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Perspective

Advances in kesterite $Cu_2ZnSn(S, Se)_4$ solar cells

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Over the past decades, the emergence of photovoltaics (PV) alleviates the energy crisis and environmental pollution of fossil fuels. Compared to the large-scale silicon-based PV technology, thin-film PV technology is still just a newcomer. Thin-film solar cells need only several microns thickness to absorb most of the sunlight effectively, enabling the application in flexible substrates. The advantages in portable wearable devices coupled with the increasing efficiency facilitate its development and it can be expected that thin-film solar cell technology will rapidly enter and occupy the market after a few years. Among various thin-film solar cell absorber materials, the kesterite semiconductor $Cu_2ZnSn(S, Se)_4$ (CZTSSe) is composed of earth-abundant and environmental-friendly elements while possessing promising optical-electrical properties. Therefore, CZTSSe thin-film solar cells are regarded as the dark horse of next-generation photovoltaic technology [1]. Though promising, CZTSSe is suffering from low power conversion efficiency (PCE). The highest PCE has hovered at 12.6% for more than 5 years, while the PCEs of solar cells based on other thin-film materials have roared. By the end of 2019, the champion device PCEs of CdTe and Cu(In, Ga)Se_2 (CIGSe) thin-film solar cells have already achieved 22.1% and 23.4% [2], respectively. Especially for emerging perovskite cells, the highest efficiency is up to 25.2% [2]. At this point, a big crisis for CZTSSe thin-film solar cells is coming. To overcome the present challenges for CZTSSe PV technology (Fig. 1) and realize its full potential, thoroughly understanding the root causes and figuring out the solutions to poor device performance are necessary.

Massive deep defects: CZTSSe semiconductor consists of at least four elements, which suggests a high degree of freedom and complexity. Abundant point defects and defect clusters in CZTSSe absorber are important manifestations [3]. Especially in Cu-poor and Zn-rich conditions (the composition ratio proved to yield high-efficiency devices), the deviation in composition from the stoichiometry leads to the formation of defects with deep levels. Explicitly, large amounts of defects and defect clusters lead to two kinds of serious hazards. One is the structural inhomogeneity. Structural inhomogeneity originated from the defects' ionization brings about the fluctuation of local stoichiometry and variation in conduction band minimum and valence band maximum, further leading to electrostatic fluctuation [4]. The fluctuation reduces the optical band gap and lowers the theoretical open-circuit voltage (V_{oc}) for the CZTSSe device. The other is poor carrier characteristics. Carrier collection includes the generation and separation of photogenerated electron-hole pairs and the transportation of electrons and holes. In all these three processes, the defects and defect clusters with deep energy levels within the bandgap capture and recombine carriers before carriers are transported to the outer circuit and thus become carrier recombination sites. This leads to a short minority carrier lifetime and diffusion length in CZTSSe solar cells, which is almost one order of magnitude lower than that in CdTe, CIGSe and perovskite, let alone silicon solar cells. The short minority carrier lifetime and diffusion length are believed to be the main reason for V_{oc} loss and poor device performance.

Severe band tailing: Owing to the different ratios of S and Se, the band gap of CZTSSe is tunable in the range of 1.0–1.5 eV. The tunable band gap is one of the advantages of CZTSSe thin-film solar cells. However, it is worth noting that V_{oc} does not show a linear rise with the increase of band gap. The band tail state is believed to be the critical factor responsible for this large V_{oc} deficit (the difference between E_g/q and V_{oc}) [5]. The more significant peak shifts of external quantum efficiency (EQE) spectra and photoluminescence (PL) spectra and larger Urbach band tail energy of CZTSSe than those of CIGSe reflect more severe band tailing issue in CZTSSe than that in CIGSe. Similar to the fluctuation of conduction and valence band edge, the existence of band tail states also narrows the optical band gap, redshifts the intrinsic absorption onset and increases V_{oc} deficit. Nevertheless, it remains controversy about the root cause of band tail states. Most researchers believed that the disorder on the Cu-Zn plane is the culprit, but some deemed $2Cu_{Zn} + Sn_{Zn}$ defect clusters. However, the low critical temperature of Cu and Zn position replacement in CZTSSe implies that the influence of the significant amount of Cu-Zn disorder cannot be eliminated during the study of other defects/defect clusters. That restricts the confirmation of the real reason for band tailing.

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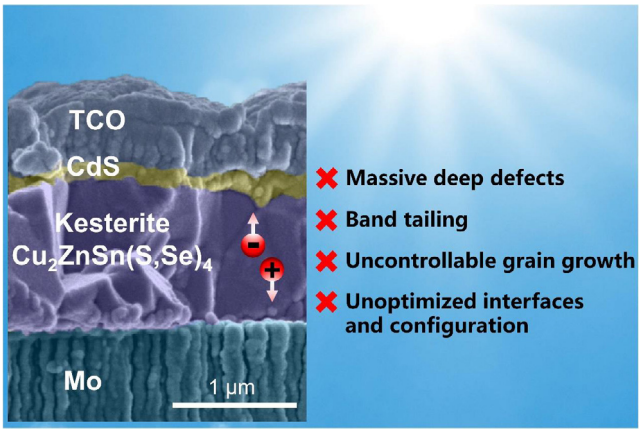

Fig. 1. (Color online) Four crucial issues of kesterite $Cu_2ZnSn(S, Se)_4$ solar cells.

Uncontrollable grain growth: High-quality crystallization is a prerequisite to fabricate decent kesterite solar cells. Although both vacuum and non-vacuum based film preparation processes can yield large grain spanning the entire layer with diameter over 1 μm, the challenge is to control the grain size distribution, compactness, grain morphology and grain boundary properties (such as chemical composition and band structure). The mechanisms about element migration, reaction pathway, phase transition, and microstructure evolution during grain growth are not clearly revealed, making the control of gain growth tricky. In addition, dislocations, twin grains and stress, which may be important factors affecting crystalline quality and device performance, have not been studied so far. The difficulty in grain growth also varies for different processes. For vacuum based process, it is more challenging to prevent the loss of the volatile components (Zn, Sn(S, Se), and chalcogen elements) to realize the controlling in nanoscale composition and morphology homogeneity. For non-vacuum based processes with advantages in grasping volatile elements through tight chemical bonds between atoms in solution, abnormal grain growth is usual prevalent, specifically, the appearance of bi-layer or even tri-layer structured CZTSSe absorber with a fine-grained sub-layer at the bottom or middle, respectively [6]. This lowers the effective volume of the absorber (thus degrades light absorbing ability) and leads to severe carrier recombination problem.

Unoptimized interfaces: There are two crucial interfaces in typical CZTSSe device: (i) the interface between the CZTSSe absorber and the Mo back contact, namely the back interface; (ii) the interface between the CZTSSe absorber and the CdS buffer layer, namely the front interface. At the back interface, the reaction between CZTSSe and Mo during the high-temperature reactive annealing treatment process is detrimental to the device performance [7]. The products of the reaction can be divided into two groups, i.e., $MoS(e)_2$ interface layer and secondary phases. The $MoS(e)_2$ layer can effectively transform Schottky contacts into quasi-Ohmic contacts with optimal thickness. However, too thick $MoS(e)_2$ acts as a huge barrier to hinder holes transport and thus increase series resistance (R_S). In terms of secondary phases, ZnS(e) secondary phases remained at back contact increase R_S. SnS(e) secondary phases volatilize and leave voids at the back contact region, which leads to high R_S and a high degree of recombination. For front interface (i.e., p-n heterojunction), electrical and chemical properties of p-n heterojunction are two critical aspects. The electrical properties strongly depended on the energy band alignment. The preferable energy band alignment is flat, or spike-like where the conduction band minimum of CZTSSe is slightly higher than that of CdS with conduction band offset less than 0.3 eV. The energy band alignment in the sulfide CZTS device is not favorable (cliff-like) and needs modification. Different from sulfide CZTS device, sulfoselenide device has a relatively decent band alignment, resulting from the lowered CBM after Se introduction. With regard to chemical properties of p-n heterojunction such as the epitaxial growth of n-type CdS and inter-diffusion are also important aspects [8]. The epitaxial growth minimizes the lattice mismatch and defect density at the interface. The moderate diffusion of cadmium (Cd) atoms, which occupy vacant Cu sites in the Cu-poor and Zn-rich CZTS matrix acting as substitutional donors, results in a beneficial buried homojunction and thus reduced recombination at the interface. Besides, Fermi-level pinning at the middle of the band gap near the p-n heterojunction is also a severe problem at the front interface [9].

In order to solve the above four problems illustrated in Fig. 1, several strategies have been pursued. One is alkali doping, which could be learned from the experience of CIGSe. Alkali doping can increase carrier concentration and p-type conductivity of CZTSSe absorbers, promote the passivation of deep defects, and facilitate the growth of grain decreasing grain boundaries. The doped alkali elements could be from soda-lime glasses (SLG) substrates or alkali metal salts added artificially. Regarding the ranking of the capability to improve device performance, an order of lithium (Li) > sodium (Na) > potassium (K) > rubidium (Rb) > cesium (Cs) based on more than 700 individual CZTSSe devices has been concluded by Haass et al. [10], which is similar to the case of CIGSe solar cells. That suggests light alkali metals with smaller migration energy are more favorable for CZTSSe than heavy alkali metals. Alkali post-deposition treatment (PDT) with heavy alkali metals (K, Rb and Cs), which improves surface and diode quality, has brought efficiency breakthrough (over 20%) for CIGSe solar cells. However, for CZTSSe, the effectiveness of PDT seems to depend on the CZTSSe preparation process and baseline efficiency, which needs further exploration. Besides, the alkali metal re-distribution with Na-accumulation at the top region of CZTSSe absorbers upon heterojunction heat treatment to improve device performance is clearly observed by Yan et al. [11], indicating that how to precisely control the distribution of alkali metal in CZTSSe absorber films is also an important subject.

Cation substitution, one of the most effective approaches to relieve the band tailing issue, has become the research hot-spot in recent years. Massive Cu-Zn antisite defects in the bulk of CZTSSe result from nearly the same cation sizes as well as small chemical mismatch of Cu^+ and Zn^+. Through cation substitution, the concentration of Cu, Zn or Sn in the bulk of CZTSSe is directly decreased, and thus defect density is lowered. Nearly one-third of the elements in the periodic table are explored to solve the defects problems. Among those elements, Cd is a relatively outstanding choice. Although people may argue that Cd is toxic and harmful to the environment, at this stage, efficiency improvement is the priority for the development of the CZTSSe PV technology and a new record is hungered to boost the confidence of the CZTSSe community. This is similar to the development pathway of perovskite solar cells. Perovskite starts with environment-hazardous methylammonium lead iodide and extremely expensive spiro. After achieving high efficiency, researchers turn back to solve high-costs, poor-stability and toxicity problems. Furthermore, the amount of Cd is actually very few in CZTSSe films with thickness of only about 1–2 μm, which would make the Cd level at a low level in the PV modules meeting the environmental protection standards. But this small amount can make a big enhancement for device performance. On the one hand, the formation energy of Cd-Cu antisite defects and $Cu_{Cd} + Cd_{Cu}$, $2Cu_{Sn} + Sn_{Cd}$ defect clusters are larger than that of Cu-Zn defects and corresponding defect clusters, indicating lower defect density. On the other hand, Cd-incorporation dramatically reduces the Urbach band tail energy

and associated band tailing through the diminution of cation disorder [12].

Although cation substitution is effective to moderate defects, it does not solve the defects problem completely. To solve the defects thoroughly, we must first understand the defects on a micro-level. The defect detection methods in use currently are too macro and not clear enough. In terms of Raman measurements, for example, the relative area changes of 176 cm^{-1} Raman peak corresponds to the concentration changes of V_{Cu} defects and 250 cm^{-1} Raman peak corresponds to Zn_{Sn} point defects. The results can only qualitatively analyze defect concentration variation, playing a supplementary role in defect analysis. As for the atomic-resolution transmission electron microscopy, though high-angle annular dark-field (HAADF) imaging at sub-0.1 nm resolution, it is still difficult to distinguish Cu and Zn atoms because of their great similarities in atomic size. Therefore, higher resolution characterization techniques are needed to distinguish Cu and Zn atoms evidently. Furthermore, if *in-situ* observation for defects could be realized in CZTSSe, the generation, diffusion, and distribution of defects can be studied thoroughly. If so, the understanding of defects must be more profound and more precise, while the strategies adopted would be more oriented.

Refer to CIGSe thin-film solar cells, the strategy of the "V" shape band gradient via V-shape In and Ga concentration gradient is effective to maximize V_{oc} and facilitate the transportation of the photogenerated carriers, which is the optimal approach to achieve trade-off between V_{oc} and short circuit current density (J_{sc}). However, for CZTSSe, the low tolerance to off-stoichiometry owing to the limitation of the narrow chemical-potential stable range makes it unrealistic to adjust the concentration of Cu or Sn to form "V" shape gradient. The small variation from the chemical-potential stable phase would lead to many secondary phases and defect clusters. Therefore, substitution-element gradient is an alternative way to fulfil the concentration gradient. Silver (Ag), the substitution element of Cu, is successfully applied to form "V" shape gradient [13]. High Ag concentration near p-n junction provides high n-type conductivity as well as large band bending and high depletion region width, so that alleviates the Fermi-level pining and effectively increases V_{oc}, while the aggregation of Ag near back interface is not beneficial for photogenerated charge collection [9]. Other substitution elements which have advantages at p-n junction region and/or back interface region should be good candidates for the "V" shape gradient. Another option, with the introduction of Ag, is to introduce another element to compensate the performance loss at back interface region caused by Ag. Germanium (Ge) preferentially accumulates at the back interface and forms the Ge gradient. Graded conduction band edge enhances the collection of photogenerated electrons and significantly increases EQE and thus J_{sc} [14]. The Ge substitution may offset the disadvantages of Ag while maintain the "V" shape gradient. The coordination of Ag and Ge, also can be popularized for other substitution elements.

In terms of interface quality, there are many approaches to improve it, which can be divided into two categories. One is inserting an intermediate layer. At the front interface, Al_2O_3 and SnO_2 have been reported as the intermediate layers. At the back interface, metal nitrides, metal oxides, metal sulfides, Ag and carbon intermediate layers have been explored. Alternatively, changing the type of back contact layer or buffer layer is the other category. The investigations on non-molybdenum back contact materials are very few whereas new buffer layers are numerous, such as In_2S_3, CeO_2, ZnO, ZnS, Zn(O, S), ZnCdS, ZnSnO, etc. However, all current approaches from both above categories have not achieved breakthrough progress in conversion efficiency although these approaches can improve device performance device moderately. Considering that the device configuration is completely duplicated from CIGSe thin-film solar cells and each kind of solar cell with high efficiency usually has its unique configuration, it is time to think carefully that whether the configuration copied from CIGSe is the optimum one for CZTSSe. In this regard, revolutionary device configuration is urgently needed. For example, i-ZnO may not be so necessary for CZTSSe thin-film solar cells. New electron/hole transfer materials in CZTSSe device can be investigated and applied. p-i-n structure or superstrate structure (similar to CdTe thin film solar cells) could be explored. Of course, other creative ideas are welcome.

After all, a suitable band gap and high absorption coefficient of CZTSSe are necessary criteria, but those are not enough to make it a good solar cell material. It absolutely needs to find the answer to the ultimate question "What holds the key to major breakthroughs for CZTSSe thin-film solar cells?" To answer this question, each aspect of the device should be researched thoroughly. Besides device structure innovation, device performance enhancement calls for an exploration of creative ideas and a "tailor-made" treatment process. Although it is difficult to precisely predict how long we have to wait for the answer, the investigation progress needs to be accelerated so that there is a leap in the efficiency of CZTSSe in the near future.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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