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

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Understanding carrier loss mechanisms at microscopic regions is imperative for the development of high-performance polycrystalline inorganic thin-film solar cells. Despite the progress achieved for kesterite, a promising environmentally benign and earth-abundant thin-film photovoltaic material, the microscopic carrier loss mechanisms and their impact on device performance remain largely unknown. Herein, we unveil these mechanisms in state-of-the-art \( \text{Cu}_2\text{ZnSnSe}_4 \) (CZTSe) solar cells using a framework that integrates multiple microscopic and macroscopic characterizations with three-dimensional device simulations. The results indicate the CZTSe films have a relatively long intragrain electron lifetime of 10–30\( \mu \)s and small recombination losses through bandgap and/or electrostatic potential fluctuations. We identify that the effective minority carrier lifetime of CZTSe is dominated by a large grain boundary recombination velocity (~\( 10^4 \) cm s\(^{-1} \)), which is the major limiting factor of present device performance. These findings and the framework can greatly advance the research of kesterite and other emerging photovoltaic materials.

Photovoltaics have been identified as the most attractive renewable energy that can be used to mitigate escalating global climate change\textsuperscript{1}. Large-scale deployments of photovoltaic energy require stable, abundant and low-toxic materials similar to silicon (Si) (ref. \textsuperscript{2}), which has stimulated the worldwide interest in new inorganic photovoltaic materials such as chalcogenides, oxides, pnictides, and halides\textsuperscript{3–5}. Kesterite \( \text{Cu}_2\text{ZnSn(S,Se)}_4 \) (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)\textsuperscript{6,7}. Although CZTSSe solar cells have reached the highest PCE (12.6\% to 13.0\%) among inorganic photovoltaic materials such as chalcogenides, oxides, pnictides and halides\textsuperscript{3–5}, it is still behind its poly- and single-crystalline cousins CdTe and CIGSSe\textsuperscript{8,9,14,15}. 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 structures\textsuperscript{16}, most efforts have been directed to the bulk and heterojunction interfaces\textsuperscript{17–20}. Although some properties of the grain interiors and grain boundaries, such as intragrain crystallinity defects and band bending at the grain boundaries, have been investigated using high-resolution structural and electrical analysis, respectively\textsuperscript{3,11,21,22}, detailed loss mechanisms in these microscopic regions, especially grain boundary 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 multiple cousins CdTe and CIGSSe, can be one of the key origins of the efficiency stagnation of CZTSSe in recent years, thus requiring urgent comprehensive investigation.

Herein, we unveil the microscopic carrier loss mechanisms in state-of-the-art efficiency selenide-kesterite \( \text{Cu}_2\text{ZnSnSe}_4 \) (CZTSe) solar cells by establishing a framework that integrates multiple micro-structural and macroscopic optoelectronic characterizations with three-dimensional (3D) device simulations, building on a recent approach demonstrated by Krause et al. for CIGSSe solar cells\textsuperscript{23}. We show that the grain boundary recombination limits the effective carrier lifetime of bulk kesterite. The associated grain
boundary recombination velocity of kesterite, at a level of 10^6 cm s^{-1}, is one to two orders of magnitude larger than that of CIGSSe and CdTe\textsuperscript{20,21}. The intragrain minority carrier lifetime is estimated to be 10–30 ns, while the net carrier density is around 1.8×10^{13} cm^{-3}. It seems that the well-recognized open-circuit voltage (V\textsubscript{OC}) losses due to bandgap fluctuation and/or electrostatic potential fluctuation are small. Instead, the dominating loss mechanisms of current state-of-the-art CZTSe solar cells are associated with the severe non-radiative recombination at grain boundaries. Further efficiency improvement towards 20% requires substantial grain boundary passivation and increase of net carrier density.

**Photovoltaic performance and device structure**

We used CZTSe absorbers fabricated by the same method used for our reported 12.5% record CZTSe cells\textsuperscript{26}. Details of the fabrication processes can be found in the Methods section. The solar cells fabricated on these absorbers achieve PCEs between 11.0% and 12.5% and an average PCE of 11.8% (Supplementary Fig. 1), representing state-of-the-art performance. Figure 1a, b shows 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\textsuperscript{2}) efficiency is 12.45 %, with a V\textsubscript{OC} of 479 mV, a fill factor (FF) of 70.45% and a short-circuit current density (J\textsubscript{SC}) of 36.9 mA cm\textsuperscript{-2} (integrated J\textsubscript{SC} from EQE is 37.0 mA cm\textsuperscript{-2}). The diode ideality factor (A) extracted from corresponding dark J–V data is 1.4 and the diode reverse saturation current density (J\textsubscript{0}) is 8.1×10\textsuperscript{-4} A cm\textsuperscript{-2} (Supplementary Fig. 2). The J\textsubscript{0} is much lower than the previous 11.6% efficiency record CZTSe device from IBM (40.6 mA cm\textsuperscript{-2}) (ref. 26), which could be attributed to the relatively low transmittance of the 200 K to ~320 K temperature range where the device behaves as an ideal diode in this temperature region\textsuperscript{26} and that the tunneling process at the CZTSe/ZnSe interface dominates the current transport in this temperature region\textsuperscript{26}. Contrastingly, A is around 1.5 without significant change when the temperature is in the range of 260–320 K, indicating the dominating current transport mechanism is likely to be thermionic emission in this temperature region, where it is possible to extract the recombination activation energy, E\textsubscript{r}, using the one-diode model\textsuperscript{26}:

\[
V_{OC} = \frac{E_A}{q} - \frac{A k_B T}{q} \ln \left( \frac{J_{00}}{J_L} \right),
\]

where q is the unit charge, k\textsubscript{B} is the Boltzmann’s constant, T is the temperature, J\textsubscript{00} is the prefactor of diode current and J\textsubscript{L} is the photocurrent. Here J\textsubscript{00}, J\textsubscript{L} and E\textsubscript{r} are assumed to be weakly temperature-dependent in the temperature region used for fitting\textsuperscript{26}. The temperature-dependent V\textsubscript{OC} shows good linear behaviour in this temperature region (Fig. 2f), and the fitted E\textsubscript{r} is 1.025 ± 0.005 eV, well-aligned to the bandgap of the CZTSe absorber (E\textsubscript{g} = 1.02 eV, as shown in Fig. 3e). This indicates that the E\textsubscript{r} deficit compared with E\textsubscript{g} is no longer a limitation in these CZTSe devices, owing to the passivated heterojunction interface by the epitaxial ZnSe nanolayer and the suppressed bandgap/potential fluctuation as reported previously\textsuperscript{26}.

The blocking barrier height of the back contact interface is derived from the temperature-dependent series resistance (R\textsubscript{s}) over the 200 K to ~320 K temperature range where the device behaves consistently with the thermal emission model\textsuperscript{26}. The fitted barrier height is only 11 ± 5 meV (Fig. 2g), much smaller than the previously reported value\textsuperscript{26}, indicating a quasi-ohmic contact at the back contact interface. The result of cross-sectional Kelvin probe force microscope (KPFM) measurements also confirms that the fine grain layer and the MoSe\textsubscript{2} layer do not introduce a hole-transporting barrier at the back contact interface (Supplementary Figs. 8 and 9).

**Potential fluctuations**

We investigated the lateral electrostatic potential fluctuation between grains and the band bending at grain boundaries by means of combining atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) on a fresh cleaved cross-section, as shown in Fig. 3a,b. The horizontal line scan of contact potential difference (CPD) (Fig. 3c) 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,
which is negligible compared with the resolution of CPD (~10 mV). The band bending at GB1 is 8 meV (Fig. 3d), which is also negligible, the same as the band bending of GB2 to GB5 (Supplementary Fig. 10). The local chemical composition near grain boundaries was investigated using an EDS line scan. A small Cu peak is observed at the grain boundary region (Supplementary Fig. 11), which has also been observed in other CZTSe and CIGS solar cells\(^\text{35,36}\), and has been deemed detrimental for device performance.

The potential fluctuation is further investigated by analysis of the internal quantum efficiency (IQE, Supplementary Fig. 12) and photoluminescence (PL) spectra. The PL emission energy, \(E_{\text{PL}}\) (1.01 eV), is only slightly lower than the bandgap (1.02 eV) determined from the inflection of the IQE curve (peak of \(-d\text{IQE}/d\lambda\), Fig. 3e). The PL peak is quite broad, though no obvious red shift is observed. This PL peak broadening can be attributed to band tailing states arising from bandgap and/or electrostatic potential fluctuation, both of which can be estimated using the absorption edge derived from the tail of the IQE curve (Supplementary Discussion 1) (ref. \(^\text{37}\)). Bandgap fluctuations can be described by a Gaussian distribution of local absorption coefficient with a standard

**Fig. 1 | Device performance, morphology and element distribution.** a, b, 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 anti-reflection coating. c, Cross-sectional SEM image of a CZTSe device. The device structure from bottom to top is soda lime glass (SLG)/Mo/MoSe\(_2\)/CZTSe/CdS/i-ZnO/ZnO:Al. d, Element SIMS depth profile of the CZTSe absorber. e, The cross-sectional TEM image and the corresponding EDS element mapping of Cu, Zn, Sn, Se, Mo, Cd and Mg. The cross-sectional STEM sample was prepared with a focused ion beam.
Fig. 2 | Structure and carrier transport performance of the front and rear interfaces. a,b. Colour-coded Raman intensity mapping at peak positions of 196 cm$^{-1}$ (A mode of CZTSe) (a) and 250 cm$^{-1}$ (A1 mode of ZnSe) (b), respectively (without baseline subtraction). The Raman mapping was performed using a 441 nm He–Cd laser as excitation. c. Average Raman spectrum of the mapping and the corresponding baseline. The unit cps. means count per second. The baseline-subtracted Raman spectrum is shown in Supplementary Fig. 6. d. HR-STEM image and the colour-coded inverse fast Fourier transformation images of the selected reflections revealing the dislocations ($T_\text{marked}$ at the CZTSe/ZnSe/CdS heterointerface. The interplanar spacings are indicated in the HR-STEM figure. The yellow dashed lines roughly indicate the boundaries of different phases. The length of all the three scale bars is 2 nm. e. Temperature-dependent series resistance ($R_s$) and diode ideality factor extracted from temperature-dependent $J$–$V$ curves (Supplementary Fig. 7). For each metric, the line on top of data is a guide to the eye. The black dashed line indicates the boundary between the ideal device region and non-ideal device region. The horizontal dashed blue line indicates where the diode ideality factor is 2. f. Plot of $V_{\text{oc}}$ versus temperature and the linear fit (dashed blue line) of the recombination activation energy $E_A$. The data points coded with blue are selected for the linear fitting. The red line on top of data is a guide to the eye. g. Plot of ln ($R_s$) versus $1/T$ and the linear fitting showing back contact barrier height. $R_s$ is the series resistance and $T$ is the temperature.

deviation of $\sigma_e$ (ref. 13). The fitted $\sigma_e$ is 48 meV (Supplementary Fig. 13), which is significantly lower than some previous analysis but in good agreement with more recent findings. Because the local bandgap fluctuation observed in cathodoluminescence (CL) mapping is within 5 meV, these fluctuations would have to occur on length scales smaller than the spatial resolution of CL measurement (several 100 nm). Alternatively, average electrostatic fluctuations, $\sigma_{\text{opt}}$, can be estimated from the Shklovskii and Efros model, yielding a value of 20 meV (Fig. 3f), which also agrees with the estimated Urbach tail energy ($E_U$). The loss of radiative limit $V_{\text{oc}}$ ($V_{\text{oc,rad,loss}}$) due to the lateral potential fluctuation can be estimated to be 44 mV or 7.7 mV due to either $\sigma_e$ or $\sigma_{\text{opt}}$, respectively, by the following equation:

$$V_{\text{oc,rad,loss}} = \gamma^2/2qk_bT$$ (2)

where $\gamma$ is either $\sigma_e$ or $\sigma_{\text{opt}}$. Nevertheless, the $V_{\text{oc}}$ loss due to these fluctuations in our cells is rather small compared with the non-radiative loss mechanisms that will be discussed in the following sections.

Carrier collection and free carrier density

We performed electron beam-induced current (EBIC) measurement to investigate the carrier collection in the CZTSe solar cell. Figure 4a,b shows the SEM and EBIC images of the corresponding cross-section of the CZTSe solar cell at a beam energy of 5 kV. Figure 4c shows a representative cross-sectional line scan extracted from a reasonably flat region without near-horizontal grain boundary and the fitting using the analytical approach described by Nichterwitz et al. The fitted electron diffusion length is around 250 nm. As the excitation depth of the acceleration voltage used in EBIC (at 5 kV) is estimated to be only about 100 nm (Supplementary Fig. 14), 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 electron diffusion length. For a given fitted electron diffusion length, the upper limit of the intragrain electron diffusion length is estimated to be 1.0 µm using the upper limit of surface recombination velocity ($10^5$ cm s$^{-1}$), according to the method described by Nichterwitz et al. However, we note that this approach is not
very accurate given that the cross-section surface is not very flat. The intragrain diffusion length will be further estimated using 3D device simulation.

Considering the large surface roughness of the CZTSe absorber (inset of Fig. 4d), the effective junction interface area can be significantly larger than the device area. On the basis of the AFM measurement (Supplementary Fig. 15), the effective junction interface area is about 1.3 times of the device area. Using the single-side abruption method (Supplementary Fig. 15), the effective junction interface area can be significantly larger than the device area. On the basis of the AFM measurement (Supplementary Fig. 15), the effective junction interface area can be significantly larger than the device area.

According to the defect activation energy measured using admittance from a similar sample (130 meV) (ref. 25), the electrical neutral condition and the Fermi–Dirac distribution, these defects are fully ionized (detailed analysis in Supplementary Discussion 2). We thus get an average free carrier density of $1.8 \times 10^{15}$ cm$^{-3}$.

In addition, the high spatial resolution of the EBIC image enables us to further investigate the electron transport across the grain boundaries. It is noteworthy that the CZTSe grains underneath near-horizontal grain boundaries, not directly connected to the buffer layer (Supplementary Fig. 16), do not contribute to the EBIC signal. This indicates significant recombination and/or a carrier transport barrier may exist near these grain boundaries or inside these grains, which may be responsible for the additional $J_{sc}$ loss in the long-wavelength region.

**Carrier recombination at grain boundaries and grain interiors**

The non-radiative recombination velocity at grain boundaries and grain interiors is first qualitatively compared by performing cathodoluminescence (CL) mapping on a directly cleaved cross-section...
sample. In the measured region, all the grain boundaries show pronouncedly lower CL intensity compared with the grain interiors (Supplementary Fig. 17), which indicates grain boundaries have much larger non-radiative recombination velocity compared with the grain interiors. To exclude the effect of morphology and quantify the non-radiative recombination velocity at the grain boundaries, $S_{\text{GB}}$, we further performed CL mapping of a focused ion beam (FIB)-prepared cross-section sample. As shown in Fig. 5a, the grains at the top and bottom of the CZTSe layer show comparable CL intensities while the CL intensities at the grain boundaries are much lower compared with the grain interiors. This verifies that the poor carrier collection efficiency in the bottom grains observed in EBIC can be attributed to their relatively larger $S_{\text{GB}}$ rather than to the recombination inside the grain interiors. Figure 5b shows CL line scans across two representative grain boundaries. No obvious CL peak energy variation is observed at the grain boundaries (Fig. 5c), indicating the bandgap does not change at the grain boundaries. The value of $S_{\text{GB}}$ can be estimated using the decay of CL intensities between grain boundaries and grain interiors, according to the model described by Mendis et al.:

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

where $\Delta I(x)$ is the relative CL intensity between the grain boundaries and grain interiors, $L$ is the apparent electron diffusion length, $S$ is the reduced recombination velocity ($S = S_{\text{GB}} \tau_{\text{GI}} / L$, where $\tau_{\text{GI}}$ is the minority carrier lifetime of grain interior) and $x$ is the position of the electron beam. The linear fittings of $S$ and $L$ are shown in Fig. 5d. Here we adopt the value of $\tau_{\text{GI}}$ of 10–30 ns based on the 3D device simulations as will be shown below.

The values of $S_{\text{GB}}$ extracted from six grain boundaries (marked in Fig. 5a) are in a range of $(0.15–3.8) \times 10^4 \text{cm s}^{-1}$, one to two orders

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**Fig. 4** | Electron beam-induced current and carrier density analysis. a, b, Cross-sectional SEM image (a) and EBIC image (b) of a cleaved CZTSe device. The beam energy was 5 keV. c, Normalized EBIC Intensity ($I_{\text{EBIC, norm}}$) profile (blue dots) along the dashed yellow arrows shown in a and b and the fitting with analytical model (red line). The space charge region (SCR) and QNR are separated with the vertical dashed lines. The fluctuation of the 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. The EBIC signal at the SCR region is severely altered by the non-flat morphology, which may lead to a large error in fitting of depletion region width. The QNR region shows a relatively flat morphology and thus is used for fitting diffusion length in this region. d, Carrier density profiles measured with capacity voltage (CV) and drive-level capacity profile (DLCP) with junction area before (blue) and after (red) modification. $N_{\text{CV}}$ and $N_{\text{DLCP}}$ are apparent carrier densities measured by CV and DLCP, respectively. $f$ is the modulation frequency used for the CV and DLCP measurements. $\varepsilon_r$ is the relative dielectric constant of CZTSe. $A_j$ is the junction area. The inset shows the plain view SEM image of a CZTSe absorber.
of magnitude larger than the value reported for high efficiency CIGSSE and CdTe solar cells32,44. As the band bending at grain boundaries is negligible, the effective grain boundary recombination velocity is not affected by band bending and should be close to the \( S_{\text{gb}} \). It is noteworthy that the high recombination velocity at the grain boundaries 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.

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 Fig. 5a, and the results are shown in Fig. 5c. The horizontal CL emission peak fluctuation at the region near the junction interface is rather small (<5 meV). In contrast, the front and rear surface regions show slightly increased CL peak energy compared with the bulk by 20–40 meV, which could be attributed to an increased bandgap correlation with the relatively high sodium concentration at the top and bottom (Supplementary Fig. 20). The incorporation of Na is known to slightly increase the bandgap of kesterite44. The minimum CL peak energy at the bulk is 1.00 eV (Supplementary Fig. 21), 0.01 eV and 0.02 eV lower than the PL peak energy and bandgap energy, respectively.

To evaluate how the large \( S_{\text{gb}} \) impacts the optoelectronic quality of CZTSe absorber, we quantitatively correlated the effective minority carrier lifetime to the \( S_{\text{gb}} \) and the grain size \( d \) (Supplementary Discussion 3):

\[
\tau_{\text{eff}} \cong \tau_{\text{GB}} \cong \frac{d}{(6 - n) \cdot S_{\text{GB}}},
\]

where \( n \) is the number of passivated faces of cubic-like grains. Equation (5) suggests that grain size \( d \) could also be a critical factor that determines \( \tau_{\text{eff}} \). Using the value of \( S_{\text{GL}} \) extracted from CL mapping, the calculated value of \( \tau_{\text{GB}} \) of our CZTSe absorber with a grain size of 1.1 \( \mu \)m is 0.6–4.7 ns, with an average value of 2.5 ns, comparable to the fast decay time measured from time-resolved PL (TRPL) (3.3 ns, Fig. 5f), which is believed to be a key parameter determining \( V_{\text{oc},\text{eff}} \). Using equation (5), the statistical average \( S_{\text{GB}} \) in the cells is estimated to be 6.7 \( \times \) 10\(^{10}\) cm\(^{-2}\) for the CZTSe absorbers with effective minority carrier lifetime of 3.3 ns (measured from TRPL) and grain size of 1.1 \( \mu \)m.

### 3D device simulations

To further investigate the critical intragrain material parameters (carrier lifetimes and mobilities) and how the microscopic carrier recombination mechanisms impact the device performance, we link the above characterizations into 3D device simulations. The simulations were based on a 3D unit cell established using the equivalent topology extracted from the morphology in the SEM and STEM images (Supplementary Figs. 22–24). The experimentally obtained photo-electronic parameters, including free carrier density, potential fluctuation, bandgap grading and the statistical average \( S_{\text{GB}} \), are integrated into the simulation model as fixed parameters (details in Methods and Supplementary Table 1).

Under a reasonable precondition that the minority carrier electrons should have a longer lifetime and mobility than holes, we can get a set of values of intragrain electron and hole lifetimes and mobilities by matching the experimental \( J-V \) and EQE data of the 12.45% efficient CZTSe cell. Meanwhile, the radiative loss due to potential fluctuations is simulated and shown to be rather small (Supplementary Fig. 25). Starting from this point, we can first estimate...
the region of intragrain carrier mobilities by fitting the value of FF and $J_{sc}$ because FF and $J_{sc}$ are sensitive to carrier mobilities while $V_{oc}$ is not. As shown in Fig. 6a, to match the value of FF (70–70.5%), the mobilities of electron and hole have to be in a range of 80–100 cm$^2$ V$^{-1}$ s$^{-1}$ and 30–50 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, which fall within the same regions as that determined by fitting the $I_{sc}$ (Supplementary Fig. 26). The fitted electron mobility is comparable to that measured using time-resolved terahertz spectroscopy (128 cm$^2$ V$^{-1}$ s$^{-1}$) (ref. 4), while the hole mobility is several times higher than that measured from time-resolved terahertz spectroscopy. Then we can estimate the value of electron and hole lifetimes under fixed electron and hole mobility (Supplementary Fig. 27). Figure 6b shows the overlapped region (dark brown) where experimental $V_{oc}$, FF and $J_{sc}$ can be all well fitted within 1% deviation. The estimated intragrain electron and hole lifetimes are 10–30 ns and 0.3–0.7 ns, respectively. This shows that the intragrain minority carrier lifetime is significantly higher than the effective carrier lifetime. The electron diffusion length thus is estimated to be 1.4–2.8 μm, comparable with the value measured using bias dependent IQE26.

To identify the efficiency limiting factors and associated step-change directions for further efficiency improvement, we simulated how the efficiency changes with intragrain electron lifetime, grain boundary recombination velocity and hole density. As shown in Fig. 6c,d, if the grain boundary recombination remains at $10^3$ cm s$^{-1}$, the efficiency can hardly be improved by increasing carrier lifetime or carrier density, suggesting that the large grain boundary recombination velocity is the current limiting factor. Additionally, if the carrier density can be improved to $5 \times 10^{16}$ cm$^{-3}$, a typical carrier density level for state-of-the-art CZTSe cells, the efficiency can be achieved by reducing grain boundary recombination velocity to $<10^3$ cm s$^{-1}$ and increasing electron lifetime to 100 ns. On the other hand, larger grain size will also lead to better performance (Supplementary Table 2) because both $r_{cb}$ and $r_{al}$ linearly increase with grain size as described by equation (5).

**Discussion**

The above results indicate the device performance of the investigated 12.4% efficient CZTSe solar cells is mainly limited by the large grain boundary recombination velocity and the relatively low net carrier density. There are reported strategies to increase the net carrier density without introducing secondary phases, such as indium and lithium doping9,20. However, investigation of grain boundary passivation for kesterite materials is rather limited.
The grain interior carrier lifetime is in a range of 10–30 ns, much higher than expected. Device simulations have shown that further improving grain interior carrier lifetime would not give any improvement in device performance if 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 (probably because grain interior lifetime is too low) but hardly further improve the efficiency if baseline efficiency is at a level of 12–13%. Therefore, strategies for effective grain boundary passivation are urgently needed. 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.

Considering the radiatively limited lifetime versus carrier density of CZTSe materials (Supplementary Fig. 29), an increase in carrier density to about 5.0 × 10^{15} cm^{-3} would be beneficial for the Voc and efficiency when the intragrain lifetime can be increased to 100 ns, which is an essential direction to improve the efficiency towards 20% and beyond.

For sulfide Cu_{2}ZnSnS_{4} (CZTS) solar cells, the microscopic carrier loss mechanisms can be investigated using the same framework, though some optoelectronic characterization such as EBIC and CL mapping could be more challenging. It is worth noting that the dominant loss mechanisms in CZTS may be different from that of CZTSe. The carrier density in CZTS is usually high (>10^{17} cm^{-3}), which, however, may impose more interfacial recombination even if the conduction band alignment is optimized. Another important issue for CZTS is the significant PL red shift due to the dominating carrier density of CZTSe materials (Supplementary Fig. 29), an increase in barrel temperature was detailed in our early publication. Some key points for controlling Se atmosphere by adjusting the Se source temperature and Se cracking and Se cracking barrel (schematic diagram in Supplementary Fig. 30). The selenization growth process. The target composition of the CZTSe absorber is Cu/Zn/Sn with a composition ratio of Mo/CZTSe/CdS/i-ZnO/ZnO:Al/Ni/Al/MgF_{2}. A 20–50 nm CdS buffer layer was deposited at 85 °C using the chemical bath deposition method. A 50 nm i-ZnO layer and a 400–450 nm ZnO/i-Al layer were subsequently deposited using radio frequency and direct current sputtering, respectively, with an Ar working pressure of 0.2 Pa. The Ni/Al grids and 110 nm MgF_{2} anti-reflector coating were deposited using electron beam evaporation. The total area of each device is about 0.24 cm^{2} defined by mechanical scribing. Total area efficiencies are reported.

**Conclusion**

We have successfully unveiled most of the important microscopic loss mechanisms in our ≥12% efficiency CZTSe solar cells. The results indicate that the junction interface is well passivated by an epitaxial ZnSe nanolayer, the radiative recombination loss through bandgap fluctuation and/or electrostatic potential fluctuation is small and that the intragrain minority carrier lifetime is between 10 ns and 30 ns, all of which are encouraging characteristics for high efficiency solar cells. Instead, the high effective recombination velocity at grain boundaries (≥10^5 cm s^{-1}) and the relatively low net carrier density (~2 × 10^{15} cm^{-3}) are the current main limiting factors of our CZTSe solar cells. This provides clear direction 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 such as perovskite and antimony chalcogenides.

**Methods**

**Cu–Zn–Sn metal precursor.** 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 Cu/(Zn + Sn) = 0.75 and Zn/Sn = 1.1, measured with X-ray fluorescence spectrometer (ARL PerformX 4200, Thermo Fisher Scientific, with Uniquant analysis software). The Cu, Zn and Sn targets have 99.999% purity. The precursor stacking order was Mo/Sn/Cu/Zn/Sn/Cu, and the sputtering pressure was about 0.2 Pa.

**CZTSe selenization process.** The metallic precursors were pre-selenized 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 ramped to 550 °C in 15 min and stayed at 550 °C for 8–10 min. The details of the annealing profile are described elsewhere. All these annealing processes were performed in a custom-made furnace that can have independent temperature control of Se source, substrates and Se cracking barrel (schematic diagram in Supplementary Fig. 30). The controlling Se atmosphere by adjusting the Se source temperature and Se cracking barrel temperature was detailed in our early publication. Some key points for the selenization processes are summarized as follows: (1) before selenization start, a pre-selenizing 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 MoSe_{2} layer; (2) a sufficient soft selenization with temperature below 300 °C (to prevent Sn loss) is important to control the bulk defects by turning Sn to Sn^{2+} and facilitating Zn diffusion to the top region before the synthesis of the CZTSe phase start at 350–400 °C (ref. 35). This Zn diffusion process enabled by the soft selenization may be a key step for the formation of the epitaxial ZnSe nanolayer. The formation of a near-continuous ZnSe nanolayer may also require a slightly high Zn/Sn ratio (close to 1:1). For example, the ZnSe layer cannot be observed in the sample with Zn/Sn ratio lower than 1.05 (Supplementary Fig. 31). In this soft selenization, it is very important to use a reactive micro-molecule Se vapour (Se_{2}) under low Se partial pressure. High Se partial pressure will lead to poor Se diffusion. (3) Sufficient Se partial pressure during high temperature annealing is important for grain growth.

**CZTSe device fabrication.** The CZTSe devices were fabricated with an architecture of Mo/CZTSe/CdS/i-ZnO/Ni/Al/MgF_{2}. A 20–50 nm CdS buffer layer was deposited at 85 °C using the chemical bath deposition method. A 50 nm i-ZnO layer and a 400–450 nm ZnO/i-Al layer were subsequently deposited using radio frequency and direct current sputtering, respectively, with an Ar working pressure of 0.2 Pa. The Ni/Al grids and 110 nm MgF_{2} anti-reflector coating were deposited using electron beam evaporation. The total area of each device is about 0.24 cm^{2} defined by mechanical scribing. Total area efficiencies are reported.

**SEM, STEM and EDS.** Morphological analysis was performed using a SEM (FEI Arpreo 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/1-Pt before milling. The transmittance electron microscopy (TEM) lamella thickness was ~100 nm. The samples were imaged on a Hitachi HD2700 STEM with high-resolution TEM mode and a JOEL JEM-F200. EDS spectra were acquired on Oxford INCA, Bruker Quantax EDS system.

**J–V and EQE measurement.** The J–V curves were performed using a solar simulator (ABET IV Tester) with AM 1.5 G illumination (100 mW cm^{-2}) at room temperature in open air. The light intensity was calibrated with a Fraunhofer World PV Scale (WPVS) reference cell (KG3 filter). The scan was from ~0.1 V to 0.5 V with a step of 4 mV and a dwell time of 2 ms. 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 Ge photodetectors as references.

**SIMS and ultraviolet photoelectron spectroscopy.** The element depth profiles were recorded by SIMS (IMS-6F; CAMECA). A primary Cs+ beam was used for 500 μm × 500 μm sampling area. Ultraviolet photoelectron spectroscopy was performed on Thermo Fisher ESCALAB 250Xi. A He I light source (21.2 eV) was used as excitation source. The spot size is 500 μm. The spectrometer was calibrated using Au 4f7/2 and Cu 2p3/2 at 83.96 eV and 932.62 eV. The data was recorded at 0 V sample bias without etching process.

**Raman mapping and Raman spectrum.** Raman spectroscopy mapping was performed using a Renishaw inVia Raman microscope fitted with a 441 nm He–Cd laser as the excitation source, 1,800 mm−1 grating and measured using a 100× objective. The focal point was above the surface of the sample to collect more signals from the surface. The pixel size was 2 μm × 2 μm. Raman spectrum on MoSe_{2} back contact was performed using a 514 nm laser as the excitation, 1,800 mm−1 grating and measured using a 100× objective. The focal point was on the surface of the sample.

**EBIC.** 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.

**Cross-section KPFM and AFM.** The cross-sectional 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) × 4.25 μm (H). A brand new PtSi probe (Bruker SCM-PFTS) was used in these measurements, and the sample was measured using a two-pass scan (one for topography in contact mode and another for CPD maps in non-contact mode). The system deviation of CPD is about ±10 mV. Surface AFM measurement was performed on an as-grown CZTSe sample using the same scan rate. Cross-section KPFM measurements, to prevent probe damage, we start the rough topology scan from the glass region, which is far from the cliff region of the cross-section, and gradually approach the glass/Mo interface. The glass/Mo interface can be identified by the sudden change of surface roughness because the cleaved glass is much smoother than the cross-section of Mo and CZTSe films.
When reaching the Mo and CZTSe interface, we slow the approach rate and then scan at the same rate until reaching the CZTSe/window layer. Once part of the window layer appears in the projected area, we stop approaching and focus on a relatively flat region for high-resolution KPFM measurements.

PL and TRPL. 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 fibre-coupled InGaAs avalanche photodiode (ID210) and processed using the time-correlated single photon counting board (TimeHarp 260). The time binning is 25 ps.

CL mapping. 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 and images were generated using the MICROWAVE software (Supplementary Fig. 14) to determine the suitable thickness of the sample and acceleration voltage used in the CL measurement. On the basis of the simulation and considering that the average grain size is around 1 μm, 10 kV and 1 μm were used for the sample and for targeting thickness of the FIB milled sample, respectively. The sample was then cleaned 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 ~1 μm thick. Before CL measurement, the sample received a final ion beam polish on both faces (Fischione NanoMill 1040) at low voltage (500 V) 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, was used to numerically examine the device physics. In this study, a 3D unit cell shown in Supplementary Fig. 24a 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 (Supplementary Figs. 22 and 23). 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, that is, the smaller mesh allows for a higher accuracy to compute the spatial distribution of key fields such as 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 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 a snapshot at a ramping step can also be saved to preserve spatial distribution of fields.

Key performance characteristics. Afterwards, the impact of grain lifetime, carrier density, grain size and the peak incident light condition was predicted, providing a guideline for future cell improvement.

Reporting summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability. The datasets analysed and generated during the current study are included in the paper and its Supplementary Information. Source data are provided with this paper.

Code availability. The codes used for simulation within this paper are available from the corresponding author upon reasonable request.

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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 J–V, EQE, J–V–T, CV/DLCR, Raman mapping, SEM, EBIC measurements and most of the data analysis; and wrote the manuscript. J.H. analysed the HR-STEM, EBIC and CL data. F.M. developed the 3D device simulation model. F.M. and J.L. performed the 3D simulation. W.Y., J.L. and H.S. conducted KPFM measurements. J.H. and J.C. fabricated the FIB sample for CL mapping and STEM-EDS measurements. K.P., J.H., R.D.T. and J.L. conducted the CL mapping. R.F.W., S.C., R.D.T. and J.H. conducted the STEM-EDS measurements. R.L.C., Z.H. and J.L. conducted the PL and TRPL measurements. X.Y. did the Raman measurements. M.H. and K.S. assisted in precursor and window layer fabrication. H.L. assisted in EBIC measurements. All authors discussed and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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## Solar Cells Reporting Summary

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### Experimental design

**Please check: are the following details reported in the manuscript?**

|   |   |   |
|---|---|---|
|  | Yes | No |
| 1. Dimensions |   |   |
| Area of the tested solar cells |   |   |
| Method used to determine the device area |   |   |
| 2. Current-voltage characterization |   |   |
| Current density-voltage (J-V) plots in both forward and backward direction |   |   |
| Voltage scan conditions |   |   |
| For instance: scan direction, speed, dwell times |   |   |
| Test environment |   |   |
| For instance: characterization temperature, in air or in glove box |   |   |
| Protocol for preconditioning of the device before its characterization |   |   |
| Stability of the J-V characteristic |   |   |
| Verified with time evolution of the maximum power point or with the photocurrent at maximum power point; see ref. 7 for details. |   |   |
| 3. Hysteresis or any other unusual behaviour |   |   |
| Description of the unusual behaviour observed during the characterization |   |   |
| Related experimental data |   |   |
| 4. Efficiency |   |   |
| External quantum efficiency (EQE) or incident photons to current efficiency (IPCE) |   |   |
| A comparison between the integrated response under the standard reference spectrum and the response measure under the simulator |   |   |
| For tandem solar cells, the bias illumination and bias voltage used for each subcell |   |   |
| 5. Calibration |   |   |
| Light source and reference cell or sensor used for the characterization |   |   |

- Methods - The total area of each device is about 0.24 cm² defined by mechanical scribing. Total area efficiencies are reported.
- Hysteresis is not observed.
- Methods - The scan was from 0.1V to 0.5V with a step of 4 mV and a dwell time of 2 ms.
- Methods - The cells were measured at room temperature in open air.
- No light soaking or other protocol for preconditioning was employed.
- Supplementary Figure 1b. The J-V characteristics was tracked after storage aging for 42 days and 167 days.
- No hysteresis and other unusual behavior has been observed by authors.
- Provided EQE in Figure 1b in main manuscript.
- See the integrated $J_{sc}$ from EQE in Figure 1b in main manuscript. The integrated $J_{sc}$ is slightly (0.1 mA/cm²) higher than the $J_{sc}$ measured under simulator.
- Not applicable.
- Methods - The J-V curves were performed using a solar simulator [ABET IV Tester] with AM1.5 G illumination [100 mW cm⁻²] at room temperature in open air. The light intensity was calibrated with a Fraunhofer WPSV reference cell [KG3 filter] reference cell.
6. Mask/aperture

Size of the mask/aperture used during testing

Variation of the measured short-circuit current density with the mask/aperture area

7. Performance certification

Identity of the independent certification laboratory that confirmed the photovoltaic performance

A copy of any certificate[s]

Provide in Supplementary information

8. Statistics

Number of solar cells tested

Statistical analysis of the device performance

9. Long-term stability analysis

Type of analysis, bias conditions and environmental conditions

For instance: illumination type, temperature, atmosphere humidity, encapsulation method, preconditioning temperature

| Yes | No |
|-----|----|
| ✔   |    |

Methods - The light intensity was calibrated with a Fraunhofer WPVS reference cell (KGS filter) reference cell.

Yes | No
---|---

Certificated silicon solar cells are commonly used as the reference solar cell for performance test of kesterite thin film solar cells. For kesterite CZTSe the band gap energy (E_g=1.0 eV to 1.05 eV) is close to silicon solar cell (E_g=1.10 eV).

Yes | No
---|---

Not applicable as no mask/aperture is used.

Yes | No
---|---

Not applicable as no mask/aperture is used.

Yes | No
---|---

A sister cell with 12.5% efficiency has been independently confirmed by Fujian Metrology Institute/National PV Industry Measurement and Testing Center, NPVM. The device performance has been cross-checked by UNSW and Jinan University. The light intensity of our solar simulator for J-V and EQE measurement was calibrated by standard Silicon and Ge cells which were calibrated by Fraunhofer.

Yes | No
---|---

The light intensity of our solar simulator for J-V and EQE measurement was calibrated by standard Silicon and Ge cells which were calibrated by Fraunhofer. We do not claim record efficiency in this work.

Yes | No
---|---

Supplementary Figure 1a.

Yes | No
---|---

Supplementary Figure 1a.

Yes | No
---|---

Supplementary Figure 1b. The J-V characteristics was tracked after storage aging for 42 days and 167 days. Long term stability testing is beyond the scope of this article.