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Impact of Nanoscale Elemental Distribution in High-Performance Kesterite Solar Cells

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The effort to develop earth-abundant kesterite solar cells has led to an approximate doubling of the power conversion efficiency over the past five years to 12.6%, primarily due to increases in short-circuit current and fill factor; open-circuit voltage has resisted similar change, limiting further efficiency improvement. In the present investigation, Auger nanoprobe spectroscopy, X-ray/ultraviolet photoelectron spectroscopy, and device characterization are used to provide a comprehensive understanding of the role of grain boundaries and interfaces in limiting performance in kesterite-based devices. High photovoltaic performance is found to correlate with grain boundaries that are Cu-depleted and enriched with SnOx. The formation of this bulk-like oxide at grain boundaries with type I band offset provides a unique effective passivation that limits electron-hole recombination. Building on these new insights, photovoltaic device simulations are performed that show optimized electrostatic designs can compensate for bulk defects, allowing efficiencies closer to the theoretical limit.

1. Introduction

Among chalcogenide solar cell absorbers, copper–indium–gallium–sulfide–selenide (CIGSSe) compounds have shown power conversion efficiencies of as high as 20.9%.^[1] However, scarcity and rising cost of In and Ga are expected to limit the maximum power production capacity to ≈100 GWp year^{-1,[2]} In kesterites like copper–zinc–tin–sulfide/selenide (Cu₂ZnSn(S_x,Se_{1–x})₄ or CZTSSe), In, and Ga are replaced with the more earth-abundant and low-cost elements, Zn and Sn; overall production capacity of >100 GWp year⁻¹ has been foreseen for CZTSSe devices.^[3–5] While power conversion efficiency of polycrystalline CZTSSe

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solar cells has increased from 0.66%^[6] to 12.6%;^[7] to compete with CIGSSe technologies, CZTSSe devices need conversion efficiencies in excess of 15%.^[4] With short-circuit current (J_{sc}) having reached >81% of the Shockley-Queisser limit, open-circuit voltage (V_{oc}) represents the predominant barrier to further efficiency improvement, currently rising to only 62% of the theoretical limit. Improvement in Voc directly relies on understanding and controlling defect-mediated recombination mechanisms within the bulk, at the grain boundaries (GBs) and at interfaces between CZTSSe and buffer layers or secondary phases.^[8-11]

Champion devices for both CIGSSe^[12] and CZTSSe^[7] employ CdS buffers deposited by chemical bath deposition (CBD). CdS/CZTSSe and CdS/CIGSSe junction qualities have been theoretically and

experimentally shown to be superior for Cu-poor absorber surfaces.^[13,14] The Cu-poor surfaces can accommodate Cd²⁺ ions from the chemical bath within the high density of Cu vacancies, forming a subsurface p-n homojunction a few nanometers below the physical CdS/CIGSSe heterojunction.^[15-18] However, Zn-rich surfaces might give rise to higher recombination rates by formation of secondary phases such as Zn(S,Se)^[19,20] and Cu₂Sn(S,Se)₃.^[21,22] CZTSSe oxides can also form during the growth or postgrowth processing. In contrast to Si-based photovoltaics, oxidation by air anneal at 300-400 °C increases CZTSSe cell efficiencies; inspired by the extensive studies on CIGSSe, it is hypothesized that during the air anneal oxygen and sodium (from the soda-lime glass substrate) diffuse through the GBs and passivate the defect sites that cause nonradiative recombination.^[23-25] However, oxide formation at the GBs has not been directly observed, and it is unknown whether this process leads to atomic scale substitution of sodium and oxygen at CZTSSe lattice sites as proposed theoretically^[26] or to formation of a bulk oxide phase selectively at the grain boundaries.

In the present investigation, the dependence of the macroscale CZTSSe photovoltaic device performance on the nanoscale elemental distributions on the surface and at the grain boundaries are determined with Auger Nanoprobe Spectroscopy (NanoAuger). This is the first time that Auger Nanoprobe elemental mapping has been employed to determine the nanoscale elemental distribution on the kesterite absorber



surfaces, and the 8 nm lateral resolution provides an unprecedented view of grain features, both at the surface and in cross-section. Device characterization and photoelectron spectroscopy data are consistent with the formation of grain boundaries enriched with tin oxide (SnOx), along with Cu-poor CdS/ CZTSSe interfaces, being crucial for high efficiency CZTSSe solar cells. These observations go beyond the models predicting passivation of GBs simply with atomic scale replacement of CZTSSe constituents with Na and O.^[23,26,27] Device simulations for the CZTSSe solar cells show that, with effective grain boundary passivation, current bulk defect densities can be compensated by engineering the electrostatics in the devices (by combination of thinner absorbers with highreflectivity, high-work-function backside contacts) to raise efficiencies to >16%.

2. Results and Discussion

Nanoscale surface compositional variations on CZTSSe films were obtained by highly surface-sensitive Auger Nanoprobe elemental mapping using Auger primary peaks for Cu, Zn, Sn, S, Se, and O (for details, see Figure S1, Supporting Information). Figure 1a shows the elemental maps in planar mode for the CZTSSe surface after air-anneal at 375 °C for 10 min (a typical treatment for high-performance devices). X-ray photoelectron spectroscopy (XPS) results show that the air anneal produces an oxide-covered, Cu-depleted surface with high Zn and Sn concentration ([Cu]/[Zn] + [Sn] = 0.32, [Sn]/[Sn] + [Zn] = 0.47; see Figure S2, Supporting Information). On the air-annealed surface, a relatively uniform distribution of S and Zn is observed between the grains and GBs. In stark contrast, both Sn and O appear as bright lines and Cu as dark lines that delineate the boundaries between the grains where grooving also occurs (GBs are denoted by ① and ⑤ in the SEM image). The bright Sn and O lines indicate the formation of SnOx-enriched layers at the GBs. However, in the compositional map a uniform background subtraction is automatically performed, which highlights enrichment at grain boundaries when the elemental composition is uniform across all grains. In

contrast, single point measurement presented in Table S1 (Supporting Information) give accurate compositional ratios since a full spectrum is recorded at each point. Based on single point spectroscopy, the amount of Zn at the GBs is comparable to Sn (Sn/(Zn + Sn) = 0.48-0.51) similar to the oxide on grains top





Figure 1. Elemental maps for air-annealed CZTSSe: a) Planar secondary electrons and elemental maps showing the lateral distribution of Cu, Zn, Sn, S, Se, and O on the surface after air anneal. Scan size is $3.75 \times 5 \ \mu m^2$. Maps reflect the intensity of primary Auger peaks. b) Secondary electrons and cross-sectional elemental maps. 2° tilt of the sample stage was applied in order to detect top surface and compare its composition with the cross-section. Tables present the composition of various points on the surface derived from the ratios between RSF-normalized Auger peak intensities for the comprising elements. [O]/CZTSSe is the ratio of oxygen peak intensity to the sum of Cu, Zn, Sn, S, and Se peak intensities. Green columns mark the GBs that have been quantified in the tables.

surfaces. In both elemental maps and spectroscopy results, the actual compositional contrast between the grains and GBs can be screened by the presence of oxide on the top surface.

The more exothermic formation reaction for SnO_2 and ZnO relative to SeO_2 and CuO, make them the more



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thermodynamically favorable native oxides on CZTSSe (Figure S6, Supporting Information). Despite a smaller enthalpy of formation, both SeO₂ and selenates (as NaSeO₂ or SnSeO₄) have been observed on the CZTSSe surfaces (Figure S2, Supporting Information).^[24] The SO_2 enthalpy of formation is as large as Sn and Zn oxide but its high vapor pressure is consistent with its evaporation in UHV. Therefore, although in principle the compositional variations depicted in Figure 1 could be understood in terms of highly oxygen-substituted CZTSSe interfaces, a combination of zinc, tin, and selenium oxides on the surface of air annealed CZTSSe can be expected from thermodynamic considerations.

а

Cross-sectional elemental maps for the cleaved air-annealed sample are shown in Figure 1b. Polycrystalline CZTSSe mechanical fracture will occur predominantly along the grain boundaries; therefore, cleavage should expose the surface of oxidized grains at the GBs (called GB faces) instead of the unoxidized grain interior.^[28] Due to a sample stage tilt of 2°, the cross-sectional maps include some view of the top film surface. Compared with the top surface, Cu, S, and Se have higher intensities on the cross-sectional GB faces while intensities of Sn. Zn. and O are smaller. However, GBs perpendicular to the imaging section (3) and (5) as well as a fraction of GB faces, are Cu-poor and Sn-/O-rich. When compared with the single points spectroscopy results in planar maps (Table in Figure 1a), GBs seen in the cross-sectional images contain more Se (higher [Se]/CZTSSe) and more Sn (higher [Sn]/([Zn] + [Sn])). Se oxidation has been previously reported on CIGSSe^[25] and CZTSSe^[24] surfaces, and it is expected that Se from CZTSSe oxidizes during the air anneal to form Sn(O,Se)_X. Formation of $Sn(O,Se)_x$ is consistent with the XPS and SIMS measurements (Figure S2, Supporting Information).

To replicate the conditions of the CdS CBD step used to make devices, samples were treated with dilute ammonium hydroxide (NH₄OH), which is present in the CdS deposition bath solution and is known for dissolving metal oxides.^[24] XPS measurements showed that NH4OH surface cleaning reduced the surface O intensity to 10% of sub-

strate intensity (sum of Cu, Zn, Sn, S, and Se intensities) and resulted in a Cu-deficient surface ([Cu]/([Zn] + [Sn]) = 0.67; see Figure S2, Supporting Information). While very low oxygen concentrations were measured by XPS and large area AES (Figures S1,S2, Supporting Information), elemental maps in Figure 2



Figure 2. Elemental maps for NH4OH-cleaned CZTSSe: a) Planar elemental maps showing the lateral distribution of Cu, Zn, Sn, S, Se, and O on the surface after cleaning by NH₄OH. Scan size is $3.75 \times 5 \,\mu\text{m}^2$ Maps reflect the intensity of primary Auger peaks. b) Cross-sectional elemental maps. 2° tilt of the sample stage was applied in order to detect top surface and compare its composition with the cross-section. Top surface has higher Cu and Se and lower Sn and O compared with the GB surfaces. Tables present the composition of various spots on the surface derived from the ratios between RSF-normalized Auger peak intensities for the comprising elements. [O]/CZTSSe is the ratio of oxygen peak intensity to the sum of Cu, Zn, Sn, S, and Se peak intensities. Green columns mark the GBs that have been quantified in the tables.

[O]/[Zn]+[Sn]

[O]/CZTSSe

clearly depict the GBs (point ① and ③) as Sn/O-rich and Cu-/Sepoor, consistent with SnOx enrichment of grain boundaries and grooves even after NH₄OH oxide removal from the top surface. Moreover, small SnOx-rich patches can be observed in planar maps (point ⑤) consistent with the NH4OH clean leaving oxide

0.73 0.64

0.38

0.29 0.33

0.66

0.60

0.28

0.76

0.42

SEM

0.34

0.14



in the all grain boundaries and in a few small regions of the top surface. After oxide removal, single point spectroscopy results for GBs in Figure 2 shows higher concentration of Sn (higher [Sn]/([Zn] + [Sn])) consistent with removal of more ZnO from the top surface of the GBs. Similar to air-annealed surfaces prior to NH₄OH cleaning, single point spectroscopy (Table in Figure 2b) and line scans of the NH₄OH-cleaned surface extracted from the elemental maps (Figure S4, Supporting Information) show that GBs are not completely depleted from Cu, Se, and S. The width of the SnOx-rich GBs extracted from line traces in the elemental maps varies between 90 and 270 nm implying that the SnOx layer is bulk-like in character and covers the GBs. However, based on the comparison between depth profiles in planar and cross-sectional NanoAuger, thickness of SnOx patches at the GB faces was estimated to be at least three times thinner than the native oxide on the grain surfaces of the air-annealed sample (Figure S5, Supporting Information). Therefore, it is hypothesized that SnOx is present at the GBs in the form of thin SnOx crystallites that when probed by NanoAuger, due to large incident electron beam size, cannot be resolved as individual features since a large area of CZTSSe matrix surrounding the crystallites is concurrently probed. Furthermore, Cu, Sn, and Se Auger electrons have larger mean escape depths than Sn and O increasing the probability of probing the CZTSSe matrix around SnOx crystallites.

Comparison of the top surface with the GB faces shown in the cross-sectional maps of the NH₄OH-cleaned CZTSSe (Figure 2b) reveals that GBs remain Sn- and O-rich after the oxide removal



from the top surface. Furthermore, consistent with the uncleaned air-annealed sample's cross-section (Figure 1b), GB faces (point O) as well as GBs perpendicular to the cross-section (① and ③) are covered in SnOx and partly Sn(O,Se)_X. More O- and Sn-rich oxide patches can also be observed on the GB surfaces, adjacent to the bottom of the film (point ⑤). This confirms that NH₄OH clean influences only the composition of the top surface and leaves the oxides at the GBs within the film.

In order to correlate the compositional variations measured by NanoAuger with PV device characteristics, solar cells were fabricated with the device structure shown in Figure 3a. CdS buffers were deposited by CBD in NH4OH solution on the top surfaces of polycrystalline CZTSSe films prepared under various conditions. To determine the effect of various surface cleaning elements on the surface composition and solar cell performance, beside NH4OH single dip two additional cleaning recipes were investigated: (1) HOOH followed by NH4OH (HOOH/NH4OH clean); (2) NH4OH clean followed by 0.3 nm Cu deposition and UHV anneal at 200 °C. Exposure of the CZTSSe to 30% HOOH generates a surface oxide that is subsequently removed by the NH₄OH; this two-step process etches down into the CZTSSe producing an oxygen-free (O intensity as low as = 5% of the substrate intensity) surface with slightly higher Cu concentration than the NH4OH-cleaned surface ([Cu]/([Zn] + [Sn]) = 0.71; Figure S2, Supporting Information). Deposition of 0.3 nm of Cu on a NH₄OH-cleaned surface followed by UHV anneal ensures formation of a Cu-rich top surface via Cu incorporation into the top few monolayers



Figure 3. Solar cell device performance: a) Cross-sectional TEM image of a complete CZTSSe device. Different layers of the device are shown with various colors on the right. HAADF refers to high angle annular dark field imaging. b) J–V curves for devices fabricated on CZTSSe surfaces prepared by NH₄OH clean and HOOH/NH₄OH clean. c) Efficiency, V_{oc} , J_{sc} , and FF for samples with surfaces prepared by NH₄OH clean, HOOH/NH₄OH clean or Cu deposition/anneal. d) Solar cell efficiency as a function of surface preparation process. High efficiency for HOOH/NH₄OH cleaned CZTSSe devices can be recovered by second air anneal followed by NH₄OH clean.



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of CZTSSe. Prior to all surface preparations, samples were annealed in air at 375 $^{\circ}\mathrm{C}$ for several minutes.

Air-annealed samples cleaned with NH₄OH (resulting in relatively Cu-poor surfaces) showed efficiencies of 11%–12% without antireflection coating (Figure 3b and 3c). HOOH/ NH₄OH-cleaning of CZTSSe devices, as well as Cu deposition and postdeposition annealing, resulted in poor device efficiencies (\approx 0.1%). Both cells suffered from low V_{oc}, J_{sc} and fill factor (FF), all giving rise to very low efficiencies. However, the efficiency of CZTSSe solar cells first etched by HOOH/ NH₄OH can be restored to 11% by a second air anneal followed by oxide etch in NH₄OH (Figure 3d). This confirms that the mechanisms limiting their performance are only limited to the top surface of the film and can be improved by repeating the proper surface treatment.

The difference in device performance results can be explained in the context of the elemental maps for the CZTSSe surface cleaned by HOOH/NH₄OH (**Figure 4**a). A majority of GBs after HOOH/NH₄OH clean are no longer Cu-deficient

and Sn- and O-rich (maps for all the elements are available in Figure S7, Supporting Information). Since HOOH/NH₄OH affects only the near surface region, only GBs adjacent to, or at the film top surface lose their SnOx termination. Conversely, air-annealed devices cleaned only with NH₄OH (Figure 3) performed comparably to the highest efficiency CZTSSe devices.^[7] Therefore, some combination of film surface/grain boundary stoichiometry modification (i.e., especially Cu content) and the passivation of the GBs with thin SnOx crystallites spanning the full film thickness and including the regions adjacent to the buffer/absorber interface must be critical to efficient device performance. NH₄OH removes the oxides on the grains at the CZTSSe/CdS interface, which is critical to high Jsc. Figure 4b depicts the band bending diagram for CdS/CZTSSe/SnOx constructed by femtosecond ultraviolet photoelectron spectroscopy (fs-UPS, see methods) measurements on CdS/CZTSSe combined with UPS results from the literature for SnO₂.^[29,30] There is at least a 1.9-eV barrier for holes between CZTSSe and SnOx due to the large valence band offset, and the electron barrier



Figure 4. Electronic and chemical properties of $SnO_2/CZTSSe$ and CdS/CZTSSe interfaces: a) SEM microscopy image and Cu and O elemental maps for CZTSSe surface after HOOH/NH₄OH cleaning. Scan size is $3.75 \times 5 \ \mu m^2$. b) Band alignment between SnOx, $Cu_2ZnSn(S_{0.45},Se_{0.55})_4$, and CdS buffer showing existence of both electron and hole barriers at the SnOx/CZTSSe interface. Band diagram has been constructed by combining the UPS measurements for CdS/CZTSSe with data from the literature for SnO₂/CdS junctions.^[31,32] c) Surface Fermi level position and surface band bending of NH₄OH-cleaned, HOOH/NH₄OH-cleaned and Cu-incorporated CZTSSe surfaces measured by fs-UPS. d) SEM image of CdS/CZTSSe interface.

varies between 0.6–0.8 eV depending on the concentration of the oxygen vacancies (as donors) and Zn (as acceptors);^[31–33] the UPS data is consistent with the SnOx crystallites neither trapping electrons nor holes. Also, note that nonconducting oxiderich grain boundaries running perpendicular to the film surface should not impede current collection, which is also primarily a vertical process. Since the grains in these films are quite large, there are relatively few horizontal grain boundaries that the current needs to traverse to be collected.

Complimentary Kelvin probe force microscopy at the grain boundaries showed 60-100 meV higher work function for GBs relative to the grains on the NH4OH-cleaned CZTSSe surfaces (Figure S8, Supporting Information). These KPFM measurements are consistent with internal fields resulting in upward band bending and negative charge at and near the GB that repels electrons and prevent recombination in the vicinity of GBs. Therefore, upward band bending combined with type I band offset at the grain boundaries prevents the photoexcited electrons or holes from entering the GBs and recombining at the GB defects. This contrasts with the hypothesis of electron collection at the GBs and electron current flow in their vicinity in the absence of CZTSSe grain boundary oxidation.^[34] Removal of the SnOx-passivation layer at the GBs at and near HOOH/NH₄OH-cleaned surface will lead to higher recombination rates near the CdS/CZTSSe junction and a significant decrease in both Voc and Jsc. Similarly poor PV device performance was observed for CZTSSe without air anneal, where Auger Nanoprobe elemental maps show the absence of SnOx at the grain boundaries (Figure S10, Supporting Information).

In order to explain the poor device performance in the sample with 0.3 nm Cu deposition, the effect of Cu concentration on the surface charge and CdS/CZTSSe heterojunction quality was assessed by measuring surface work function, band bending and flat band Fermi level positions (relative to the valence band) using fs-UPS (Figures 4c and S9, Supporting Information).^[24] Surface band bending is an important indication of charged defects at or near the surface. Particularly, the density of ionized, and hence negatively charged, Cu vacancies (V_{Cu}) near the Cu-depleted surface directly corresponds to the magnitude and direction of the band bending, consistent with the mechanisms suggested for CIGS. [17,25,35] As shown in Figure 4c, for the most Cu-depleted (NH₄OH-treated) surfaces, an upward band bending of 180 meV was measured indicating substantial negative charge; this value dropped by only 50-130 meV for the HOOH/NH₄OH-etched surface possessing a higher Cu concentration. Finally, the surface following 0.3 nm Cu deposition and anneal displayed a switch to downward band bending of 100 meV indicating the full eradication of negative charge at and near the surface.

By linking the spectroscopy and device results, the critical role of V_{Cu} in solar cell performance can be hypothesized. Angle-resolved XPS and transmission electron microscopy (TEM) studies on Cu-poor CIGSSe samples, suggest that Cd²⁺ from the CdS bath diffuses up to 30 nm into the substrate.^[15,16] Cd²⁺ is believed to occupy vacant Cu sites (V_{Cu}) forming positively-charged donor states (Cd_{Cu}⁺) in CIGSSe and resulting in a thin n-doped region a few tens of nanometers away from the CdS/CIGSSe junction.^[18,36–38] Cd has been predicted to behave similarly at the CdS/CZTSSe interface, although in this system



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there is also the likelihood of Cd occupying the Zn site.^[13,39,40] Therefore, poor PV performance after 0.3 nm of Cu deposition followed by postdeposition anneal can be attributed to removal of the majority of V_{Cu} at or near the surface. Conversely, since surface negative charge (equivalent to V_{Cu} concentration) has not been eliminated for HOOH/NH₄OH, the deterioration in its performance can be attributed to the removal of SnOx crystallites at the GBs near the CdS/CZTSSe junction.

Compositional measurements along a line from the CdS top surface to the bottom of the CZTSSe film in Figure 4d,e show that Cd and S signals do not reach their minimum until 260 nm beyond the point where Cu and Se (representing the CZTSSe substrate) reach their maximum intensity. The data is consistent with CdS depositing conformally on the surfaces as well as within GBs over a distance of 200–300 nm from the surface. Therefore, the CdS/CZTSSe interface extends to the grain sidewalls at the GBs, increasing the CdS/CZTSSe junction area and necessitating Cu-poor sidewalls for better device performance.

While a thin SnOx barrier layer and a Cu-depleted surface can passivate grain boundaries and improve the CdS/CZTSSe junction properties, high densities of antisite disorder lead to band tailing, thereby providing another pathway for $V_{\rm oc}$ reduction driven by the bulk of the CZTSSe grains.^[41] The presence of an internal electric field across the film can overcome the adverse effect of the bulk defects in an absorber and result in substantially higher Voc and power conversion efficiency.[42] Effective internal electric fields can be introduced by modification of the back contact work function in concert with an optimal CZTSSe absorber thickness. Coupling CZTSSe, whose work function (WF) is 5.2 eV, to a back contact material with a greater WF (for instance MoO_{3} , WF = 6.5 eV) will result in electron transfer and a resulting electric field that will drive the photoexcited electrons to the front contact. Since the sum of the minority carrier diffusion length and depletion width in CZTSSe is less than 1 $\mu m^{[43]}\!,$ the absorber thickness is an important parameter. In order to model this device architecture, device simulations were performed with WXAMPS, whose parameters were first extracted from detailed modeling of 12.6% efficiency devices.^[44] A schematic showing the electronic structure of the device and results of WXAMPS modeling for efficiency, V_{oc} and J_{sc} are shown in Figure 5. The model compares the performance of a CZTSSe device for a standard Mo/ glass substrate with that achieved for a high WF back contact such as MoO₃, which possesses a 6.5 eV WF. Additional comparisons are made for a reflective (R = 1) layer added to the contact. For absorber thicknesses below 1 µm, substantial increases in V_{oc} are observed with decreasing thickness, while J_{sc} peaks near 600 nm; below this the CZTSSe is simply too thin to fully absorb the incoming light. With this approach, efficiencies as high as 15%-16% result within the device simulation for a reflective back contact and absorber thicknesses $\approx 0.5 \ \mu m$.

3. Conclusion

It has been shown for the first time that the nanoscale elemental compositions of the grain boundaries and absorber/buffer interface strongly influence performance of polycrystalline CZTSSe

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Figure 5. Solar cell device simulation for various CZTSSe thicknesses and back contact work functions: a) Band diagram for the proposed PV device architecture with thin absorber and high work function (HWF) back contact. b,c) V_{oc} and J_{sc} as a function of CZTSSe thickness for PV devices with film baseline (FB) or high work function (HWF) materials as the back contact. Reflectivites (R) of 0 and 1 were tested. V_{oc} and J_{sc} for thin devices strongly depend on backside contact work function and reflectivity. d) Device efficiency vs. CZTSSe film thickness with variable back contact configuration. Using a high work function backside contact with a large reflectivity, CZTSSe device efficiency may be boosted up to 16% for thinner films.

photovoltaic devices. In particular, the presence of tin oxide at the grain boundaries, formed after annealing the bare absorber in air, is found to correlate with high device performance and is proposed to passivate GB recombination sites. Observation of a distinct tin-oxide layer suggests that GB passivation by an air anneal may occur due to thin bulk-like crystallite formation rather than simple atomic-scale O and Na defect passivation, thereby providing a new method of grain boundary passivation. NanoAuger and photoelectron spectroscopy experiments are consistent with a Cu-deficient buffer/absorber interface being required for the formation of a proper p-n junction to guide electrons from the CZTSSe top surface into the buffer and subsequent top contacts. PV device modeling shows that, given the effective passivation of the grain boundaries and interfaces using mechanisms described in this study, internal electrostatic fields may be used to reduce the effect of remaining bulk defects and substantially raise both $V_{\rm oc}$ and power conversion efficiency. Utilization of a high work function, reflective back contact coupled with careful selection of absorber thickness introduces an internal electrostatic field to efficiently drive the separation of photoexcited electrons and holes. This work provides a detailed evaluation of interface properties in highperformance CZTSSe devices and, given an effective pathway to interface passivation, provides a roadmap for fabrication of higher efficiency, earth abundant, kesterite thin-film photovoltaic devices, even in the presence of bulk defects.

4. Experimental Section

Solution-Phase Thin Film CZTSSe Preparation and Surface Cleaning: 2-µm-thick CZTSSe films were prepared by spin coating of hydrazinebased precursor solutions onto Mo-coated soda lime glass substrates in a nitrogen-filled glovebox. Further details of the synthesis have been published.^[6,7] The bulk [Cu]/[Zn] and [Se]/[S] + [Se] measured by X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) analysis were 1.8 and 0.7, respectively. The resulting bandgap for the CZTSSe films was 1.13 eV. After spin coating, all samples were subjected to a 15-min hard bake (HB) heat treatment at 600 °C in a nitrogen-filled glovebox followed by an air anneal (AA) at temperatures in the range of 300-400 °C for several minutes.^[24,45,46] To remove the surface oxide, two surface cleaning recipes were used: (1) 5 min dip in 7% aqueous NH_4OH solution followed by N_2 drying for 20 s; (2) 1 min dip in 30% aqueous H_2O_2 solution followed by 5 min dip in 7% aqueous NH_4OH solution and N_2 dry for 20 s. Subsurface incorporation of Cu into CZTSSe has been conducted on the samples, cleaned with 5 min NH₄OH dip, by 3–5 A° Cu e-beam evaporation deposition and post deposition annealing in N2-filled glove box at 200 °C.

Solar Cell Device Fabrication: The typical device structure for champion CIGSSe and CZTSSe was employed throughout the study.^[7,12] 25-nm-thick CdS buffers were deposited onto CZTSSe films by standard chemical-bath deposition followed by RF magnetron deposition of 10-nm-thick ZnO window and 50-nm-thick ITO top transparent contacts. Patterned 2-µm-thick Ni/Al collector grids were also applied. The total device area defined by mechanical scribing was 0.45 cm².

Solar Power Conversion Efficiency Characterization: Current-voltage measurements were performed using a Newport solar simulator

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with simulated AM1.5G illumination and 6 in \times 6 in beam. A Keithley 2400 sourcemeter was used for bias application and current measurement. The system is equipped with custom-designed software that controls light stabilization and automates data acquisition using a Keithley 2400.

X-ray Photoelectron Spectroscopy (XPS) and Femtosecond-Ultraviolet Photoelectron Spectroscopy (fs-UPS): XPS measurements were carried out using a monochromatic XM 1000 MkII/SPHERA (by Omicron Nanotechnology) XPS system with an Al-K α source (E = 1486.7 eV). For all measurements, a take-off angle of 30° from the sample surface was used. Surface compositional analysis using XPS spectra was performed using CASA XPS v.2.3. Femtosecond UPS (fs-UPS) has been previously described in detail.^[24,47,48] In the fs-UPS measurement, a regeneratively amplified, 1 kHz repetition rate Ti:Sapphire laser is utilized for pump and probe steps, with probe photon energies of 15–40 eV and light pulse widths of 50 fs. For CZTSSe surfaces, 1.55 eV pump pulses were focused on the probe area.

Auger Nanoprobe Spectroscopy and Microscopy (NanoAuger): Auger spectroscopy and compositional mapping has been performed using a Physical Electronics PHI-700 Auger Nanoprobe Microscope at the Stanford Nanocharacterization Laboratory. For spectroscopy and mapping, a 10 KeV and 1.0 nA electron beam was focused on the sample (with 3.75 × 5 μ m² raster) and secondary and Auger electrons were collected by the two separate detectors, both located above the sample (take off angle of 90°). The base pressure for the measurements was $\approx 1-2 \times 10^{-9}$ torr. Intensities used for single point and line trace composition measurements were normalized to the relative sensitivity factors of the elements' primary Auger peaks.

Solar Cell Device Simulations: Device simulations were carried out using the WXAMPS software with parameters optimized for hydrazine-processed CZTSSe samples with world record efficiency of 12.6%.^[44]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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