Underlying mechanism of the efficiency loss in CZTSSe solar cells: Disorder and deep defects

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ABSTRACT Although $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (CZTSSe) is a promising candidate for thin-film photovoltaics, its cell performance is currently limited by the large voltage loss. Although a series of studies on the efficiency loss mechanism of CZTSSe solar cell have been carried out in the past few years, no convincing understanding has been obtained until now. In this review, the current findings regarding the underlying mechanism of the efficiency loss in CZTSSe solar cells are systematically summarized and analyzed. The properties of atomic disorder and deep defects in CZTSSe materials and their effects on device performance are discussed. The synergistic effect is proposed to help understand the defect-related charge loss in the absorber. Furthermore, the experimental methods of defect identification and defect control are presented, in an attempt to identify the killer defects that can be responsible for the ultra-short minority lifetime of CZTSSe material. By comprehensively and dialectically understanding these defect properties of the CZTSSe solar cell, we believe breakthrough in the cell efficiency will come soon with our concentrated effort.

Keywords: CZTSSe solar cell, voltage loss, disorder, defect

INTRODUCTION

Photovoltaics (PV) have been an important renewable energy to meet the increasing global energy demand, with a cumulative power installed capacity of 515 GW [1]. The silicon-wafer-based PV technology accounted for more than 90% of the total production in 2017. Since silicon is an indirect bandgap semiconductor, silicon wafers need a thickness up to few hundreds of microns to fully absorb the longer wavelength light [2,3]. Compared with silicon-based PV, thin-film solar cells have significant advantages

in raw material consumption and multiple scenarios application [4]. At present, the widely studied and commercialized thin-film solar cells, $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS) and CdTe, have achieved over 22% power conversion efficiency (PCE) [5]. Nevertheless, the rare elements (In, Ga, and Te) limit the large-scale production and application of these cells [6]. In this case, kesterite $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (CZTSSe, $0 \leq x \leq 1$) has emerged as one of the most promising candidate materials, because of its ideal direct bandgap (1.0–1.5 eV), high optical absorption coefficient (10^4 – 10^5 cm^{-1}) and earth-abundant raw materials [7–11]. During the last decades, the efficiency of CZTSSe solar cell has been significantly increased from about 2.6% in 2001 to 12.6% in 2013 [12–14]. However, the development seems to be experiencing a bottleneck, without any significant breakthrough in efficiency during the past six years. Currently, the performance of kesterite solar cells is much far below the Shockley-Queisser (S-Q) limit [15]. For the further progress, it is crucial to deeply understand the performance loss mechanism of CZTSSe solar cells. Some research groups have contributed their comprehensions from different aspects in recent years [16–20].

Firstly, the non-ideal interface properties of the CZTSSe solar cell can limit the PV performance [21,22]. Both of the top CZTSSe/CdS interface and the bottom Mo/CZTSSe interface should be concerned. The bandgap of CZTSSe could be adjusted by changing the ratio x of S and Se, $x = \text{S}/(\text{S} + \text{Se})$. When $x = 1$, namely pure CZTS ($E_g = 1.5 \text{ eV}$), a so-called “cliff-type” band alignment is formed between CZTS and CdS [23,24]. With such a negative conduction band offset (CBO), high recombination between electrons injected into the buffer

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and holes in the CZTS may arise in the top interface on account of reduced recombination activation energy. Comparatively, when $x=0$, namely pure CZTSe ($E_g=1.0$ eV), an electrically benign “spike-type” band alignment is formed [23]. Other buffer layers have also been attempted, and the CZTSSe solar cell based on $\text{In}_2\text{S}_3/\text{CdS}$ double buffer layers also exhibited the highest efficiency in the latest report [25–28]. Regarding the bottom interface, CZTSSe could react with the standard back contact, Mo, during the necessary high-temperature sulfoselenization, thus creating a $\text{Mo}(\text{S}, \text{Se})_2$ thin film [29–31]. The $\text{Mo}(\text{S}, \text{Se})_2$ film is a double-edged sword, which could act as a buffer layer to promote the back contact but may introduce high series resistance when the film is too thick [32,33]. Besides, secondary phases, such as $\text{ZnS}_{(\text{e})}$, $\text{SnS}_{(\text{e})}$, and $\text{Cu}_2\text{S}_{(\text{e})}$, could be generated at this interface because of the reaction between CZTSSe and Mo [29]. Therefore, the non-ideal electrical properties of the top and bottom interfaces could be one of the causes for the performance loss of the cell. Although a series of efforts have been made to control and optimize the interfaces [32,34–36], it is still difficult to make substantial breakthrough and progress so far.

Apart from the interfaces, the CZTSSe absorber itself is a multiterinary semiconductor, which possesses complicated defect properties. First-principles calculation to the intrinsic lattice defects in pure $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and pure $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) have revealed that various isolated defects and self-compensated defect clusters widely exist in both stoichiometric and non-stoichiometric alloys [37]. The defects with low ionization level, including V_{Cu} , Cu_{Zn} , $[\text{Cu}_{\text{Zn}}+\text{Zn}_{\text{Cu}}]$, could on the one hand enhance the intrinsic p-type conductivity, but on the other hand increase the band tail states. Experiments have exhibited that CZTSSe has much more band tail states than the parent compound CIGS [38]. The Cu/Zn antisite defect was once considered as the main reason for limiting the efficiency of CZTSSe devices, and various methods (such as elements substitution) have been used to suppress this defect, but recently this claim has been questioned [21,39–41]. Another kind of defects located deeply at the mid-gap, such as Sn_{Zn} , V_{S} , $[2\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}]$, could act as non-radiative recombination centers of photogenerated electron-hole pairs [42,43]. It is suggested that both the band tail states and the non-radiative recombination centers are detrimental to the cell performance, especially to the open-circuit voltage [41]. Honestly, we are still far away from clearly revealing the defect-related charge loss mechanisms, and it is also hard to experimentally identify and control the defects. Re-

cently, new theoretical and experimental findings about the defect physics of the CZTSSe material have been reported, providing us with more opportunities to understand this material and the performance loss of the cell. For the CZTSSe community, it is urgent to systematically summarize current findings and understandings about the defect-related charge loss mechanism and to dialectically extract valuable information from the previously published numerous studies. This is the topic and aim of this review. We hope this review about exploration of the underlying mechanism of the efficiency loss could help the readers to better understand the material and device physics of the CZTSSe solar cell and to develop more effective approaches for the device performance improvement.

For clarity, this review is presented in five main sections in addition to the introduction and conclusion. Firstly, we will give a brief summary of the development history of the CZTSSe solar cell with a comparison with the CIGS cell. Secondly, we will introduce the band tail states and their widespread existence in CZTSSe. The following section will aim at the atom disorder in CZTSSe and its impact on device properties. Then, we will focus on the deep defects as effective non-radiative recombination centers in CZTSSe. Furthermore, the experimental characterization and controlling methods towards defects will be summed up in the last. In this review, we present dialectical discussions on previously reported theoretical and experimental results, and more importantly extract more abundant charge recombination dynamics information and provide our understandings on the charge recombination processes of the CZTSSe. These discussions may help recognize the status, deficiencies and the future direction of the study on the performance loss mechanism of the CZTSSe solar cell.

DEVELOPMENT STATUS AND MAIN PROBLEM

The efficiency of CZTSSe solar cell has indeed improved significantly over the past few decades, from 2.67% in 2001 to 12.6% in 2013 [12,13]. Fig. 1 shows the efficiency evolution of CZTSSe solar cells from year 0 (first reported working device) up to date, in comparison with the CIGS technology [5,12,44–46]. From this comparison, we can clearly see that the kesterite technology is still in the primary development stage, with no more than twenty years' history. CIGS technology is more mature with more than forty years of evolution. Interestingly, the CZTSSe cell exhibited a slightly faster development trend in the initial twelve years compared with the CIGS. This is

Figure 1 Efficiency evolution of CZTSSe and CIGS from the first reported working solar cell. Year 0 is 1977 for CIGS and 2001 for CZTSSe.

a positive signal although the CZTSSe cell is experiencing a bottleneck. This bottleneck not only arises from the cell itself but also correlates to the limited research community. The emerging and rapid development of the perovskite solar cell from 2013 has affected the research enthusiasm of the CZTSSe cell more or less [5]. Nonetheless, we can still see the development promise of the CZTSSe from the history of CIGS and CZTSSe if the research community can be expanded and more efforts can be gathered together.

Performance parameters including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor

(FF) of the reported CZTSSe solar cells with efficiencies above 11% are summarized and shown in Fig. 2a–d [13,28,47–63]. These devices were prepared by different processes, including non-vacuum (i.e., hydrazine-based and non-hydrazine spin coating) and vacuum (i.e., co-evaporation, and sputtering) methods. Besides the hydrazine-based method, the sputtering method also produced highly efficient CZTSSe devices, 12.6% for a small cell size and 11.3% for a larger cell size (1.176 cm^2), as shown in Fig. 2d [60]. Obviously, the highest efficiency was achieved in CZTSSe absorber with low S content ($E_g \approx 1.1 \text{ eV}$). This depends on the different defect nature of CZTS and CZTSe. The energy level of point defects in CZTS is usually deeper than that in CZTSe, which may lead to more non-radiative recombination loss in the absorber [37]. High efficiency seldom occurs in the bandgap of 1.2–1.3 eV regime because CZTSSe materials with a medium S/(S+Se) ratio usually possess a high formation energy and serious phase separation [24]. Meanwhile, the change of the CBO at buffer/absorber interface caused by different S/(S+Se) ratios will also affect the device efficiency [64]. By comparing these performance parameters with the S-Q theoretical limit (Fig. 2a–d), it is clearly seen that the efficiency loss mainly lies in the V_{oc} and the FF [65]. In particular, the V_{oc} is less than 60% of the S-Q limit. The V_{oc} deficit ($E_g/q - V_{oc}$,

Figure 2 The single-junction solar cell parameters. (a) J_{sc} , (b) V_{oc} , (c) FF, (d) PCE are shown as a function of bandgap energy according to the S-Q limit (black solid lines) and experimental values for reported highly efficient (PCE>11%) CZTSSe solar cells. The green dots represent devices made by vacuum processes, and the orange dots are for the devices made by non-vacuum processes. (e) Schematic diagram of carrier dynamics processes within a CZTSSe solar cell.

where q is the charge of an electron) of CZTSSe (> 0.57 V) is much larger than that of the parent CIGS solar cell (< 0.40 V) [21].

The V_{OC} of a solar cell refers to the potential difference formed by carriers accumulated in the front and back electrodes. As shown in Fig. 2e, the photons are incident from the front surface of the solar cell, transmitted through the window layer and the buffer layer, and then absorbed by CZTSSe, thereby generating free electrons and holes. Due to the presence of the built-in electric field, the photogenerated carriers in the depletion region are rapidly separated. The electrons drift into the CdS and ZnO layers, and are laterally transported within the indium tin oxide (ITO) or Al-doped ZnO (AZO) layer and eventually collected by the front electrode. The carrier recombination loss in the bulk material and at the charge extraction interfaces can cause a large V_{OC} deficit [66].

Many efforts have been made to clarify the origins of large V_{OC} deficit, which resulted in various interpretations and ongoing debates. Some time ago, researchers generally believed that the high-density shallow defects (i.e., Cu_{Zn} , Zn_{Cu}), which are formed by widespread atomic

disorder in CZTSSe, cause band tail states and reduction of the bandgap of the bulk material [41]. However, some recent studies show that the deep defects with strong carrier capture ability (i.e., Sn_{Zn}^{2+} , V_S) are killer defects for V_{OC} deficit [42,43]. It is critical for achieving efficiency breakthroughs to analyze the properties of different defects and their effects on device performance, which will be reviewed and discussed in detail below.

BAND TAIL STATES

Band tailing in the CZTSSe film has been widely verified by experiments [38,67,68]. Band tailing arises because the density of states (DOS) in the bandgap, especially near the band edge, is usually not zero, which leads to the narrowing of the effective bandgap, as shown in Fig. 3a [69]. Fig. 3b shows that the falling edge of internal quantum efficiency (IQE) curve of the CZTSSe solar cell is severely tailed, and the peak position of film photoluminescence (PL) is significantly red-shifted compared with the bandgap [38]. These are representative signatures of the band tailing effect.

Theoretically, the band tail states mainly arise from

Figure 3 (a) Schematic of total DOS plot in conventional semiconductor materials and modified DOS plot in disordered materials. Reprinted with permission from Ref. [69]. Copyright 2017, Wiley-VCH. (b) The IQE, the bandgap determined from the IQE inflection point, and the PL spectra (taken using a 532 nm solid state laser) of high-performance CZTSSe solar cell (10.7% efficiency). (c) Schematic of bandgap fluctuations (left) and electrostatic potential fluctuations (right). (d) Absorption coefficient (as deduced from the IQE) vs. photon energy plots below the bandgap energy of CZTSSe (10.7% efficiency) and CIGS (15.0% efficiency) solar cells. Fits corresponding to the electrostatic potential fluctuations and bandgap fluctuations models are shown by blue and red lines, respectively. Reprinted with permission from Ref. [38]. Copyright 2013, AIP publishing. (e) PL spectra of a CZTS device (8.3% efficiency) as a function of excited laser power (identified in legend, $W cm^{-2}$) at 4 K. Reprinted with permission from Ref. [70]. Copyright 2013, AIP publishing.

spatial fluctuation of bandgap or electrostatic potential in the semiconductor as seen in Fig. 3c [38]. In the case of pure bandgap fluctuations, the spatial variation of the conduction and valence bands are inversely correlated. This kind of fluctuations originates from non-uniformity of the components, disorder of the structure or coexistence of different lattice phases. For example, the distribution of S and Se atoms in CZTSSe may be uneven or random, forming S-rich or Se-rich region. The bandgap of the Se-rich region is smaller than that of the S-rich region. Both photogenerated electrons and holes can spontaneously transfer to the Se-rich region driven by the energy gradient. Another example, the formation of the antisite defects and the charge compensation pairs of Cu and Zn in CZTSSe will simultaneously introduce defect states below the conduction band minimum (CBM) and above the valence band maximum (VBM), which is equivalent to reducing the local bandgap of the material. For any direct bandgap semiconductor without band tail states, the absorption coefficient is given by $\alpha \propto \sqrt{\hbar\omega - E_g} / \hbar\omega$, where $\hbar\omega$ is the incident photon energy. For bandgap fluctuations, the above equation should be modified by turning E_g into a Gaussian probability distribution function. So the absorption coefficient is described as

$$\alpha \propto \int_0^\infty \frac{1}{\sigma_g \sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{E_g - E_{g,\text{mean}}}{\sigma_g}\right)^2\right) \left(\frac{\sqrt{\hbar\omega - E_g}}{\hbar\omega}\right) dE_g, \quad (1)$$

where $E_{g,\text{mean}}$ and σ_g are the mean and the standard deviation of the spatially varying bandgaps, respectively. Obviously, the bandgap fluctuations cause that the photons with energy lower than the true E_g can also produce photogenerated carriers, hence easily accounting for the experimentally observed IQE curve tailing.

The electrostatic potential fluctuations mainly come from the influence of impurity atoms with positive or negative charges on the local electrostatic potential. The conduction and valence bands follow the same electrostatic potential, thereby resulting in little spatial variation in E_g . Sub-bandgap absorption is realized by the tunneling effects. Using the model developed by Shklovskii and Efros [71], which assumes a random distribution of charged defects, the absorption coefficient below E_g is given by

$$\alpha \propto \exp\left(-\frac{2}{5\sqrt{\pi}} \left(\frac{E_g - \hbar\omega}{\gamma_{\text{opt}}/2}\right)^{5/4}\right), \quad (2)$$

where γ_{opt} is the amplitude of the electrostatic potential fluctuations relevant for optical transitions, and it is related to the total charged defect density and material properties, e.g., the relative dielectric constant, and the electron/hole effective mass [72]. It was found that when the temperature dropped from room temperature to extremely low temperature (4 K), the carrier lifetime of CZTSSe increased from ~5 ns to ~10 μ s, while the carrier lifetime of CIGS was only slightly enhanced (Fig. 4) [38]. This was believed to be a signature of the existence of electrostatic potential fluctuations in CZTSSe.

The IQE data obtained by experimental characterization can also reflect the semiconductor absorption coefficient. For the IQE curve tailing, when $\text{IQE} < 0.3$, there is a relationship:

$$\alpha \propto -\ln(1 - \text{IQE}(\hbar\omega)). \quad (3)$$

Based on Equations (1–3), the σ_g and γ_{opt} can be deduced by fitting the α vs. $\hbar\omega$ data. Through this way, Gokmen *et al.* [38] obtained the parameters of their solar cells: $\sigma_g^{\text{CIGS}} = 44.2$ meV, $\sigma_g^{\text{CZTSSe}} = 80.3$ meV or $\gamma_{\text{opt}}^{\text{CIGS}} = 35.5$ meV, $\gamma_{\text{opt}}^{\text{CZTSSe}} = 56.4$ meV (Fig. 3d), indicating that both the fluctuation amplitude and the bandgap standard

Figure 4 Time-resolved PL (TRPL) curves at 4 and 300 K for (a) CIGS and (b) CZTSSe solar cells. Reprinted with permission from Ref. [38]. Copyright 2013, AIP publishing.

deviation of CZTSSe are roughly twice those of CIGS. Mattheis *et al.* [73] used PL spectra to estimate the fluctuations. Under the assumption that the length scale of the fluctuations is smaller than the diffusion length, the red shift of the PL peak can be calculated with σ_g of ~40 and ~150 meV for CIGS and CZTSSe, respectively. Although the IQE and PL tests cannot distinguish between bandgap fluctuations and electrostatic potential fluctuations, it is undeniable that the band tail states of CZTSSe are much more severe than that of CIGS, which can account for the larger V_{OC} deficit to some extent.

Excitation intensity-dependent PL spectra presented more direct evidence of the existence of tail or subgap states within the CZTSSe [70]. As reported in Fig. 3e, at low excitation power, the PL peak was centered at 1.15 eV, showing a giant red shift of approximately 0.35 eV. As the excitation power increased, the peak position blue-shifted and gradually saturated, showing a state filling behavior. In the meanwhile, a new higher-energy peak appeared at 1.45 eV, close to CZTS bandgap. These results mean that under normal working conditions, the photogenerated charge of the cell is mainly localized within the subgap states. The resulting severe non-radiative recombination and charge transportation loss eventually lead to the V_{OC} loss of the device.

DISORDER

Cu/Zn disorder: formation

It is now generally accepted that CZTS crystals adopt a kesterite (KS) structure (space group $I\bar{4}$), which is a tetragonal derivative of the cubic sphalerite ZnS structure [23]. When the Cu atoms at the (1/2,0,1/4), (0,1/2,3/4) position are interchanged with the Zn atoms at the (1/2, 1/2,0), (0,0,1/2) position, the stannite (ST) structure (space group $I\bar{4}2m$) CZTS is obtained (Table 1 and Fig. 5a) [74,75]. First principle calculations show that the KS structure has lower energy and is more stable in the thermodynamic equilibrium state, while the energy of the ST structure is only 4.6 meV atom⁻¹ higher than that of

the KS structure [74]. As limited by the dynamic process during the high-temperature annealing and cooling, the CZTSSe lattice may not be completely relaxed to the KS structure and the final product may be in a mixture structure comprised of KS and ST or in a Cu/Zn antisite random state. Fig. 5b shows the theoretically calculated formation energy of a series of point defects in the CZTSSe [37]. It is clear that Cu_{Zn} antisite possesses the lowest formation energy of <0.25 eV in both CZTS and CZTSe. Moreover, the formation energy of [Cu_{Zn}⁻+Zn_{Cu}⁺] ([Cu_{Zn}+Zn_{Cu}]) defect cluster is extremely low of 0.2 eV and independent to the element chemical potential. This means that the Cu/Zn disorder is always easy to form in the CZTSSe lattice whatever the element composition is.

Cu/Zn disorder: characterization

Due to the similarity of Cu and Zn in atomic number and size, these disordered structures are not distinguishable by using standard X-ray diffraction (XRD) techniques. Neutron diffraction and nuclear magnetic resonance (NMR) can be used to identify the cation distribution in the crystal structure, and have confirmed the widely existing disorder between Cu and Zn in the $z=1/4$ and $z=3/4$ Cu/Zn planes [76–78]. However, neutron diffraction and NMR are unsuitable for thin film samples. How to accurately quantify the Cu/Zn disorder in film samples is still a challenge for CZTSSe solar cell investigations.

The classic description of order-disorder transitions in crystalline materials was made by Bragg and Williams [79]. According to them, the crystal is in a state of dynamical equilibrium, where the rate at which atoms are thrown out of ordered positions into disordered positions by thermal fluctuations is equal to the rate at which the reverse process takes place. The perfectly ordered structure with a lowest energy is the ground state, while thermal fluctuations have the effect of creating a random atomic arrangement, leading to a temperature-dependent equilibrium ordering degree. The degree of order can be quantified by a long-range order parameter, S , which ranges from 1 (perfectly order) to 0 (totally disorder).

Table 1 Atomic occupancies, calculated lattice sizes and energies corresponding to different lattice structures of CZTS [74]

Structure	Cu	Zn	Sn	a (Å)	c (Å)	c/a	Energy (meV per atom)
CZTS KS	(0,0,0)	(1/2,1/2,0)	(0,1/2,1/4)	5.443	10.786	1.982	0
	(1/2,1/2,1/2)	(0,0,1/2)	(1/2,0,3/4)				
	(1/2,0,1/4)						
	(0,1/2,3/4)						
CZTS ST	(0,0,0)	(1/2,0,1/4)	(0,1/2,1/4)	5.403	10.932	2.023	4.6
	(1/2,1/2,1/2)	(0,1/2,3/4)	(1/2,0,3/4)				
	(1/2,1/2,0)						
	(0,0,1/2)

Figure 5 (a) Crystal structures of kesterite and ST CZTS. Reprinted with permission from Ref. [75]. Copyright 2009, AIP publishing. (b) The formation energy of defects in CZTS (top) and CZTSe (bottom) as a function of the chemical potential. Reprinted with permission from Ref. [37]. Copyright 2013, Wiley-VCH.

This method has been used to study the Cu/Zn order/disorder of the CZTS_{Se}. Considering a Cu/Zn plane of the kesterite, the long-range order parameter can be described as $S = 2(P_{\text{Cu}}^{\text{Cu}} - 1/2)$. $P_{\text{Cu}}^{\text{Cu}}$ is the probability that a Cu atom occupies its native site, which decreases from 1 in perfectly ordered to 0.5 in fully disordered material. In Vineyard's theory of order-disorder kinetics [80], the order parameter equilibrium value, S_{eqm} , is a function of temperature: S_{eqm} equals 1 at absolute 0 K. As temperature increases, S_{eqm} drops and falls rapidly to zero when approaching a certain critical temperature, T_C , as shown with the dashed line in Fig. 6a [81]. However, in practical experiments, the crystal structure cannot be completely relaxed to equilibrium state during the annealing and cooling processes. The solid curves in Fig. 6a illustrate the effect of annealing to a sample with an initially low degree of ordering (non-equilibrium), S_0 , for two different time durations t_1 and t_2 ($t_1 > t_2$). In Fig. 6a, the evolution of the long-range order parameter is divided into three stages. (I) When the temperature is much lower than T_C , thermal fluctuations mainly cause atomic vibration, which is not high enough to cause atomic positional interchange. (II) At intermediate temperatures, the order parameter in-

creases towards S_{eqm} with the occurrence of atomic exchange. (III) As the temperature approaching T_C , S drops rapidly and then remains zero at higher temperatures. Annealing for a longer period of time allows the crystal structure to obtain a fuller relaxation to approach the equilibrium state. Thus, in stage II, $S(T, t_1)$ is higher than $S(T, t_2)$. In theory, infinite-time annealing can bring the crystal to the equilibrium state, but this is not realistic in practical preparations of CZTS_{Se} absorbers.

Scragg *et al.* [81] proposed that near-resonant Raman scattering can detect the degree of Cu/Zn disorder. The Raman scattering depends on the symmetry of the crystal structure, the strength of the chemical bonds and the mass and charge of the constituent elements, which is sensitive to the local atomic environment [82]. In their study [81], two CZTS powder samples which were prepared at different cooling rates were firstly measured by NMR to make an evaluation of the Cu/Zn disorder. The slowly cooling sample (sample VS in Fig. 6b) was proved to be highly ordered, while the other sample (sample VF) that quenched in ice-water was disordered. They then collected the Raman spectra of these two samples excited at 785 nm, as shown in Fig. 6b. It can be clearly seen that

Figure 6 (a) The curves of the order degree, S , with the temperature. The dashed line indicates the equilibrium case. The solid lines show the effect of annealing initially disordered samples for fixed time periods t_1 and t_2 ($t_1 > t_2$). (b) Raman spectra with peak fitting for stoichiometric CZTS powder reference samples, VS (slowly cooled, ordered) and VF (rapidly cooled, disordered), with excitation wavelength of 785 nm. (c) Variation in Q for initially identical CZTS films post-annealed for different time periods (top). The triangles show the effect of temperature cycling on a single sample to test the reversibility of changes in Q . The full width at half maximum (FWHM) of the main Raman A mode for the 1 h post-annealed samples (bottom). The shaded region indicates the probable location of the critical temperature T_c . Reprinted with permission from Ref. [81]. Copyright 2014, AIP publishing.

the Raman spectra are different from each other. Sample VF exhibited a larger full width at half maximum (FWHM) of the main A mode (m_{1A}) at $\sim 339 \text{ cm}^{-1}$. The second A mode (m_{2A}) at $\sim 288 \text{ cm}^{-1}$ was about twice as strong as the E and B modes at 368 and 376 cm^{-1} (m_{4E} and m_{5B}). Comparatively, for sample VS, the relative intensity of m_{2A} was significantly increased compared with that of m_{3A} mode, and both the m_{4E} and m_{5B} modes were obviously suppressed.

Based on the above observations, Scragg *et al.* [81] extracted two important parameters from the Raman spectra. One is the Q , which is defined as $I(m_{2A})/I(m_{3A})$, where $I(m)$ is the intensity of certain Raman mode derived from full spectrum fitting, and the other parameter is the FWHM of m_{1A} . The relationship between Q and annealing condition was obtained as in Fig. 6c, which showed a similar shape to the curves of $S(T, t)$. Together with more multi-step annealing experiment, they found that the parameter Q can be used to reflect the Cu/Zn disorder of CZTS film, that is, a larger Q represents a more ordered structure. In addition, the estimated T_c of pure CZTS is $533 \pm 10 \text{ K}$ ($260 \pm 10^\circ \text{C}$). As seen in Fig. 6c, the FWHM of the main m_{1A} mode also increased rapidly

at $\sim 533 \text{ K}$, further supporting the above finding. It is worth noting that the Raman scattering can be influenced by the bandgap and composition of CZTSSe, which makes it unrealistic to directly use the Q value to compare the degree of order between the samples with different compositions.

Cu/Zn disorder: influence

Based on the observation of structural changes induced by thermal treatment, Rey *et al.* [83] investigated the variation of the optical bandgap of pure CZTSe as a function of the annealing temperature. After successive annealing/quenching of the sample, the state before quenching can be sustained and detected. As shown in Fig. 7a, the change of E_g with the temperature was completely reversible, which helped to exclude the possible influence of the formation of secondary phases, the loss of element, and the contamination of glass substrate during the annealing process. Further, the calculated shape of equilibrium long-range order parameter (S_{eqm}) vs. T exhibited a good agreement to the measured changes of E_g vs. T (Fig. 7b), which means that the Cu/Zn disorder has a direct influence on the E_g . Ordering the atomic

Figure 7 (a) Evolution of the CZTSe bandgap with the temperature during the annealing/quenching sequence. In the inset, Tauc's plots for different temperatures are presented. (b) Calculated evolution of the long-range order parameter during successive annealing treatments. The inset presents the evolution of E_g for the same annealing sequence. Annealing times (dwell times) are shown as labels. Reprinted with permission from Ref. [83]. Copyright 2014, AIP publishing.

arrangements of the CZTSe can increase the E_g by about 110 meV as compared with the fully disordered material, and the estimated T_C of pure CZTSe is $200 \pm 20^\circ\text{C}$ (473 ± 20 K), lower than that of pure CZTS. They also calculated that the E_g can be decreased by 24 meV when the density of the $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ defect cluster reaches $3.4 \times 10^{20} \text{ cm}^{-3}$.

Despite these efforts, the influence of Cu/Zn disorder on the E_g has not been clearly clarified because various research groups sometimes give different theoretical or experimental results. Chen *et al.* [37] calculated the band edge shift caused by one $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ cluster in the 128-atom supercell of CZTS and CZTSe and found that a high population of $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ cluster can indeed decrease the optical bandgap. Interestingly, other deep defect clusters, like $[\text{Sn}_{\text{Cu}} + \text{Cu}_{\text{Sn}}]$, $[\text{Sn}_{\text{Zn}} + \text{Zn}_{\text{Sn}}]$ and $[\text{Sn}_{\text{Zn}} + 2\text{Cu}_{\text{Zn}}]$, have a more significant impact on the bandgap. Huang *et al.* [84] reported that when a 64-atom CZTS supercell contains one $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ cluster, the bandgap will be reduced by approximately 110 meV. Comparatively, the cluster $[\text{Zn}_{\text{Cu}} + \text{V}_{\text{Cu}}]$ was found to be able to increase the E_g by 70 meV. The presence of Cu-poor $[\text{Zn}_{\text{Cu}} + \text{V}_{\text{Cu}}]$ cluster can lower the formation energy of the antisite $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ cluster, which may lead to a complicated influence on the E_g . Thus, the bandgap evolutions observed by Rey *et al.* [83] should be a result of the joint influence of various defects.

It is more widely recognized that the increase of Cu/Zn disorder could result in more band tail states. As charged defects, isolated Cu_{Zn}^- or Zn_{Cu}^+ can induce the electrostatic potential fluctuations, which were considered as an

important factor limiting CZTS solar cell efficiency by Gokmen *et al.* [38]. The uneven distribution of $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ clusters will lead to the bandgap fluctuations. Both these two types of fluctuations can locally separate the electron and hole and thus suppress the radiative recombination. Scragg *et al.* [85] carried out excitation-intensity-dependent PL measurements on ordered ($S \sim 0.8$) and disordered ($S \sim 0$) CZTS samples (Fig. 8a). When increasing the excitation intensity, the ordered sample exhibited a higher PL response. The lower PL response of the disordered sample may also come from the severe non-radiative recombination induced by the tail states.

According to our discussion above, the band tail states may lead to the V_{OC} deficit of the device. In this case, it is a question how much the band tail states caused by Cu/Zn disorder can influence the V_{OC} . Rau *et al.* [86] proposed to quantify the relationship between bandgap fluctuations and the V_{OC} , that is

$$V_{\text{OC}} = \frac{E_g}{q} - \frac{\sigma_g^2 q}{2kT} - \frac{kT}{q} \ln \left(\frac{J_{00}}{J_{\text{SC}}} \right), \quad (4)$$

where J_{00} is the pre-exponential factor of the dark saturation current density, and J_{SC} is the short circuit current density. It was assumed that at a given anion ratio, the amplitude of bandgap fluctuations caused by Cu/Zn disorder is 150 meV, corresponding to a reasonable $\sigma_g = 150/4 = 38$ meV. Taking this value into Equation (4), it can be found that the maximum V_{OC} deficit is only 47 mV [41]. Apparently, this value is negligible compared

Figure 8 (a) Dependence of PL intensity on excitation intensity for ordered ($S \sim 0.8$) and disordered ($S \sim 0$) pieces of a CZTS sample. The straight lines indicate the regions of data from which the k -factors were calculated. Reprinted with permission from Ref. [85]. Copyright 2015, Wiley-VCH. (b) Grain-to-grain variation evaluated from 24 data points measured on various grains from a few sections, with 1 data point per grain. The relationship between the bandgap energy and Urbach energy E_U (c), and the relationship between Urbach energy E_U and the lowest voltage deficit (d) for various photovoltaic materials reported. Reprinted with permission from Ref. [41]. Copyright 2016, Wiley-VCH.

with current V_{OC} deficit of the CZTSSe device in the experiment (> 570 mV). In addition, although the bandgap and the V_{OC} can indeed be increased more or less by suppressing the Cu/Zn disordering, the reduction in V_{OC} deficit is very limited until now. These studies show that whether the large V_{OC} loss occurring in the CZTSSe solar cell arises from the Cu/Zn disorder is still an open question.

S/Se disorder

S/Se disorder, that is, non-uniform anionic distribution, could also exist in the CZTSSe system [87]. Currently, the CZTSSe thin films are mainly prepared through a post sulfo-selenization route; during this process, slow atomic diffusion may result in different concentrations of anions inside and outside the grain. The scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX) characterization proved that the grains of the active absorber exhibited different S/(S+Se)

ratios as seen in Fig. 8b [41]; the Se concentration on the upper surface was higher than that on the bottom surface. Such S/Se disorder will lead to bandgap fluctuations in the real-space of the absorber. Its influence on the V_{OC} was also estimated by Equation (4). The calculation results showed that the S/Se non-uniformity and the spatial bandgap fluctuations only made a negligible contribution (less than 2.8%) to the V_{OC} deficit [41].

Based on the above discussions, it can be found that the CZTSSe material indeed possesses more serious atomic disorder and band tail states compared with other semiconductors. A previous summary of the Urbach energy (E_U) of the CZTSSe and other materials clearly shows this fact [41,88–90]. E_U is also a featured parameter reflecting the band tail states. As seen in Fig. 8c, at the same bandgap, the CZTSSe exhibits a much higher E_U . However, these serious band tail states seem not to be the origin for the large V_{OC} loss of the CZTSSe solar cell. As in Fig. 8d, even under the same E_U , the CZTSSe cell still

gives a much larger V_{OC} loss than other devices. These results imply that there should be another hidden mechanism limiting the device voltage and that there is an unknown correlation between the atomic disorder and the large voltage loss of the CZTSSe solar cell.

DEEP DEFECTS

Effective non-radiative recombination centers (NRRCs)

As mentioned above, the high V_{OC} deficit of CZTSSe solar cell should stem from rapid non-radiative recombination, as reflected by the extremely short minority carrier lifetime observed in experiments. The CZTSSe exhibited a carrier lifetime of only few nanoseconds ($\sim$ ns), far less than that of CIGS (>100 ns) [91–93]. It is of great significance to explore and regulate the non-radiative recombination centers (NRRCs) in CZTSSe for promoting the device efficiency. The non-radiative recombination is a process in which an NRRC captures an electron from the CBM and a hole from the VBM, while releasing phonons. The NRRC is mainly the defected electronic state in the forbidden band located in the bulk or at the surface/interface of the semiconductor device. According to the Shockley-Read-Hall theory, deep defects play a dominant role in causing the recombination because of its large overlap with the Fermi energy level [94,95]. Nonetheless, whether a deep defect could act as an effective NRRC still depends on its carrier capture cross-section (σ). As a p-type semiconductor, the minority carrier of CZTSSe is electron, and its maximum lifetime can be determined from defect concentration N_t and electron capture cross-section (σ_n), that is

$$\tau_n = \frac{1}{v_{th}\sigma_n N_t}, \quad (5)$$

where v_{th} is the thermal velocity of the CZTSSe determined by the carrier effective mass. It is reported that the σ_n highly depends on the energy barrier of the non-radiative electronic state transition (E_b), while the E_b is closely associated to the lattice relaxation process according to the Huang-Rhys theory [96–99], that is

$$E_b = \frac{(\Delta E - E_{rel})^2}{4E_{rel}}, \quad (6)$$

$$E_{rel} = \sum_k \frac{1}{2} \omega_k^2 \Delta Q_k^2. \quad (7)$$

The lattice relaxation energy (E_{rel}) is determined by the frequency of the defect correlated phonon modes (ω_k) and the coordination difference between the initial and final states (ΔQ_k). The phonon frequency ω_k is strongly correlated with the strength of the chemical bonds

around the defect. Once acquiring both the phonon frequencies and the coordination change, one can calculate E_{rel} and E_b , and thus determine whether the defect is an effective NRRC or not.

Deep defects in CZTSSe

As shown in Fig. 9, there is a variety of point defects in multiterinary CZTS and CZTSe materials. Cu vacancy (V_{Cu} , acceptor), Cu-Zn substitutions (Cu_{Zn} acceptor or Zn_{Cu} donor) are shallow defects, and others, including Cu_{Sn} , Zn_{Sn} , V_{Zn} , and V_{Sn} acceptors, Sn_{Cu} , Sn_{Zn} , Zn_i , V_S , and V_{Se} donors, are all deep defects [37]. Chen *et al.* [37] made a systematical calculation on the energy levels and formation energy of these defects. However, few reports have been presented on their carrier capture cross-section. It is a great challenge to evaluate the carrier capture cross-section of these defects from experimental measurements or theoretical calculations. Experimentally, many deep defects coexist and interact with each other, resulting in giant difficulty in determining and analyzing a specific defect. The defect energy levels measured in experiments were generally around 100 meV; the deep defect levels were rarely observed. Due to the complexity of the CZTSSe system, only a few theoretical studies have been done to investigate the carrier capture cross-section

Figure 9 The ionization levels of intrinsic defects in the bandgaps of (a) CZTS and (b) CZTSe. The red bars show the acceptor levels and the blue bars show the donor levels, with the initial and final charge states labeled in parentheses. Reprinted with permission from Ref. [37]. Copyright 2013, Wiley-VCH.

and the non-radiative recombination mechanism of several certain deep defects.

Li *et al.* [42] theoretically compared the electron capture capabilities of three deep defects (i.e., $\text{Sn}_{\text{Zn}}^{2+}$, Sn_{Zn}^+ , and $[\text{Cu}_{\text{Zn}}-\text{Sn}_{\text{Zn}}]^+$) in CZTS and found that the strength of Sn-S bonds around the defect has a significant effect on the carrier capture cross-section. At 300 K, the electron capture cross-section (σ_n) of $\text{Sn}_{\text{Zn}}^{2+}$, Sn_{Zn}^+ , and $[\text{Cu}_{\text{Zn}}-\text{Sn}_{\text{Zn}}]^+$ were estimated to be 8.8×10^{-14} , 4.7×10^{-18} , and $4.5 \times 10^{-14} \text{ cm}^2$, respectively. $\text{Sn}_{\text{Zn}}^{2+}$ and $[\text{Cu}_{\text{Zn}}-\text{Sn}_{\text{Zn}}]^+$ can be considered as effective NRRCs. Further calculations showed that $\text{Sn}_{\text{Zn}}^{2+}$ (2+/+) and $[\text{Cu}_{\text{Zn}}-\text{Sn}_{\text{Zn}}]^+$ (+/0) have relatively larger lattice relaxation energies E_{rel} (0.50, 0.52 eV), thus resulting in a small E_b (0.01, 0.02 eV), which makes them easier to capture electron. Comparatively, Sn_{Zn}^+ (+/0) exhibits a relatively small $E_{\text{rel}}(\text{Sn}_{\text{Zn}}^+)$ of 0.23 eV and thus a large $E_b(\text{Sn}_{\text{Zn}}^+)$ of 0.44 eV. The coordinate diagram for $\text{Sn}_{\text{Zn}}^{2+}$ (2+/+) and Sn_{Zn}^+ (+/0) are plotted in Fig. 10a–c. Li *et al.* [42] explored deeply into these results. Due to the differences in size and charge

number between the substitutional and the original atoms, the lattice around the antisite defect is distorted. Every Sn atom in these three antisite defects coordinates with four S atoms, and lattice distortion occurs when S atoms relax towards or away from the defects. As shown in Fig. 10d–f, for $\text{Sn}_{\text{Zn}}^{2+}$ and $[\text{Cu}_{\text{Zn}}-\text{Sn}_{\text{Zn}}]^+$, the Sn-S bonds become shorter and stronger because the S atoms relax towards the Sn atom, corresponding to high-frequency vibration phonons. According to Equations (6) and (7), it can be inferred that they have larger E_{rel} and smaller E_b . In contrast, the Sn-S bond near Sn_{Zn}^+ becomes longer and softer, and thus its carrier capture cross-section becomes much smaller. This work provides a theoretical way to evaluate whether a deep defect is an effective NRRC. Nonetheless, it is still difficult to operate this evaluation in complex situations where multiple defects may interact with each other.

Kim *et al.* [100] proposed that the rapid carrier recombination through NRRCs is closely related to the ($5s^2$) lone pair electronic state of Sn. At first, it was shown that

Figure 10 (a) Schematic diagram of non-radiative recombination induced by deep defect. Configuration coordinate diagram (under the harmonic approximation) of the non-radiative electronic state transition for (b) $\text{Sn}_{\text{Zn}}^{2+}$ capturing an electron and converting to Sn_{Zn}^+ and (c) Sn_{Zn}^+ capturing an electron and converting to neutral Sn_{Zn}^0 . The non-radiative electronic state transition mainly occurs at the cross point of energy curves, it is necessary for a system to overcome energy barrier E_b with the help of phonon. $\Delta E = E_{10}' - E_{10}$ is the electronic energy difference at the equilibrium states, and ΔQ corresponds to the difference in the equilibrium coordinates between the initial and final states. Lattice relaxation energy, E_{rel} , originates from the equilibrium configuration coordinate difference between the initial and final states. The phonon modes and the electronic states induced by the defects (d) $\text{Sn}_{\text{Zn}}^{2+}$, (e) Sn_{Zn}^+ , and (f) $[\text{Cu}_{\text{Zn}}-\text{Sn}_{\text{Zn}}]^+$. The green isosurfaces represent the squared norms of wavefunctions of the transition energy levels of defects, whereas the red arrows denote the vibration of the S atoms (marked in yellow) around the Sn_{Zn} antisite (marked in blue) associated with the defect-induced phonon modes. Reprinted with permission from Ref. [42]. Copyright 2019, ACS publishing.

the sulfur vacancy (V_S) can be an effective NRRC through the aid of an intermediate excited state where electron is captured by Sn [43]. When Sn(IV) near a neutral V_S captures an electron, the Sn(IV) is reduced to a metastable Sn(III) and V_S^0 becomes V_S^+ . The unoccupied level of V_S^+ is close to the VBM of CZTS and thus it can capture a hole under illumination and turns into V_S^{2+} . The hole capturing promotes the V_S^{2+} energy level close to the CBM of CZTS. V_S^{2+} can efficiently capture an electron and recover the +1 charge state, thus completing the electron-hole non-radiative recombination process. Furthermore, V_S , $[V_S+Cu_{Zn}]$, Sn_{Zn} under S-poor conditions and Sn_{Zn} under S-rich conditions have also been investigated. They were all proved to be effective NRRCs, limiting the minority carrier lifetime, and all of them are associated with Sn $5s^2$ lone-pair state. In CZTS, the formation of an inert lone pair ($5s^2$) reduces the oxidation state of Sn from +4 to +2. Due to the difference in ionic radii between Sn(II) and Sn(IV), large lattice distortions around the lone-pair defect centers were found. The high stability of the lone pair suppresses the ionization of certain point defects and induces deep carrier transition level in the bandgap. Therefore, the lone-pair effect associated with Sn is responsible for both the deep defect levels and large lattice distortions in CZTS, thereby resulting in rapid electron-hole non-radiative recombination.

These reported studies have highlighted a connection between the Sn atom and the effective NRRCs. A number of experimental studies have also shown that the CZTSSe solar cell efficiency is very sensitive to the Sn composition [52,101,102]. However, the details of the effects of Sn composition on specific deep defects are rarely reported. Compared with the Cu/Zn disorder, studies on deep defects of CZTSSe are relatively lacking, and most of reported results are based on theoretical calculations. The experimental characterization or regulation is still difficult to realize at present, which should be regarded as an

important direction for the development of CZTSSe.

Synergy effect

Considering the complexity of CZTSSe material structures and the diversity of defect types, the V_{OC} deficit of the CZTSSe cell may not be caused by a single type of defect. Considering a perfectly crystalline CZTSSe absorber without any undesirable defects in the solar cell (Fig. 11a), it absorbs incident photons to generate free carriers. The free electrons diffused into the depletion region are extracted by the n-type material, and the free holes diffused to the back side are collected by the back electrode. The perfect crystal has a very low probability of carrier recombination, thus the free carriers have a long lifetime and a long diffusion length, which will lead to a high V_{OC} . When the band tail states (induced by Cu/Zn disorder) are formed at the band edge of the absorber semiconductor, the effective E_g of the absorber is slightly reduced. In addition, some free carriers will be trapped in the band tail states and thus decreasing the V_{OC} of the solar cell (Fig. 11b). Nonetheless, this decrease may be much smaller than the experimental result, as predicted by Equation (4). The deep defects can further decrease the V_{OC} by accelerating the non-radiative recombination processes. Although it was experimentally found that the CZTSSe possessed an ultra-short carrier lifetime, the contribution of the deep defects has not been confirmed until now in experiments. In this case, we prefer to propose that there is a synergy effect between the shallow and deep traps in causing the charge loss of the cell, as shown in Fig. 11c. Compared with the deep defect, the shallow defect usually has much smaller energy barrier of carrier capturing and the carrier trapping can be completed within a picosecond timescale. For the deep defect, carrier capturing from the shallow defect may be much easier than from the continuum band. In addition, the carrier exchange between the tail states and the continuum band could significantly decrease the carrier mobility and thus

Figure 11 Schematic diagrams of the charge processes in solar cells prepared with (a) perfect CZTSSe absorber without any undesirable defects, (b) CZTSSe absorber only with Cu/Zn disorder, and (c) CZTSSe absorber with Cu/Zn disorder and deep defects.

slow down the carrier transport. This will give the deep defect more time and opportunity to capture carriers that transport around it.

EXPERIMENTAL IDENTIFICATION AND CONTROL OF DEFECTS

Experimental identification of defects

There are so many kinds of defects in CZTSSe materials, and different defects have different influence mechanisms on the solar cell performance, which requires us to characterize and control specific defects, especially the killer defects. Several experimental characterization methods for semiconductor defects have been used in the CZTSSe field, and four methods will be discussed here, that is, deep level transient spectroscopy (DLTS), thermal admittance spectroscopy (TAS), temperature-dependent PL spectroscopy (TPL), and transient photocapacitance spectroscopy (TPC). The defect information of CZTSSe materials obtained by these methods is listed in Table 2.

DLTS is one of the most useful methods to detect deep defects of a semiconductor, which can measure the activation energy, concentration, electron- or hole-capture cross-section of each defect [103,104]. This method comes from the concept of p-n junction capacitance transients due to the filling and emptying of defects at fixed temperatures. The sign of the capacitance-mode DLTS (C-DLTS) signal peak can help determine whether the deep defect is a minority carrier trap or a majority carrier trap. The height of the DLTS signal peak is proportional to the defect concentration, and the position of the peak is determined by the thermal emission rate of the defect. The Arrhenius curve of corresponding DLTS peak is $\ln(e_{n,p}/T^2)$ vs. $1/T$, where $e_{n,p}$ is the carrier emission rate of the defect. By linearly fitting the Arrhenius curve, the defect activation energy (E_a) can be calculated from the slope, and the carrier capture cross-section ($\sigma_{n,p}$) of the defect can be calculated from the intercept, that is

$$e_{n,p}(T) = \gamma \sigma_{n,p} T^2 \exp\left(-\frac{E_a}{kT}\right), \quad (8)$$

where γ is a constant for a given material. Das *et al.* [105] used the current-mode DLTS (I-DLTS) to analyze two CZTSSe solar cells (Fig. 12a–c). The pure CZTSe cell, with an efficiency of 7.1%, showed only a shallow V_{Cu} level at $E_v+0.03$ eV, whereas the CZTSSe (S/Se=1.4) cell, with an efficiency of 4.1%, showed two dominant deep acceptor levels at $E_v+0.12$ eV and $E_v+0.32$ eV corresponding to Cu_{Zn} and Cu_{Sn} antisites. The result of the pure CZTSe cell indicates that although Cu_{Zn} has a lower

formation energy, V_{Cu} may be the predominant lattice defect in kesterite. However, the efficiency of the CZTSe device with only benign defect is still low. Qi *et al.* [106] also detected Cu_{Zn} and Cu_{Sn} defects by conventional C-DLTS, with the E_a of 175 and 366 meV, respectively. Campbell *et al.* [107] calculated the E_{a1} to be 86 ± 7 meV according to a broad DLTS peak at around 115 K (Fig. 12d and e). They thought the observed peak may in fact be comprised of a distribution of deep levels closely spaced in energy, and tried to separate those levels *via* a Laplace analysis method but failed. Thus this peak was vaguely identified as Cu_{Zn} antisite. They also observed an energy level of $E_{a2}=167 \pm 10$ meV (Fig. 12d and e), which was considered as a Sn-related defect, and finally identified as Zn_{Sn} according to the Cu-poor and Zn-rich composition condition. Besides, other shallower defects beyond the scope of DLTS were detected by TPL, which will be mentioned below. In the meantime, Campbell *et al.* [107] acquired the minority carrier lifetime (0.20 ns) and minority carrier diffusion length (203 nm) of the CZTSSe film by relevant photoelectric measurement and analysis. We can see from these different reports that there is still no convincing understanding on the defects because the experimental identification of defects has strong subjectivity. In different studies, similar energy levels, measured by the same method on the samples with nearly identical bandgap, have been regarded to be corresponding to different defects.

According to the reported information, such as the density and the carrier capture cross-section of the defects, measured by DLTS, here we can estimate the shortest carrier lifetime of CZTSSe by Equation (5). The calculated carrier lifetimes τ_c are listed in Table 2 [89,90,101,105–112]. Unexpectedly, the τ_c values derived from the DLTS are in the order of microsecond or even millisecond, which is several orders of magnitude larger than the measured result (τ_m). As shown in Fig. 12f, the τ_m values measured by time-resolved PL (TRPL) are mainly in the range of ~1 to ~10 ns for the CZTSSe solar cells with efficiencies of 9%–11% [91]. Such a large gap suggests that some fundamental properties about CZTSSe materials remain undiscovered. More effective NRRCs may have not been detected for some reasons until now. Possibly, the synergy effect we proposed above has indeed accelerated the non-radiative recombination of the carriers. In our opinion, more new and independent methods are desired to be developed and exploited to probe the defect properties of the CZTSSe and to establish a closer correlation between the defect and the non-radiative recombination.

Table 2 Defect states information in CZTSSe materials obtained by different test methods

Method	Reference	E_a (meV)	N_t (cm ⁻³)	σ (cm ²)	τ_c (μ s)	Possible defect
I-DLTS	Das <i>et al.</i> [105]	30±10	6.46×10 ¹⁵	2.52×10 ⁻²⁰	166	V _{Cu}
		120±40	6.17×10 ¹⁴	1.31×10 ⁻²⁰	28	Cu _{Zn}
		320±60	6.73×10 ¹⁴	2.04×10 ⁻¹⁸		Cu _{Sn}
C-DLTS	Qi <i>et al.</i> [106]	175	6.69×10 ¹⁴	1.06×10 ⁻²¹	6.98	Cu _{Zn}
		366	9.46×10 ¹⁴	4.10×10 ⁻¹⁸		Cu _{Sn}
	Campbell <i>et al.</i> [107]	86±7	(1.70±0.22)×10 ¹⁴	(1.08±0.95)×10 ⁻²⁰	10690	Cu _{Zn}
		167±10	(3.17±0.32)×10 ¹³	(2.20±1.99)×10 ⁻²⁰		Zn _{Sn}
TAS	Fernandes <i>et al.</i> [108]	44.7±0.7	–	–	–	V _{Cu}
		112.7±3.5	–	–	–	Cu _{Zn}
	Gunawan <i>et al.</i> [109]	130–200 ^a	–	–	–	Cu _{Zn}
		Duan <i>et al.</i> [110]	134	4.96×10 ¹⁵	5.20×10 ^{-17b}	0.1
	163		5.24×10 ¹⁵	1.56×10 ^{-17b}	0.47	Cu _{Zn}
	183		1.14×10 ¹⁶	8.00×10 ^{-18b}	0.42	Cu _{Zn}
	Larramona <i>et al.</i> [101]	120–170 ^c	–	–	–	Cu _{Zn}
		600±100	–	–	–	V _{Sn} or Cu _{Sn}
TPL	Larramona <i>et al.</i> [101]	25–30 ^c	–	–	–	Potential fluctuation
		120–130 ^c	–	–	–	Donor
	Luckert <i>et al.</i> [111]	7±2	–	–	–	Donor
		27±3	–	–	–	Acceptor
	Grossberg <i>et al.</i> [112]	277±6	–	–	–	Cu _{Sn} or Zn _{Sn}
		289±7	–	–	–	
	Campbell <i>et al.</i> [107]	38.3±3.8	2.1×10 ^{18d}	–	–	V _{Cu}
		3.2±0.5		–	–	Sn _{Cu}
Measurement results						
TPC	Miller <i>et al.</i> [89]	1.0 eV≤ E_g ≤1.2 eV; E_U ≤18 meV; E_t = E_v +800 meV				
		1.4 eV≤ E_g ≤1.5 eV; E_U =25–30 meV; E_t = E_v +800 meV				
	Islam <i>et al.</i> [90]	S/(S+Se)=0.15; E_U =54 meV; E_t = E_v +1000 meV				
		S/(S+Se)=0; E_U =69 meV; E_t = E_v +1000 meV				

a) The different E_a values in this range are for CZTSSe films with various bandgaps; b) the σ values are estimated from the Arrhenius curves in Ref. [110]; c) the different E_a values in these ranges are for CZTSSe films with various Sn additions; d) the total density of the two shallow defects was calculated from the PL peak blue-shift value in excitation-dependent PL spectra.

TAS is also widely used in CZTSSe to detect deep defects [113]. The Arrhenius relationship of TAS exists between $\ln(\omega_0/T^2)$ and $1/T$ [114], where ω_0 is a characteristic frequency for capacitance transition. Fernandes *et al.* [108] successfully fitted the complex admittance plane with an expanded equivalent circuit (Fig. 13a and b), in which two recombination centers (C_1 – R_1 , C_2 – R_2) were considered [108]. The characteristic frequency was defined as $\omega_0 = 1/(R_i C_i)$, $i = 1, 2$. Through temperature-dependent measurements, two defect levels were detected, that is, $E_{a1} = 44.7 \pm 0.7$ meV for V_{Cu}, and $E_{a2} = 112.7 \pm 3.5$ meV for Cu_{Zn} (Fig. 13c). Using TAS, Gunawan *et al.*

[109] and Duan *et al.* [110] found that the E_a values (130–200 meV) of Cu_{Zn} defect tended to increase with higher S/(S+Se) ratio in CZTSSe alloys (Fig. 14a and b). Gunawan *et al.* [109] thought the reason might be the concomitant decrease in the dielectric constant or in the crystal lattice constant when increasing anion substitution from Se to S (Fig. 14c). Duan *et al.* [110] thought that the VBM moves down as the S content increase, potentially yielding defects with higher activation energies. In Enkhbat's recent TAS study [115], the detected activation energy even rose from 59 to 367 meV with S-alloying. This implies that the dominant defect state of the CZTSSe becomes deeper at

Figure 12 (a) Arrhenius plots corresponding to the peaks from I-DLTS signal of (b) Cell 1 (S/Se=1.4) and (c) Cell 2 (pure CZTSe) obtained by Das *et al.* Reprinted with permission from Ref. [105]. Copyright 2014, AIP publishing. (d) Arrhenius plots corresponding to the peaks from (e) C-DLTS signal obtained by Campbell *et al.* Reprinted with permission from Ref. [107]. Copyright 2019, IOP publishing. (f) Minority carrier lifetime and mobility *versus* minority carrier diffusion length. Reprinted with permission from Ref. [91]. Copyright 2013, AIP publishing.

Figure 13 (a) AC response equivalent circuit of CZTS solar cell constructed by Fernandes *et al.* (b) Complex admittance plane of the studied solar cell measured at 293 K and the fitting results for the AC response equivalent circuits. (c) Arrhenius plot for the estimation of the defect energies. Reprinted with permission from Ref. [108]. Copyright 2012, AIP publishing.

higher S content. This may explain why high-efficiency CZTSSe solar cells are rarely based on S-rich materials. Larramona *et al.* [101] detected an ultra-deep defect at $E_a=600\pm100$ meV, and thought it was V_{Sn} or Cu_{Sn} . From the reported TAS results, we can also estimate the shortest carrier recombination lifetimes (Table 2), which are also larger than the τ_m values measured by TRPL. We need to note that although the shallow defects such as the Cu_{Zn} exhibit fast charge capturing, they should not be effective NRRCs because they may not be simultaneously active to both electrons and holes. Nonetheless, these defects may have played a critical role in the synergy process for realizing charge recombination.

TPL was also used to estimate the defect levels. It was generally believed that there is a relationship between the steady-state PL intensity and the temperature [116], that is

$$I_{PL}(T) = I_0 / \left[1 + A_1 \exp\left(-\frac{E_{a1}}{kT}\right) + A_2 \exp\left(-\frac{E_{a2}}{kT}\right) \right], \quad (9)$$

where I_0 is the intensity at the lowest temperature, A_1 and A_2 are fitting parameters. In the original theory, the E_{a1} or E_{a2} represented the activation energy of PL quenching due to the thermal activated non-radiative charge transition, similar to the E_b in Equation (6). In some studies later, this activation energy was also thought as the defect en-

Figure 14 (a) Admittance spectra of devices with various sulfur contents: sample A ($S/(S+Se)=0.35$), sample B ($S/(S+Se)=0.8$), sample C ($S/(S+Se)=1$), measured by Duan *et al.* (b) Defect spectra derived from admittance spectra in (a). Reprinted with permission from Ref. [110]. Copyright 2013, Wiley-VCH. (c) Summary of the acceptor levels (dashed line is guide to the eye) and relative dielectric constants determined from the admittance spectra obtained by Gunawan *et al.* The blue filled circles are the theoretical values of the relative dielectric constants, and the star points are the experimental data. Reprinted with permission from Ref. [109]. Copyright 2012, AIP publishing.

ergy level. Whether this usage is reasonable or not is a question. Nonetheless, we still collect some studies here for the readers' reference. Larramona *et al.* [101] used TPL to find two defect levels that were not detected by TAS (Fig. 15a and b). One was classified as the potential fluctuation with a smaller energy level (25–30 meV), and the other was considered as a donor defect with its activation energy of 120–130 meV. Campbell *et al.* [107] detected a shallow donor (3.2 ± 0.5 meV) for Sn_{Cu} and a shallow acceptor (38.3 ± 3.8 meV) for V_{Cu} , and neither of them had been detected by the DLTS. In addition, Campbell *et al.* [107] calculated the density of the donor-acceptor-pair (Sn_{Cu} and V_{Cu}) to be $2.1 \times 10^{18} \text{ cm}^{-3}$ from the blue-shift value of excitation-dependent PL spectra. Luckert *et al.* [111] studied pure CZTSe, for which two activation energies of $E_{a1} = 7 \pm 2$ meV and $E_{a2} = 27 \pm 3$ meV were determined. Later, Grossberg *et al.* [112] proposed that the deep defects in pure CZTS were detected by TPL for the first time. Two PL peaks were observed in their study (Fig. 15c), corresponding to similar activation energies of 287 ± 7 and 277 ± 6 meV (Fig. 15d). It was considered that these two peaks arise from the band-to-impurity recombination process involving the same deep acceptor defect (Cu_{Sn} or Zn_{Sn}) but the different CZTS phase with different bandgap. Notably, Grossberg *et al.* [112] abandoned the activation energy derived from the low-temperature regime, whose value was usually a few meV in other studies. In the low temperature regime, the PL intensity evolution exhibited an approximate T^{-2} de-

Figure 15 (a) TPL spectra of a CZTSSe film fabricated with 2% Sn addition. (b) Arrhenius plots of the PL intensity for CZTSSe films with various Sn additions. Reprinted with permission from Ref. [101]. Copyright 2015, Wiley-VCH. (c) Low-temperature PL spectrum of CZTS polycrystals together with the fitting result. (d) Arrhenius plots derived from the temperature-dependent PL spectra of CZTS polycrystals. Reprinted with permission from Ref. [112]. Copyright 2012, AIP publishing.

pendence, similar to correlation between defect's capture cross-section and temperature [117]. This may indicate that the activation energy obtained from the TPL is not a true defect energy level.

TPC has also been used to study defect state distributions in CZTSSe with various bandgaps [118]. Miller *et al.* [89] investigated five CZTSSe solar cells with different S/Se ratios (Fig. 16a and b). The TPC spectra indicated that E_U of band tail states was limited within 18 meV when the bandgap was smaller than 1.2 eV, whilst E_U was in the range of 25–30 meV for higher-bandgap samples. Besides, a deep defect centered at E_v+800 meV existed in most samples. Islam *et al.* [90] measured two samples (Fig. 16c and d), and the E_U values were determined to be 54 and 69 meV for pure CZTS and CZTSSe (S/(S+Se)=0.15), respectively. A deep defect centered at around 1.0 eV above the VBM was observed in the CZTS sample.

At present, the experimental measurements of the defects in CZTSSe show that the Urbach energies or the activation energies of the shallow defects increase with the width of the bandgap, while the location of the deep defect seems to remain unchanged, as seen in Fig. 17

[119]. The activation energies obtained in most studies are smaller than 200 meV and only a few deep defects have been observed. In our opinion, these results on the defects are not enough to explain the ultra-short minority lifetime of the CZTSSe materials. The undiscovered information may be the key for understanding the efficiency loss mechanism of the cell.

Experimental control of defects

So far, many efforts have been made to suppress the detrimental defects in CZTSSe. Intrinsic doping (i.e., composition regulation of Cu, Zn, and Sn), cationic substitution with iso-electronic elements (i.e., the elements from the same family as Cu, Zn, and Sn), and extrinsic doping with alkaline elements are the most investigated ones. Meanwhile, less conventional options such as Ba, Mn, Fe, Co, and Ni have also been reported for alloying [120–123].

From the early-stage development of kesterite materials, it has been known that an off-stoichiometric composition is required to obtain high-efficiency devices [23,124–126]. Generally, the grains of absorber grow

Figure 16 (a, b) TPC spectra for five CZTSSe samples obtained by Miller *et al.* The bandgaps of samples 1 to 5 are 1.07, 1.15, 1.20, 1.47 and 1.51, respectively. Reprinted with permission from Ref. [89]. Copyright 2012, AIP publishing. TPC spectra of (c) CZTS and (d) CZTSSe (S/(S+Se)=0.15) solar cells measured by Islam *et al.* Solid black line is the Gaussian fitting of the defect band, OH1. Insets of figures show schematic diagram of the sub-band-gap optical transitions in the films. Reprinted with permission from Ref. [90]. Copyright 2015, AIP publishing.

Figure 17 A schematic defect band diagram of the defect levels for CZTSSe devices. Dashed lines are guides to the eye. Reprinted with permission from Ref. [119]. Copyright 2016, APS publishing.

under Cu-poor and Zn-rich conditions, which can help to suppress the formation of secondary phases, such as Cu-X, Sn-X, and Cu-Sn-X (X=S or Se). Meanwhile, V_{Cu} tends to form in CZTSSe under such conditions, helping increase the conductivity. The Sn content has also exhibited an important effect on the defect properties of CZTSSe thin films. Larramona *et al.* [101] eliminated the deep defect (V_{Sn} or Cn_{Sn}) centered at E_v+600 meV by fine-tuning the Sn content, and achieved 10.8% solar cell efficiency from a spray-deposition method. Haass *et al.* [52] proposed that there is complex interplay between the doped alkali elements and absorber composition, especially the Sn content. The most efficient solar cells doped with different alkali metals correspond to different optimized Sn compositions, and a champion device with 12.3% efficiency has been achieved. In the view that Sn-related defects are all deep defects, the influence mechanism of Sn component on CZTSSe needs to be further studied and controlled.

The complexity of kesterite means that, even in the most favorable cases, there are intrinsic harmful defects due to composition or processing issues. The extrinsic doping with iso-electronic elements has been introduced to compensate such defects. Research on Ag replacing Cu has received widespread attention in this regard [106,127–129]. The formation energy of Ag_{Zn} in Ag_2ZnSnS_4 (AZTS) is larger than that of Cu_{Zn} in CZTS, as well as the formation energies of related defect clusters, such as $[Ag_{Zn}+Zn_{Ag}]$ and $[2Ag_{Sn}+Sn_{Zn}]$ in AZTS [130]. Besides, the energy level of Ag- and Zn-related defects in AZTS is lower than that in CZTS. Therefore, Cu substitution by Ag in CZTSSe has been expected to suppress

the Cu/Zn disorder and associated band tail states. Qi *et al.* [51] reported that Ag_{Cu} substitution can decrease both the density and the energy level of Cu_{Zn} and Cu_{Sn} defects (Fig. 18a and b), and achieved an 11.2% efficiency for Ag-graded device. Cd doping was also applied in CZTSSe [131–134]. Although the theoretical calculation showed that replacing Zn with Cd cannot significantly reduce the formation energy of antisite defects or defect clusters [130], some studies have still exhibited that Cd-alloying has positive influence on the CZTSSe. Yan *et al.* [59] found that the E_U of Cd-alloying CZTS became smaller (Fig. 18c) and up to 11.5% efficiency solar cell was obtained. Sun *et al.* [58] showed that the activation energy of dominant defect turned from 118 meV in CZTSSe to 38 meV in Cd-alloying CZTSSe (Fig. 18d). Besides eliminating Cu/Zn disorder, approaches of replacing Sn with Ge were also developed to reduce the probability of formation of Sn-reduced species like Sn^{2+} that are commonly associated with deep defects. Kim *et al.* [61] prepared Ge-alloying CZTSe solar cell by co-evaporating Cu, Zn, Sn, Ge, and Se, which resulted in an improved minority lifetime and an efficiency of 12.3%. Neuschitzer *et al.* [135] analyzed Ge-alloying CZTSe samples, and found that appropriate Sn content can eliminate deep defects such as the Cu_{Sn} or V_{Sn} ($E_a=428$ meV), while excess Sn content can lead to the formation of other deep defects such as Sn_{Cu} and Ge_{Cu} ($E_a=438$ meV) that deteriorate the cell performance, as shown in Fig. 19. Despite these positive and valuable efforts, the efficiencies of the kesterite devices that incorporated element alloying have not yet broken through the maximum record of 12.6%.

Apart from the substitution of cations, alkaline element doping that is inherited from the CIGS field has also shown a strong positive impact on CZTSSe [136]. It was found that Na-doping can increase the carrier concentration of CZTSSe [137–139]. There are two compatible explanations for this phenomenon. The first is that the introduced Na atoms naturally occupy the Cu positions, replacing Zn in Zn_{Cu} antisite defects, thus decreasing the concentration of shallow donor and increasing the p-type conductivity [140]. Another possible explanation has considered the change in the alloying solubility of Na with temperature. Under the high temperature condition of the CZTSSe synthesis ($>500^\circ\text{C}$), Na is highly soluble in kesterite, occupying the Cu position. During the cooling process, Na solubility strongly decreases, separating out toward the grain boundaries and leaving V_{Cu} in the grains [141]. Besides Na, K-doping exhibited the similar result. Studies on the doping of the smallest-sized alkali metal Li indicated that the properties

Figure 18 (a) C-DLTS signals of $(Cu, Ag)_2ZnSn(S, Se)_4$ solar cells with different ratios of $Ag/(Ag+Cu)$. (b) Arrhenius plots corresponding to the peaks derived from C-DLTS spectra. Reprinted with permission from Ref. [106]. Copyright 2017, ACS publishing. (c) Absorption coefficients for CZTS and Cd-alloying CZTS (CZCTS) obtained from photothermal deflection spectroscopy. The inverse of the slope from the linear part below the band gap energy provides the E_U . Reprinted with permission from Ref. [59]. Copyright 2017, ACS publishing. (d) Defect density spectra derived from admittance spectra. Reprinted with permission from Ref. [58]. Copyright 2017, Elsevier.

of grain and grain boundary are affected simultaneously. Yang *et al.* [142] proposed that Li atoms can enter into the lattice to form $(Li, Cu)_2ZnSn(S, Se)_4$ alloy, and thus can adjust the bandgap value of the absorber. Xin *et al.* [47] observed that the contact potential difference at the grain boundaries turned from positive to negative after Li-doping, which may be caused by the formation of the insulating thin layer such as LiO_2 , LiS_2 , $LiSe_2$, and Li_2SnO_3 . In this case, the grain boundaries can act as the hole channel and electron barrier, which is considered to be superior to that where the grain boundaries act as the electron channel. After trying a variety of alkali metals, Haass *et al.* [52] obtained the highest efficiency of 12.3% by the Li-doping. The synergy effect of the above three methods, such as alkali metal+Sn [52], and Na+Ge [135,143], has also been studied. In our opinion, compared with these doping strategies, improving the fabrication technology of CZTSSe absorption layer is the most

direct and effective way to control the defects and enhance the efficiency. A systematic improvement of the preparation process is based on a deep understanding of the crystallization mechanism, which is another topic and we will not talk here.

CONCLUSION AND PERSPECTIVES

In this review, we present a systematical discussion about the efficiency loss-related atomic disorder and defect properties of the CZTSSe. Ever since the record efficiency of 12.6% in CZTSSe solar cell was realized by a hydrazine-based method in 2013, the efficiency has been experiencing a bottleneck with a V_{OC} deficit in the range of 0.57–0.62 V. However, the material and physics mechanism behind this giant voltage loss has not been clearly clarified until now. The large V_{OC} deficit was once believed to be associated with the prevalence of severe band tailing induced by atomic disorder. To understand

Figure 19 (a, c, e) Temperature-dependent admittance spectra and (b, d, f) defect spectra derived from them for CZTSe solar cells with different Ge doping quantities. Reprinted with permission from Ref. [135]. Copyright 2018, RSC publishing.

and resolve this issue, researchers have steered their study interest towards the Cu/Zn disorder, adjusting the disordering by long annealing, tracking the order level change by Raman spectra, and quantifying the bandgap fluctuations amplitude caused by Cu/Zn disorder. Recently, the research of deep defects in CZTSSe, especially the effective non-radiative recombination centers, has been on the rise. Theoretical calculations have shown that the lone-pair ($5s^2$) effect associated with Sn is responsible for both the deep defect levels and larger lattice distortions that facilitate the electron-hole non-radiative recombination. Nevertheless, this explanation still lacks direct experimental proof. Based on the findings about disorder and deep defects, we suggest that a synergy effect may exist between different defects in causing the charge recombination, that is, deep defects act as the killer de-

fects while Cu_{Zn} and Zn_{Cu} antisites assist fast charge capturing. Furthermore, the defect identification in the CZTSSe system has been summarized and discussed in this review. Although several shallow defects (V_{Cu} , Cu_{Zn} , Zn_{Sn}) and few deep defects (Cu_{Sn} , V_{Sn}) have been detected in the CZTSSe samples, the obtained defect information are still not enough to explain the extremely short carrier lifetime in kesterite. Many efforts have been made to suppress the detrimental defects in CZTSSe, doping isoelectronic/alkaline elements. Nonetheless, the record of the CZTSSe device is still waiting to break through.

Although numerous published studies have explored the defect properties of CZTSSe, there are still some important issues unresolved. The hidden mechanisms limiting the minority lifetime of the CZTSSe materials and the device voltage need to be further investigated.

Figure 20 Schematic diagram of the two ways to the “high efficiency” destination. The mountain background is a photo taken by a Chinese netizen [144].

The properties of different defects and their effects on the device performance have not been fully clarified yet. It is still a challenge to accurately evaluate the Cu/Zn disorder in film samples and the carrier capture cross-section of defects from experimental measurements to theoretical calculations. More new and independent methods are desired to be developed and exploited to probe the defect properties of the CZTSSe and to investigate the defect-related charge recombination processes. It is necessary to explore new experimental characterization methods and regulation methods, combining with complicated theoretical calculations and the establishment of mechanism models to deal with these problems, which is indeed a huge challenge, just like climbing a steep cliff, requiring the cooperation and efforts of numerous researchers. Nonetheless, there may be another way waiting to be discovered (Fig. 20 [144]), which can bypass this obstacle and then make it easier to reach our destination. We sincerely hope more and more research interest and resources can be focused on the study of CZTSSe solar cell. Overcoming the defect and efficiency limit of the CZTSSe device is not just an issue for the thin-film photovoltaic field, but more importantly has giant implications for the compound semiconductor science and technology.

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- 1 Burger B, Kiefer K, Kost C, *et al.* Photovoltaics Report. Freiburg: Fraunhofer ISE, 2019
- 2 Xiong S, Zhu M. Fundamentals and Applications of Solar Cells. 1st ed. Beijing: Science Press, 2007
- 3 Luque A, Hegedus S. Handbook of Photovoltaic Science and Engineering. 2nd ed. Chichester: Wiley, 2011

- 4 Polman A, Knight M, Garnett EC, *et al.* Photovoltaic materials: Present efficiencies and future challenges. *Science*, 2016, 352: aad4424
- 5 NREL. Best Research-Cell Efficiencies. <https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.pdf> (accessed 6 November, 2019)
- 6 Pthenakis V, Wang W, Kim HC. Life cycle inventory analysis of the production of metals used in photovoltaics. *Renew Sustain Energy Rev*, 2009, 13: 493–517
- 7 Chen S, Yang JH, Gong XG, *et al.* Intrinsic point defects and complexes in the quaternary kesterite semiconductor $\text{Cu}_2\text{ZnSnS}_4$. *Phys Rev B*, 2010, 81: 245204
- 8 Scragg JJ, Dale PJ, Peter LM, *et al.* New routes to sustainable photovoltaics: Evaluation of $\text{Cu}_2\text{ZnSnS}_4$ as an alternative absorber material. *Phys Stat Sol B*, 2008, 245: 1772–1778
- 9 Kamoun N, Bouzouita H, Rezig B. Fabrication and characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films deposited by spray pyrolysis technique. *Thin Solid Films*, 2007, 515: 5949–5952
- 10 Park D, Nam D, Jung S, *et al.* Optical characterization of $\text{Cu}_2\text{ZnSnSe}_4$ grown by thermal co-evaporation. *Thin Solid Films*, 2011, 519: 7386–7389
- 11 Zhang X, Han Y, Chai SZ, *et al.* Advances in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin film solar cells. *Acta Physico-Chim Sin*, 2016, 32: 1330–1346
- 12 Katagiri H, Saitoh K, Washio T, *et al.* Development of thin film solar cell based on $\text{Cu}_2\text{ZnSnS}_4$ thin films. *Sol Energy Mater Sol Cells*, 2001, 65: 141–148
- 13 Wang W, Winkler MT, Gunawan O, *et al.* Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. *Adv Energy Mater*, 2014, 4: 1301465
- 14 Fan Y, Qin H, Mi B, *et al.* Progress in the fabrication of $\text{Cu}_2\text{ZnSnS}_4$ thin film for solar cells. *Acta Chim Sin*, 2014, 72: 643–652
- 15 Siebentritt S. Why are kesterite solar cells not 20% efficient? *Thin Solid Films*, 2013, 535: 1–4
- 16 Mitzi DB, Gunawan O, Todorov TK, *et al.* The path towards a high-performance solution-processed kesterite solar cell. *Sol Energy Mater Sol Cells*, 2011, 95: 1421–1436
- 17 Yang KJ, Sim JH, Son DH, *et al.* Effects of the compositional ratio distribution with sulfurization temperatures in the absorber layer on the defect and surface electrical characteristics of $\text{Cu}_2\text{ZnSnS}_4$ solar cells. *Prog Photovolt-Res Appl*, 2015, 23: 1771–1784
- 18 Zhou H, Hsu WC, Duan HS, *et al.* CZTS nanocrystals: A promising approach for next generation thin film photovoltaics. *Energy Environ Sci*, 2013, 6: 2822–2838
- 19 Azimi H, Hou Y, Brabec CJ. Towards low-cost, environmentally friendly printed chalcopyrite and kesterite solar cells. *Energy Environ Sci*, 2014, 7: 1829–1849
- 20 Wang D, Zhao W, Zhang Y, *et al.* Path towards high-efficient kesterite solar cells. *J Energy Chem*, 2018, 27: 1040–1053
- 21 Kim J, Shin B. Strategies to reduce the open-circuit voltage deficit in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin film solar cells. *Electron Mater Lett*, 2017, 13: 373–392
- 22 Gao S, Jiang Z, Wu L, *et al.* Interfaces of high-efficiency kesterite $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin film solar cells. *Chin Phys B*, 2018, 27: 018803
- 23 Walsh A, Chen S, Wei SH, *et al.* Kesterite thin-film solar cells: Advances in materials modelling of $\text{Cu}_2\text{ZnSnS}_4$. *Adv Energy Mater*, 2012, 2: 400–409
- 24 Chen S, Walsh A, Yang JH, *et al.* Compositional dependence of structural and electronic properties of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ alloys for thin film solar cells. *Phys Rev B*, 2011, 83: 125201
- 25 Sun K, Huang J, Yan C, *et al.* Self-assembled nanometer-scale ZnS

- structure at the CZTS/ZnCdS heterointerface for high-efficiency wide band gap $\text{Cu}_2\text{ZnSnS}_4$ solar cells. *Chem Mater*, 2018, 30: 4008–4016
- 26 Gour KS, Parmar R, Kumar R, *et al.* Cd-free Zn(O,S) as alternative buffer layer for chalcogenide and kesterite based thin films solar cells: A review. *J Nanosci Nanotechnol*, 2020, 20: 3622–3635
 - 27 Yu J, Zheng Z, Dong L, *et al.* Effect of deposited temperatures of the buffer layer on the band offset of CZTS/ In_2S_3 heterostructure and its solar cell performance. *Chin Phys B*, 2017, 26: 046802
 - 28 Kim J, Hiroi H, Todorov TK, *et al.* High efficiency $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cells by applying a double $\text{In}_2\text{S}_3/\text{CdS}$ emitter. *Adv Mater*, 2014, 26: 7427–7431
 - 29 Scragg JJ, Wätjen JT, Edoff M, *et al.* A detrimental reaction at the molybdenum back contact in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin-film solar cells. *J Am Chem Soc*, 2012, 134: 19330–19333
 - 30 Shin B, Bojarczuk NA, Guha S. On the kinetics of MoSe_2 interfacial layer formation in chalcogen-based thin film solar cells with a molybdenum back contact. *Appl Phys Lett*, 2013, 102: 091907
 - 31 Yang KJ, Sim JH, Jeon B, *et al.* Effects of Na and MoS_2 on $\text{Cu}_2\text{ZnSnS}_4$ thin-film solar cell. *Prog Photovolt-Res Appl*, 2015, 23: 862–873
 - 32 Gao S, Zhang Y, Ao J, *et al.* Tailoring $\text{Mo}(\text{S,Se})_2$ structure for high efficient $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cells. *Sol Energy Mater Sol Cells*, 2018, 176: 302–309
 - 33 Li J, Zhang Y, Zhao W, *et al.* A temporary barrier effect of the alloy layer during selenization: Tailoring the thickness of MoSe_2 for efficient $\text{Cu}_2\text{ZnSnSe}_4$ solar cells. *Adv Energy Mater*, 2015, 5: 1402178
 - 34 Min X, Guo L, Yu Q, *et al.* Enhancing back interfacial contact by *in-situ* prepared MoO_3 thin layer for $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ solar cells. *Sci China Mater*, 2019, 62: 797–802
 - 35 Sun K, Yan C, Liu F, *et al.* Over 9% efficient kesterite $\text{Cu}_2\text{ZnSnS}_4$ solar cell fabricated by using $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ buffer layer. *Adv Energy Mater*, 2016, 6: 1600046
 - 36 Park J, Huang J, Yun J, *et al.* The role of hydrogen from ALD- Al_2O_3 in kesterite $\text{Cu}_2\text{ZnSnS}_4$ solar cells: Grain surface passivation. *Adv Energy Mater*, 2018, 8: 1701940
 - 37 Chen S, Walsh A, Gong XG, *et al.* Classification of lattice defects in the kesterite $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ earth-abundant solar cell absorbers. *Adv Mater*, 2013, 25: 1522–1539
 - 38 Gokmen T, Gunawan O, Todorov TK, *et al.* Band tailing and efficiency limitation in kesterite solar cells. *Appl Phys Lett*, 2013, 103: 103506
 - 39 Kumar MS, Madhusudanan SP, Batabyal SK. Substitution of Zn in earth-abundant $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ based thin film solar cells—A status review. *Sol Energy Mater Sol Cells*, 2018, 185: 287–299
 - 40 Moore JE, Hages CJ, Agrawal R, *et al.* The importance of band tail recombination on current collection and open-circuit voltage in CZTS solar cells. *Appl Phys Lett*, 2016, 109: 021102
 - 41 Bourdais S, Choné C, Delatouche B, *et al.* Is the Cu/Zn disorder the main culprit for the voltage deficit in kesterite solar cells? *Adv Energy Mater*, 2016, 6: 1502276
 - 42 Li J, Yuan ZK, Chen S, *et al.* Effective and noneffective recombination center defects in $\text{Cu}_2\text{ZnSnS}_4$: Significant difference in carrier capture cross sections. *Chem Mater*, 2018, 31: 826–833
 - 43 Kim S, Park JS, Walsh A. Identification of killer defects in kesterite thin-film solar cells. *ACS Energy Lett*, 2018, 3: 496–500
 - 44 Katagiri H. $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells. *Thin Solid Films*, 2005, 480–481: 426–432
 - 45 Jimbo K, Kimura R, Kamimura T, *et al.* $\text{Cu}_2\text{ZnSnS}_4$ -type thin film solar cells using abundant materials. *Thin Solid Films*, 2007, 515: 5997–5999
 - 46 Katagiri H, Jimbo K, Yamada S, *et al.* Enhanced conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ -based thin film solar cells by using preferential etching technique. *Appl Phys Express*, 2008, 1: 041201
 - 47 Xin H, Vorpahl SM, Collord AD, *et al.* Lithium-doping inverts the nanoscale electric field at the grain boundaries in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ and increases photovoltaic efficiency. *Phys Chem Chem Phys*, 2015, 17: 23859–23866
 - 48 Haass SG, Diethelm M, Werner M, *et al.* 11.2% efficient solution processed kesterite solar cell with a low voltage deficit. *Adv Energy Mater*, 2015, 5: 1500712
 - 49 Todorov TK, Tang J, Bag S, *et al.* Beyond 11% efficiency: Characteristics of state-of-the-art $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cells. *Adv Energy Mater*, 2013, 3: 34–38
 - 50 Duan B, Guo L, Yu Q, *et al.* Highly efficient solution-processed CZTS solar cells based on a convenient sodium-incorporated post-treatment method. *J Energy Chem*, 2020, 40: 196–203
 - 51 Qi YF, Kou DX, Zhou WH, *et al.* Engineering of interface band bending and defects elimination via a Ag-graded active layer for efficient $(\text{Cu,Ag})_2\text{ZnSn}(\text{S,Se})_4$ solar cells. *Energy Environ Sci*, 2017, 10: 2401–2410
 - 52 Haass SG, Andres C, Figi R, *et al.* Complex interplay between absorber composition and alkali doping in high-efficiency kesterite solar cells. *Adv Energy Mater*, 2017, 8: 1701760
 - 53 Cabas-Vidani A, Haass SG, Andres C, *et al.* High-efficiency $(\text{Li}_x\text{Cu}_{1-x})_2\text{ZnSn}(\text{S,Se})_4$ kesterite solar cells with lithium alloying. *Adv Energy Mater*, 2018, 8: 1801191
 - 54 Lee YS, Gershon T, Gunawan O, *et al.* $\text{Cu}_2\text{ZnSnSe}_4$ thin-film solar cells by thermal co-evaporation with 11.6% efficiency and improved minority carrier diffusion length. *Adv Energy Mater*, 2015, 5: 1401372
 - 55 Kim SY, Son DH, Kim YI, *et al.* Void and secondary phase formation mechanisms of CZTS solar cells using Sn/Cu/Zn/Mo stacked elemental precursors. *Nano Energy*, 2019, 59: 399–411
 - 56 Yang KJ, Son DH, Sung SJ, *et al.* A band-gap-graded CZTS solar cell with 12.3% efficiency. *J Mater Chem A*, 2016, 4: 10151–10158
 - 57 Yan C, Huang J, Sun K, *et al.* $\text{Cu}_2\text{ZnSnS}_4$ solar cells with over 10% power conversion efficiency enabled by heterojunction heat treatment. *Nat Energy*, 2018, 3: 764–772
 - 58 Sun R, Zhuang D, Zhao M, *et al.* Beyond 11% efficient $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin film solar cells by cadmium alloying. *Sol Energy Mater Sol Cells*, 2018, 174: 494–498
 - 59 Yan C, Sun K, Huang J, *et al.* Beyond 11% efficient sulfide kesterite $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ solar cell: Effects of cadmium alloying. *ACS Energy Lett*, 2017, 2: 930–936
 - 60 Son DH, Kim SH, Kim SY, *et al.* Effect of solid- H_2S gas reactions on CZTS thin film growth and photovoltaic properties of a 12.62% efficiency device. *J Mater Chem A*, 2019, 7: 25279–25289
 - 61 Kim S, Kim KM, Tampo H, *et al.* Improvement of voltage deficit of Ge-incorporated kesterite solar cell with 12.3% conversion efficiency. *Appl Phys Express*, 2016, 9: 102301
 - 62 Giraldo S, Saucedo E, Neuschitzer M, *et al.* How small amounts of Ge modify the formation pathways and crystallization of kesterites. *Energy Environ Sci*, 2018, 11: 582–593
 - 63 Green MA, Dunlop ED, Levi DH, *et al.* Solar cell efficiency tables (version 54). *Prog Photovolt Res Appl*, 2019, 27: 565–575
 - 64 Kim SY, Rana TR, Kim JH, *et al.* Limiting effects of conduction band offset and defect states on high efficiency CZTS solar cell.

- [Nano Energy](#), 2018, 45: 75–83
- 65 Shockley W, Queisser HJ. Detailed balance limit of efficiency of p - n junction solar cells. [J Appl Phys](#), 1961, 32: 510–519
- 66 Sze SM, Ng KK. Physics of Semiconductor Devices. 3rd ed. Hoboken: Wiley, 2006
- 67 Tai KF, Gershon T, Gunawan O, *et al.* Examination of electronic structure differences between CIGS_{Se} and CZTS_{Se} by photoluminescence study. [J Appl Phys](#), 2015, 117: 235701
- 68 Romero MJ, Du H, Teeter G, *et al.* Comparative study of the luminescence and intrinsic point defects in the kesterite Cu₂ZnSnS₄ and chalcopyrite Cu(In,Ga)Se₂ thin films used in photovoltaic applications. [Phys Rev B](#), 2011, 84: 165324
- 69 Shin D, Saparov B, Mitzi DB. Defect engineering in multinary earth-abundant chalcogenide photovoltaic materials. [Adv Energy Mater](#), 2017, 7: 1602366
- 70 Gershon T, Shin B, Bojarczuk N, *et al.* Photoluminescence characterization of a high-efficiency Cu₂ZnSnS₄ device. [J Appl Phys](#), 2013, 114: 154905
- 71 Shklovskii BI, Efros AL. Electronic Properties of Doped Semiconductors. 1st ed. Berlin: Springer, 1984
- 72 Dirnstorfer I, Wagner M, Hofmann DM, *et al.* Characterization of CuIn(Ga)Se₂ Thin Films. [Phys Stat Solidi A](#), 1998, 168: 163–175
- 73 Mattheis J, Rau U, Werner JH. Light absorption and emission in semiconductors with band gap fluctuations—A study on Cu(In,Ga)Se₂ thin films. [J Appl Phys](#), 2007, 101: 113519
- 74 Khare A, Himmetoglu B, Johnson M, *et al.* Calculation of the lattice dynamics and Raman spectra of copper zinc tin chalcogenides and comparison to experiments. [J Appl Phys](#), 2012, 111: 083707
- 75 Chen S, Gong XG, Walsh A, *et al.* Crystal and electronic band structure of Cu₂ZnSnX₄ (X=S and Se) photovoltaic absorbers: First-principles insights. [Appl Phys Lett](#), 2009, 94: 041903
- 76 Schorr S. The crystal structure of kesterite type compounds: A neutron and X-ray diffraction study. [Sol Energy Mater Sol Cells](#), 2011, 95: 1482–1488
- 77 Choubrac L, Paris M, Lafond A, *et al.* Multinuclear (⁶⁷Zn, ¹¹⁹Sn and ⁶⁵Cu) NMR spectroscopy—an ideal technique to probe the cationic ordering in Cu₂ZnSnS₄ photovoltaic materials. [Phys Chem Chem Phys](#), 2013, 15: 10722–10725
- 78 Schorr S, Hoebler HJ, Tovar M. A neutron diffraction study of the stannite-kesterite solid solution series. [ejm](#), 2007, 19: 65–73
- 79 Bragg WL, Williams EJ. The effect of thermal agitation on atomic arrangement in alloys. [Proc R Soc Lond A](#), 1934, 145: 699–730
- 80 Vineyard GH. Theory of order-disorder kinetics. [Phys Rev](#), 1956, 102: 981–992
- 81 Scragg JJS, Choubrac L, Lafond A, *et al.* A low-temperature order-disorder transition in Cu₂ZnSnS₄ thin films. [Appl Phys Lett](#), 2014, 104: 041911
- 82 Valakh MY, Dzhagan VM, Babichuk IS, *et al.* Optically induced structural transformation in disordered kesterite Cu₂ZnSnS₄. [JETP Lett](#), 2013, 98: 255–258
- 83 Rey G, Redinger A, Sessler J, *et al.* The band gap of Cu₂ZnSnSe₄: Effect of order-disorder. [Appl Phys Lett](#), 2014, 105: 112106
- 84 Huang D, Persson C. Band gap change induced by defect complexes in Cu₂ZnSnS₄. [Thin Solid Films](#), 2013, 535: 265–269
- 85 Scragg JJS, Larsen JK, Kumar M, *et al.* Cu-Zn disorder and band gap fluctuations in Cu₂ZnSn(S,Se)₄: Theoretical and experimental investigations. [Phys Status Solidi B](#), 2016, 253: 247–254
- 86 Rau U, Werner JH. Radiative efficiency limits of solar cells with lateral band-gap fluctuations. [Appl Phys Lett](#), 2004, 84: 3735–3737
- 87 Roelofs KE, Guo Q, Subramoney S, *et al.* Investigation of local compositional uniformity in Cu₂ZnSn(S,Se)₄ thin film solar cells prepared from nanoparticle inks. [J Mater Chem A](#), 2014, 2: 13464–13470
- 88 De Wolf S, Holovsky J, Moon SJ, *et al.* Organometallic halide perovskites: Sharp optical absorption edge and its relation to photovoltaic performance. [J Phys Chem Lett](#), 2014, 5: 1035–1039
- 89 Miller DW, Warren CW, Gunawan O, *et al.* Electronically active defects in the Cu₂ZnSn(S,Se)₄ alloys as revealed by transient photocapacitance spectroscopy. [Appl Phys Lett](#), 2012, 101: 142106
- 90 Islam MM, Halim MA, Sakurai T, *et al.* Determination of deep-level defects in Cu₂ZnSn(S,Se)₄ thin-films using photocapacitance method. [Appl Phys Lett](#), 2015, 106: 243905
- 91 Gokmen T, Gunawan O, Mitzi DB. Minority carrier diffusion length extraction in Cu₂ZnSn(S,Se)₄ solar cells. [J Appl Phys](#), 2013, 114: 114511
- 92 Gunawan O, Todorov TK, Mitzi DB. Loss mechanisms in hydrazine-processed Cu₂ZnSn(S,Se)₄ solar cells. [Appl Phys Lett](#), 2010, 97: 233506
- 93 Kumar M, Dubey A, Adhikari N, *et al.* Strategic review of secondary phases, defects and defect-complexes in kesterite CZTS-Se solar cells. [Energy Environ Sci](#), 2015, 8: 3134–3159
- 94 Shockley W, Read WT. Statistics of the recombinations of holes and electrons. [Phys Rev](#), 1952, 87: 835–842
- 95 Hall RN. Electron-hole recombination in germanium. [Phys Rev](#), 1952, 87: 387–387
- 96 Alkauskas A, Yan Q, Van de Walle CG. First-principles theory of nonradiative carrier capture *via* multiphonon emission. [Phys Rev B](#), 2014, 90: 075202
- 97 Li J, Zhu HF, Zhang YY, *et al.* Large carrier-capture rate of PbI antisite in CH₃NH₃PbI₃ induced by heavy atoms and soft phonon modes. [Phys Rev B](#), 2017, 96: 104103
- 98 Kubo R, Toyozawa Y. Application of the method of generating function to radiative and non-radiative transitions of a trapped electron in a crystal. [Prog Theor Phys](#), 1955, 13: 160–182
- 99 Huang K. Lattice relaxation and multiphonon transitions. [Contemp Phys](#), 2006, 22: 599–612
- 100 Kim S, Park JS, Hood SN, *et al.* Lone-pair effect on carrier capture in Cu₂ZnSnS₄ solar cells. [J Mater Chem A](#), 2019, 7: 2686–2693
- 101 Larramona G, Levchenko S, Bourdais S, *et al.* Fine-tuning the Sn content in CZTS_{Se} thin films to achieve 10.8% solar cell efficiency from spray-deposited water-ethanol-based colloidal inks. [Adv Energy Mater](#), 2015, 5: 1501404
- 102 Min X, Shi J, Guo L, *et al.* Regulation of Zn/Sn ratio in kesterite absorbers to boost 10% efficiency of Cu₂ZnSn(S,Se)₄ solar cells. [Chin Phys B](#), 2018, 27: 016402
- 103 Lang DV. Deep-level transient spectroscopy: A new method to characterize traps in semiconductors. [J Appl Phys](#), 1974, 45: 3023–3032
- 104 Yang D. Semiconductor Materials Testing and Analysis. 1st ed. Beijing: Science Press, 2014
- 105 Das S, Chaudhuri SK, Bhattacharya RN, *et al.* Defect levels in Cu₂ZnSn(S_xSe_{1-x})₄ solar cells probed by current-mode deep level transient spectroscopy. [Appl Phys Lett](#), 2014, 104: 192106
- 106 Qi Y, Tian Q, Meng Y, *et al.* Elemental precursor solution processed (Cu_{1-x}Ag_x)₂ZnSn(S,Se)₄ photovoltaic devices with over 10% efficiency. [ACS Appl Mater Interfaces](#), 2017, 9: 21243–21250

- 107 Campbell S, Qu Y, Major JD, *et al.* Direct evidence of causality between chemical purity and band-edge potential fluctuations in nanoparticle ink-based $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells. *J Phys D-Appl Phys*, 2019, 52: 135102
- 108 Fernandes PA, Sartori AF, Salomé PMP, *et al.* Admittance spectroscopy of $\text{Cu}_2\text{ZnSnS}_4$ based thin film solar cells. *Appl Phys Lett*, 2012, 100: 233504
- 109 Gunawan O, Gokmen T, Warren CW, *et al.* Electronic properties of the $\text{Cu}_2\text{ZnSn}(\text{Se},\text{S})_4$ absorber layer in solar cells as revealed by admittance spectroscopy and related methods. *Appl Phys Lett*, 2012, 100: 253905
- 110 Duan HS, Yang W, Bob B, *et al.* The role of sulfur in solution-processed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ and its effect on defect properties. *Adv Funct Mater*, 2013, 23: 1466–1471
- 111 Luckert F, Hamilton DI, Yakushev MV, *et al.* Optical properties of high quality $\text{Cu}_2\text{ZnSnSe}_4$ thin films. *Appl Phys Lett*, 2011, 99: 062104
- 112 Grossberg M, Krustok J, Raudoja J, *et al.* The role of structural properties on deep defect states in $\text{Cu}_2\text{ZnSnS}_4$ studied by photoluminescence spectroscopy. *Appl Phys Lett*, 2012, 101: 102102
- 113 Kask E, Grossberg M, Josepson R, *et al.* Defect studies in $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSn}(\text{Se}_{0.75}\text{S}_{0.25})_4$ by admittance and photoluminescence spectroscopy. *Mater Sci Semiconductor Processing*, 2013, 16: 992–996
- 114 Walter T, Herberholz R, Müller C, *et al.* Determination of defect distributions from admittance measurements and application to $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ based heterojunctions. *J Appl Phys*, 1996, 80: 4411–4420
- 115 Enkhbat T, Kim SY, Kim JH. Device characteristics of band gap tailored 10.04% efficient CZTSSe solar cells sprayed from water-based solution. *ACS Appl Mater Interfaces*, 2019, 11: 36735–36741
- 116 Lee J, Giles NC, Rajavel D, *et al.* Donor-acceptor pair luminescence involving the iodine A center in CdTe. *J Appl Phys*, 1995, 78: 5669–5674
- 117 Krustok J, Collan H, Hjelt K. Does the low-temperature Arrhenius plot of the photoluminescence intensity in CdTe point towards an erroneous activation energy? *J Appl Phys*, 1997, 81: 1442–1445
- 118 Cohen JD, Unold T, Gelatos AV, *et al.* Deep defect structure and carrier dynamics in amorphous silicon and silicon-germanium alloys determined by transient photocapacitance methods. *J Non-Crystalline Solids*, 1992, 141: 142–154
- 119 Levchenko S, Just J, Redinger A, *et al.* Deep defects in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells with varying Se content. *Phys Rev Appl*, 2016, 5: 024004
- 120 Chen R, Persson C. Electronic and optical properties of Cu_2XSnS_4 ($\text{X} = \text{Be}, \text{Mg}, \text{Ca}, \text{Mn}, \text{Fe}, \text{and Ni}$) and the impact of native defect pairs. *J Appl Phys*, 2017, 121: 203104
- 121 Xiao Z, Meng W, Li JV, *et al.* Distant-atom mutation for better earth-abundant light absorbers: A case study of $\text{Cu}_2\text{BaSnSe}_4$. *ACS Energy Lett*, 2016, 2: 29–35
- 122 Cui Y, Deng R, Wang G, *et al.* A general strategy for synthesis of quaternary semiconductor Cu_2MSnS_4 ($\text{M} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$) nanocrystals. *J Mater Chem*, 2012, 22: 23136
- 123 Li X, Hou Z, Gao S, *et al.* Efficient optimization of the performance of Mn^{2+} -doped kesterite solar cell: Machine learning aided synthesis of high efficient $\text{Cu}_2(\text{Mn},\text{Zn})\text{Sn}(\text{S},\text{Se})_4$ solar cells. *Sol RRL*, 2018, 2: 1800198
- 124 Xiao W, Wang JN, Zhao XS, *et al.* Intrinsic defects and Na doping in $\text{Cu}_2\text{ZnSnS}_4$: A density-functional theory study. *Sol Energy*, 2015, 116: 125–132
- 125 Altamura G, Vidal J. Impact of minor phases on the performances of CZTSSe thin-film solar cells. *Chem Mater*, 2016, 28: 3540–3563
- 126 Katagiri H, Jimbo K, Tahara M, *et al.* The influence of the composition ratio on CZTS-based thin film solar cells. *MRS Proc*, 2009, 1165: M04
- 127 Gershon T, Lee YS, Antunez P, *et al.* Photovoltaic materials and devices based on the alloyed kesterite absorber $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnSe}_4$. *Adv Energy Mater*, 2016, 6: 1502468
- 128 Guchhait A, Su Z, Tay YF, *et al.* Enhancement of open-circuit voltage of solution-processed $\text{Cu}_2\text{ZnSnS}_4$ solar cells with 7.2% efficiency by incorporation of silver. *ACS Energy Lett*, 2016, 1: 1256–1261
- 129 Qi Y, Liu Y, Kou D, *et al.* Enhancing grain growth for efficient solution-processed $(\text{Cu},\text{Ag})_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells based on acetate precursor. *ACS Appl Mater Interfaces*, 2020, 12: 14213–14223
- 130 Yuan ZK, Chen S, Xiang H, *et al.* Engineering solar cell absorbers by exploring the band alignment and defect disparity: The case of Cu- and Ag-based kesterite compounds. *Adv Funct Mater*, 2015, 25: 6733–6743
- 131 Su Z, Tan JMR, Li X, *et al.* Cation substitution of solution-processed $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cell with over 9% efficiency. *Adv Energy Mater*, 2015, 5: 1500682
- 132 Fu J, Tian Q, Zhou Z, *et al.* Improving the performance of solution-processed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ photovoltaic materials by Cd^{2+} substitution. *Chem Mater*, 2016, 28: 5821–5828
- 133 Sun K, Yan C, Huang J, *et al.* Minority lifetime and efficiency improvement for CZTS solar cells via Cd ion soaking and post treatment. *J Alloys Compd*, 2018, 750: 328–332
- 134 Yan Q, Cheng S, Yu X, *et al.* Mechanism of current shunting in flexible $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{Sn}(\text{S},\text{Se})_4$ solar cells. *Sol RRL*, 2020, 4: 1900410
- 135 Neuschitzer M, Rodriguez ME, Guc M, *et al.* Revealing the beneficial effects of Ge doping on $\text{Cu}_2\text{ZnSnSe}_4$ thin film solar cells. *J Mater Chem A*, 2018, 6: 11759–11772
- 136 Salomé PMP, Rodriguez-Alvarez H, Sadewasser S. Incorporation of alkali metals in chalcogenide solar cells. *Sol Energy Mater and Sol Cells*, 2015, 143: 9–20
- 137 Zhou H, Song TB, Hsu WC, *et al.* Rational defect passivation of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ photovoltaics with solution-processed $\text{Cu}_2\text{ZnSnS}_4\text{:Na}$ nanocrystals. *J Am Chem Soc*, 2013, 135: 15998–16001
- 138 Yang Y, Kang X, Huang L, *et al.* Facile and low-cost sodium-doping method for high-efficiency $\text{Cu}_2\text{ZnSnSe}_4$ thin film solar cells. *J Phys Chem C*, 2015, 119: 22797–22802
- 139 Li JV, Kuciauskas D, Young MR, *et al.* Effects of sodium incorporation in co-evaporated $\text{Cu}_2\text{ZnSnSe}_4$ thin-film solar cells. *Appl Phys Lett*, 2013, 102: 163905
- 140 Giraldo S, Jehl Z, Placidi M, *et al.* Progress and perspectives of thin film kesterite photovoltaic technology: A critical review. *Adv Mater*, 2019, 31: 1806692
- 141 Yuan ZK, Chen S, Xie Y, *et al.* Na-diffusion enhanced p-type conductivity in $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$: A new mechanism for efficient doping in semiconductors. *Adv Energy Mater*, 2016, 6: 1601191
- 142 Yang Y, Kang X, Huang L, *et al.* Tuning the band gap of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ thin films via lithium alloying. *ACS Appl Mater Interfaces*, 2016, 8: 5308–5313
- 143 Becerril-Romero I, Acebo L, Oliva F, *et al.* CZTSe solar cells

developed on polymer substrates: Effects of low-temperature processing. *Prog Photovolt Res Appl*, 2018, 26: 55–68

144 Lvmama, <http://www.lvmama.com/comment/3465012>

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Conflict of interest The authors declare that they have no conflict of interest.

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基于原子无序和深缺陷态分析铜锌锡硫硒太阳能电池效率损失的机理

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摘要 铜锌锡硫硒(CZTSSe)是具有前景的薄膜光伏材料,但目前其太阳能电池的效率仍受限于较大的开路电压损失.近年来,研究者们对CZTSSe太阳能电池效率损失的机理进行了一系列研究,但尚未有令人信服的结论.本综述对有关CZTSSe太阳能电池效率损失的潜在机理的研究结果进行了系统的总结和分析.讨论了CZTSSe材料中原子无序和深能级缺陷态的特征及其对器件性能的影响.提出了协同效应以辅助理解吸收层中缺陷态相关的电荷损失.此外,总结了缺陷态识别和调控的实验方法,并试图找到可导致CZTSSe中极短的少子寿命的关键缺陷态.通过全面和辩证地理解CZTSSe太阳能电池的缺陷特性,我们相信在研究人员的不懈努力下电池效率将很快有新的突破.