Unveiling microscopic carrier loss mechanisms in 12% efficient $\text{Cu}_2\text{ZnSnSe}_4$ solar cells

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Unveiling microscopic carrier loss mechanisms in 12% efficient $\text{Cu}_2\text{ZnSnSe}_4$ solar cells

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Abstract

Carrier loss mechanisms at microscopic regions is imperative for high-performance polycrystalline inorganic thin-film solar cells. Despite the progress on Kesterite, a promising environmental-benign and earth-abundant thin-film photovoltaic material, the microscopic carrier loss mechanisms and their impact on device performance remain unknown. Herein, we unveil these mechanisms in state-of-the-art $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) solar cells using a framework that links microscopic-structural and optoelectronic characterizations with three-dimensional device simulations. The results indicate the CZTSe films have an encouraging intragrain minority carrier lifetime of >10 ns, a marginal radiative recombination loss

through sub-band recombination and electrostatic potential fluctuation, whilst a large effective grain boundary recombination velocity of around 10^4 cm s^{-1} and a low net carrier density of $\sim 1 \times 10^{15} \text{ cm}^{-3}$. We identify that severe grain boundary recombination and low net carrier density are the current limiting factors of device performance. The established framework can greatly advance the research of kesterite and other emerging photovoltaic materials.

Introduction

Photovoltaics have been identified as the most attractive renewable energy that can be used to mitigate the escalating global climate change.¹ Large scale deployments of photovoltaic energy require stable, abundant, and low-toxic materials similar to silicon (Si),² which has stimulated the worldwide interest in new inorganic photovoltaic materials such as chalcogenides, oxides, pnictides, and halides.³⁻⁶ Kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has emerged as one of the most compelling candidates due to its stable structure, abundancy, environmental benefits, and its large potential for high power conversion efficiency (PCE).^{7, 8} Although, CZTSSe solar cells have reached the highest PCE (12.6% to 13.0 %) among the thermodynamically stable emerging inorganic materials,⁹⁻¹¹ their PCE is still far from a commercialization-viable level.

To allow low-cost processing, CZTSSe like many other emerging inorganic solar cells, often uses polycrystalline thin-films as light absorbers and follows the heterojunction architecture.⁴ This device architecture accommodates a significant amount of imperfect crystalline structures, mainly grain boundaries (GBs) and grain surfaces. At these regions, dangling bonds, elastic strain fields, and atomic composition segregations may introduce electronic states within the energy bandgap with higher density than that in the grain interiors (GIs).¹² These bandgap states may act as carrier traps and/or effective recombination centers depending on their transition energy level and relative capture cross-section for

holes and electrons, thus, imposing serious limitations to the minority carrier lifetime and carrier mobilities.¹³ Consequently, the photovoltaic performance of polycrystalline absorbers is usually inferior to that of crystalline absorbers^{14, 15}, unless the grain boundaries and grain surfaces are electrical-benign, like the case of hybrid halide perovskite¹⁶, or can be well passivated such as in the cases of CdTe and CuInGa(S,Se)₂ (CIGSSe)¹⁷⁻²⁰. Therefore, understanding the carrier loss mechanisms at these microscopic regions is imperative for achieving high-performance CZTSSe and other emerging inorganic thin-film solar cells.

Despite the critical importance of these microscopic carrier loss mechanisms in inorganic materials, the number of investigations regarding these processes is rather limited. For CZTSSe, due to the multiple competitive secondary phases and complex intrinsic defect system,²¹ most efforts have been paid to the bulk and heterojunction interfaces, through modifications of the chemical composition and growth conditions,²²⁻²⁵ extrinsic cation/alkali doping or alloying,^{7, 26, 27} alternative buffer materials,^{28, 29} or interface passivation.³⁰⁻³² Although some properties of the GIs and GBs such as intragrain crystallinity defects and band bending at the GBs have been investigated using high-resolution structural and electrical analysis respectively,^{33, 34} detailed loss mechanisms in these microscopic regions especially GB recombination and grain interior carrier lifetime, and their impact on the device performance remain unknown. This, as a critical gap between the understanding of CZTSSe and its mature cousins CdTe and CIGSSe, can be one of the key origins of the efficiency stagnation of CZTSSe in recent years, thus requiring comprehensive investigation urgently.

Herein, we unveil the microscopic carrier loss mechanisms in state-of-the-art efficiency selenide-kesterite Cu₂ZnSnSe₄ (CZTSe) solar cells by establishing a framework that links micro-structural and optoelectronic characterizations with three-dimensional (3D) device simulations. We show that the GB recombination limits the effective carrier lifetime of bulk kesterite. The associated GB recombination

velocity of kesterite, at a level of 10^4 cm s^{-1} , is 1-2 orders of magnitude larger than that of CIGSSe and CdTe.^{35 36} The intragrain minority carrier lifetime is estimated to be $>10 \text{ ns}$ while the net carrier density is around $1 \times 10^{15} \text{ cm}^{-3}$. It seems that the well-recognized open-circuit voltage (V_{OC}) losses due to electrostatic potential fluctuation and bandgap fluctuation are actually small. Instead, the dominating loss mechanisms of current state-of-the-art CZTSe solar cells are associated with the severe non-radiative recombination at GBs and the relatively low net carrier density.

Results

Photovoltaic performance and absorber structure

We used CZTSe absorbers fabricated by the same method used for our reported 12.5% record CZTSe cells.²² Details of the fabrication processes can be found in the Methods section. The solar cells fabricated on these absorbers achieve PCEs between 11.0% to 12.5% and an average PCE of 11.8% (**Figure S1**), representing state-of-the-art performance. **Figure 1a** and **1b** show the current density-voltage (J-V) and external quantum efficiency (EQE) of one of the best devices used for characterizations in this study. The total area (0.24 cm^2) efficiency is 12.45 %, with a V_{OC} of 479 mV, a fill factor (FF) of 70.45%, and a short-circuit current density (J_{SC}) of 36.9 mA/cm^2 (integrated J_{SC} from EQE is 37.0 mA/cm^2). The diode ideality factor (A) extracted from corresponding dark J-V data is 1.4 and the diode reverse saturation current (J_0) is $8.1 \times 10^{-8} \text{ A/cm}^2$ (**Figure S2**). The J_{SC} is much lower than the previous 11.6% efficiency record CZTSe device from IBM (40.6 mA/cm^2),³⁷ which could be attributed to the relatively low transmittance of the window layer at the long wavelength region, as discussed in our previous work,²² and the recombination in the microscopic regions as will be discussed in the following sections.

On the top, the CZTSe absorber shows large and compact grains ($> 1 \mu\text{m}$) while at the bottom the grains are smaller and voids can be seen (**Figure 1c**). The secondary ion mass spectroscopy (SIMS) depth profile

(**Figure 1d**) indicates the CZTSe absorber has a high Zn concentration at the surface and high Sn concentration at the bottom. Segregations of Zn (probably ZnSe) could be observed at both the top and the bottom of the CZTSe film in the energy-dispersive X-ray spectroscopy (EDXS) mapping (**Figure 1e**). Many Sn-rich small grains (probably SnSe_x) and Cu-rich grains (probably Cu_{2-x}Se) can be noticed at the bottom region near the MoSe_2 layer, in agreement with the SIMS profile. The signal of Cd is fully confined between CZTSe and ZnO, showing no significant diffusion into the CZTSe absorber or GBs.

Figure 1. Device performance, morphology, and element distribution. J-V (a) and EQE (b) measurements of one of the best CZTSe cells with total area (0.24 cm^2) efficiency of 12.45% with antireflection coating. c Cross-section SEM image. d Element SIMS depth profile of the CZTSe absorber. e The cross-section TEM image and the corresponding EDXS element mapping of Cu, Zn, Sn, Se, Mo, Cd, and Mg. The cross-section TEM sample was prepared with a focused ion beam (FIB).

Carrier transport at front and rear interfaces

Results of surface Raman mapping on a $40 \times 40 \text{ }\mu\text{m}^2$ bare CZTSe absorber indicate that the front surface of the CZTSe absorber may be fully covered with a ZnSe layer (**Figures 2 a-c**). Further high-resolution TEM (HRTEM; **Figure 2d**) shows the presence of a locally epitaxially grown 8-12 nm thick ZnSe nano-layer (confirmed by EDS line-scan, **Figure S3**) along with the (200) orientation. With the almost identical (200) interplanar spacing between CZTSe and ZnSe (0.283 nm, **Figure 2d**), no dislocation is observed at the CZTSe/ZnSe interface, indicating a near-perfect CZTSe/ZnSe heterointerface with largely suppressed interfacial lattice defects. In comparison, the CZTSe absorber without this ZnSe nano layer shows a high density of dislocations at the CZTSe/CdS heterointerface (**Figure S4**). Additionally, ZnSe has a wide bandgap of 2.7 eV,³⁸ with a conduction band minimum (CBM) 0.86 eV higher and a valence band maximum (VBM) 0.78 eV lower than that of CZTSe.²³ These large electron and hole barriers could repel electrons and holes respectively, preventing them from recombining at the heterojunction interface, i.e., effectively suppressing interfacial recombination. On the other hand, due to the large “spike-like” conduction band offset (CBO, 0.86 eV) at the ZnSe/CZTSe interface, transport of the photogenerated electrons across this interface may rely on the tunnelling process with the assistance of the built-in electric field and thermal energy. It is noted that a continuous ZnSe layer with 8-12 nm thickness may block the electron current as tunneling would be very difficult under this condition. Fortunately, in the large scale, the thickness of ZnSe nano layer has a significant fluctuation as indicated by the varying ZnSe signal intensity in the Raman mapping, which facilitates electron transport across the CZTSe/ZnSe interface.

We performed temperature-dependent I-V measurements to further investigate the carrier transport and recombination at the front and rear interfaces (**Figure S5**). **Figure 2e** shows the temperature-dependent A extracted from the dark J-V curves. A is larger than 2 when the temperature is lower than 200 K, suggesting that the device does not behave as an ideal diode in this temperature region.³⁹ One possible explanation is that the tunnelling transport process at the CZTSe/ZnSe/CdS heterostructure starts to limit the current when the temperature is lower than 200 K. This limitation is more severe when the temperature is lower because of the lack of sufficient thermal energy that is required for the tunnelling transport.⁴⁰ Since the A is around 1.5 without significant change when the device temperature is within the range of 260–320 K, the device behaves like an ideal diode in this temperature region. Therefore, it is possible to extract the recombination activation energy, E_A , within this temperature region using the ideal one diode model:⁴¹

$$V_{OC} = \frac{E_A}{q} - \frac{Ak_B T}{q} \ln \left(\frac{J_{00}}{J_L} \right), \quad (1)$$

where q is the unit charge, k_B is the Boltzmann's constant, T is the temperature, J_{00} is the prefactor of diode current, and J_L is the photocurrent. Here, J_{00} , J_L , and E_A are assumed to be weakly temperature-dependent in the temperature region used for fitting.⁴¹ The temperature-dependent V_{OC} shows good linear behavior in this temperature region (**Figure 2f**) and the fitted E_A is 1.025 ± 0.005 eV, well aligned to the bandgap of the CZTSe absorber (1.03 eV, **Figure S6**). This indicates that the E_A deficit compared to E_g is no longer a limitation in these CZTSe devices, owing to the passivated heterojunction interface by the epitaxial ZnSe nano-layer and the suppressed bandgap/potential fluctuation as reported previously.²²

The blocking barrier height of the back contact interface is derived from the temperature dependent series resistance (R_s) over the 200 ~ 320 K temperature range where the device behaves consistently with the thermal emission model.^{42, 43} The fitted barrier height is only 11 ± 5 meV (**Figure 2g**), much smaller than the previously reported value,^{44, 45} indicating a quasi-ohmic contact at the back contact interface. This

greatly contributes to the relatively high FF of over 70%, indicating that the fine grain layer at the bottom of the CZTSe layer is not a significant limitation to the back contact resistance. This is highly likely as the involved Cu_{2-x}Se and SnSe_x phases at the back contact interface are known to be heavily doped p-type materials, allowing for good conductance.^{46,47}

Figure 2. Structure and carrier transport performances of the front and rear interfaces. **a** and **b** Color coded Raman mapping at peak positions of 196 cm^{-1} (A mode of CZTSe) and 250 cm^{-1} (A1 mode of ZnSe), respectively. **c** Average Raman spectrum of the mapping. The Raman mapping was performed using 441 nm He-Cd laser as excitation. **d** HRTEM image and the color-coded inverse fast Fourier transformation (FFT) images of the selected reflections revealing the dislocations (T marked) at the CZTSe/ZnSe/CdS heterointerface. The yellow dashed lines roughly indicate the boundaries of different phases. **e** Temperature-dependent series resistance (R_s) and diode ideality factor extracted from temperature dependent J-V curves (**Figure S5**). The black dashed line indicates the boundary between the ideal device region and nonideal device region. **f** Plot of V_{oc} vs. temperature and the linear fit of the recombination activation energy E_A . The data of blue dots are selected for fitting. **g** Plot of $\ln(R_s T)$ vs. $1/T$ and the linear fitting showing back contact barrier height.

Carrier collection behavior at GBs and GIs

We performed electron beam induced current (EBIC) measurement to directly investigate the carrier collection in the CZTSe solar cell. **Figures 3 a** and **b** show the SEM and EBIC images of the corresponding cross-section of the CZTSe solar cell at a beam energy of 5 keV. The high spatial resolution of the EBIC image enables us to further investigate the electron transport across the GBs. It is noteworthy that the CZTSe grains underneath near-horizontal GBs, not directly connected to the buffer layer (indicated by the yellow and red frames in **Figures 3 a** and **b**), do not contribute to the EBIC signal. This indicates significant recombination and/or a carrier transport barrier may exist near these GBs or inside these grains, which may be responsible for the additional J_{SC} loss in the long wavelength region.

Figure 3. Electron beam-induced current and carrier density analysis. **a** Cross-section SEM image and **b** EBIC image of a cleaved CZTSe device. The yellow frames are eye guides locating the boundaries of the CZTSe grains which do not contribute to the EBIC signal (the regions within the red frames in EBIC image). The beam energy was 5 keV. **c** extracted EBIC profile along the yellow dash line (blue dots) and the fit with analytical model (red line); scan is from top to bottom of the yellow line in **b**. The space charge region (SCR) and quasi-neutral region (QNR) are highlighted with the vertical dash lines. The fluctuation of EBIC signal is induced by the rough morphology. The regions with protrusions show weak EBIC because of the higher reflection of electron beam, and vice versa. **d** Carrier density profiles measured with C-V and DLCP with junction area before (blue) and after (red) modification. The depletion region W_d in of the area-modified data is calibrated with the value fitted from EBIC data. Inset: the surface SEM image of CZTSe absorber.

Figure 3 c shows a representative cross-sectional line-scan extracted from a reasonably flat region without near-horizontal GB, and the fitting of these data using the analytical approach described in Ref.[⁴⁸]. The

fitted space charge region (SCR) width is around 660 nm, the electron diffusion length is around 250 nm, and the back surface recombination velocity is around 10^7 cm s^{-1} . As the excitation depth of the acceleration voltage used in EBIC (at 5 kV) is estimated to be only about 100 nm (**Figure S7**), it can be expected that the decay of EBIC in the quasi-neutral region (QNR) may be significantly enhanced by recombination at the unpassivated cross-section surface, thus, underestimating the intragrain electron diffusion length. The intragrain electron diffusion lengths in the QNR can be estimated roughly to be about 0.6-0.7 μm for assumed surface-recombination velocities of 10^6 – 10^7 cm s^{-1} using the analytical approach described in Ref.[⁴⁹].

Considering the rough surface of the CZTSe absorber (inset of **Figure 3 d**), the effective junction interface area can be significantly larger than the device area. Therefore, we calibrated the space charge region (SCR) width determined by capacitance-voltage (C-V) measurements and the drive level capacity profile (DLCP) measurements using the value obtained from the EBIC (660 nm), which enables us to better estimate the real net carrier density in the CZTSe absorber and the charged interface defect density. Using the single-side abrupt junction mode (ignoring the depletion region in the n-type buffer and window layer), the SCR width (W_{SCR}) and the doping density (N_{DL}) of the CZTSe absorber can be calculated as following:⁵⁰

$$W_{SCR} = \varepsilon_0 \varepsilon_r A_j / C_0, \quad (2)$$

$$N_{DL} = -C_0^3 / 2q \varepsilon_0 \varepsilon_r A_j^2 C_1, \quad (3)$$

where ε_0 and ε_r are the vacuum permittivity and relative permittivity of CZTSe respectively, A_j is the junction interface area, and C_0 and C_1 are the static capacitance and the first order differential capacitance, respectively. When A_j is set to the device area, W_{SCR} is 330 nm and N_{DL} is $3.1 \times 10^{15} \text{ cm}^{-3}$ (**Figure 3d**). The fitted W_{SCR} from the cross-section EBIC profiles is in the range of 650 to 750 nm (**Figure S8 and S9**).

When W_{SCR} is set to 660 nm, the effective junction interface area is calculated to be twice of the device area, and the real average N_{DL} is about $8.0 \times 10^{14} \text{ cm}^{-3}$. This relatively low net carrier density may significantly limit the quasi-fermi level splitting (QFLS) given the limited minority carrier lifetime, thus leading to large V_{OC} loss ($V_{OC,loss}$) as will be revealed by the following 3D device simulation.

We investigated the electrostatic potential fluctuation between grains and the band bending at GBs by means of combining atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) on a fresh cleaved cross-section, as shown in **Figure 4a** and **b**. The horizontal line-scan of CPD (**Figure 4c**) indicates a relatively uniform electrostatic potential distribution between the grains even though the topology fluctuation is large, highlighting that the impact of the topology on the CPD is small. The electrostatic potential fluctuation is only 5.4 meV. The $V_{OC,loss}$ due to the lateral electrostatic potential fluctuation, $\Delta\phi$ could be estimated using the following equation:⁵¹

$$V_{OC,loss} = \Delta\phi^2 / 2qk_B T \quad (4)$$

The $V_{OC,loss}$ estimated via Equation (4) is only about 0.6 mV, which is negligible. The extracted band bending at the GB1 to GB5 is very small. As shown in **Figure 4d**, the band bending at GB1 is 8 meV (upward), while the band bending of GB2 to GB5 is negligible (**Figure S10**). The local chemical composition near GBs was investigated using an EDXS Line-scan. A small Cu peak is observed at the GB region (**Figure S11**), which has also been observed in other CZTSe and CIGS solar cells,^{52, 53} and has been deemed detrimental for device performance.

Figure 4. Kelvin Probe Force Microscope and GB composition analysis. Topology image measured with AFM (a) and the corresponding KPFM image (b) of a fresh cleaved CZTSe cell. The blue dash lines labeled with numbers indicate where the GB profiles were extracted. c Contact potential difference (CPD) and topology profiles extracted along the yellow (horizontal) dash line in b. Inset of c: the statistic CPD distribution of horizontal scan, showing a mean CPD of 237.2 mV and a standard deviation of 5.4 mV. d The CPD and topology profiles of GB1 (indicated in a and b). The bend bending at GB1 is about -8 meV (upward). The CPD and topology profiles of GB2-GB5 are shown in **Figure S10**.

Radiative and non-radiative recombination at GBs and GIs

To quantify the non-radiative recombination velocity at the GBs, S_{GB} , we performed cathodoluminescence (CL) mapping of a cross-section CZTSe absorber prepared using an FIB. As shown in **Figure 5a**, the grains at the top and bottom of the CZTSe layer show comparable CL intensities whilst the CL intensities at the GBs are much lower compared to the GIs. This verifies that the poor carrier collection efficiency in the bottom grains observed in EBIC can be attributed to their relatively larger S_{GB} rather than to the recombination inside the GIs. **Figure 5b** shows CL line-scans across two representative GBs. No obvious luminescence emission peak variation is observed at the GBs which could indicate that the band gap does

not change at the GBs. The value of S_{GB} can be estimated using the decay of CL intensities between GBs and GIs (shown in **Figure 5c**), according to the model described in Ref. [54]:

$$\ln[\Delta I(x)] = \ln[S/(S + 1)] - x/L, \quad (5)$$

where $\Delta I(x)$ is the relative CL intensity between the GBs and GIs, L is the electron diffusion length, S the reduced recombination velocity ($S = S_{GB} \tau_{GI}/L$), and x is the position of the electron beam. The linear fittings of S are shown in **Figure 5d**. Assuming the photoluminescence (PL) decay time τ_{eff} is dominated by the GB recombination, i.e. τ_{eff} is in the range of 3.3-8.6 ns as measured by time-resolved photoluminescence (TRPL; **Figure 5e**). Here, we adopt an intragrain lifetime, τ_{GI} of 10 ns, the lower limit based on the 3D device simulation as will be shown below. The estimated S_{GB} is in a range of $(1.3-1.7) \times 10^4 \text{ cm s}^{-1}$, 1-2 orders of magnitude larger than the value reported for high efficiency CIGSSe and CdTe solar cells.^{35, 36} As the band bending at GBs is negligible, the effective GB recombination velocity is not affected by band bending and should be close to the S_{GB} .⁵⁵ It is noteworthy that the high recombination velocity at the GBs may also exist in sulfur-mixed CZTSSe and CZTS materials, indicating that more pertinent research efforts such as grain boundary chemistry and passivation strategies are urgently needed for kesterite solar cells.

Figure 5. Cathodoluminescence and photoluminescence analysis. **a** Hyperspectral and intensity combined CL map acquired at 10 keV from an FIB prepared cross-section sample of CZTSe absorber. The SEM image is shown in **Figure S12**. **b** Spectro-, spatial-, and intensity- resolved CL maps of the two GBs indicated in **a**. **c** Extracted CL intensity profiles across the two GBs. **d** $\ln[\Delta I]$ plots of the CL intensity profiles for positive distance values. The red and blue solid lines are the linear regressions. **e** Time-resolved photoluminescence (TRPL) measured with 532 nm laser and its corresponding double exponential decay fit. **f** the extracted CL peak energy profiles along the horizontal and vertical blue dash arrows indicated in **a**.

In addition, we further investigated the bandgap fluctuation in the CZTSe absorber by horizontal and vertical line-scans of CL peak energies. The positions of these line-scans are indicated in **Figure 5a** and the results are shown in **Figure 5g**. The horizontal CL emission peak fluctuation at the region near the junction interface is rather small (<5 meV), suggesting that the radiative recombination owing to lateral bandgap fluctuation is negligible. In contrast, the front and rear surface regions show slightly increased CL emission peak compared to the bulk by 20-40 meV, which could be attributed to an increased band gap correlating with the relatively high sodium concentration at the top and bottom (**Figure S13**). The incorporation of Na is known to slightly increase the bandgap of kesterite.⁵⁶ The minimum CL peak energy

at the bulk is around 1.00 eV, slightly lower than the PL peak energy (1.02 eV, **Figure S14**) and the optical bandgap (1.03 eV), which may contribute to ~ 30 mV $V_{OC,loss}$ due to sub-bandgap radiative recombination.

3D device simulations

To further investigate how the GB and GI recombination impacts the device performance, we employed 3D device simulations to fit the 12.45% efficiency CZTSe device and estimate pathways for further improvement. The simulations were based on a 3D unit cell established using the experimental photo-electronic parameters and the equivalently topology extracted from the morphology in the SEM and TEM images (see the details in **Methods: 3D device simulation**, **Table S1**, and **Figure S15-S17**). The 12.45% efficient CZTSe cell was reasonably reproduced using this unit cell by matching the J-V and EQE curves (**Figure S18**). The fitted S_{GB} is 0.7×10^4 cm s⁻¹, which is slightly smaller than the value measured from CL mapping. Assuming that the grains of CZTSe absorber are approximately cubic-like, S_{GB} is uniformly distributed at GBs including the top and bottom surfaces, the minority carrier lifetime determined by GB recombination, τ_{GB} , in a cubic-like grain with a grain size d can be estimated using the following equation:⁵⁷

$$\tau_{GB} \cong \frac{V}{S_{GB} \cdot S_a} + \frac{\alpha d^2}{D_e} = \frac{d}{6S_{GB}} + \frac{\alpha q d^2}{\mu_e k_B T}, \quad (6)$$

where V is the volume of the grain, S_a is the surface area, α is the constant determined by the cubic-like boundary conditions, D_e is the diffusivity of minority carriers, and μ_e is the minority carrier mobility. The first term at the right side of Equation (6) is determined by the recombination rate at GBs, while the second term is determined by the arrival rate of minority carriers diffusing from GI to GBs. Considering that the value of α should be much smaller than that for Si wafers ($\alpha = 1/\pi^2$)⁵⁷ as there are four more recombination active surfaces for cubic-like grains, and that the electron mobility of CZTSe is relatively

large compared to the grain size d ,^{37, 58} we believe the second term determined by the arrival rate can be negligible. Therefore, using the simulated value of S_{GB} , the calculated value of τ_{GB} of our CZTSe absorber with a grain size of 1.1 μm is 2.6 ns. Assuming the top surface is well passivated by the ZnSe nano layer, the constant 6 in Equation (6) should be changed to 5 and the amended τ_{GB} is 3.1 ns, very close to the fast decay time measured from TRPL (3.2 ns) which is believed to be a key parameter determining V_{OC} .⁵⁹ The effective minority carrier lifetime τ_{eff} could be expressed as:⁶⁰

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{GB}} + \frac{1}{\tau_{GI}} + \frac{1}{\tau_{int}} + \frac{1}{\tau_{rad}}, \quad (7)$$

where τ_{GI} is the intragrain minority carrier lifetime, τ_{int} the interface recombination lifetime, τ_{rad} the radiative recombination lifetime. Due to the low carrier density in the CZTSe absorber, the radiative recombination is negligible under low injection condition (one sun). According to the simulated impact of τ_{GI} (**Table S2**), the photovoltaic parameters fit best when τ_{GI} is 50-100 ns. On the other hand, considering that slight deviations could be involved in the device simulation, it is possible that the lower limit of τ_{GI} can be 10 ns. Assuming that the junction interfacial recombination is also negligible, and the rear interfacial recombination can be included in the GB recombination, the value of τ_{eff} is dominated by τ_{GB} . Equation (6) predicts that τ_{GB} approximately linearly increase with grain size d . Therefore, grain size could be a critical factor that determines τ_{eff} assuming that the S_{GB} stays the same.

The impact of grain boundary recombination velocity is simulated and shown in **Table 1**. It shows that reducing the value of S_{GB} to 10^2 - 10^3 cm s^{-1} (comparable with high efficiency CIGS and CdTe solar cells) gives rise to only an additional 30 mV to V_{OC} , 5% absolute increase of FF, a marginal increase of J_{SC} , and a ~2% absolute increase of PCE. The improved V_{OC} is in good accordance with the value of the etched single-crystalline CZTSe solar cells.⁶¹ The device performance in this region is mainly limited by the

relatively low carrier density and the limited τ_{GI} . However, if S_{GB} increases to above 10^4 cm s^{-1} , all the photovoltaic performance parameters significantly decrease, indicating large S_{GB} is the limiting factor in this region. The simulations indicate only a marginal benefit by further improving τ_{GI} (**Table S2**). This is because the effective minority carrier lifetime τ_{eff} is limited by the low τ_{GB} as discussed above. However, if the grain quality is degraded, the cell performance is severely impacted. **Table 2** shows the impact of the carrier density on the device performance. The results indicate that significant V_{OC} and FF increases could be achieved if the carrier density is improved to $5 \times 10^{16} \text{ cm}^{-3}$, a typical carrier density level for >20% efficient CIGS and CdTe solar cells,^{35, 62} resulting in efficiency beyond 15%. The impact of grain size on device performance was also simulated. Larger grain size will lead to better performance (**Table S3**) because both τ_{GB} and τ_{eff} linearly increases with grain size as described by Equation (6) and Equation (7).

Table 1. Simulated impact of GB recombination on device performance, with intragrain lifetime 50 ns and net carrier density $8 \times 10^{14} \text{ cm}^{-3}$.

$S_{GB} (\text{cm s}^{-1})$	10^0	10^2	10^3	10^4	10^5	10^6	10^7
$V_{oc} (\text{mV})$	508	507	500	473	438	411	406
$\eta (\%)$	14.4	14.3	13.9	11.9	8.9	7.0	6.6
$J_{sc} (\text{mA cm}^{-2})$	37.5	37.4	37.4	36.7	33.9	31.2	30.6
FF (%)	75.6	75.5	74.5	68.8	60.0	54.7	52.8

Table 2. Simulated impact of carrier density on device performance, with intragrain lifetime 50 ns and $S_{GB} 7000 \text{ cm s}^{-1}$.

Carrier density (cm^{-3})	10^{14}	5×10^{14}	10^{15}	5×10^{15}	10^{16}	5×10^{16}
$V_{oc} (\text{mV})$	34.9	36.7	37.0	36.9	36.5	35.1
$\eta (\%)$	438	482	486	499	507	549
$J_{sc} (\text{mA cm}^{-2})$	8.9	11.9	12.6	13.8	14.2	15.2
FF (%)	58.2	67.1	70.0	75.1	77.0	79.1

The above results indicate the device performance of the investigated 12.45% efficient CZTSe solar cells is limited by the recombination at GBs and the low net carrier density. Although grain interior lifetime is important when its value is lower than 10 ns, further improving grain interior lifetime to longer than 50 ns would not give any improvement in device performance if the grain boundary recombination cannot be reduced. This may explain why various extrinsic doping/alloying strategies that are anticipated to improve bulk qualities can improve device performance when the baseline efficiency is low, but hardly further improve the efficiency if the baseline efficiency is at a level of 12-13% and GBs are not passivated. On the other hand, as long as the density of acceptor-like interface defects can be kept low, higher net carrier density will not lead to significant interfacial recombination.⁶³ Considering the radiatively limited lifetime versus carrier density of CZTSe materials (**Figure S19**), an increase in carrier density to about $5.0 \times 10^{16} \text{ cm}^{-3}$ would be beneficial for the open-circuit voltage when the intragrain lifetime is 50-100 ns, which is an essential direction to improve the efficiency to 15% and beyond.

Conclusion

In summary, we have successfully unveiled most of the important microscopic loss mechanisms in our $\geq 12\%$ efficiency CZTSe solar cells. The results indicate that the junction interface is well passivated by an epitaxial ZnSe nano layer, the radiative recombination loss through sub-band recombination and electrostatic potential fluctuation is small, and that the intragrain minority carrier lifetime is larger than 10 ns, all of which are encouraging characteristics for high efficiency solar cells. Instead, the high effective recombination velocity at grain boundaries ($\geq 10^4 \text{ cm s}^{-1}$) and the low net carrier density ($\sim 10^{15} \text{ cm}^{-3}$) are the current main limiting factors of our CZTSe solar cells. This provides clear directions for improving the performance of Se-based kesterite solar cells. We believe the established framework to reveal the important microscopic loss mechanisms of thin-film solar cells could also be applicable to other emerging materials like perovskite and antimony chalcogenides.

Methods

Film and Device fabrication:

CZTSe films were fabricated with sputtering stacked Cu-Zn-Sn metallic precursors on Mo-coated glass substrates, followed by a selenization growth process. The target composition of the CZTSe absorber is $\text{Cu}/(\text{Zn}+\text{Sn}) \approx 0.75$ and $\text{Zn}/\text{Sn} \approx 1.1$, measured with X-ray Fluorescence spectrometer (XRF). The Cu, Zn, and Sn targets are with 99.999% purity. The precursor stacking order was Mo/Sn/Cu/Zn/Sn/Cu, and the sputtering pressure was about 0.2 Pa. The metallic precursors were pre-alloyed at 250 °C for 15 min, followed by a soft-selenization at 250 - 280°C for 15 min in controlled low Se partial pressure. Then the substrates were ramp to 550°C in 15 min and dwell at 550°C for 8-10 min. The details of the annealing profile are described in Ref.[22]. All these annealing processes were performed in a custom-made furnace which can have independent temperature control of Se source, substrates, and Se cracking barrel (see the schematic diagram in **Figure S20**). The controlling Se atmosphere by adjusting the Se source temperature and Se cracking barrel temperature was detailed in our early publication.⁶⁴ Some key points for the selenization processes are summarized as follows: i) Before selenization start, a pre-alloying treatment with temperature higher than 250°C is important to fabricate compact films, and also important to control the Sn loss and the thickness of MoSe₂ layer;⁴⁴ ii) a sufficient soft selenization with temperature below 300°C (to prevent Sn loss) is important to control the bulk defects by turning Sn to Sn⁴⁺ and facilitating Zn diffusing to the top region before the synthesis of CZTSe phase start at 350 - 400°C.²² In this soft selenization, it is very important to use a reactive micro-molecule Se vapor (Se₂) under low Se partial pressure. High Se partial pressure will lead to poor Se diffusion.⁶⁴ iii) Sufficient Se partial pressure during high temperature annealing is important for grain growth.

The CZTSe devices were fabricated with an architecture of Mo/CZTSe/CdS/i-ZnO/ZnO:Al/Ni/Al/MgF₂. A 20-50 nm CdS buffer layer was deposited at 85 °C using the chemical bath deposition (CBD) method. A 50 nm i-ZnO layer and a 400-450 nm ZnO:Al layer were subsequently deposited using radio frequency (RF) and direct current (DC) sputtering, respectively. The Ni/Al grids and 110 nm MgF₂ anti-reflector coating were deposited using electron beam evaporation. The total area of each device is about 0.24 cm² defined by mechanical scribing. Total area efficiencies are reported.

Characterization:

The compositions of the films were analyzed using an X-ray Fluorescence spectrometer (XRF; ARL Performance'X 4200, Thermo Fisher Scientific) with Uniquant analysis software. Morphological analysis was performed using a Scanning Electron Microscope (SEM; FEI Apreo LoVac). The TEM-ready samples were prepared using the in-situ FIB lift out technique on an FEI Dual Beam FIB/SEM. The samples were capped with sputtered C and e-Pt/I-Pt prior to milling. The TEM lamella thickness was ~100nm. The samples were imaged on a Hitachi HD2700 STEM with high-resolution (HR) TEM mode. EDS spectra were acquired on Oxford INCA, Bruker Quantax EDS system. The current-voltage (J-V) data were acquired using a Keithley 2400 source meter and a Newport solar simulator (ORIEL-SOI3A) under the standard condition (1000 W/m², 25°C, AM 1.5 G). A certificated mono-crystalline Si reference solar cell was used to calibrate the light intensity of the solar simulator. The temperature dependent J-V data were measured using a vacuumed cryostat with quartz windows. The light intensity was adjusted according to the J_{SC} measured at standard condition (AM 1.5 G, without cryostat). EQE data were acquired by measuring the short-circuit current with spectrally resolved monochromatic beam and locked-in amplifier, using calibrated Si and InGaAs photodiodes as references.

The element depth profiles were recorded by secondary ion mass spectroscopy (SIMS; IMS-6F, CAMECA). Raman spectroscopy was performed using a Renishaw inVia Raman microscope fitted with a 441 nm He-Cd laser as the excitation source, 1800 l mm^{-1} grating, and measured using a 1000 $\times$ objective. The focal point was above the surface of the sample to collect more signals from the surface of the sample. The pixel size was 2 $\mu\text{m} \times 2 \mu\text{m}$.

The EBIC measurements were performed on the cross-section of the finished device using an SEM (Zeiss SIGMA) extended with a tunable current amplifier. The devices were connected to a circuit that provided tunable bias. The EBIC images were obtained with a splitting mode, which was combined with SEM images of the same scanned region. The electron beam energy was 5 keV.

The cross-section KPFM measurements were conducted on a fresh cleaved CZTSe cell using atomic force microscopy (Bruker Dimension ICON SPM) with a scan rate of 0.200 Hz in a scan size of 8.5 μm (W) $\times$ 4.25 μm (H). A brand new PtSi probe (Bruker SCM-PTSI) was used in these measurements and the samples were measured using a two-pass scan (one for topography in contact mode and another for contact potential difference [CPD] maps in non-contact mode). The system deviation of CPD is about ± 10 mV.

PL and TRPL were measured using a microscope customized for micro-PL measurements. The excitation source was a 532 nm pump from an EKSPLA PT210 laser at 1 MHz repetition rate and 10 ps pulse width. The TRPL signal was detected using a fiber-coupled InGaAs avalanche photodiode (ID210) and processed using the time-correlated single photon counting board (TimeHarp 260). The time binning is 25 ps.

A cross-section sample was prepared for CL by a plasma FIB (Thermo Fisher Helios G4 PFIB) with an in-situ lift-out platform. The electron excitation profile was simulated by the Monte Carlo method using the CASINO software⁶⁵ (**Figure S7**) to determine the suitable thickness of the sample and acceleration voltage used in the CL measurement. Based on the simulation and considering that the average grain size

is around 1 μm , 10 kV and 1 μm were used for the voltage and targeting thickness of the FIB milled sample, respectively. The sample was transferred and mounted on an in-situ TEM grid with Pt welding after rough milling to about 2 μm thick. The sample was further polished using low beam current (0.3 nA) after lift-out to achieve $\sim 1 \mu\text{m}$ thickness. Prior to CL measurement, the sample received a final ion beam polish on both faces (Fischione NanoMill 1040) at low voltage (500V) to ensure a clean and fresh surface for analysis. Analysis was conducted using a Delmic SPARC spectral cathodoluminescence system coupled to an FEI Nova Nano SEM 450 field-emission SEM.

3D device simulation:

A commercial software package, Sentaurus technology computer-aided design (TCAD) was used to numerically examine the device physics. In this study, a 3D unit cell shown in **Figure S 16a** was established in the simulator. In this unit cell, the absorber consists of five grains, one is larger (1.1 μm) and the other four are smaller with the same size (0.5 μm). The sizes of these grains were averaged from the TEM and SEM results (Figure S13 and S14). After all constitutional regions were generated in the simulator, the whole structure went through a meshing process to break down into millions of small elements i.e. cuboids. A smaller element allows for a higher accuracy to compute the spatial distribution of key fields like carrier concentration. Meanwhile, it demands more computer resources as well. Hence the element size was refined only where the field variation is significant to balance between speed and accuracy. Afterwards, photogeneration was computed with the simple optical beam absorption method using the Beer-Lambert law. The complex refractive index of each layer was obtained from inhouse characterization. The key semiconductor material parameters for electron simulation are listed in **Table S1** and obtained from either inhouse characterization or the literature.⁶⁶⁻⁶⁸ The ambient temperature in simulation is also 298.15 K to match the standard test condition. The tuned lifetime and mobility values are well within the reported range in the literature.

After initialising all important fields and model parameters, the thermal equilibrium condition was first computed by solving five semiconductor equations i.e. the Poisson, drift-diffusion and carrier continuity equations numerically. A well-established mesh and suitable solver help reach self-consistency fast. Subsequently, the impact of carrier generation and bias voltage was investigated by ramping these parameters dynamically. For each ramping step, the steady state was computed so that key fields can be extracted for further analysis. If necessary, a snapshot at a ramping step can also be saved to preserve spatial distribution of fields. Following this practice, the champion cell was reproduced by matching key performance characteristics. Afterwards, the impact of grain lifetime, doping, size and boundary recombination on cell performance was predicted, providing a guideline for future cell improvement.

Author contributions

J.L. and X.H conceived the idea, X.H. and M. A. G supervised the project. J. L. fabricated the CZTSe films and solar cells, conducted most of the characterizations and data analysis, and wrote the manuscript. J.H. analyzed the HR-TEM and EBIC data. F.M. did the 3D device simulation. J.L. and H.L. conducted the EBIC measurements. Y.Y., J.L., H.S. conducted KPFM measurements. J.H. and J.C. fabricated the FIB sample for CL mapping. K.P., R.T., J.H., J.L. conducted the CL mapping. R.L.C., Z.H., J.L. conducted the PL and TRPL measurements. M.H. and K.S. assisted in precursor and Window layer fabrication. All authors discussed and commented on the manuscript.

Supporting Information.

Supporting Information is available at <https://doi/xxxxxxx>.

Notes

The authors declare no competing financial interest.

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