Suppressing Deep-Level Trap and Energy Band Alignment Enable Air-Solution-Processed Cu2ZnSnS4 Thin Film Solar Cell with Certified Record Efficiency

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Abstract

The sulfide kesterite Cu$_2$ZnSnS$_4$ (CZTS) is widely recognized as a highly competitive photovoltaic material, especially for use in multi-junction solar cells, due to its excellent photoelectric properties. However, the power conversion efficiency (PCE) of CZTS solar cells has remained stagnant for years. The presence of deep level defects, such as V$_S$ (sulfur vacancies), has been demonstrated to provide a kind of effective non-radiative recombination pathway, leading to serious open-circuit voltage ($V_{OC}$) deficit and reduced efficiency in carrier migration and separation. Herein, we propose a novel directional passivation strategy for V$_S$ through an easily operable heterojunction heat treatment. By introducing O$_2$ during this process, sulfur vacancies can be readily occupied by oxygen atoms in an oxygen-rich environment, thus contributing to eliminating the already-existing V$_S$ defects. In addition, the thermal movement of ions during this process induces Cd diffusion to the absorption layer to occupy the Cu or Zn lattice sites, these collective effects lead to a reduced charge recombination and more favorable band alignment. As a result, CZTS thin film solar cell with a PCE of 11.89% and a certified record efficiency of 11.51% was achieved. The present study offers valuable insights into defect passivation mechanism of kesterite thin-film solar cells.
1. Introduction

Kesterite Cu$_2$ZnSn(S, Se)$_4$ (CZTSSe), widely recognized for its exceptional light absorption capabilities, abundant and non-toxic elemental composition, tunable band gap properties, environmental friendliness, and excellent stability, is a highly promising material for thin-film solar cells$^{1-4}$. It is a direct derivative of commercial CdTe and CuIn$_x$Ga$_{1-x}$Se$_2$ (CIGS) cells in diamond configurations, known for their potential to achieve high efficiency. Although the photoelectric conversion efficiency of current laboratory-prepared CZTSSe thin film solar cells falls significantly below its detailed balance limiting efficiency of 33% and the efficiency record of commercial CIGS$^5$, recent advancements in CZTSSe thin film solar cells have showcased progress, with a jump in efficiency from 12.6% to 14.6% by Meng et al.$^6$-$^8$, re-establishing their prominence among inorganic thin film solar cells. However, pure sulfide CZTS thin film solar cells, which possess fewer constituent elements and a similar crystal structure, have experienced a stagnant photoelectric conversion efficiency (about 11%) for years$^9$. The substantial $V_{OC}$ deficit ($E_g/q-V_{OC}$) exhibited by kesterite CZTS is commonly attributed to the primary factor contributing to this predicament$^{10}$. Several factors have been proposed to explain the $V_{OC}$ deficit, such as a high density of charged defects linked to band tailing$^{11}$, an overly thick MoS$_2$ layer at the back of the CZTS device$^{12}$, $^{13}$, the presence of secondary phases, and unfavorable band alignment at the CZTS/CdS heterojunction interface$^{14-17}$. The current research stage emphasizes the CZTS absorber layer itself to address these challenges. The CZTS absorber is primarily optimized through doping engineering and heat treatment technology, with a focus on enhancing the crystal quality and indirectly impact the interface. While selenide CZTSSe thin film solar cells have achieved a photoelectric conversion efficiency of over 14% through optimized absorber operation$^{18}$, factors like element doping, sulfurization adjustment, and solvent engineering seem to play a limited role, in pure sulfide CZTS thin film solar cells$^{19}$. Currently, CZTS absorber films are typically fabricated using either magnetron sputtering or solution spinning coating methods for the precursor, followed by
sulfurization to obtain highly crystalline films. Regardless of the chosen method, process optimization consistently achieves a high degree of crystallinity in the absorber film. Unlike CZTSSe, CZTS films exhibit large grains, suggesting that the heterojunction interface is key to improved photoelectric performance. Therefore, heightened attention is required for controlling interface properties between adjacent functional layers such as the Mo electrode, absorber layer, buffer layer, window layers, and grid lines. Defects at interfacial and unfavorable band alignment can lead to nonradiative recombination and charge losses, impacting both the open-circuit voltage ($V_{OC}$) and fill factor (FF). Specifically, the formation of P-N junctions is crucial as abundant defects may exist near the CZTS/CdS heterojunction including interface and space charge region defects. These defects contribute to severe recombination near the heterojunction, introduce band tail states within the bandgap, and reduce carrier lifetime, directly leading to $V_{OC}$ deficit. Post-heat treatment is considered a simple and effective strategy to enhance the quality of the heterojunction, as demonstrated by Yan et al. who achieved a record efficiency for pure sulfide CZTS thin-film solar cells through post-heat treatment, which induced mutual diffusion of elements and reduced recombination caused by defects. Su et al. enhanced the charge transport efficiency and carrier concentration by incorporating alkali metal ions at the heterojunction interface to optimize band alignment, ultimately achieving a photoelectric conversion efficiency exceeding 11%. However, research primarily focuses on cation substitution and exchange, with limited in-depth investigations on anion vacancies defect, such as $V_S$. The prevalent formation $V_S$, a point defect in CZTS films, impacts crystal structure crystal, stability, and introduce deep-level defects as non-radiative recombination centers, affecting charge transport capacity by reducing carrier lifetime and diffusion length. The lack of understanding regarding the formation and transformation mechanisms of these defects imposes barriers on the development of efficient strategies for defect passivation.

In this work, the passivation mechanism of defects in CZTS/CdS heterojunctions is elucidated by employing heat treatment in an oxygen-rich environment to effectively passivate sulfur vacancy defects. We demonstrate that some O being introduced into
both the CdS and the CZTS absorber is able to occupy the Vs, the harmful deep level vacancy defects are transformed into benign Os defects. With this defect passivation, the devices shown enhanced charge transport efficiency and prolonged minority carrier lifetime. As a result, we achieved a pure sulfide kesterite solar cell with 11.89% PCE and a certified record efficiency of 11.51%.

2. Results

In our experimental approach for fabricating CZTS solar cells, two crucial steps are involved: spin-coating of CZTS precursor, followed by high-temperature sulfurization annealing. Simultaneously, the addition of sulfur powder incorporates stannous sulfide to mitigate the evaporation of tin-related phases during annealing, thereby promoting the formation of high-quality kesterite CZTS absorber films. Detailed information about this experiment can be found in the experimental section, where the fundamental procedure results in a solar cell photoelectric conversion efficiency of 9.14%. After the deposition of CdS, the heterojunction heat treatment was conducted in a constant temperature water bath, as shown in Fig. 1. The CZTS/CdS heterojunction underwent heat treatment in an atmosphere of oxygen and nitrogen, resulting in samples labeled as CZTS/CdS (N-HT) and CZTS/CdS (O-HT), respectively. Various processing temperatures and treatment times were explored, ranging from 100 °C to 370 °C and 1 minute to 9 minutes. (Supplementary Figs. 1-2 for device performances at different HT temperatures and duration time) Among these conditions, treating the samples at 280 °C for 5 minutes yielded the most optimal and reproducible performance results, making it the preferred choice for comprehensive analysis. The schematic diagram of the CZTS solar cell fabrication is illustrated in Fig. 1. Upon heat treatment in a nitrogen environment, the interdiffusion of cadmium and copper zinc ions at the interface led to ion substitution. Conversely, when the heat treatment was conducted in oxygen, mutual diffusion of metal ions and occupation of sulfur vacancies by oxygen were observed. The untreated device displayed a VOC of 695 mV, a $J_{SC}$ of 22.48 mA cm$^{-2}$, an FF of 59.8%, and an overall PCE of 9.14%. The N-HT device showed improved parameters with values increasing to 701 mV, 23.73 mA cm$^{-2}$, 64.93%, and 10.81% for $V_{OC}$, $J_{SC}$,
FF, and PCE, respectively, after heat treatment in N\textsubscript{2} atmosphere. Furthermore, heat treatment in oxygen led to an increase in the PCE of thin-film solar cells to 11.89\%, with $V_{\text{OC}}$ rising to 728 mV, and $J_{\text{SC}}$ and FF increasing to approximately 25.15 mA/cm\textsuperscript{2} and 68.29\%, respectively. As a result of a statistical analysis of these parameters, there were significant differences in the performance of the three devices types (Supplementary Figs. 3). Additionally, the champing device received certified performance from the National PV Industry Measurement and Testing Center (NPVM), (Fig. 1g and Supplementary Figs. 4), with a certified photoelectric conversion efficiency of 11.51\%, $V_{\text{OC}}$ of 708.7 mV, $J_{\text{SC}}$ of 24.17 mA cm\textsuperscript{-2} and FF of 67.18\%. The certified efficiency achieved by this pure sulfide Cu$_2$ZnSnS$_4$ solar cell is currently the highest recorded, with a current density exceeding 24 mA/cm\textsuperscript{2}, approaching its theoretical maximum value while maintaining a high $V_{\text{OC}}$, surpassing previous literature reports\textsuperscript{5}.

The External quantum efficiency (EQE) spectra of different heat treatments and control cells are shown in Fig. 1h, which is consistent with the aforementioned results. The enhancement of N-HT in $J_{\text{SC}}$ by approximately 2 mA cm\textsuperscript{-2} primarily originates from an increase in EQE within the wavelength range of 300 to 600 nm, while the improvement of O-HT in $J_{\text{SC}}$ by approximately 4 mA cm\textsuperscript{-2} is attributed to an enhanced EQE within the wavelength range of 600 to 1000 nm. These findings suggest a more efficient extraction of photocarriers generated within the bulk absorber. The reduction in charge losses is also responsible for the significant improvements in $V_{\text{OC}}$ and FF. Both absorbers showed similar bandgaps close to 1.51 eV based on EQE spectra as depicted in Fig. 1i. This indicates that the substantial increase in current is not attributed to alterations in the band gap. However, it is noteworthy that there is a significant augmentation in the band gap of buffer CdS within the heat-treated heterojunction. This could potentially have a profound impact on the band arrangement of the heterojunction, which will be further substantiated through subsequent tests. Urbach energy (E\textsubscript{U}) (Fig. 1j) is calculated from EQE spectra to be 35.7, 33.3 and 32.7 meV for the W/O, N-HT and O-HT CZTS thin-film solar cells, respectively. The heat treatment results in a decrease in Urbach energy, indicating a reduction in the number of band trailing states\textsuperscript{23}. 
Moreover, when the heat treatment is conducted in an oxygen environment, there is further suppression of carrier recombination, which greatly benefits device performance. **Fig. 1k** shows the PL spectra of different samples. The PL peak intensity of the N-HT CZTS is significantly sharper due to the reduction of nonradiative recombination in the CZTS absorber layer. It has an important contribution to the improvement of $V_{oc}$ and short-circuit current. Moreover, the reduced $\Delta E_g = E_g (\text{EQE}) - E_g (\text{PL})$ from $\approx 30 \text{ meV (pristine)}$ to $\approx 10 \text{ meV (O-HT)}$ suggests a decline in electrostatic potential fluctuations within the absorber film, providing evidence that suppressed defects may be attributable to a reduction in Cu–Zn antisite defects in the CZTS absorption layer\textsuperscript{24-27}.

It has been established that PCE significantly increases in cells treated with a heterojunction in an oxygen-rich environment, with the heterojunction regions showing substantially reduced non-radiative recombination. The next phase of investigation will focus on exploring the alterations occurring in the space charge region (SCR) following heat treatment in an oxygen atmosphere. **Fig. 2a** illustrates element distribution mapping of the device cross-section, revealing a discernible diffusion of metal components from the absorption layer into the buffer layer CdS, as well as Cd diffusion from the buffer layer into the absorption layer near the interface. Additionally, **Supplementary Fig. 5** illustrates the element distribution curve obtained from the TEM-EDS line scan, revealing a noticeable influx of O atoms with a uniform concentration throughout the buffer layer to the absorption layer after slight reduction.

In high-resolution high-angle annular dark field imaging (HAADF), we examined the upper CZTS region adjacent to the CZTS/CdS interface. An atomic column's contrast in a HAADF-STEM image is approximately proportional to the constituent atom's mean square atomic number ($Z^2$)\textsuperscript{28, 29}. The magnified image in **Fig. 2d** clearly shows distinct contrasts between ion columns. **Fig. 2f** presents the intensity profile of a row of ions, as indicated by the yellow rectangle in **Fig. 2d**. The significantly lower intensity of the weakness peaks, being less than half of those observed in the higher peaks, strongly suggests an association with an anion site. Moreover, it is apparent that both
columns exhibit considerably weaker intensities compared to the remaining lower peaks and are far below half of the represented metal cations' peak. This provides a robust indication that some oxygen atoms occupy sulfur sites. Subsequently, we conducted deep etched XPS tests on various heterojunction surfaces to further investigate elemental changes during this process.

Given that CdS fabricated by the chemical bath deposition (CBD) method is known to exhibit sulfur deficiency, the presence of S vacancies originating from the preparation method may significantly influence the photoelectrochemical (PEC) performance. It is likely that these untreated sulfur vacancies will act as recombination centers in CZTS/CdS heterojunctions, causing inefficient charge separation. This could be a crucial factor explaining why the current heterojunction heat treatment scheme fails to further enhance the photoelectric conversion efficiency of CZTS thin film solar cells, even when a high-quality heterojunction interface is achieved. The chemical states of CZTS/CdS(W/O), CZTS/CdS (N-HT), and CZTS/CdS (O-HT) were characterized using Deep X-ray photoelectron spectroscopy (XPS). The peak position at approximately 531.5 eV in the O 1s spectrum for CZTS/CdS (W/O) is attributed to the presence of oxygen-containing groups incorporated during the CBD process. With increasing depth of CZTS/CdS, the intensity of the O 1s signal diminishes, indicating that oxygen is predominantly located on the surface of CdS. Interestingly, no signals related to oxygen were observed in samples annealed in nitrogen. We propose that a small amount of water may be present on the surface of CBD-treated samples, which evaporates completely upon annealing in nitrogen and eliminates all traces of oxygen.

In contrast, when CZTS/CdS was heat treated in O2, an O 1s signal was still detected even at greater etching depths, suggesting that oxygen doping occurred due to heterojunction heat treatment in O2. The S 2p peaks of CZTS/CdS (NHT) at approximately 161.3 eV exhibit a shift towards lower binding energies, which may be attributed to the detachment of some sulfur atoms during the heat treatment of CZTS/CdS, indicating an increase in the concentration of sulfur vacancies. Conversely, we observed positive shifts in the binding energies of S 2p spectra for CZTS/CdS (O-HN), suggesting a decrease in the amount of sulfur vacancies. The introduction of
oxygen through heat treatment occupies these sulfur vacancies and binds to low-
coordination cadmium atoms, thereby reducing electron density around Cd and S\textsuperscript{32}.
This also explains the positive shift in Cd 3d and S 2p peak binding energy after
annealing the heterojunction as shown in Supplementary Figs. 6. Furthermore, Figs.
6a reveals that with increasing etching depth and decreasing peak intensity, there is a
negative displacement observed for O-HT's O 1s peak, indicating a decrease in oxygen
doping concentration. Revealing a gradual decrease in oxygen content from a high
concentration in the CdS buffer layer to a weak content the CZTS absorption layer as
depth increased, which is highly consistent with the analysis of the TEM test above.
Additionally, XRD and Raman tests (Supplementary Figs. 8) do not detect any
oxygen-related quadratic terms, strongly suggesting that oxygen doping predominantly
occupies sulfur vacancies. Fewer sulfur vacancies are associated with fewer
recombination centers, which is beneficial for improving charge transport efficiency,
consistent with the enhanced \(J_{SC}\) and PCE demonstrated in Fig. 1.
The surface potential distribution of the CZTS film was examined by conducting Kelvin
probe force microscopy (KPFM) analysis. After heterojunction heat treatment, all
samples were etched with CdS, followed by KPFM characterization of the absorbing
layer. The KPFM images in Fig. 3 a-c depict the contact potential difference (CPD)
distribution for W/O, N-HT, and O-HT films as -111.3 to 172.6 mV, -66.1 to -80.1 mV,
and -60.8 mV to 81.2 mV respectively. The CPD mapping results suggested that the
heterojunction heat treatment significantly modified the energy band bending behaviors
of the CZTS absorber film. Specifically, in the untreated film, a higher CPD was
observed in the grain boundary region, indicating band bending towards lower energy
levels. Consequently, photogenerated minority carriers were drawn to this defective
grain boundary region, resulting in carrier loss. In contrast, after heat treatment of the
heterojunction, a significant reduction in CPD values (as shown in Fig. 3b-e and c-f
indicated a substantial inhibition of this phenomenon. Band bending was considerably
weakened due to reduced receptor defects at grain boundaries. As depicted in the
schematic diagram (Fig. 3h) illustrating the energy band bending in the vicinity of the
grain boundary (GB) regions, O-HT samples exhibit a more favorable and a lesser
degree of band bending due to an effective reduction of the Vs donor defects, which facilitates spatial separation of electrons and thus reduces carrier recombination\textsuperscript{33-35}. The obtained result is in line with the analysis of steady-state photoemission spectra test conducted previously.

Ultraviolet photoelectron spectroscopy (UPS) analysis (Supplementary Figs. 11) was utilized to delve deeper into the fundamental physical mechanisms and acquire a more detailed understanding of the band alignment, which plays a crucial role in determining the charge transport mechanism. This analysis unveiled the spectra of valence band maximum (VBM) and secondary electron cut-off ($E_{\text{cutoff}}$) for both untreated and O$_2$-heat-treated CZTS and CdS films. The band alignment diagram of CZTS/CdS is illustrated in Fig. 3i. Prior to heat treatment (HT), these positions relative to the Fermi energy ($E_F$) were determined to be 1.46 eV for CdS and 0.51 eV for CZTS. Subsequent to the HT process, these positions shifted to 1.51 eV for CdS and 0.38 eV for CZTS. The movement of the Fermi level of CZTS towards its VBM following heat treatment suggests an elevation in the CZTS doping level. The conduction band offset (CBO) is commonly utilized as a quantitative measure of the band alignment at the heterojunction (the details are shown in Supplementary Note2), with values estimated at -0.1 eV pre-heat treatment and 0.11 eV post-heat treatment. A CBO value in the range of -0.1 to -0.3 eV signifies a cliff-like band structure. Such a configuration introduces a barrier for injected electrons under forward bias, leading to increased majority carrier recombination via defects at the interface and consequent deterioration in device performance\textsuperscript{36,37}. However, the temperature-induced ion diffusion causes the conduction band minimum (CBM) and VBM of both the CZTS absorber and CdS buffer layers to shift towards an optimal band arrangement. Consequently, the CBO at the heterojunction is reversed to spike-like structure the device after HT, facilitating a more favorable band alignment that effectively mitigates hetero-interface recombination and prevents charge carrier accumulation near the interface. This improvement notably enhances charge carrier collection and boosts the $J_{SC}$ in the device.
To gain a better understanding of how oxygen atom injection affects defect properties and device performance. We measured capacitance-voltage profiles (N\textsubscript{CV}) and driven level capacity profiles (N\textsubscript{DL}) at different frequencies in order to characterize interface defects and bulk defects caused by carrier concentrations, as shown in Fig. 4a (the details are shown in Supplementary Note3 Figs. 12). The interfacial defect concentration of the W/O, N-HT, and O-HT was estimated to be 2.8 × 10\textsuperscript{15} cm\textsuperscript{-3}, 5.3 × 10\textsuperscript{14} cm\textsuperscript{-3}, and 2.3 × 10\textsuperscript{14} cm\textsuperscript{-3}, respectively. As a result of heterojunction heat treatment, interfacial defect concentrations are significantly reduced, thereby improving the quality of P-N junctions. Additionally, the disparity in carrier concentrations between low and high frequencies can be used to determine bulk defect concentrations. The difference in DLCP curves between high and low frequencies of the three devices resulted in estimated bulk defect concentrations of W/O, N-HT, and O-HT as 8.6 × 10\textsuperscript{15} cm\textsuperscript{-3}, 7.3 × 10\textsuperscript{15} cm\textsuperscript{-3}, and 5 × 10\textsuperscript{15} cm\textsuperscript{-3}, respectively\textsuperscript{38}. Obviously, the reduced bulk defect concentration and interfacial defects attributed to the optimization of CZTS/CdS heterojunction treatment. Additionally, O-HT devices exhibit higher \textit{V}\textsubscript{bi} as determined from C\textsuperscript{-2}–V analysis (Supplementary Figs. 13), which is considered more favorable for facilitating charge carrier transport and consequently leading to enhanced \textit{V}_{OC} and \textit{J}_{SC}\textsuperscript{39,40}.

Conducting modulated electrical transient measurements is an effective approach for examining the impact of heterojunction heat treatment on cell performance. This method enables the investigation of charge transfer and recombination dynamics properties under different operating voltages, as well as the quantification of bulk and interface charge loss in the device. Supplementary Figs. 14 display the photocurrent decay of CZTS/CdS samples under different conditions, revealing that the decay rate of the modulated transient photocurrent (M-TPC) curve for the heat-treated sample is notably faster than that of the untreated sample at specific voltages (-1 V and 0 V), indicating enhanced charge transport capability post heat treatment. The photocurrent peak position of the heat-treated sample shows minimal shifts with bias changes compared to the untreated samples, suggesting improved stability in charge transport, particularly pronounced for the O-HT sample due to its favorable band arrangement.
and reduced trap states. Moreover, the modulated transient photovoltage (M-TPV) results in Supplementary Figs. 14d-f highlight distinct differences in carrier recombination properties among the three samples. The untreated samples exhibit a fast dual-exponential decay dynamic at 0 V bias, implying carrier recombination at both the CZTS bulk and heterojunction interface. In contrast, the heat-treated samples, particularly the O-HT sample, display slower photovoltage decay, indicating reduced recombination centers resulting from S-vacancy replacement and thus inhibiting carrier recombination. Furthermore, the quantitative assessment of charge loss in the cell based on M-TPC and M-TPV results reveals that heat-treated samples with heterojunctions demonstrate enhanced charge collection efficiency ($\eta_c$), suggesting a reduction in interface defect-induced charge loss. Additionally, the O-HT solar cell shows higher charge collection efficiency ($\eta_e$) due to reduced defects in the CZTS absorber. Also, the efficiency of charge collection is closely related to the minority carrier diffusion length ($L_d$) (Supplementary Figs. 17), which was investigated for different CZTS devices using bias-dependent EQE (Supplementary Figs. 16 Note 4). The device subjected to heat treatment exhibits a reduced dependence on $X_d$ and yields a deduced $L_d$ value of 0.68 \(\mu\)m, which closely matches the thickness of the CZTS absorber layer. This proximity offers advantages for efficient collection of photogenerated carriers, thereby enhancing quantum efficiency and current density. According to the formula of $L_d$ for O-HT device (Note 4 formula S12), it exhibits a maximum electron mobility ($\mu_e$) at 156 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\). Given that charge carriers in solar cells predominantly travel along the out-of-plane direction, the absence of grain boundary scattering offers an advantage by facilitating the migration of minority carriers through single-layer large grains. This observation aligns with the findings obtained from SEM cross-section analysis (Supplementary Figs. 9). The increase in carrier diffusion length and electron mobility may also indicate a decrease in defect levels. To validate these conclusions, the electrical properties of the device were examined.

To gain a deeper understanding of the generation of defects and passivation mechanisms during heterojunction heat treatment, capacitance-mode deep-level
transient spectroscopy (C-DLTS) and temperature-dependent admittance spectroscopy (AS) and were carried out on these three devices to detect specific defects. A pair of DLTS signals for W/O and N-HT shows both negative and positive peaks (Fig. 4c), respectively, corresponding to majority and minority carrier traps, including one electron trap (E1) and one hole trap (H1)\textsuperscript{44,45}. Only a single negative peak is observed in the O-HT sample, indicating the presence of one hole trap in O-HT-CZTS films. Detailed information about the defects (shown in Table 3) is derived by linearly fitting the points near the DLTS peak on the Arrhenius curves (Supplementary Note6), where $E_T$ represents the trap activation energy and $N_T$ represents the trap concentration. The hole trap activation energies range from 0.5 to 1 eV (relative to the valence band maximum (VBM)), which is attributed to the $V_S$ doner defect. Besides, the defects with $E_T$ range from 0.4 to 0.68 eV and from 0.2 to 0.4 eV [relative to the conduction band minimum (CBM)] can be classified into [2Cu$_{Sn}$+Sn$_{Zn}$] and [2Cu$_{Zn}$+Sn$_{Zn}$] defect clusters\textsuperscript{46, 47}. By comparison, it can be observed that both W/O and N-HT devices exhibit a hole trap (H1) located approximately 0.75 eV above the VBM. Notably, there is an increase in defect density when the heterojunction undergoes nitrogen heat treatment. This suggests that nitrogen heat treatment exacerbates sulfur vacancy defects, likely due to the disordered movement of sulfur atoms during the process. In contrast, donor defects associated with sulfur vacancies completely disappear after the heterojunction is heat-treated in oxygen. These deep-level defects, which are situated very close to the middle of the bandgap, can cause significant trap-assisted Shockley-Read-Hall (SRH) recombination. The elimination of H1 in the CZTS absorber following oxidative heat treatment effectively inhibits non-radiative recombination, thereby mitigating the degradation of device performance. The admittance spectra (AS) within the temperature range of 110–340 K are presented in Supplementary Figs. 18. A significant frequency dependence of the capacitance in the W/O device suggests a higher density of traps within the absorber layer, and the Arrhenius plots for three distinct devices were illustrated in Fig. 4e, with the activation energy (Ea) derived from these plots approximating the difference between the defect level and valence band edge.
The $E_a$ values range from 0.10-0.20 eV [relative to the valence band maximum (VBM)] can be assigned to $\text{Cu}_{\text{Zn}}$ antisite acceptor defects\textsuperscript{47}. The energy level and concentration of both shallow defects and deep-level defects were illustrated in Fig. 4g through a schematic diagram. Considering the figure, it is evident that all three devices have similar activation energies for electron traps attributed to the $[2\text{Cu}_{\text{Zn}}^+\text{Sn}_{\text{Zn}}]$ and $[2\text{Cu}_{\text{Sn}}^+\text{Sn}_{\text{Zn}}]$ defect cluster, which shifts the conduction band edge downward, resulting in photoelectric capture. It has been identified that deep-level defects induce electron-trapping states and act as recombination centers, resulting in band tailing in kesterite CZTS semiconductors, thereby reducing device performance by decreasing the device $V_{oc}$. However, compared to W/O devices, heat-treated samples, especially O-HT ones, exhibit lower defect levels and density as well as a narrower defect distribution. This feature of defects leads to reduced defect loss and improved device performance. Therefore, this suggests that reducing the energy level and density of defects and consequently minimizing the band tail state is also crucial for enhancing device performance. This finding is consistent with previous results showing a reduction in band-tail energy $E_u$. The high concentration and/or deep energy level of defects would exacerbate carrier recombination, as defects more readily act as centers for carrier recombination. As depicted in the figure, the generation of shallow $\text{Cu}_{\text{Zn}}$ antisite defects (ranging from 0.10 to 0.20 eV) is also not impeded; however, heat treatment effectively reduces both defect energy levels and densities. These findings once again demonstrate that a rational heterojunction treatment scheme effectively inhibits photogenerated carrier recombination.

Moreover, the O-HT device exhibits superior $R_{\text{rec}}$ and minimal $R_s$ values when assessed using electrical impedance spectroscopy (EIS) and depicted as Nyquist plots alongside their corresponding equivalent circuit (Fig. 4h). This indicates that the implementation of efficient interfacial modifications has effectively minimized charge recombination and improved charge transportation. The diffusion-recombination model ($\tau_n = R_{\text{rec}} \times C$) indicates the extension of carrier lifetime to 6.76 ms for the O-HT device, consequently decreasing recombination and enhancing carrier transport due to superior heterojunction quality. In addition, an extension was pursued to determine the lifetime
of minority carriers through the time-resolved photoluminescence (TRPL) technique, employing a 532 nm laser to explore the effects of defects on nonradiative recombination processes. The lifetimes \( \tau_1 \) and \( \tau_2 \) were obtained through appropriate fitting procedures (Supplementary Note7). As per Fig. 4i, it is evident that W/O exhibited an average minority carrier lifetime of 4.93 ns, whereas N-HT and O-HT displayed longer lifetimes at about 11.00 ns and 14.25 ns respectively. This outcome implies a decrease in free carrier recombination, leading to enhanced efficiency in charge collection and overall performance of the cell.

**Conclusion**

In summary, a straightforward heterojunction heat treatment process was developed to enhance the interfacial properties and performance of CZTS thin-film solar cells. This process involves conducting heat treatment in an O\(_2\) environment, to achieve element inter-diffusion near the interface, resulting in effective oxygen doping while preserving a gradient of zinc in cadmium sulfide and a gradient of cadmium in the CZTS layer. The presence of oxygen has a positive impact on minimizing S-vacancy defects in the CdS and CZTS layers, resulting in an overall reduction in imperfections and improved p-type properties of the CZTS absorber. This leads to a significant suppression of non-radiative recombination losses and prolongation of carrier lifetime within the CZTS solar cell. The elemental inter-diffusion also helps in attaining a more favorable band alignment, resulting in a substantial reduction in recombination at the heterojunction interface. As a result, of these improvements, sulfurized CZTS thin-film solar cells demonstrated a PCE of 11.89\%, with a certified efficiency of 11.51\%, representing the highest reported performance for pure sulfide kesterite CZTS thin-film solar cells. This work provides novel insights into post-treatment strategies for enhancing heterojunctions in efficient kesterite solar cells, which could potentially be extended to various types of inorganic thin-film solar cells and supports the development of wide-band gap tandem solar cells.
Materials and Methods

Materials

CuCl (99.995%, Aladdin), Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O (99.99%, Aladdin), and SnCl\textsubscript{4}·5H\textsubscript{2}O (99.995%, Macklin), thiourea (99.99%, Aladdin), 2-methoxyethanol (99.8%, Aladdin), S powder (99.95%, Aladdin), SnS\textsubscript{2} (99.99%, Macklin), CdSO\textsubscript{4}·8/3H\textsubscript{2}O (99.99%, Aladdin), ammonium (95%, Aladdin) (without additional purification) were used to prepare precursor solution.

Film preparation

CZTS precursor film preparation: The mixture of CuCl\textsubscript{2}, SnCl\textsubscript{4}·5H\textsubscript{2}O, Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O and thiourea was dissolved in 2-methoxyethanol, followed by continuous stirring at a constant temperature of 60 °C for 1 hour until a fully dissolved solution was obtained. All the above steps are carried out in a glove hood. The concentration of Cu/Zn+Sn in the solution was 0.85, and the ratio of Zn/Sn was maintained at 1.2. The precursor solution was applied onto a Mo substrate using spin-coating at a speed of 4000 rpm for a duration of 20 seconds. Subsequently, the coated substrate was annealed in the air at a temperature of 280°C. This process was repeated twelve times to achieve a CZTS precursor thin film with an approximate thickness of 1.2 μm. The resulting thin film was then placed inside a graphite box and subjected to sulfur atmosphere annealing, wherein two glass boats containing SnS\textsubscript{2} (0.06 g) were positioned on opposite sides of the precursor film. The detailed sulphuration condition was as followed: the temperature was initially increased to 610 °C in a span of 50 minutes and then held steady for a duration of 20 minutes. Subsequently, all samples were allowed to cool down naturally inside the graphite box along with the furnace until completion.

Device preparation

The CZTS devices were produced using a standard configuration of Mo/CZTS/CdS/ITO/Ag/MgF\textsubscript{2}. A chemical bath deposition (CBD) technique was employed to deposit a CdS buffer layer of approximately 50 nm thickness at a
temperature of 80 °C. The solution was prepared by combining 20 mL of CdSO₄, 20 mL of thiourea, 20 mL of ammonia, and 140 mL of deionized water. Subsequently, the precursor solution containing the sample was continuously stirred in water at a temperature of 80 °C for 8 min 30 s. The CZTS/CdS samples were subsequently subjected to a negative pressure heat treatment at 280 °C for a duration of 5 minutes in quartz tubes filled with N₂ and O₂ respectively. The ITO window layer, approximately 200 nm thick, was prepared using RF magnetron sputtering under an O₂/Ar ratio atmosphere of about 2% at a working power of 100 W and a working pressure of 0.4 Pa for a duration of 25 minutes. Subsequently, silver electrodes with a thickness of 500 nm were evaporated onto the surface of the ITO layer. To provide comprehensive anti-reflection coating (ARC) coverage for the entire device, a MgF₂ layer with a thickness of 70 nm was applied.

**Film Characterization**

The top-view and cross-sectional images of the CZTS thin films were characterized by a scanning electron microscope (SEM, SUPPA 55). Raman spectroscopic data were acquired using an excitation wavelength of 532 nm. X-ray diffraction measurements were conducted on a "Rigaku Ultima IV" instrument, employing CuKα radiation source (40 mA, 40 kV). XPS analysis was performed utilizing an ESCALAB 250Xi (Thermo Fisher) 359 spectrometer. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) were recorded using a Fluo Time 300 spectrograph with an excitation wavelength of 532 nm. Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) images were obtained via a Bruker Dimension Icon system. Ultraviolet Photoelectron Spectroscopy (UPS) measurements were carried out using the PHI 5000 Versa Probe III instrument with He I source at energy level of 21.22 eV and -9.0 V bias voltage applied. Transmission electron microscopy (TEM) imaging was performed on an FEI Titan Cubed Themis G2 300 microscope, while sample preparation for TEM analysis involved the use of focused ion beam technique provided by the FEI Scios system.
Device Characterization

The Keithley 2400 m and Zolix SS150 solar simulator, calibrated with a standard Si reference cell, were used to measure the dark and illuminated J-V pattern. The Zolix solar cell QE/IPCE measurement system (Solar Cell Scan 100) was employed to measure the external quantum efficiencies (EQE) of the device, using calibrated Si and InGaAs photodiodes as references. For capacitance-voltage (C-V) profiling and drive level capacitance profiling (DLCP), we utilized the Keithley 4200A-SCS system with JANIS cryogenic platform. To ensure precise temperature conditions, temperature-dependent dark J-V characterization was performed using the Keithley 4200A-SCS system in conjunction with a Lakeshore 325 temperature controller. The electrochemical workstation (CHI660e) was utilized to conduct measurements of electrochemical impedance spectroscopy (EIS) across a frequency range spanning from 1 Hz to 100 kHz. Pulsed laser technology at a wavelength of 532 nm (Brio, 10 Hz, 4 ns) was employed to obtain modulated transient photocurrent and photovoltage (m-TPC/TPV) measurements. The decay process was recorded using a sub-nanosecond resolved digital oscilloscope (Tektronix, DPO7104). Deep-level transient spectroscopy (DLTS) data were acquired through the FT-1030 HERA DLTS system in conjunction with the JANIS VPF-800 heat controller.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Cu$_2$ZnSnS$_4$, Defect Passivation, Photoelectric performance, Interface optimization

16. Duan, B. et al. Underlying mechanism of the efficiency loss in CZTSSe solar cells: Disorder


### Table 1 Photovoltaic performance parameters of the W/O, N-HT and O-HT thin film solar cells.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω•cm$^2$)</th>
<th>$R_{sh}$ (Ω•cm$^2$)</th>
<th>$A$ (mA/cm$^2$)</th>
<th>$J_0$ $V_{OC}/V_{OC}^{SQ}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/O</td>
<td>22.48</td>
<td>695</td>
<td>59.8</td>
<td>9.14</td>
<td>1450</td>
<td>3.07</td>
<td>3.8×10$^{-3}$</td>
<td>53.2</td>
</tr>
<tr>
<td>N-HT</td>
<td>23.73</td>
<td>701</td>
<td>64.93</td>
<td>10.81</td>
<td>1206</td>
<td>1.96</td>
<td>1.0×10$^{-7}$</td>
<td>55.3</td>
</tr>
<tr>
<td>O-HT</td>
<td>25.15</td>
<td>728</td>
<td>68.29</td>
<td>11.89</td>
<td>1059</td>
<td>1.57</td>
<td>1.5×10$^{-7}$</td>
<td>58.3</td>
</tr>
</tbody>
</table>

### Table 2 The device characteristics of the CZTSSe, ACZTSSe and ACZITSSe solar cells derived from EQE, TRPL, DLCP and bias-dependent IQE data.

<table>
<thead>
<tr>
<th>Device</th>
<th>$E_g$ EQE (eV)</th>
<th>$E_g$ PL (eV)</th>
<th>$E_U$ (meV)</th>
<th>$N_{it}$ (cm$^{-3}$)</th>
<th>$N_{bulk}$ (cm$^{-3}$)</th>
<th>$L_d$ (μm)</th>
<th>$R_S$ (Ω)</th>
<th>$R_{rec}$ (kΩ)</th>
<th>$C_{rec}$ (nF)</th>
<th>$\tau_n$ (ms)</th>
<th>$\tau_{TRPL}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/O</td>
<td>1.51</td>
<td>1.48</td>
<td>35.7</td>
<td>2.8×10$^{15}$</td>
<td>8.6×10$^{15}$</td>
<td>0.3</td>
<td>117.2</td>
<td>63.4</td>
<td>1.45×10$^8$</td>
<td>0.92</td>
<td>4.93</td>
</tr>
<tr>
<td>N-HT</td>
<td>1.52</td>
<td>1.49</td>
<td>33.3</td>
<td>5.3×10$^{14}$</td>
<td>7.3×10$^{15}$</td>
<td>0.6</td>
<td>76.13</td>
<td>175.9</td>
<td>1.74×10$^8$</td>
<td>3.06</td>
<td>11.00</td>
</tr>
<tr>
<td>O-HT</td>
<td>1.50</td>
<td>1.49</td>
<td>33</td>
<td>2.3×10$^{14}$</td>
<td>5×10$^{15}$</td>
<td>0.68</td>
<td>26.2</td>
<td>205.1</td>
<td>3.3×10$^8$</td>
<td>6.76</td>
<td>14.25</td>
</tr>
</tbody>
</table>

### Table 3 Summary of defect properties measured by AS and C-DLTS.

<table>
<thead>
<tr>
<th>Device</th>
<th>Label</th>
<th>Possible defect</th>
<th>Activation energy $E_a$ [eV]</th>
<th>Trap conc. $N_T$ [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/O</td>
<td>E1</td>
<td>2Cu$<em>{Sn}$+Sn$</em>{Zn}$</td>
<td>$E_C$-0.634</td>
<td>1.04×10$^{12}$</td>
</tr>
<tr>
<td></td>
<td>H1</td>
<td>Vs</td>
<td>$E_V$+0.797</td>
<td>1.45×10$^{12}$</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>Cu$_{Zn}$</td>
<td>$E_V$+0.152</td>
<td>7.07×10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>E1</td>
<td>2Cu$<em>{Sn}$+Sn$</em>{Zn}$</td>
<td>$E_C$-0.480</td>
<td>9.95×10$^{11}$</td>
</tr>
<tr>
<td>N-HT</td>
<td>H1</td>
<td>Vs</td>
<td>$E_V$+0.711</td>
<td>1.67×10$^{12}$</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>Cu$_{Zn}$</td>
<td>$E_V$+0.157</td>
<td>9.91×10$^{16}$</td>
</tr>
<tr>
<td>O-HT</td>
<td>E1</td>
<td>2Cu$<em>{Zn}$+Sn$</em>{Zn}$</td>
<td>$E_C$-0.289</td>
<td>8.52×10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>Cu$_{Zn}$</td>
<td>$E_V$+0.166</td>
<td>4.75×10$^{16}$</td>
</tr>
</tbody>
</table>
Fig. 1. Schematic diagram of production procedure and device photovoltaic performance.

(a) (b) Schematic diagram of CZTS precursor and sulfured post-annealing. (c) Schematic diagram of the CBD process for CdS. (d) The heterojunction undergoes two distinct heat treatment strategies: the upper treatment is conducted in a high-purity nitrogen-filled quartz tube, while the lower treatment takes place on a high-purity oxygen-filled quartz tube. (e) Diagram of changes in atomic thermal motion at heterojunction. (f) Current-voltage (I-V) characteristics of the champion W/O, N-HT and O-HT devices. (g) Certified I-V curves of the cell at both forward and reverse
scanning directions. (h) EQE spectra of W/O, N-HT and O-HT devices. (i) The band data of absorption layer CZTS calculated from EQE. (j) Urbach energy was derived from the EQE data of three samples. (k) PL spectra of W/O, N-HT and O-HT devices.

Fig. 2. Characterization of element changes in champion devices after heat treatment in O₂.
(a) Cross-sectional TEM image and mapping analysis of the O-HT devices. (b) Cross-sectional TEM image of the device. (c) HRTEM image of the selected area near the CZTS/CdS heterojunction interface. (d) (e) Filtered atomic resolution HAADF image taken at the region of CZTS absorber layer and CdS buffer layer. (f) The intensity profile of S and O atoms (O occupying the S vacancy). (g) X-ray photoelectron spectra (XPS) spectra of S 2p for W/O, N-HT and O-HT sample.
Fig. 3. Characterization of the CZTS absorbers and CdS buffers. Kelvin probe force microscopy (KPFM) images of the (a) W/O, (b) N-HT and O-HT processed CZTS absorbers, the absorbers were prepared by selectively etching the CdS layer using dilute hydrochloric acid, resulting in a single thin film of CZTS as the absorbing layer. Line profiles extracted from the AFM and contact potential difference map for (d)W/O, (e) N-HT and (f) O-HT processed CZTS absorbers. (g) Contact potential difference (CPD) distribution of the three samples. (h) Schematic diagram of the energy band bending near the GB regions, “e” represents electron and “h” represents hole. (i) Schematic diagram of the band alignment for W/O and O-HT device.
Fig. 4. Characterization of defects property and devices performance for CZTS/CdS heterojunction. (a) Charge profiles of the cells measured by DLCP and C-V. (b) Charge collection efficiency ηc and extraction efficiency ηe of the cells derived from the modulated electrical transient measurements. (c) DLTS signals from the three devices. (d) The Arrhenius plots derived from C-DLTS spectra and corresponding to the peaks of DLTS spectra. (e) The Arrhenius plots and (f) the defect density spectra derived from admittance spectra. (g) The schematic diagram of the band energy levels and defect energy levels of three devices. (h) Nyquist plots of the three devices. (i) Normalized time-resolved photoluminescence decay excitation wavelengths of 532 nm for the three devices.
Supplementary Materials

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Supplementary Notes

Supplementary Note 1 Open circuit voltage deficit

The Open circuit voltage deficit \( (V_{oc-def}) \) can be evaluated by \( V_{oc}/V_{oc}^{SQ} \), where \( V_{oc}^{SQ} \) is the maximum achievable \( V_{oc} \) based on Shockley–Queisser limit and can be calculated by following equation\(^1\):

\[
V_{oc}^{SQ} = 0.932 \times E_g - 0.1667 \quad (S1)
\]

Supplementary Note 2 Conduction band offset (CBO)

There are two types of band alignment at heterojunctions: cliff-type and spike-type. In the case where the electron affinity energy of the buffer layer exceeds that of the absorber, a negative conduction band offset (CBO) is observed at the heterojunction, resulting in a cliff-type energy band alignment. This configuration significantly enhances interface recombination and diminishes the open-circuit voltage \( (V_{oc}) \). Conversely, when the electron affinity energy of the buffer layer is lower than that of the absorber, a positive CBO arises at the heterojunction leading to a spike-type energy band alignment. Spike-type band alignment effectively prevents electron backflow and reduces interface compounding; however, excessive spikes (large CBO values) can impede electron tunneling at interfaces thereby compromising device performance.

Literature suggests an optimal range for CBO between 0 to 0.4 eV with larger CBO values favorably reducing interface recombination\(^2\).

The UPS measurements were conducted to determine the cutoff edge \( (E_{cutoff}) \) and energy gaps \( (E_{cutoff}) \) of the samples. The \( E_{cutoff} \) values for the W/O and O-HT CZTS samples were determined as 16.73 eV and 16.78 eV, respectively, while those for the
W/O and O-HT CdS samples were found to be 16.74 eV and 17.12 eV, respectively. Furthermore, by extrapolating the linear region at low binding energies, we obtained $E_{\text{cutoff}}$ values of 0.51 eV and 0.38 eV for the W/O and O-HT CZTS samples, respectively; whereas for the W/O and O-HT CdS samples, these values were calculated as 1.46 eV and 1.51 eV correspondingly. From these, the conduction band ($E_c$), and valence band ($E_v$) were calculated from the equation\textsuperscript{3,4}:

$$\varphi = h\nu - E_{\text{cutoff}} \quad (S2)$$
$$E_v = E_{\text{onset}} + E_{\text{onset}} \quad (S3)$$
$$E_c = E_v - E_g \quad (S4)$$

Where $\varphi$ denotes the work function, $h\nu$ represents the UV photoelectron energy of 21.22 eV.

**Supplementary Note 3** CV and DLCP measurement

CV and DLCP are often used to analyze carrier concentration and depletion width in thin film solar cells. The formulas for the calculations are as follows\textsuperscript{5}:

$$N_{CV} = \frac{c^3}{qA^2\varepsilon_0\varepsilon}(\frac{dC}{dV})^{-1} \quad (S5)$$
$$W_{d-CV} = \frac{\varepsilon_0EA}{C} \quad (S6)$$
$$N_{DL} = -\frac{c_0^3}{2q\varepsilon_0\varepsilon A^2C_1} \quad (S7)$$
$$W_{d-DL} = \frac{\varepsilon_0EA}{C_0} \quad (S8)$$

Where $\varepsilon$ and $\varepsilon_0$ stand for the dielectric constant of the CZTS and vacuum dielectric constant, respectively; $C$, $A$ and $q$ is the measured capacitance, the active area of the cell, and elementary charge, $C_0$ and $C_1$ are two quadratic fitting parameters derived from the DLCP. Besides, The CV measurement is more sensitive to the interface state ($N_{\text{IT}}$) than the DLCP, so the interface state density can be obtained from the difference between the CV and the DLCP:

$$N_{\text{IT}} = N_{CV} - N_{DL} \quad (S9)$$

**Supplementary Note 4** Minority carrier diffusion length

The calculation formulas were as follows\textsuperscript{6,7}:

$$IQE(\lambda, V) = \frac{EQE(\lambda V)}{1-R(\lambda)} \quad (S10)$$
\[ IQE(X_d, \lambda) = \frac{\exp(-a(\lambda)X_d)}{1+a(\lambda)L_d} \] (S11)

where EQE \((\lambda, V)\) as a function of wavelength \((\lambda)\) and voltage bias \((V)\) is measured, and \(R(\lambda)\) is determined by the reflectivity as a function of wavelength. The bias dependence of \(X_d\) was determined on the basis of the \(C\)-\(V\) measurement using, where \(\varepsilon_i\) is the relative dielectric constant of CZTS. The array of IQE \((X_d, \lambda)\) data is fit to the analytic expression given by Equation 6 to extract a single \(L_d\) value and the absorption coefficient \((\alpha)\) at each \(\lambda\). The electron mobility \((\mu_e)\) can be estimated by following formula:

\[ L_d = \sqrt{\tau \mu_e k_B T / q} \] (S12)

Where \(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(q\) is the elementary charge.

**Supplementary Note 5** AS analysis

Admittance spectral measurements are used to estimate the defect level within the bandgap. The inflection frequency \(\omega_0\) of each admittance spectral curve is determined by the corner frequency point at the maximum of the \(-\omega dC/d\omega\) plot, which was fitted by follow equation\(^8:\)

\[ \omega_0 = 2\pi v_0 T^2 e^{\frac{E_a}{kT}} \] (S13)

Where \(T\) is testing temperature, \(E_a\) was derived from the slope of the Arrhenius plots, and \(v_0\) was extracted from the y-axis intercept \(\ln(2\pi v_0)\). Then, the energy distribution and density of defects was presented in follow equation:

\[ E(\omega) = kT \ln \left( \frac{2\pi v_0 T^2}{\omega} \right) = kT \left[ \ln(2\pi v_0) - \ln \left( \frac{\omega}{T^2} \right) \right] \] (S14)

\[ N_t[E(\omega)] = -\frac{V_{bi}}{qW_d kT} \omega \frac{dC}{d\omega} \] (S15)

where \(V_{bi}\) and depletion region width \(W_d\) are extracted from the plots of \(\frac{1}{C^2}\) and \(N_{CV}\) vs. \(X\), which were obtained by Capacitance-Voltage measurement.

**Supplementary Note6** DLTS analysis

Deep-level transient spectroscopy (DLTS) is vital to gain insights into defect
concentration, type, and defect energy level of a photovoltaic device. The corresponding parameters can be derived by the following equation:\(^9\):

\[
\ln\left(\tau_e \nu_{\text{th},n} N_N\right) = \frac{E_C - E_T}{k_B T} - \ln(X_n, \sigma_n) \quad (S16)
\]

\[
\ln\left(\tau_e \nu_{\text{th},p} N_V\right) = \frac{E_T - E_V}{k_B T} - \ln(X_p, \sigma_p) \quad (S17)
\]

Where \(N_N\), \(N_V\) is conduction band state density and valence band state density, respectively. \(\tau_e\) is the emission time constant, \(X_n\) and \(X_p\) are the entropy factor for election and hole, \(\nu_{\text{th},n}\) and \(\nu_{\text{th},p}\) is the thermal velocity.

**Supplementary Note 7** TRPL analysis

The minority carrier lifetime is obtained by fitting TRPL curve with bi-exponential function\(^{10}\):

\[
y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} \quad (S18)
\]

and the final lifetime was calculated by the average function:

\[
\tau_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_2^2 + A_2 \tau_2} \quad (S19)
\]

where \(\tau_1\) and \(\tau_2\) are lifetime; \(A_1\) and \(A_2\) are the respective ratio of \(\tau_1\) and \(\tau_2\).

**Supplementary Note 8** Dark \(J-V\) Characteristics

Accurate diode parameters are essential to investigate the recombination mechanism of CZTS devices, including shunt conductance (\(G\)), series resistance (\(R\)), diode ideality factor (\(A\)), and reverse saturation current density (\(J_0\)). The calculated parameters of the three different devices are summarized in Table 1. The shunt conductance was plotted by \(dJ/dV-V\) curve (Figure S18). Series resistance and diode quality factor were calculated by the following equation and shown in figure S18 b:

\[
r(J) = \frac{dV}{dJ} = R + \frac{akT}{q} \frac{1-\frac{e^V}{j+jL-GV}}{j+jL-GV} = R + V_0 \frac{1-\frac{e^V}{j+jL-GV}}{j+jL-GV} \quad (S20)
\]

And the reverse saturation current density is obtained by plotting the \(\ln(J + J_{SC} - GV)\)–(\(V-RJ\)) curve and calculated by the following equation\(^{11}\):

\[
\ln(J + J_L - GV) = \ln J_0 + \frac{V}{akT} (V - RJ) = \ln J_0 + \frac{V - RJ}{V_0} \quad (S21)
\]

where \(J_L\) is the light current density. The lower series resistance (\(Rs\)) and ideality factor (\(A\)) values indicated a suppressed defect recombination at the interface and in bulk regions. Additionally, the O-HT device showed a lower reverse saturation current
density \(J_0\), indicating a reduction in nonradiative recombination loss due to a lower deep defect concentration.

Furthermore, the curves can be categorized into three regimes: the ohmic zone (characterized by a low voltage and an exponent \(n=1\)), the trap-filled limit (TFL) region (occurring at intermediate voltages with an exponent greater than 3), and the trap-free Child region (appearing at high voltages with an exponent greater than 2). When the bias voltage in the TFL region surpasses the kink point, a sharp increase in current is observed, indicating complete injection of all carriers into trap states. The space charge-limited current model was employed to investigate the trap density of solar cells. The trap density \(N_{\text{trap}}\) can be estimated using the following equation\(^{12, 13}\):

\[
N_{\text{trap}} = \frac{2\varepsilon_0 \varepsilon_r V_{\text{TFL}}}{qL^2} \quad (S22)
\]

Where \(\varepsilon_0\) is the relative permittivity, \(\varepsilon_r\) is the vacuum permittivity, \(q\) is the elementary charge, and \(L\) represents the thickness of the CZTS absorber thin film. The calculated defect density \(N_{\text{trap}}\) values of the W/O, N-HT, and O-HT devices are observed to be 2.76\(\times10^{12}\) cm\(^{-3}\), 2.85\(\times10^{12}\) cm\(^{-3}\), and 2.25\(\times10^{12}\) cm\(^{-3}\), respectively. This indicates that a lower concentration of recombination defects signifies enhanced absorber quality and improved effectiveness in passivating defects.
Supplementary Figure 1. Statistical performance parameters of the CZTS devices without and with HT at 100 °C, 190 °C, 280 °C and 370 °C, respectively.
Supplementary Figure 2. Statistical performance parameters of the CZTS devices HT on 1 min, 3 min, 5 min, 7 min, and 9 min, respectively.
Supplementary Figure 3. Statistical performance parameters of the CZTS devices without and with HT in different atmosphere.
1. **Standard Test Condition (STC):**
   - Total Irradiance: 1000 W/m²
   - Temperature: 25.0 °C
   - Spectral Distribution: AM1.5G

2. **Measurement Data and I-V/P-V Curves under STC**

   **Forward Scan**
   - $I_{sc} (mA)$: 0.9866
   - $V_{oc} (V)$: 0.7087
   - $I_{mp} (mA)$: 0.8413
   - $V_{mp} (V)$: 0.5583
   - $P_{mp} (mW)$: 0.4697
   - $FF (%)$: 67.18
   - $η (%)$: 11.51
   - $A (cm^2)$: 0.0408

   **Reverse Scan**
   - $I_{sc} (mA)$: 0.9872
   - $V_{oc} (V)$: 0.7095
   - $I_{mp} (mA)$: 0.8365
   - $V_{mp} (V)$: 0.5611
   - $P_{mp} (mW)$: 0.4694
   - $FF (%)$: 67.02
   - $η (%)$: 11.50
   - $A (cm^2)$: 0.0408

Mismatch Factor: 1.003

**Figure 1.** I-V and P-V characteristic curves of the measured sample under STC
Supplementary Figure 5. TEM-EDS line scan results of the champion O-HT device.
(a) The element distribution ranges from ITO window layer to CZTS absorption layer,
(b) The element distribution near the interface.
Supplementary Figure 6. XPS spectra of S 2p, O 1s Cu 2p\(_{3/2}\), Zn 2p\(_{3/2}\), Cd 3d\(_{5/2}\) and Sn 3d\(_{5/2}\) CZTS/CdS heterojunction. The curves of different colors represent the XPS signal detected at different etching depths.
Supplementary Figure 7. Element distribution curves of XPS depth test for W/O, N-HT and O-HT devices.
Supplementary Figure 8. XRD patterns (a) of W/O, N-HT and O-HT CZTS thin films; Raman spectra (b) of W/O, N-HT and O-HT CZTS/CdS samples. The absorber films all exhibit characteristic peaks of the kesterite phase without any additional diffraction peaks, indicating the absence of noticeable secondary phases formed after the HT process. The reduction in the half-peak width of the CdS displacement signal peak observed in the Raman test indicates an improvement in the crystallinity of the film.
Supplementary Figure 9. The cross-sectional (a-c) and the surface SEM images (g-l) of W/O, N-HT and O-HT samples.
Supplementary Figure 10. The band gap of CdS for three devices calculated by $\frac{d(-\ln(1-EQE))}{dE}$. 
Supplementary Figure 11. Ultraviolet photoelectron spectroscopy (UPS) results of the (a) W/O CdS sample, (b) W/O CZTS sample, (c) O-HT CdS sample, and (d) O-HT CZTS sample.
Supplementary Figure 12. DLCP measured at frequencies from 1 to 100 kHz for W/O, N-HT and O-HT devices.
Supplementary Figure 13. (a) The bias–dependent Wd of W/O, N-HT and O-HT devices. (b) $1/C^2$-V plots of the three devices.
Supplementary Figure 14. Modulated transient photocurrent and photovoltage spectra of W/O, N-HT and O-HT solar cells.
Supplementary Figure 15. The reflection data of CZTS absorber layer.
**Supplementary Figure 16.** The bias–dependent EQE of W/O, N-HT and O-HT devices.
Supplementary Figure 17. Minority carrier diffusion length extraction of W/O, N-HT and O-HT devices.
Supplementary Figure 18. The admittance spectra and plots of \(-\omega dC/d\omega\) vs. frequency at different temperature for W/O, N-HT and O-HT devices.
Supplementary Figure 19. Electrical behaviors of the three devices: (a) shunt conductance \( G \) characterizations, (b) series resistance \( R \) and ideality factor \( A \) characterizations, (c) reverse saturation current density \( J_0 \) characterizations, (d)-(f) Logarithmic \( J-V \) curves of the W/O, N-HT and O-HT devices.
Supplementary Figure 20. $J-V-T$ plots of W/O, N-HT and O-HT devices.
Supplementary Figure 21. PCE evolution of the champion device after 60 days storage in air ambient without special encapsulation.
**Supplementary Figure 22.** Progress curve of PCE of pure sulfurized kesterite CZTS thin film solar cell in recent ten years.
References


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