. Due to the similar structure and properties of CIGS thin films, the application of similar methods for CZTS thin films was widely studied. Most of the research focuses on the quaternary CZTS or binary-based process. Guo et al have fabricated CZTSSe TFSC with 9.6% efficiency from binary/ternary sulfide nanoparticles [26]. Those nanoparticles were synthesized by hot injection technique, which includes the injection of a cold solution of precursors into a hot surfactant solution (oleylamine) with the protection of inert gas. Such a complex process will increase production costs and be difficult to scale up, which needs to be solved before the commercialization of the CZTS solar cells [27]. Meanwhile, the nanoparticles capped with stabilizing molecules will be decomposed into carbon impurity, which will prohibit crystal growth in the CZTS film during thermal treatment [28].

On the other hand, coat oxide nanoparticles ink onto a substrate offers an extremely promising method for depositing a CIGS thin film precursor layer and such an approach led to CIGS solar cells with efficiencies of over 13.6% [24]. However, such a successful route in CIGS TFSC is rarely reported to be adopted in CZTS TFSC. The following sections will emphatically consider the deposition of oxides nanoparticles precursor layers for high quality CZTS and related materials CMTS ($M = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$).

3. Oxides nanoparticles-based routes for CZTS/Se thin films

The reason for adopting oxide precursors for CZTS thin films can be claimed as following: (I) Preparation of oxide precursors is appealing because the published literature is full of information about synthesized method. (II) The stable oxides precursor is in favor of controlling the component of the final thin films during the sintering because oxides are stable against phase segregation during sintering. (III) Metal oxides are similar to metals in exhibiting a volume change during reactive conversion to a sulfide, due to S atom is larger than O atom. So the oxides-based method can lead to densification of the films.

Although there are so many advantages, oxide nanoparticles process is rarely reported. Washio et al fabricated 6% efficiency CZTS solar cell using oxide precursors by CVD [29]. However, as we know, CVD deposition process is complicated. Tang et al had reported a facile, low-cost route to fabricate CZTS thin films by sulfurization of the Cu–Zn–Sn composite oxides thin films [30]. This mixed oxide powder is prepared by the chemical co-precipitation of all metallic ions from solution. They have studied the effects of sulfurization temperature on the properties of the CZTS thin films. The resulted CZTS thin films show porous morphology and

an optical band gap about 1.35 eV. Such a CZTS thin films was applied in solar cells and showed a conversion efficiency of 1.22%. However, the chemical precipitation and sequential dry process may result in agglomeration of particles [31]. Meanwhile, the incorporation of organic binder in the ink also deteriorates the CZTS thin film during sulfurization treatment.

In our previous work, we tried to prepare $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin films by the selenization of the oxide precursors [32]. This is exploration of applying the oxides-based approach into CZTSe thin films. To alleviate the hard agglomeration during the synthesis of oxide nanoparticles, a novel solvent-free (also called low temperature solid phase reaction) method was introduced to prepare oxides nanoparticles, as seen in **Figure 1**.

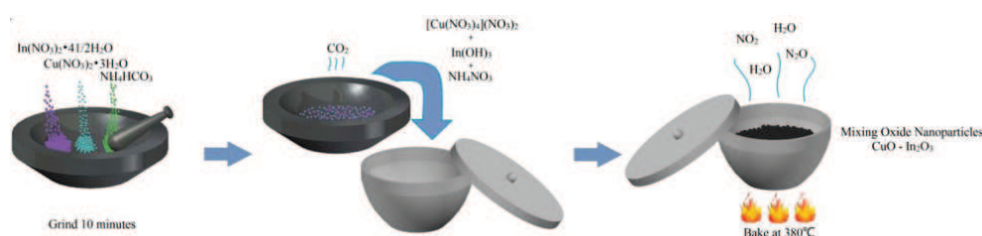


Figure 1. Illustrative diagram of oxide nanoparticles synthesis processes.

In a typical synthesis, the required amount of mixed nitrates and excess ammonium bicarbonate were mixed and reacted. The resulted mixture was then baked to obtain mixed oxide nanoparticles. During this heating process, those additional components were discharged as gases, leaving behind pure oxide nanoparticles. If the solvent free synthesis was properly extended, it would be also possible for the low cost and large-scale preparation of other mixed oxides nanoparticles for practical application. The XRD and SEM indicated that pure CZTSe thin films with micron-sized grains were obtained by selenization of the oxide precursors in our work, as shown in **Figure 2**. However, the films also were rough and porous.

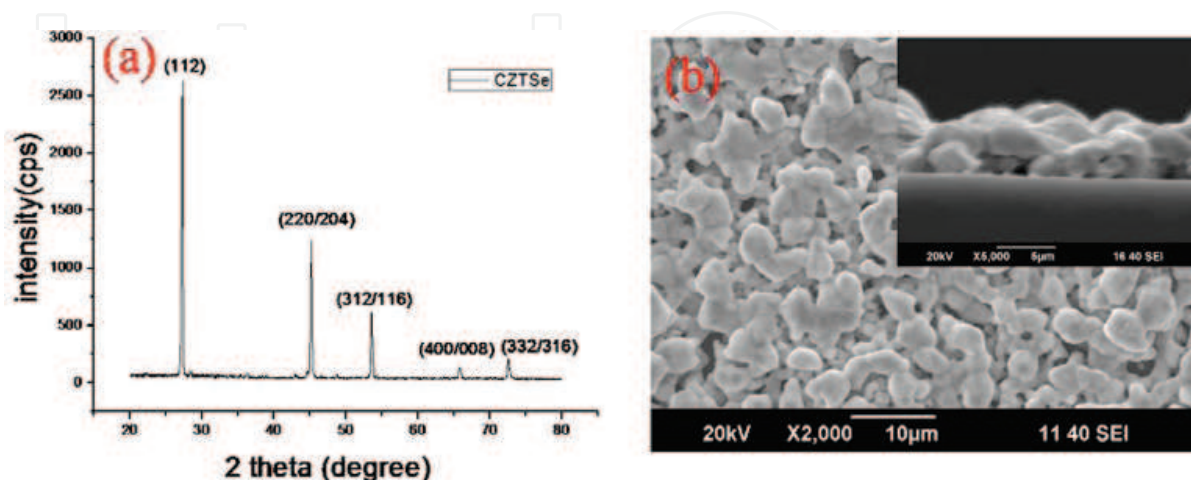


Figure 2. XRD patterns and morphology/cross-sections of CZTSe thin films.

It is well known that it is difficult to coat a uniform and dense precursor from nanoparticles, which is due to the irregular stacking of the nanoparticles. The rough and porous morphology of the precursor thin films will lead to corrosion of the back contact by excessive interaction with the sintering atmosphere. Therefore, before the heat treatment was carried out, the precursor must be densified. During the preparation of ceramic targets, the compression treatment was usually applied to obtain a compact green body [33]. Such an efficient method was introduced to compress the porous precursor thin films in the previous work, as shown in the **Figure 3**.

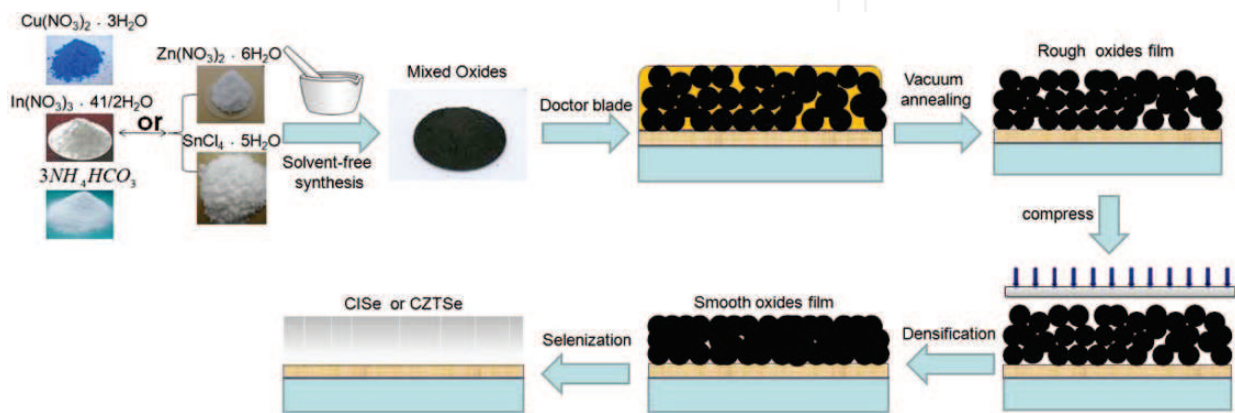
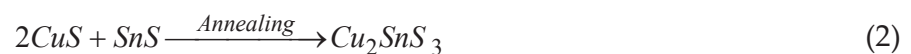


Figure 3. Schematic diagram of oxide-based CZTSe thin film fabrication processes [34].

Regardless of which coating technique, for example printing and spraying techniques as well as doctor blade and spin coating are used, to ensure that the technique is able to form porosity free thin films still exist with some difficulties. However, the density of precursor thin films is essentially improved after pressing. The introduction of compression in packing nanoparticles obviously has a beneficial effect on densification, which helps to achieve a sintered thin film with high quality. It is due to that, that the compact density significantly affects the phase transition during the selenization. The nucleation and growth of CZTSe or CZTS phase are considered to be facilitated by the mass transfer around the particle contacts.

To convert the oxides precursor into CZTSe or CZTS thin films, selenization or sulfurization was carried out respectively. Se or S sources were used to replace toxic H_2S and H_2Se gas. During the annealing process, oxides were translated into binary sulfide or selenide. Finally, the intermediate binary would react with each other under high temperature. According to references, such a conversion can generally be expressed as the following two routes:





For the first reaction path, the CZTS phase was directly obtained through reacting with each other. The moment product Cu_2SnS_3 was formed, it will react with ZnS. As shown in the **Figure 4**, all the XRD data confirmed the formation of CZTSe or CZTS by annealing the oxide precursors. Through comparing the pressured CZTSe and unpressed CZTSe thin films, it was found that the compression can effectively improve the crystallite of the CZTSe thin films. The study of the effect of annealing temperature on the CZTS thin films revealed the process of CZTS crystal growth. It was found that the order of stability of oxides was: $\text{SnO}_2 > \text{ZnO} > \text{CuO}$. The moderate stability of SnO_2 can reduce the loss of Sn through evaporation of SnS [35].

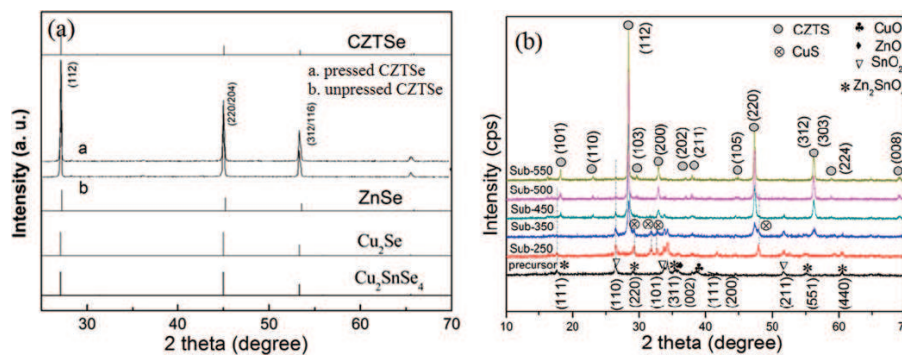


Figure 4. XRD patterns of oxide nanoparticles-based CZTSe (pressed and unpressed CZTSe) and CZTS (under different sulfurization temperature) thin films [36, 37].

XRD is generally considered as the main tool to analyze the structure of such compounds, but it is difficult to identify most of the minors phases and the possible secondary phase with similar crystal structure, for example, Cu_2SnS_3 , CuS , ZnS , or SnS_2 . Raman scattering is a useful complementary technique to detect the presence of secondary phases. Raman results (**Figure 5**) again distinguished the formation of pure CZTSe or CZTS thin films from oxide precursors.

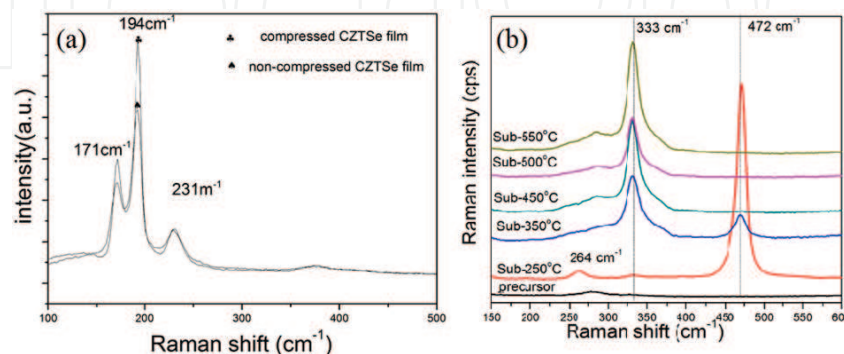


Figure 5. Raman patterns of oxide nanoparticles-based CZTSe (pressed and unpressed CZTSe) and CZTS (under different sulfurization temperature) thin films [36, 37].

The oxides-based CZTSe thin films showed a smooth film with very large grain. Many grains indeed extended across the entire thickness of the film from the cross-sectional SEM (**Figure 6(a)**). However, the pure sulfur CZTS thin films presented small grain size indicating poor crystalline. As we know, the large amount of grain boundary resulted from small grain size will deteriorate the performance of CZTS TFSC.

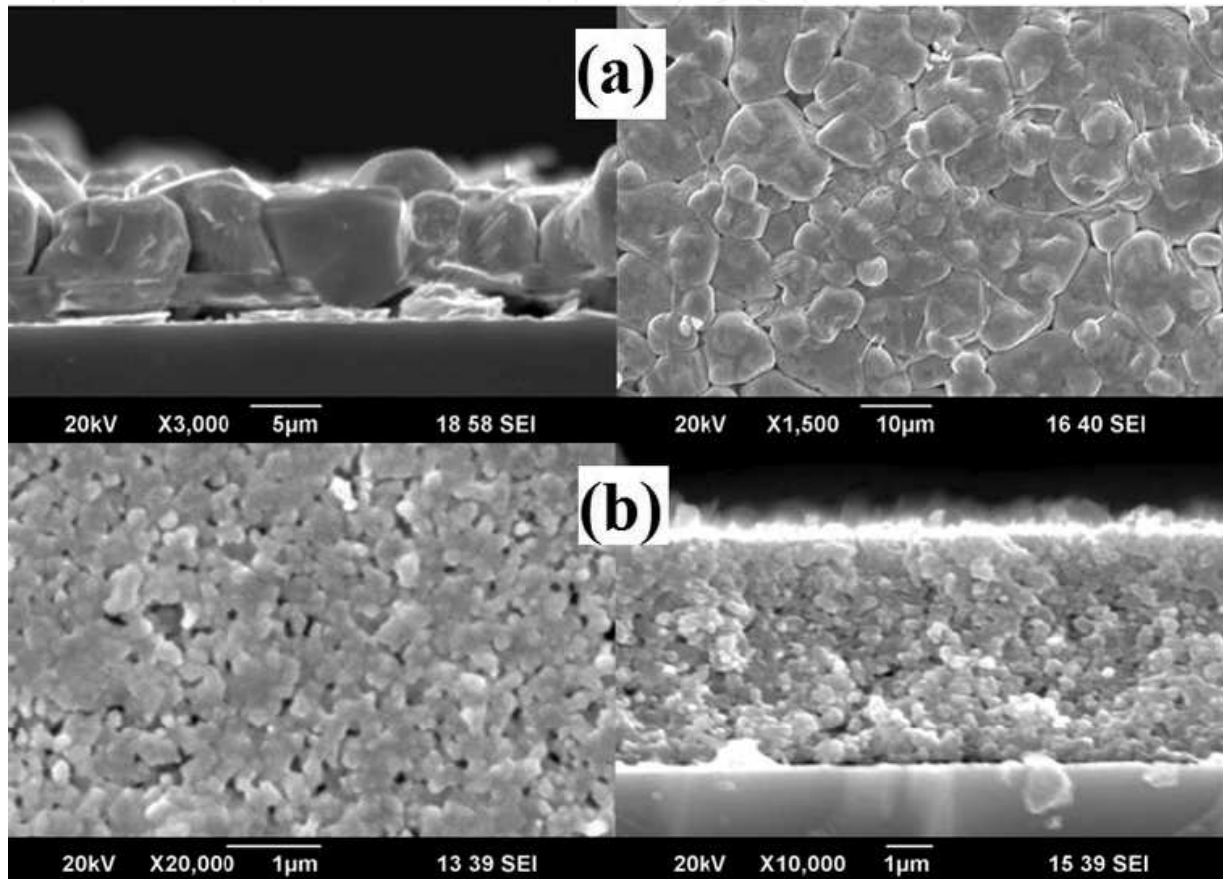


Figure 6. Morphology and cross-sections of oxide nanoparticles-based (a) CZTSe and (b) CZTS thin films [36, 37].

Grain growth is the key challenge for the preparation of pure sulfide CZTS thin films with large grain during annealing, due to the lack of suitable fluxing agent. The high thermal energy is expected to supply driving force for grain growth. As shown in the **Figure 7**, the crystal quality of CZTS thin films were improved significantly by using relatively high sulfurization temperature. The high quality CZTS thin films were comparable with the CZTS thin films prepared by the vacuum-based method. However, such high quality CZTS thin films did not produce CZTS TFSC with high conversion efficiency. From the J-V characteristics of CZTS TFSC (red curve of **Figure 8**), it can be seen that CZTS device prepared by sulfurizing oxide precursors at high temperature achieves a high V_{oc} , but low J_{sc} . As the oxide precursors suffered from high temperature sulfurization, the sulfur gas with high activity and pressure will erode Mo back electrode. The thick MoS_2 layers with high resistance were formed during this high temperature sulfurization process, which sequentially reduce J_{sc} and FF.

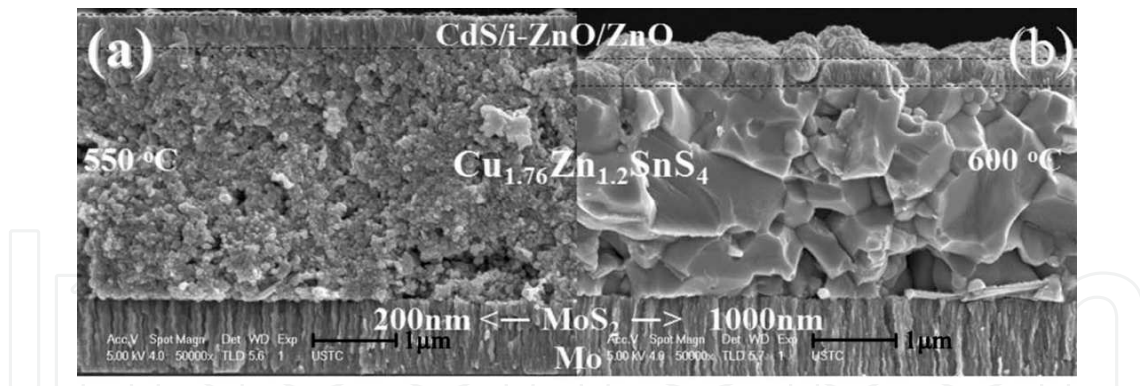


Figure 7. Cross-sectional SEM micrographs of photovoltaic devices using oxide nanoparticles-based CZTS thin films annealed under (a) 550°C and (b) 600°C [37].

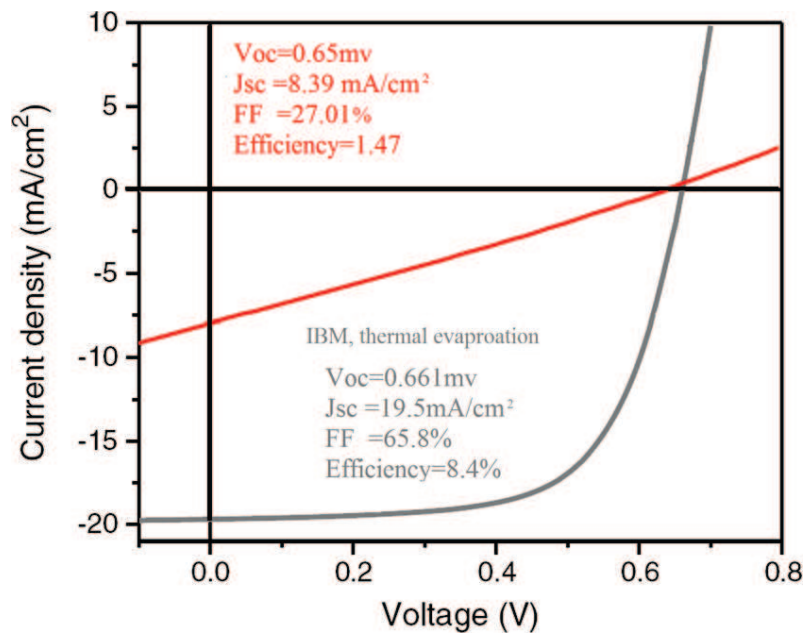


Figure 8. J-V characteristics of oxide-based CZTS TFSC and thermal evaporation based CZTS TFSC.

Such a similar phenomenon was also observed by Jin et al [38], they developed a novel combustion method for CZTS TFSC. The probable formation mechanism of oxide precursors drive CZTS thin films during the sulfurization process is analyzed. The preparation process is similar to our oxides-routes, excluding the synthesis of oxide nanoparticles. A relatively low efficiency of 1.6% was also obtained in their work, the resulted CZTS device present Voc of 505 mV, Jsc of 10.5 mA/cm² and FF of 30.3%. The thickness of MoS₂ layer was 1.4 μm in their work, which markedly deteriorate the performance of CZT TFSC.

In a word, the oxide nanoparticles-based method showed a great potential for preparation of CZTSe and CZTS thin films with high quality, which is expected to reduce the cost of production. However, a lot of efforts still need to be made to fabricate oxide nanoparticles-based CZTSe and CZTS thin films solar cell with high efficiency.

4. A general, low cost oxide nanoparticles routes for preparation of Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) thin films

Besides CZTSe and CZTS, other earth abundant $\text{Cu}_2(\text{X}^{\text{II}})(\text{Y}^{\text{IV}})(\text{S}, \text{Se})_4$ ($\text{X}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cd}, \text{Hg}$; $\text{Y}^{\text{IV}} = \text{Si}, \text{Ge}, \text{Sn}$) chalcogenide semiconductor recently have caused widespread interest in the TFSCs because of their analogous structures to CZTSe and CZTS, suitable direct band gaps, and high absorption coefficients [39]. As Cd and Hg element are high toxic, the other quaternary Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) compounds are supposed to be important potential solar cell materials. Recently, there are some reports on the synthesis of $\text{Cu}_2\text{CoSnS}_4$, $\text{Cu}_2\text{FeSnS}_4$, $\text{Cu}_2\text{NiSnS}_4$ and $\text{Cu}_2\text{MnSnS}_4$ compounds. Zhang et al [40] have reported the synthesis of monodisperse $\text{Cu}_2\text{CoSnS}_4$ nanocrystals with wurtzite phase by using a simple solution-based method. The wurtzite $\text{Cu}_2\text{CoSnS}_4$ nanocrystals can be obtained in a certain temperature range. The band gap of wurtzite $\text{Cu}_2\text{CoSnS}_4$ nanocrystals is determined to be 1.58 eV, which suggest the potential use of $\text{Cu}_2\text{CoSnS}_4$ as an active layer in low-cost thin-film solar cells. Murial et al [41] also presented a sol-gel solution routes for $\text{Cu}_2\text{CoSnS}_4$ thin films. The $\text{Cu}_2\text{CoSnS}_4$ thin films with larger grains have textured structures of stannite phase. Kamble et al [42] have synthesized $\text{Cu}_2\text{NiSnS}_4$ nanoparticles via hot injection. Phase transition of $\text{Cu}_2\text{NiSnS}_4$ was observed from wurtzite phase to cubic phase by changing the solvent. The obtained band gap (1.4 eV) and photo response behavior under illumination suggests $\text{Cu}_2\text{NiSnS}_4$ to be the potential absorber material for TFSCs. Cui et al [43] have reported the preparation of quaternary semiconductor Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) nanocrystals through solvothermal method. The four types of nanocrystals exhibit significantly different morphology, but have similar band gaps in the range of 1.2-1.5 eV. Oze [44] have also reported the fabrication and characterization of earth-abundant quaternary semiconductor Cu_2MSnS_4 ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{and Mn}$) nanofibers. Recently, Li et al [45] have reported the fabrication of Cu_2MSnS_4 ($\text{M} = \text{Zn}, \text{Cd}, \text{Mn}$) thin films from stacked layers by CBD-annealing route. Such a simple and low cost route is proposed for large-scale preparation of multi-elements TFSC.

As described above, the oxide nanoparticles process is one of the successful approaches to synthesize CIGS/CZTSe/CZTS. The electro negativity of Co, Fe, Ni, and Mn are about 1.88, 1.83, 1.91, and 1.55 respectively, which was also close to that of Zn (1.65). From the aspect of electro negativity, the Co, Fe, Ni, and Mn elements can be theoretically replaced by Zn element. Therefore, oxides based route is also regarded as an extremely promising method for the deposition of Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) thin films. The oxide nanoparticles precursor can be synthesized by solvent free method. During the sequential sulfurization, the relative stable oxide can reduce the loss of elements. Therefore, the expanding of our earlier work that is called "low cost oxide ink for CIGS/CZTSe/CZTS thin films solar cell" is expected to prepare low cost, high quality Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) thin films.

Except the above quaternary semiconductors Cu_2MSnS_4 ($\text{M} = \text{Zn}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$), a class of $\text{I}_2\text{-II-IV-VI}_4$ can be designed. Through element-substitution, a series of quaternary semiconductors had been synthesized, for example, $\text{I}_2\text{-II-IV-VI}_4$ with $\text{I} = \text{Cu}, \text{Ag}$, $\text{II} = \text{Zn}, \text{Cd}$, $\text{IV} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$, and $\text{VI} = \text{S}, \text{Se}$, were designed as early as 1960s [46]. Recently, Wang et al [47] have evaluated the thermodynamic stability limit and chemical trend in kesterite-structured $\text{I}_2\text{-II-}$

IV-VI₄ semiconductors. Using the first-principles calculations, they found that I₂-II-IV-VI₄ with I = Cu, Ag, II = Zn, Cd, Hg, IV = Si, Ge, Sn, and VI = S, Se, Te are stable quaternary compounds, however those with II = Mg, Ca, Sr, Ba, IV = Ti, Zr, Hf, and VI = O are unstable on account of the phase separate into the competing binary and ternary compounds [47]. As shown in the **Table 1**, the calculated energy change of reaction of I₂-II-IV-VI₄ compound is exothermic ($\Delta E < 0$), implying that the phase separation of Cu₂II-SnS₄ (II = Mg, Ca, Sr, Ba) will occur spontaneously. Therefore, I₂-II-IV-VI₄ with II = Zn, Cd, Hg, those with II = Mg, Ca, Sr, Ba are unstable from a thermodynamic perspective. It's worth noting that the above calculation is based on the equilibrium state, but the annealing process is always carried out under the high sulfur vapor pressure. The high sulfur vapor pressure may promote the reaction and avoids the phase separation of Cu₂II-SnS₄. Therefore, we propose preparation of some new type Cu₂II-SnS₄ (II = Mg, Ca, Sr, Ba) from oxide nanoparticles precursor in the future. The advantages of oxides-based routes will be integrated in those new compounds.

Compd.	Phase separation	Compd.	Phase separation		
	Cu ₂ S+ZnS+SnS ₂	0.56	Cu ₂ S+MgS+SnS ₂	0.47	
Cu ₂ ZnSnS ₄	2CuS+ZnS+SnS	0.40	Cu ₂ MgSnS ₄	2CuS+MgS+SnS	0.31
	Cu ₂ SnS ₃ +ZnS	0.08		Cu ₂ SnS ₃ +MgS	-0.01
	Cu ₂ +CdS+SnS ₂	0.51		Cu ₂ S+CaS+SnS ₂	-0.23
Cu ₂ CdSnS ₄	2CuS+CdS+SnS	0.35	Cu ₂ CaSnS ₄	2CuS+CaS+SnS	-0.39
	Cu ₂ SnS ₃ +CdS	0.03		Cu ₂ SnS ₃ +CaS	-0.71
	Cu ₂ S+HgS+SnS ₂	0.56		Cu ₂ S+SrS+SnS ₂	-0.35
Cu ₂ HgSnS ₄	2CuS+HgS+SnS	0.37	Cu ₂ SrSnS ₄	2CuS+SrS+SnS	-0.51
	Cu ₂ SnS ₃ +HgS	0.08		Cu ₂ SnS ₃ +SrS	-0.83
				Cu ₂ S+BaS+SnS ₂	-0.48
			Cu ₂ BaSnS ₄	2CuS+BaS+SnS	-0.64
				Cu ₂ SnS ₃ +BaS	-0.97

Table 1. Calculated energy change ΔE (in eV/formula unit) of different phase-separation reactions of Cu₂-II-SnS₄ (II=Zn, Cd, Hg, and Mg, Ca, Sr, Ba) [47].

5. Remarks and conclusions

The rapid development of low-cost, abundant CZTSe/CZTS TFSC has aroused wide concern among the researchers. Out of the many possible technical solutions available for preparation of CZTSe/CZTS thin films, oxide nanoparticles based route is considered as one of low cost, facile, and green technologies. As the successful application of such an oxides-based route on CIGS thin films solar cells, it has also been successfully explored to fabricate CZTSe/CZTS thin films with high quality. This oxides-based route is appropriate deposition techniques in terms

of low production cost and high quality thin films. Also, the application perspectives of oxides nanoparticle-based for other Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) thin films are also promising because of similar structure and element electro negativity, comparing CZTSe/CZTS thin films. What is more, the unstable $\text{Cu}_2\text{IISnS}_4$ ($\text{II} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) in thermodynamic perspective is expected to be synthesized under the high sulfur vapor pressure. In order to further develop the oxides-based CZTSe/CZTS or other $\text{Cu}_2\text{IISnS}_4$ compound, CIGS TFSC technology and related technologies can be transferred to the research of CZTSe/CZTS TFSC technology due to the great similarity between these two materials.

Acknowledgements

We acknowledge the financial support from National Natural Science Foundation of China (Grant No. 51502037), Natural Science Foundation of Fujian Province, China (Grant No. 2015J05096).

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