



Substitution of Zn in Earth-Abundant $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ based thin film solar cells – A status review

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ARTICLE INFO

Keywords:

Solar cell
 $\text{Cu}_2\text{ZnSnS}_4$ (CZTS)
 Cation substitution
 $\text{Cu}_2\text{CdSnS}_4$ (CCTS)
 $\text{Cu}_2\text{FeSnS}_4$ (CFTS)
 $\text{Cu}_2\text{MnSnS}_4$ (CMTS)
 $\text{Cu}_2\text{NiSnS}_4$ (CNTS)
 $\text{Cu}_2\text{CoSnS}_4$ (CCoTS)
 $\text{Cu}_2\text{BaSnS}_4$ (CBTS)

ABSTRACT

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) are the most promising quaternary earth abundant photo-absorber materials for thin film solar cells, with reported power conversion efficiencies (PCE) of more than 12%. In CZTS and CZTSSe based solar cells, similar atomic sizes of Cu and Zn is thought to be the main reason for Cu_{Zn} and Zn_{Cu} antisite defect formation, resulted in severe potential fluctuations and tail states that can be inhibited by an incorporation of alternative bigger atoms such as Cd and Mn. In addition, the large open-circuit voltage deficit observed in CZTS and CZTSe device because of existence of Cu and Zn cation disorder in kesterite crystal. Recently, in the development of CZTS based thin film solar cells the reduction of antisite defects by cation substitution has received considerable attention. This also opens up the possibility to explore materials with similar crystal structures and band gaps as CZTS/CZTSSe such as Cu_2XSnS_4 (where X = Mn, Cd, Fe, Co, Ni and Ba). In this review, the effect of substituting other metals for Zn is discussed, providing a way to alter defects and tail states in the absorber material of CZTS/CZTSSe thin film solar cells.

1. Introduction

The global consumption of energy has increased dramatically with the growth of the world's population and industrialization. Currently, the amount of energy generated to meet demands for sustainable development of civilization remains insufficient. On the other hand, the conventional energy sources from fossil fuels such as oil, coal and natural gas pose many challenges such as significant global warming as well as rising prices, which has led to the search for alternative sources of energy. In this context, solar energy is seen as a potential alternative that tends to some of these concerns with respect to its sustainability. Recently, solar cells including $\text{Cu}(\text{In},\text{Ga})\text{Se}_{2-x}\text{S}_x$ (CIGS) and CdTe exhibit efficiencies very near to first-generation photovoltaic technology and use reduced materials thereby reducing associated costs. Among the different types of solar cells, the CIGS based thin film solar cells have received great attention due to their good stability and high power conversion efficiency (PCE). The risk of cadmium and scarcity of raw materials such as indium, gallium and tellurium hinders progress in the field of thin film solar cells and obstructs the inevitable terawatt or petawatt scale power generation. Consequently, a great deal of research work has been realized to develop alternative thin film solar absorber materials that includes abundant, economical and non-toxic earth elements that can produce highly efficient devices that are economically

competitive with conventional sources of energy, in order to realize terawatt (TW) - scale photovoltaic (PV) era sooner rather than later.

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has attracted more and more research interests in the recent decades as a low-cost alternative to conventional absorber materials such as CIGS and CdTe absorbers in thin film solar cells [1]. CZTS is considered as an ideal absorber for thin film solar cells due to its tuneable direct band gap in 1.0–1.5 eV range, high optical absorption coefficient ($> 10^4 \text{ cm}^{-1}$) and p-type conductivity [2–4]. Decades of device optimization efforts for CZTS solar cells have made significant progress in device performance from the first reported device with PCE of 0.66% [5] to the current PCE of 12.6% [6]. In addition, Cu-poor ($\text{Cu}/\text{Zn} + \text{Sn} \sim 0.85$) and Zn-rich ($\text{Zn}/\text{Sn} \sim 1.25$) conditions are an optimal combination used to obtain highly efficient solar cells [6]. During the growth of bulk/thin film CZTS the efficiency limiting factors such as vacancy defects, antisite defects, and interstitial defects are created. The existence of defects like point defects and deviations from the ideal stoichiometry may result in self-doping and intrinsic p-type conductivity of CZTS. Theoretical and experimental studies have shown that intrinsic p-type conductivity of CZTS is determined by the high concentrations of acceptor Cu_{Zn} antisites and Cu vacancies. Unfortunately, since the ionic radii of Cu and Zn are similar, it is also easy to form undesirable Zn_{Cu} antisite defects in CZTS. In addition, the Zn_{Cu} defect can have a significant negative impact on the electrical

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properties of CZTS [7].

Assuming that the band gap vs. efficiency (S-Q limit) calculation is best fitted to the solar spectrum, the optimum band gap for the absorber materials is about 1.4 eV. [8] In addition, the open circuit voltage is proportional to the band gap of the absorber material. In order to improve the efficiency of CZTS solar cells, several studies have shown that the band gap of 1.0–1.5 eV can be obtained by adjusting the S/Se ratio to obtain an optimal band gap, crystallinity and microstructure. Moreover, it is difficult to control the ratio of S/Se anions precisely during annealing processes such as Sulfurization and Selenization, since S and Se have different volatilities. Another approach to tailor the optical band gap was by partial substitution of the metal cations during film depositions, as for example, in the case of CIGS system, the band gap can be altered by controlling the ratio of metal cations (i.e., Ga/(In + Ga)), which could be the potential alternative [9]. To further improve the efficiency of CZTS based solar cells, the best approach was found to be fabricating multi-junctions, since different band gaps of the different junctions can cover the entire range of wavelength in the solar spectrum. For example, $\text{Cu}_2\text{Zn}_x\text{Cd}_{1-x}\text{SnS}_4$ alloys have been used to fabricate multi-junction solar cells due to adjustment by controlling the content of Zn and Cd [9,10]. Though there is considerable motivation in research to enhance the efficiency of CZTS and CZTSSe based solar cells, the highest efficiency is limited to 12.6%, which hinders the potential commercialization of this earth abundant photovoltaic technology. The identical atomic radii of Cu and Zn and their nearby site in the kesterite crystals give rise to the issue of Cu_{Zn} and Zn_{Cu} antisite defect formation, which probably is the main cause of severe potential fluctuations and tail states formations. Substituting Zn with a larger atom can inhibit these problems, so there is a trend to develop some CZTS based photo absorber by substituting Zn with some other cations. This strategy can reduce the formation of antisite defects and the cation disorder between Cu and Zn ion in the kesterite CZTS. In addition, the open circuit voltage deficit in CZTS can be controlled. This review covers the discussion of the effect of cation substitution on the performance of CZTS solar cells by providing an approach to alter the defects and tail states in the thin-film solar cell absorber material in order to realize the goal of band gap engineering and to reduce the antisite defects common in CZTS based solar cells.

2. Crystal structure of CZTS

In most devices, CZTS compounds are present in two main crystal structures namely Kesterite (space group $\bar{1}\bar{4}$) and Stannite (space group $\bar{1}\bar{4}2m$). The two crystal structures are similar with cations located at tetrahedral sites, but the arrangement of Cu and Zn atoms along the c-axis is different. This stack is quite identical to the zinc-blende structure. Theoretically predicted, the CZTS sample typically has a kesterite-structure because kesterite has lower formation energy than the stannite and is therefore thermodynamically more stable than the Stannite counterpart. The crystal structure and the atomic arrangements for the Kesterite and Stannite structures are shown in Fig. 1. Interestingly in the structure of CZTS compound, the substitution of Zn by Cd results in a stannite structure which is quite similar to kesterite structure. [9] Both structures have eight atoms per primitive cell with body-centred tetragonal symmetry, with only the distribution of cations being different. It is also possible to explore the possibility of materials with similar crystal structures and band gaps as CZTS such as Cu_2XSnS_4 (where X = Mn, Cd, Fe, Co, Ni and Ba).

3. Defects of CZTS

Defects play a vital role in the optoelectronic properties of the resulting semiconductor material. As the number of component elements increases, the chemical and structural freedom of CZTS increases significantly resulting in a series of intrinsic defects, such as interstitials, vacancies and antisites compared to binary and ternary

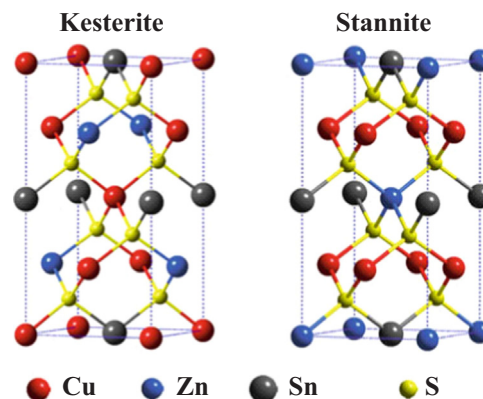


Fig. 1. Crystal structure of a Kesterite $\text{Cu}_2\text{ZnSnS}_4$, and Stannite $\text{Cu}_2\text{ZnSnS}_4$.

semiconductors. Several theoretical defect studies based on density functional theory (DFT)/ first-principle calculations have been used to examine the defect mechanism and formation energies of different possible point defects in crystal structures [11–14]. These defects and secondary phases affect the generation, separation and recombination of electron-hole pairs, which in turn impacts on the efficiency of photovoltaic devices. In the case of CZTS based solar cells, similar Cu and Zn atomic sizes are considered to be the main cause of Cu_{Zn} and Zn_{Cu} antisite defects that results in severe potential fluctuations and tail states, and can be inhibited by an incorporation of larger atoms, such as Cd and Mn. In addition, the presence of Cu and Zn cation disorder in $\text{Cu}_2\text{ZnSnS}_4$ kesterite crystal structure may be the cause of poor open-circuit voltage. Cu_{Zn} and Zn_{Cu} are said to be the lowest-energy acceptor and donor defects respectively, in case of both $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$. Their compensation can result in the formation of the antisite pair $[\text{Cu}_{\text{Zn}}^- + \text{Zn}_{\text{Cu}}^+]$ with extremely low formation energy. This is due to the fact that the Cu_{Zn} antisite defects are easily produced in high concentrations due to the similar ionic radii of Cu and Zn. Recent reports suggest that the substitution of cations with much larger size than Cu can increase the formation energy of antisite defects [8–10]. Recently, in the fabrication of CZTS based thin film solar cells, the reduction of antisite defects by cation substitution has received considerable attention.

4. Cation substitution of CZTS

The disorder among Cu and Zn metals is considered to be one of the performance limiting factors encountered with the large loss in the open-circuit voltage (V_{OC}) of CZTSSe devices. Such a large deficit in V_{OC} is attributed to a number of reasons such as point defects, defect clusters (i.e., cation disordering) and associated band tailing, the removal of which is the biggest challenge with current CZTSSe technology [11,12,14]. The similarity in the ionic size of the two species, which are nearest neighbours in the periodic table, facilitates the formation of Cu_{Zn} and Zn_{Cu} antisite defects and associated band-tailing in the kesterite system. To date, several studies reported in the literature on the synthesis of Cu_2XSnS_4 materials, replacing Zn^{2+} by cations with larger ionic sizes (X = Mn, Cd, Fe, Co, Ni, Ba), which makes it suitable for use in photonic applications due to similarities in the optical and electronic properties as that of CZTS. The Fig. 2 describes the schematic diagram of the widely studied cation exchange of the CZTS.

There are several reports on the fabrication of photovoltaic (PV) devices using cation exchanged CZTS photo-absorber materials. The highest efficiencies among this cation exchanged CZTS are shown in Table 1.

4.1. Substitution of Zn with Mn

It is well known that $\text{Cu}_2\text{MnSnS}_4$ (CMTS) exhibits the stannite

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