

Sputtered p-Type $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ Back Contact to CdTe Solar Cells

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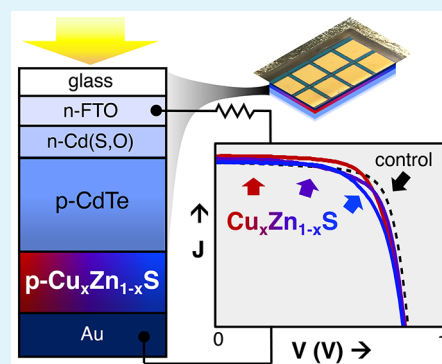
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Supporting Information

ABSTRACT: As thin-film cadmium telluride (CdTe) solar cells gain prominence, one particular challenge is optimizing contacts and their interfaces to transfer charge without losses in efficiency. Back contact recombination is still significant and will prevent CdTe solar technology from reaching its full potential in device efficiency, and transparent back contacts have not been developed for bifacial solar technology or multijunction solar cells. To address these challenges, this study investigates sputtered $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ as a p-type semi-transparent back contact material to thin-film polycrystalline CdTe solar cells at Cu concentrations $x = 0.30, 0.45$, and 0.60 . This material is selected for its high hole conductivity ($160\text{--}2120\text{ S cm}^{-1}$), wide optical band gap ($2.25\text{--}2.75\text{ eV}$), and variable ionization potential (approximately $6\text{--}7\text{ eV}$) that can be aligned to that of CdTe. We report that without device optimization, CdTe solar cells with these $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ back contacts perform as well as control cells with standard ZnTe:Cu back contacts. We observe no reduction in external quantum efficiency, low contact barrier heights of approximately 0.3 eV , and carrier lifetimes on par with those of baseline CdTe. These cells are relatively stable over one year in air, with V_{OC} and efficiency of the $x = 0.30$ cell decreasing by only 1 and 3%, respectively. Using scanning electron microscopy and scanning transmission electron microscopy to investigate the $\text{Cu}_x\text{Zn}_{1-x}\text{S}/\text{CdTe}$ interface, we demonstrate that the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ layer segregates into a bilayer of Cu-Te-S and Zn-Cd-S, and thermodynamic reaction calculations support these findings. Despite its bilayer formation, the back contact still functions well. This investigation explains some of the physical mechanisms governing the device stack, inspires future work to understand interfacial chemistry and charge transfer, and elicits optimization to achieve higher-efficiency CdTe cells.

KEYWORDS: CdTe photovoltaics, copper zinc sulfide, solar cell back contact design, transparent semiconductors, solar cell interfaces



INTRODUCTION

Cadmium telluride (CdTe) solar cell devices have reached efficiencies up to 22.1% ¹ and are the most dominant thin-film photovoltaic (PV) technology on the market today.² However, several material challenges remain that prevent this technology from meeting its theoretical detailed balance limit efficiency of 30% .³ One such challenge is the identification and implementation of buffer layers (also called contact layers, carrier selective contacts, carrier transport layers, and so forth) that are adequately aligned to the absorber such that photogenerated charge carriers are efficiently collected and transported out of the device with minimal losses.^{4,5} Prominent contact materials in commercial and research-grade superstrate CdTe cells are Cd(O,S)^{6,7} or $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ^{8,9} for the electron-selective front interface and ZnTe:Cu for the hole-selective back interface.^{10–12} However, interfacial losses due to Schottky barrier formation and recombination will prevent CdTe solar technology from reaching its full potential.^{5,13} Back contact barrier heights have been reported to be of $\sim 0.3\text{--}0.5\text{ eV}$ for ZnTe:Cu back contact cells, and Cu migration can lead to changes in series resistance and fill factor (FF), causing stability issues.^{14–16}

Thus, development of a semi-transparent hole-selective contact with adequate interfacial alignment to CdTe could lead to higher future conversion efficiencies. Furthermore, CdTe is currently limited to a superstrate configuration of p-type CdTe with an n-type emitter and transparent n-type top contact; this is in part because of the lack of a p-type transparent conductor aligned to CdTe's high work function of approximately 5.7 eV .¹⁷ Such a material could enable a variety of novel CdTe device configurations including a substrate configuration, a top cell configuration in tandem PV, and bifacial PV devices.¹⁸

Here, we focus on hole-selective back contacts to conventional superstrate CdTe devices. According to the literature, future back contacts require the following key design criteria that serve as guidelines for this study:

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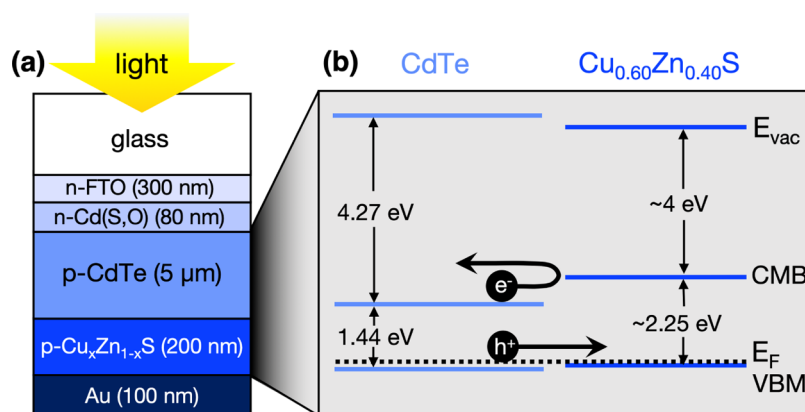


Figure 1. (a) Schematic of the as-deposited superstrate polycrystalline CdTe solar cells investigated in this study, with the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ as a p-type back contact (not to scale). (b) Approximate alignment of the as-deposited CdTe/ $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ interface for $x = 0.60$ under zero bias, guiding our selection of this material system. Note that the electron affinity of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ is an estimate based on Figure 2; band bending at the interface is not included, and the x -axis (thickness) is not to scale.

1. p-type doping: the hole concentration should place the Fermi energy E_F (i.e., chemical potential at 0 K) of the back contact close to or within the CdTe valence band maximum (VBM) such that it is sufficiently p-type-doped. The exact hole density depends on absorber hole density, so tunability of the hole concentration could also be advantageous.
2. VBM alignment: the VBM of the back contact preferably should be aligned within approximately 0–0.3 eV of CdTe's VBM to prevent barrier effects.¹⁹
3. E_F alignment: the initial Fermi level offset should be positive such that the E_F of the back contact material is below that of CdTe at zero bias.¹⁹
4. Electron reflection: the conduction band minimum (CBM) of the back contact should be higher in energy than the CdTe CBM such that electrons are reflected at the interface. This suggests a “semi-transparent” material with a band gap E_G greater than the CdTe band gap of approximately 1.5 eV (cf. Condition 2).
5. Interfacial chemical stability: the interface between CdTe and the back contact should be stable, without spurious reactions and formation of a detrimental secondary phase.
6. Passivation: the contact should be passivating such that it does not introduce recombination-inducing defects into the CdTe absorber.^{5,13}

Maintaining a low thermal budget (synthesis temperatures of less than $\sim 200^\circ\text{C}$) is usually preferable to avoid thermal reconstruction at the interface, especially for thin-film polymer contacts, but this condition depends on the specific device configuration so is not included above. Cu-free contacts are another possible criterion the community is moving toward.

In the early days of CdTe, metal contacts were applied directly to the absorber but resulted in Schottky barriers because of CdTe's high work function, so “buffer” back contacts such as ZnTe:Cu are now used. Researchers over the past decades have also investigated alternate back contact materials to ZnTe:Cu, primarily Cu-containing contacts, for example, Cu_xTe ,^{20–22} Cu_xS ,^{23–25} Cu/HgTe ,²⁶ CuI ,²⁷ CuSCN ,²⁸ and Cu nanowires with graphene,²⁹ with a variety of different metallization schemes. Non-Cu-containing contacts have also been explored, for example, Sb_2Te_3 ,^{30–32} As_2Te_3 ,³³ FeS_2 ,³⁴ MoO_x ,^{35,36} NiO_x ,³⁷ Ni-P ,³⁸ and ZnTe, but

results are not definitive and efficiencies are usually lower than Cu-containing counterparts unless the absorber utilizes group V dopants.^{33,39} None of these materials have yet resulted in a completely loss-free Ohmic hole-transport and electron-reflecting buffer layer, so the formation of a chemically stable barrier-free back contact without recombination remains a great challenge.

One material space that warrants exploration in CdTe is the ternary chalcogenide $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ —also written as $\text{ZnS}:\text{Cu}_x\text{S}$ to indicate a composite, or as Cu-Zn-S to indicate the full ternary space—which has been gaining traction as a wide band gap p-type semiconductor for PV and optoelectronic applications.^{40–42} Its optoelectronic properties are highly tunable within the cation chemical potential space, allowing for band gaps between 2.4 and 3.4 eV⁴³ and hole conductivities ranging orders of magnitude (reported up to 1000 S cm^{-1} for $x = 0.65$).⁴¹ Development of facile chemical bath deposition (CBD) and incorporation into $\text{np}^+\text{:Si}$ devices as a transparent hole-selective contact with V_{OC} up to 535 mV demonstrated its potential PV applications.⁴¹ One of the most remarkable properties of the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ system is the ability for enhanced properties and high crystallinity even at low synthesis temperatures, compatible with the thermal budget of CdTe, as well as its strong chemical and aqueous stability despite being a sulfide. Nanocomposite CBD synthesis of $\text{ZnS}/\text{Cu}_x\text{S}$ has been recently investigated as a back contact to polycrystalline p-type CdTe,⁴⁴ but this configuration still relies on ITO for carrier transport. Additionally, this synthesis method has a limited range of thickness tunability. CBD-synthesized $\text{ZnS}:\text{Cu}_x\text{S}$ has also been studied as a top contact to n-type CdTe,⁴⁵ but nonuniform film quality leading to pinhole formation was problematic. Neither study investigated device stability or interfacial chemistry.

In this study, we explore sputtered $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ as a p-type back contact to polycrystalline CdTe solar cells. We focus on sputtered layers rather than CBD to enhance film quality and finely control thickness. The CdTe solar cell film stack is depicted in Figure 1a where $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ is the as-deposited back contact. We report a high V_{OC} of 837 mV at $x = 0.30$, efficiencies commensurate with control samples, strong stability in air over one year for all devices, and high carrier lifetimes. We additionally investigate the CdTe/ $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ interface (interfaces are notated herein with “/” separating

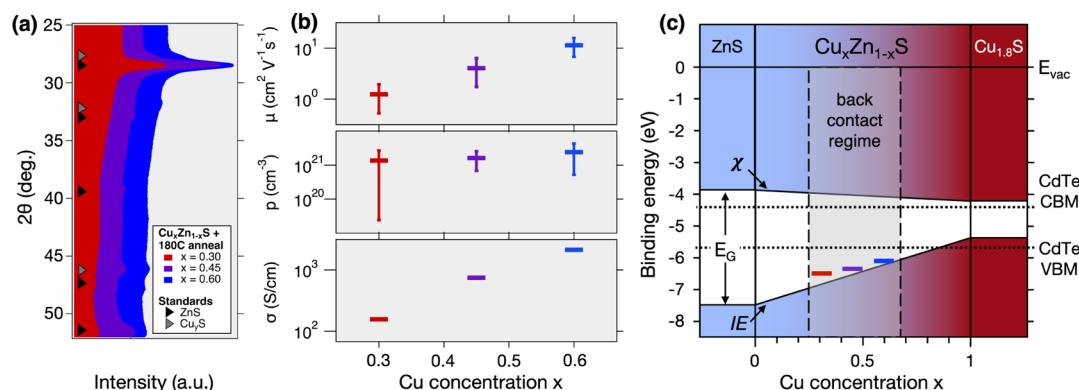


Figure 2. (a) Representative XRD peaks for $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ synthesized at ambient temperature and annealed at 180°C . (b) Electronic properties for films with $x = 0.30, 0.45$, and 0.60 , where μ is hole mobility, p is hole concentration, and σ is hole conductivity. (c) Schematic of estimated non-equilibrium band edges within the solid solution phase space of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$, with bars corresponding to approximate Fermi levels at the compositions used in devices and dotted lines corresponding to the band edges of CdTe.

each layer) with cross-sectional microscopy, demonstrate bilayer phase segregation, use first principles calculations to assess thermochemical stability, and suggest pathways for improved device performance.

METHODS

Device Fabrication. Polycrystalline CdTe thin-film solar cell devices with a superstrate configuration were fabricated using commercially available $\text{SnO}_2:\text{F}$ (FTO) coated Pilkington TEC-12D glass substrates. An 80 nm n-type Cd(S,O) layer was sputtered from a 3" target in a 6% O_2/Ar environment. CdTe was deposited in a closed-space sublimation (CSS) system with a source-to-substrate distance of 3 mm and source and substrate temperatures of 660 and 600°C , respectively. After CdTe deposition, the samples were annealed in the CdCl_2 treatment at 420°C for 10 min in a separate CSS chamber,⁴⁶ and residual CdCl_2 was rinsed off in DI water after the treatment. No other surface treatment was pursued other than water rinsing.

$\text{Cu}_x\text{Zn}_{1-x}\text{S}$ was then RF sputter-deposited at ambient temperature on the CdTe half-cell from 50 mm diameter zincblende ZnS and chalcocite Cu_2S targets. $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ standards were also deposited on glass for characterization, and we have recently reported similar films on glass substrates.⁴³ The compositions used in this study, $x = 0.30, 0.45$, and 0.60 , were achieved by fixing the ZnS target gun power at 40 W and setting the Cu_2S target gun power to 20, 30, and 40 W, respectively. As a finishing step, 100 nm of Au was evaporated for metallization. To make a baseline cell, 2.5 nm Cu followed by 350 nm of ZnTe were sputtered on a CdTe half-cell to form a control back contact device. After back contact formation, all of the samples were annealed in a tube furnace at 180°C with 100 sccm He flow for 30 min. For statistical analysis, 4–10 finished devices were fabricated for each composition and an example photograph is shown in the Supporting Information.

Material and Interfacial Characterization. Stoichiometry of the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ layer was quantified using X-ray fluorescence and corroborated by Rutherford backscattering spectrometry.⁴³ Structural analysis was performed with X-ray diffraction (XRD) on a Bruker D8 Discover with a θ - 2θ geometry, Cu $K\alpha$ radiation, and a proportional 2D detector. Hall measurements were performed using a van der Pauw configuration with indium contacts on corners of square size

samples, a 0.31 T magnet, and four-point probe contact. Optical characterization is described elsewhere.⁴³ The interfaces of cleaved devices were analyzed with cross-sectional scanning electron microscopy (SEM), using an FEI field emission Nova NanoSEM 630 at 2.0 kV, 64 pA current, and a working distance of 5.9 mm. Cross-section scanning transmission electron microscopy (STEM) specimens were prepared using the focused ion beam (FIB) lift out technique with the final Ga^+ ion milling performed at 3 kV. Ga^+ ion FIB damage was subsequently removed using low energy (<1 kV) Ar^+ ion milling in a Fischione Nanomill with the sample cooled using liquid nitrogen. STEM imaging and energy-dispersive X-ray spectrometry (EDS) analysis were performed in a FEI Tecnai F20 UltraTwin field emitting gun STEM operated at 200 kV and equipped with an EDAX Octane T Optima Si drift detector EDS system.

Device Performance Characterization. After completing the back contact, device areas of 0.25 cm^2 were defined by mechanical scribing. The solar cell devices were tested with current density–voltage (JV) measurements using a Newport solar simulator with AM1.5G filter under one sun conditions. The solar simulator light intensity was calibrated with a GaAs reference cell to match the current readings. External quantum efficiency (EQE) was measured with a 10 nm increment in wavelength on a Newport (Oriel) IQE 200. Devices were measured on three different occasions over the course of one year under identical experimental conditions.

Current density–voltage curves as a function of temperature (JVT) were collected using a current–voltage source/meter (Agilent B2912A) connected to a sample mounted in a closed-cycle helium cryostat. Because samples were deposited on thick glass, a separate temperature sensor was mounted on the top of the sample near the measured device to more accurately record the device temperature. Temperature was swept through the desired range using a temperature controller (Lakeshore 331) that stabilizes the sample temperature to within 1°C . An automated data collection program was set to maintain a stabilized temperature for 1 min before the current–voltage data were collected. Time-resolved photoluminescence (TRPL) measurements were collected using a mode-locked femtosecond pulsed laser with a pulse repetition rate of 1.1×10^6 pulses per second. Measurements were performed at an open-circuit on the glass side of the full device stack (with Au back contacts included). Using an optical parametric amplifier,

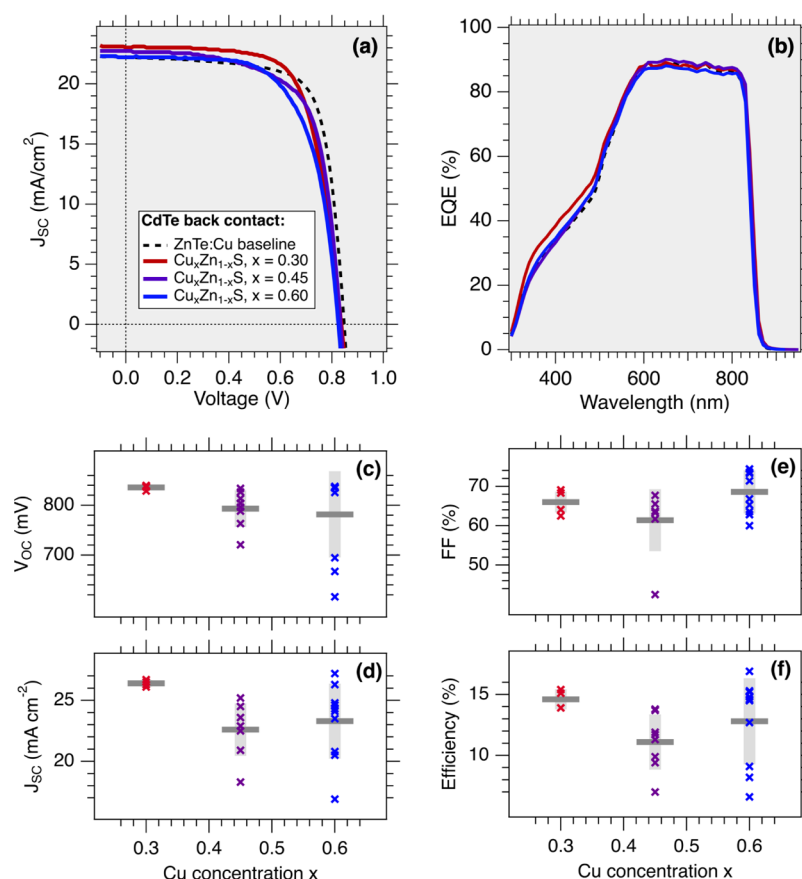


Figure 3. (a) J-V and (b) EQE measurements of different stoichiometries of Cu_xZn_{1-x}S films as back contacts to CdTe for highest performing cells. Control devices using ZnTe:Cu are plotted for comparison. The distribution of (c) open-circuit voltage (V_{OC}), (d) short-circuit current (J_{SC}), (e) fill factor (FF), and (f) efficiency (η) values are plotted across all measured cells in this study. Note that (a) is corrected from EQE measurements, but (d,f) are not.

the laser wavelength was tuned to 640 nm, laser power was 0.1 mW, a dichroic filter was chosen to block reflections and pass long wavelengths, and the carrier injection level was approximately 5×10^{16} cm⁻³ (see the [Supporting Information](#)). A 20× microscope objective was used to focus light and collect photoluminescence from a spot diameter of approximately 60 μm. A PicoQuant PicoHarp 300 time-correlated single-photon counting system was used to build up the TRPL decay curve.

Thermodynamic Calculations. The Materials Project's interfacial reaction calculator⁴⁷ was used to compute thermodynamic equilibrium reactions and energies based on the computed energies of materials from the Materials Project database.⁴⁸ Materials Project density functional theory calculations were performed using the projector-augmented wave method^{49,50} as implemented in the Vienna Ab initio Simulation Package (VASP)^{51,52} within the Perdew–Burke–Erzerhof generalized gradient approximation formulation of the exchange–correlation functional.⁵³ Cutoff, convergence, and correction criteria are described elsewhere.^{48,54} The calculations assume a closed system, where low-temperature (e.g., negligible entropic contributions) and ambient pressure conditions are appropriate.

RESULTS AND DISCUSSION

Materials Properties for the Device Design. In as-deposited sputtered Cu_xZn_{1-x}S films grown at ambient temperature, an alloy has been observed previously across

most of the cation chemical composition space; however, phase segregation occurred around $x = 0.60$.⁴³ Here, sputtered Cu_xZn_{1-x}S films are annealed at 180 °C in He to mimic processing conditions used for CdTe devices, and [Figure 2a](#) illustrates the XRD results. These films phase-segregate into zinc blende ZnS and metastable cubic Cu₃S (*Fm3m*) ($1 < y < 2$) for $x = 0.45$ and 0.60 , and appear to be single-phase zinc blende alloys for $x = 0.30$ (the data do not rule out the possibility of phase segregation with nanoscale domains). These films demonstrate strong peaks from zinc blende ZnS, highly textured in the (111) direction. There may also be traces of wurtzite ZnS, as was observed around $x = 0.30$ for ambient temperature films,⁴³ although this phase may destabilize at higher temperatures and, because of peak overlaps, it is difficult to resolve. Although we demonstrate some phase segregation, this may be acceptable for Cu_xZn_{1-x}S contacts, as has been shown with phase-segregated CBD films.^{41,44} Additionally, having one composition where phase segregation is not observed can allow us to compare whether this is in fact detrimental. Herein, we refer to all three compositions as “Cu_xZn_{1-x}S” for consistency.

In [Figure 2b](#), we plot the electronic properties for annealed Cu_xZn_{1-x}S films. The bottom panel indicates that the hole conductivity, σ , increases with Cu concentration from 160 to 2120 S cm⁻¹. The hole concentration, p , remains relatively constant at $\sim 10^{21}$ cm⁻³, increasing somewhat with Cu concentration, while hole mobility, μ , increases more

Table 1. Best Achieved CdTe Solar Cell Parameters for a Given Contact Material

back contact to CdTe	V_{OC} (mV)	J_{SC} (mA/cm ²)	$J_{SC}^{from\ EQE}$ (mA/cm ²)	FF (%)	η (%)	$\eta^{from\ EQE}$ (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
Cu _{0.30} Zn _{0.70} S	837	26.7	23.03	69.1	15.4	13.3	4.3	2600
Cu _{0.45} Zn _{0.55} S	834	24.5	22.74	67.7	13.8	12.8	3.1	2200
Cu _{0.60} Zn _{0.40} S	836	24.6	22.22	74.4	15.3	13.8	3.9	1700
ZnTe:Cu baseline	848	26.6	22.40	73.3	16.6	14.0	2.6	1200

prominently with Cu concentration from 1.2 to 11 cm² V⁻¹ s⁻¹.

One major advantage of highly tunable alloys or composites is the ability to tailor optical absorption and band alignment toward desired PV applications. In Figure 2c, we assume a linear composition grading between binary endpoints compatible with Vegard's law^{55,56} to estimate the range of band gap, E_G , electron affinity, χ , and ionization potential, IE , for Cu_xZn_{1-x}S. As x increases, we predict relatively constant χ at 3.8–4.0 eV, IE tunable between approximately 7–6 eV, and E_G tunable from approximately 2.75–2.25 eV, which corroborates optical measurements reported elsewhere.^{41,43} For comparison, we show the band offset of CdTe⁵⁷ as dotted lines, demonstrating IE values in Cu_xZn_{1-x}S close to or below that of CdTe. In a composite material, the electronic band edges are not well defined, but we retain this schematic as an estimate to guide device integration. This schematic also neglects any alloy band bowing which would likely lead to VBM positions slightly farther from vacuum (i.e., larger IE). We acknowledge that future X-ray photoelectron spectroscopy (XPS) experiments are necessary to accurately assess the valence band and conduction band positions.

PV Device Performance. Figure 2c suggests an optimal valence band alignment to CdTe somewhere in the mid-range regime of $0.25 < x < 0.75$, which is denoted as the “back contact regime.” Accordingly, we use predicted alignments as a guide for selecting the optimal Cu concentration and then vary the thickness in experiments to achieve desirable transparency or conductivity. Based on the IE estimates, we focus on $x = 0.30$, 0.45 , and 0.60 , and layer thicknesses of 200–300 nm. Figure 1b illustrates the approximate band offsets at the CdTe/Cu_xZn_{1-x}S interface under no bias for the as-deposited device with $x = 0.60$. Such an interface follows the back contact design criteria outlined previously; holes should be injected from the CdTe layer into Cu_xZn_{1-x}S, and electrons reflected.

Figure 3a plots the JV curves for the three highest performing cells (colored lines) and a baseline cell with a ZnTe:Cu back contact for reference (black dotted line). Derived solar cell performance parameters, namely, open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill factor (FF), and efficiency (η) are plotted across all cells measured in Figure 3c–f, respectively. The parameters of the highest performing cells are listed in Table 1. V_{OC} of the Cu_xZn_{1-x}S devices ranges from approximately 834 to 837 mV. This is nearly as high as the heavily optimized ZnTe:Cu back contact baseline (~848 mV) and higher than the V_{OC} of Cu_xZn_{1-x}S devices previously reported in the literature.⁴⁴ The results indicate that the Cu_xZn_{1-x}S back contact does not appear to affect the front interface adversely through diffusion or other effects. The FF for the $x = 0.60$ film is even higher than the baseline cells. We note that some J_{SC} values were measured to be greater than 25 mA cm⁻², and are likely miscalibrated because of inaccurate measurements of the cell area. For this reason, we use EQE to estimate J_{SC} and efficiency and report these derived values for comparison in Table 1 as “ $J_{SC}^{from\ EQE}$ ”

and “ $\eta^{from\ EQE}$ ”, as described in the Supporting Information. The current densities in Figure 3a have been calibrated accordingly, but (d) and (f) remain uncalibrated. From this calibration, we observe that the efficiency is the highest for the $x = 0.60$ cell at 13.8%, and all the compositions have efficiency comparable to the ZnTe:Cu baseline efficiency of 14.0%.

Statistically, the solar cell parameters are least variant across the $x = 0.30$ cells, where the average efficiency is the highest, and the highest EQE-corrected efficiency is achieved for $x = 0.60$. However, overall, the efficiencies of all three samples are very similar, within a percentage or so and all within statistical uncertainty of one another. It may be of interest that the $x = 0.30$ data are the least scattered and that the scatter and average V_{OC} increase with increasing x where materials are expected from XRD to phase-segregate,⁴³ although we note there are fewer cells measured for $x = 0.30$. Statistical analysis across all solar cells measured is elaborated upon in the Supporting Information.

EQE measurements of the same highest performing cells are plotted in Figure 3b, revealing EQEs equal to or greater than the optimized baseline back contact cells. We comment that EQE differences at low wavelengths are likely from parasitic absorption at the Cd(O,S) front buffer layer, as reported elsewhere⁵⁸ rather than from the back contact region. Shunt resistances (R_{sh}) and series resistances (R_s) are estimated from the slopes at J_{SC} and V_{OC} , respectively. R_{sh} values greater than 1000 Ω cm² and FFs of nearly 75% for Cu_xZn_{1-x}S contacts with little optimization is very encouraging, to date. R_s is low but could be addressed by further optimizing composition, thickness, and material quality of the Cu_xZn_{1-x}S layer using insights from this study. It is also important to note that the grain size of the contact layer may influence V_{OC} , J_{SC} , and resistances in these devices, as the absorber and contact grain size has been shown to influence performance in the literature.^{59,60} However, our previous study of Cu_xZn_{1-x}S suggests a grain size of approximately 10–50 nm to be relatively constant in the range $0.3 < x < 0.9$, so here, the grain size is unlikely to be responsible for significant differences between samples.⁴³

Device Stability in Air. Next, Figure 4 illustrates the stability of the three highest performing cells over one year (approximately 9000 h) in air. Assessing stability is particularly important in chalcogenide-based devices because chalcogenide materials are known to experience enhanced degradation pathways due to of oxidation. Additionally, the presence of highly diffusive Cu⁺ ions has been shown in many cases to contribute detrimentally to CdTe device stability by inducing spurious rectification so this effect must be assessed.^{16,61} Figure 4 plots the stability of the (a) V_{OC} , (b) J_{SC} from EQE, (c) FF, and (d) η as a function of time over the course of a year for the three devices investigated in this study. With a few exceptions, device properties generally decrease monotonically and only negligibly over the course of a year. V_{OC} decreases by 1–3%, and efficiency decreases by 3–6%. Unfortunately, the control cell was damaged shortly after the first measurement so could

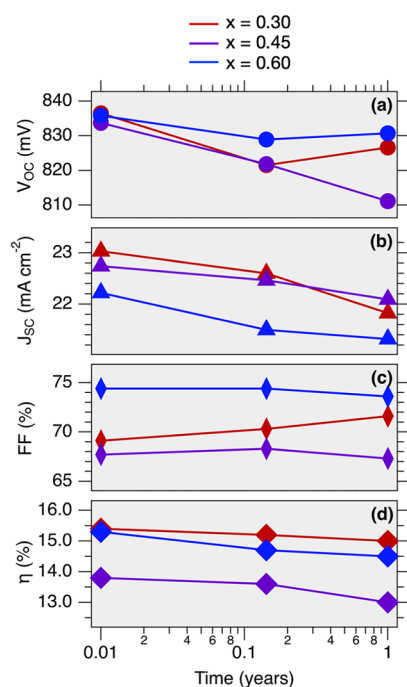


Figure 4. Stability of (a) open-circuit voltage (V_{OC}), (b) short-circuit current (J_{SC}), (c) fill factor FF , and (d) efficiency (η) as a function of time for $Cu_xZn_{1-x}S$ back contact CdTe devices stored in air. Note that (a) values are corrected from EQE measurements.

not be compared for this analysis, but this assessment should be included in follow-up work. Such a shelf-life stability test shows that Cu diffusion at room temperature is not prohibitively bad, but long-term degradation studies under illumination at maximum power point, continuous operation, and elevated temperatures are warranted in the future. First Solar modules with optimized ZnTe:Cu back contacts are warranted to have 0.5%/yr (relative) degradation or less in the field,⁶² so competitor contacts would have to hold up to this metric.

Contact Barrier Height and Carrier Lifetime Measurements. As described previously, back contact interfacial resistance can lead to a significant deviation from ideality in CdTe solar cells, and an optimal contact has a small or negligible Schottky barrier. To assess this barrier height Φ_b , we measured dark JV curves at a variety of sub-ambient temperatures (JVT), as described in the literature.^{63,64} The “turning current” J_t at which a JV curve transitions from a positive to negative second derivative, is fit for each temperature (see [Supporting Information](#) for details), as shown in [Figure 5a](#). Then, the Richardson equation⁶⁵ is used to calculate the barrier height

$$J_t = A^* T^2 e^{-q\Phi_b/kT} \quad (1)$$

where A^* is the Richardson constant and k is the Boltzmann constant. We find Φ_b values for $x = 0.30, 0.45$, and 0.60 of $298 \pm 13, 304 \pm 11$, and 316 ± 13 meV, respectively, and plot each in [Figure 5b](#). As depicted in [Figure 5b](#), typical CdTe barrier

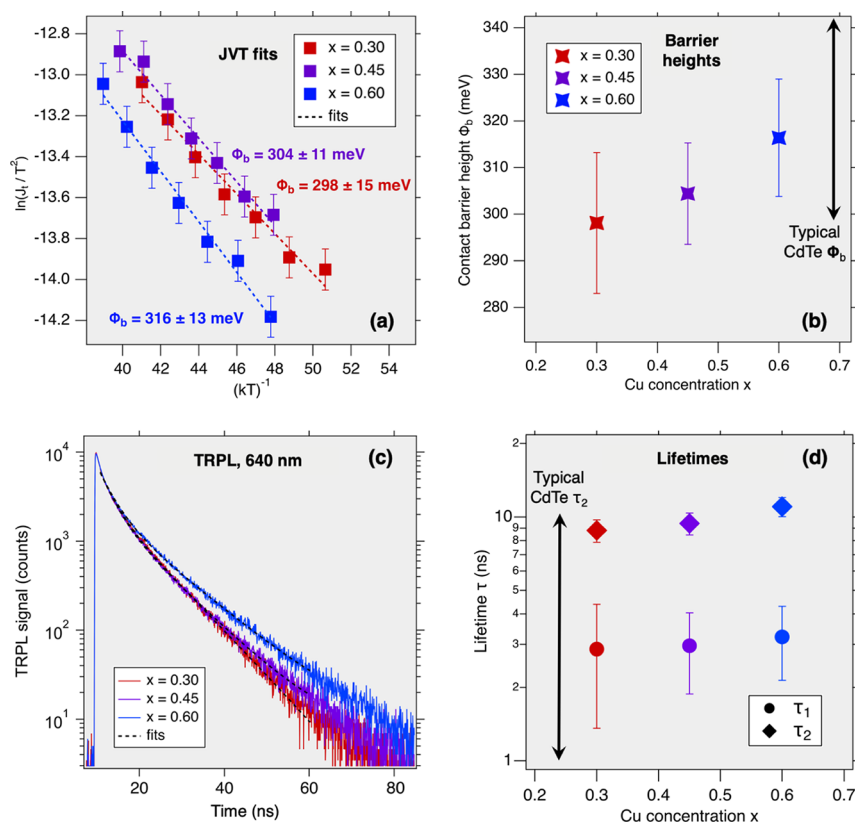


Figure 5. (a) Linear fits to temperature-dependent JV (JVT) measurements, as described in the [Supporting Information](#), and (b) back contact barrier heights as quantified by (a) in the three devices of interest, with the typical CdTe range boxed. (c) TRPL of the three highest performing $Cu_xZn_{1-x}S$ back contact devices in this study, with bi-exponential decay fits plotted, and (d) resulting carrier lifetimes from fits to these measurements. Parameters τ_1 and τ_2 correspond to the former and latter sections of the decay curve, respectively, and error bars are from uncertainty in the fit.

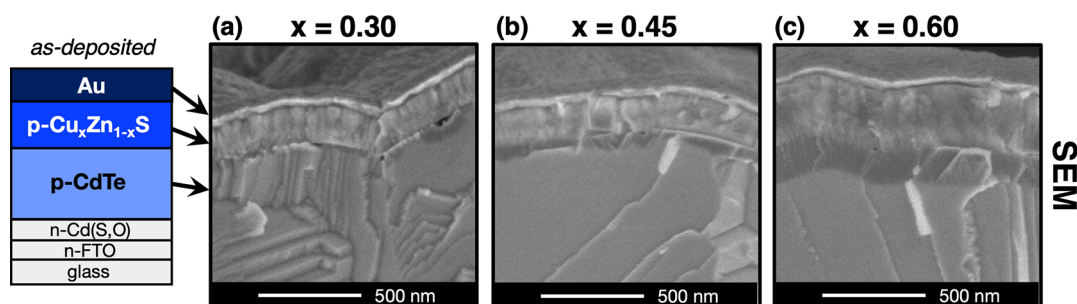


Figure 6. SEM images of the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ back-contact interfacial region for devices with (a) $x = 0.30$, (b) $x = 0.45$, and (c) $x = 0.60$. As-deposited schematic layers from Figure 1 are illustrated on the left for clarification.

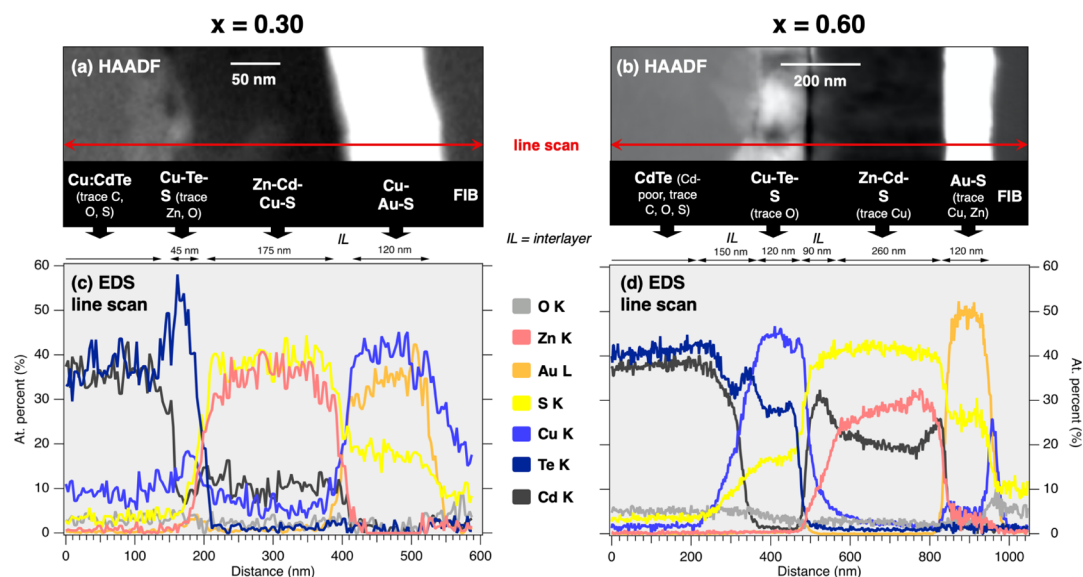


Figure 7. Cross-sectional STEM HAADF images of the $\text{CdTe}/\text{Cu}_x\text{Zn}_{1-x}\text{S}/\text{Au}$ interfacial region of representative (a) $x = 0.30$ and (b) $x = 0.60$ cells, with corresponding elemental EDS line scans for the (c) $x = 0.30$ and (d) $x = 0.60$ cells. The red lines in (a,b) indicate the region through which the EDS line scan was measured. “IL” indicates interlayer regions. Elemental profiles in (c,d) are indicated by the trace color. These images reveal complex interfacial chemistry, with a bilayer in place of the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ as-deposited layer, and depict diffusion profiles of various elements.

heights using standard back contacts are approximately 300–500 meV. Thus, these values are in the range considered small for the CdTe devices, which is consistent with the shapes of the JV curves and the JV parameters achieved. A slight increase in the barrier height with x , coupled with the slight increase in conductivity with x observed in Figure 2b, may explain why the solar cell performance dips at the mid-range of $x = 0.45$ (see Figure 3, although this is mere speculation, and there could be many simultaneous effects occurring).

Contacts must effectively passivate the CdTe absorber such that recombination is minimal. Thus, characterizing the minority carrier recombination lifetime of these devices can help assess whether the absorber layer has been compromised because of the addition of the new back contact. As described in the Introduction section, the presence of Cu can be detrimental because of its tendency to diffuse into the absorber and induce compensation, which can then reduce lifetime.^{21,66,67} Shown in Figure 5c,d, TRPL measurements on our three devices indicate $\tau_2 = 9\text{--}10$ ns and $\tau_1 = \sim 3$ ns, respectively. Lifetime τ_2 is generally on the order of several ns (depicted with an arrow in Figure 5d), whereas τ_1 is typically about 0.5–1.5 ns, assuming the CdCl_2 treatment. As-deposited lifetimes are on the order of tens to hundreds of picoseconds. We can assert that our values are typical for CdTe solar cells,

and thus, $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ back contacts demonstrate no significant degradation of the CdTe absorber.

Imaging the Interface. The above results beget the following questions: what is the nature of the $\text{CdTe}/\text{Cu}_x\text{Zn}_{1-x}\text{S}$ interface, why is there a larger statistical distribution of solar cell parameters with increasing x , and from which mechanism does observed degradation originate? To assess these, we first investigate the interfacial back contact regions of each device stack using cross-sectional SEM after a year of aging in air. Images in Figure 6 denote the as-deposited CdTe, $\text{Cu}_x\text{Zn}_{1-x}\text{S}$, and Au regions, with the Au surface visible at the top of each image. We observe the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ layer to be conformal on the surface of polycrystalline CdTe in all three devices, with columnar grains. These images confirm $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thicknesses between 200 and 300 nm. What is surprising is that there appears to be an additional interfacial layer forming, indicated by the darker region between $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ and CdTe. This interfacial effect appears in all samples, increasing in thickness as x increases. The dark region appears to extend into the grains of the CdTe layer rather than the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ layer. We also observe a few dark spots in the $x = 0.30$ sample between the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ and CdTe.

To further understand interfacial chemistry and identify the dark interfacial region observed in SEM, we performed cross-

sectional STEM on the CdTe/Cu_xZn_{1-x}S/Au interface prepared by FIB lift-out on Mo TEM grids for an $x = 0.30$ and an $x = 0.60$ sample after a year of aging. These samples are selected because they possess the thinnest and thickest dark interfacial regions and highest cell performances. The interfaces are shown as STEM high-angle annular dark-field (HAADF) images in Figure 7a,b, respectively, with stoichiometry determined by an EDS line scan (red horizontal arrows) in (c,d), respectively. The HAADF images are aligned with the x axis of the EDS scans, and we note different scaling in the two samples. Regions are labeled to contain a particular element if the concentration is greater than 10%; otherwise, the element is notated as “trace.” Quantified EDS results are included in the Supporting Information, and we note that EDS concentration is in atomic percentage and a detection limit of approximately 1%.

These measurements show that the dark interfacial regions observed in SEM are phase-segregated bilayers, and the identities of these regions are revealed as follows (going left to right across each image in Figure 7). For the interface of the $x = 0.30$ sample, the CdTe region contains approximately 10% excess Cu, and then, the Te concentration spikes at the interface. This thin (approx. 45 nm) Te-rich region contains Cu and S, so it is labeled “Cu-Te-S” and has “trace” amounts of Zn and Cd. Cu-rich inclusions were observed in some regions of the CdTe/Cu-Te-S interface (cf. Supporting Information). Next, a 175 nm layer of primarily Zn and S emerges, with ~10% Cd and just under ~10% Cu (labeled “Zn-Cd-Cu-S”). This layer gradually transitions through the interlayer (labeled “IL”) into the Au contact region (“Cu-Au-S”) in which we observe a higher elemental concentration of Cu than that of Au, as well as approx. 18% S (although this may be an analysis artifact from overlapping S K and Au M peaks). In the $x = 0.60$ sample, first, we observe that the CdTe region is somewhat Cd-poor and contains trace O and S. Next, in place of the as-deposited Cu_{0.60}Zn_{0.40}S layer, we observe a bilayer containing (1) a 150 nm thick Cu-Te-S layer in contact with CdTe, which is the dark interfacial region from the SEM and (2) a 300 nm thick Cd-Zn-S layer (with trace Cu), located between (Cu-Te-S) and Au. Then, the Au contact contains approximately 25% S (potentially an artifact, see above) as well as “trace” Cu and Zn. The far right region in both images is a Pt-protective layer from the FIB sample preparation process.

Because STEM was performed after aging cells for one year, it is unclear from this investigation whether the bilayer formation is induced by aging in air at room temperature, from the anneal step during cell fabrication, or from some other energetic transition. It is also unclear whether the segregation is the cause of the slight degradation in cell performance. We acknowledge that there is concern for additional ion migration and additional shunt resistance under operation and upon exposure to high temperature and UV radiation; this has not been explicitly studied here and certainly warrants future investigation. However, it is significant that in all cells, this phase-segregated bilayer interfacial configuration still leads to good carrier lifetimes, sufficient hole transport, and PV performance effectively equivalent to the control samples.

Chemical Stability Analysis. From the STEM-EDS analysis, it is unclear whether these bilayer phases are alloys or composites because the crystal structure of each phase is not determined. There is evidence in the literature of a ternary S-rich Cu₁₀Te₄S₁₃ phase,⁶⁸ although the Cu-Te-S layers are Te-rich. We observe inversely correlated Cu and Te fluctuations in

the Cu-Te-S layer on the order of 50–100 nm. This suggests phase segregation and perhaps a Cu_xTe:Cu_yS composite with fluctuating Cu concentration x (cf. Supporting Information). Both of these binaries are p-type semiconductors. The Zn-Cd-S layer contains inverted fluctuations of Zn and Cd, suggesting a phase segregation into Zn-rich and Cd-rich ternary phases, with smaller phase coherence on the order of 40–80 nm. These layers could be an n-type wurtzite Cd_xZn_{1-x}S solid solution or a composite, both of which have been synthesized extensively in the literature.^{69,70}

We calculate thermochemical stability of the as-deposited interface from first principles to help understand our resulting bilayer. Using the interfacial reaction calculator from the Materials Project,^{47,48} we investigate the reactions and resulting phases expected to occur at a Cu_xZn_{1-x}S/CdTe interface for $x = 0.30, 0.45, \text{ and } 0.60$, at lowest formation enthalpy (δH), and report reactions and their associated reaction energies (E_{rxn}) in Table 2. We note that this calculator is based on convex hull analysis such that reactants are phase-segregated Cu_yS:ZnS, and only yields reaction products with a convex hull energy of 0 eV/atom (i.e., only thermodynamically stable phases), although metastable phases may actually form experimentally. We calculate products of ZnS, CdS, and CuTe, with negative E_{rxn} values of $-1.898, -2.553, \text{ and } -3.085$ kJ/mol for $x = 0.30, 0.45, \text{ and } 0.60$, respectively. From these calculations, and negative E_{rxn} values, we hypothesize that a zinc blende or wurtzite ZnS phase, wurtzite CdS phase (*P6₃mc*, mp-672), and layered CuTe phase (*Pmmn*, mp-20826) are favorable to form under canonical thermodynamic conditions. Indeed, the STEM results are suggestive of a similar phase separation behavior. The CdS and ZnS products coexist in a single layer. CuTe also separates into its own layer, with some residual S present. The lower E_{rxn} in the $x = 0.60$ sample may explain why the dark phase-segregated Cu-Te-S layer is more prominent in the SEM images of Figure 6 and why the bilayers observed by STEM are thicker. Because $x = 0.45$ has a E_{rxn} between that of $x = 0.30$ and $x = 0.60$, we could expect a similar phase segregation to occur, likely with a Cu-Te-S layer thickness larger than 45 nm and smaller than 120 nm.

For comparison, we calculate equilibrium reactions of Cu_xZn_{1-x}Te/CdTe (standard back contact) to yield an additional CuTe product (see the Supporting Information). It has been shown that in CdTe cells with a ZnTe:Cu buffer layer, the activation (i.e., annealing) step can induce a bilayer structure at the CdTe/CuZnTe interface with a disordered layer because of Cd–Zn interdiffusion and a Cu_xTe phase-segregated layer at defects,⁷¹ supported by our reaction calculations. Thus, it is reasonable that a similar effect is occurring at the CdTe/Cu_xZn_{1-x}S interface because nearly all of the same elements are participating. For reference, in the Supporting Information, we also report thermodynamic stability calculations of CdTe interfaces for other back contacts in the literature, demonstrating stable interfaces for Sb₂Te₃ and As₂Te₃ and unstable interfaces for Cu_xS, CuI, CuCSN, NiO_x, and MoO_x, although we acknowledge the simplicity of our assumptions.

Implications. Here, we discuss the extent to which our experimental results correspond to the design criteria (1–6) outlined in the Introduction section. We confirmed with Hall measurements that Cu_xZn_{1-x}S is p-type-doped (Condition 1), but the doping of each of the bilayers, their E_{F} position (Condition 3), and the band bending at the interface are not assessed qualitatively here. We have measured a back contact

Table 2. Lowest Enthalpy Interfacial Reactions under Thermodynamic Equilibrium, Assuming a Closed Reaction, at Three $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ Interfaces with CdTe

interface with CdTe	interfacial reaction equation (normalized)	E_{rxn} of eqn (kJ/mol)
$\text{Cu}_{0.30}\text{Zn}_{0.70}\text{S}$	$0.769 \text{ Cu}_{0.30}\text{Zn}_{0.70}\text{S} + 0.231 \text{ CdTe} \rightarrow 0.538 \text{ ZnS} + 0.231 \text{ CdS} + 0.231 \text{ CuTe}$	−1.898
$\text{Cu}_{0.45}\text{Zn}_{0.55}\text{S}$	$0.69 \text{ Cu}_{0.45}\text{Zn}_{0.55}\text{S} + 0.31 \text{ CdTe} \rightarrow 0.379 \text{ ZnS} + 0.31 \text{ CdS} + 0.31 \text{ CuTe}$	−2.553
$\text{Cu}_{0.60}\text{Zn}_{0.40}\text{S}$	$0.625 \text{ Cu}_{0.60}\text{Zn}_{0.40}\text{S} + 0.375 \text{ CdTe} \rightarrow 0.25 \text{ ZnS} + 0.375 \text{ CdS} + 0.375 \text{ CuTe}$	−3.085

valence band barrier height of approximately 0.3 eV from JVT, which is relatively low for CdTe and allows transport of holes with minimal losses (Condition 2). However, because we observe a bilayer back contact, this could be a compounded barrier height from both layers and thus is difficult to interpret directly. Band offsets would need to be probed experimentally to confirm the exact VB offset and whether the contact is actually electron-reflecting (Condition 4). In contrast to the expected criteria (Condition 5), we demonstrate with STEM and thermochemistry calculations that the back contact interface is *not* chemically stable, at least not initially, although only slight degradation in cell performance after a year suggests it may stabilize after operation. From τ_2 lifetimes of 9–10 ns, we can claim that even though it contains Cu, the contact does not destroy the CdTe absorber; however, we cannot claim passivation without further analysis (Condition 6). Additionally, processing was carried out at temperatures below 200 °C, which is considered to be a low enough thermal budget to minimize damage to the absorber, although it is unclear from this study whether the interfacial instabilities occur immediately after processing or after operation.

Previous study assumes that the $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ back contact remains in its as-deposited composite form,⁴⁴ but here, we have demonstrated that is actually not the case, contributing to knowledge in the field. Rather than a $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ back contact, we instead have observed effectively a buffer bilayer of Cu-Te-S and Zn-Cd-S. This interfacial complexity is not uncommon in device applications—as previously mentioned, current CdTe contact materials like ZnTe:Cu have also been shown to form more complexity at the interfaces than assumed.⁷¹ In our study, the thickness of the Cu-Te-S layer appears to increase with as-deposited Cu concentration x , correlating with an increase in barrier height Φ_b , slight decrease in solar cell performance, and increase in statistical scatter of J_{SC} , V_{OC} , FF , and efficiency. Both Cu_xTe and Cu_xS have been explored as hole-selective back contacts to CdTe for decades;^{20–23} for example, optimized single-phase Cu_xTe back contacts with rapid thermal processing have yielded efficiencies up to 13.9% and have been reported to minimize back contact recombination,²² and Cu_xS back contacts have recently reported efficiencies up to 13%, although VBM offsets are slightly too high at 0.4–0.6 eV.²⁵ $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ has also been used as a contact with CdTe, but as an electron-selective *front* contact rather than a back contact. The charge transport mechanism at this bilayer interface is particularly elusive because $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ is usually a n-type semiconductor. However, Zn-Cd-S carrier concentrations here are unknown, and the Zn-Cd-S region could be p-type, for example, because of Cu substitutions. We still do not know the band alignment of the bilayer; to understand this requires future investigation. For insight into

the charge transport through our bilayer, we can look into other literature reports of bilayer back contacts.

A recent report investigated an intentional bilayer, ZnTe and Cu_xTe ($x = 1.4$), as a back contact to CdTe solar cells, resulting in high FF s > 73%.⁷² In our study, the Cu_xTe component of the bilayer is in contact with Au, rather than with CdTe, yet it still achieves similar solar cell properties, suggesting pathways to further optimization. Other bilayer CdTe back contacts have been reported elsewhere in the literature, for example, p-type SrCuSeF and n-type $\text{In}_2\text{O}_3\text{:Sn}$ bilayer Ohmic tunnel junctions have demonstrated higher efficiencies together than the efficiencies each material as a single back contact.⁷³ We note that bilayer quasi-Ohmic tunnel junctions have been used to convert the carrier type from electrons such that n-type layers can transport holes.⁷⁴ Bilayer and even tri-layer carrier selective contacts are used extensively for other PV device applications—for example, p-type a-Si and n-type transparent conductive oxide bilayer hole-selective contacts in silicon heterojunction solar cells^{75–77}—such that one material does not need to satisfy all requirements. In this study, formation of a stable bilayer back contact with good PV performance may suggest a promising design route for CdTe back contact exploration.

CONCLUSIONS

We have investigated the use of sputtered $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ ($x = 0.30, 0.45, 0.60$) as a hole-selective back contact for polycrystalline CdTe solar cells. We demonstrate a phase separation of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ into a bilayer of Cu-Te-S and Zn-Cd-(Cu-)S at the back interface for $x = 0.30$ and $x = 0.60$ cells, yet these cells still yield device performance nearly as high as cells with standard control back contacts. Specifically, we report a FF of 74.4% without optimization. Relatively low contact barrier heights of approximately 300 meV suggest small losses because of charge transport. V_{OC} measurements of 837 mV and high τ_2 lifetime measurements of approximately 9–10 ns suggest that the back contact is not degrading either the absorber or the front interface through Cu diffusion or other mechanisms. Efficiency is similar to control devices. After one year of aging in air, V_{OC} is reduced by only 1–3% and efficiencies by 3–6%. Although these samples use Cd(O,S) buffers and the JV parameters are far from the best polycrystalline CdTe devices in the literature, it is significant that these results are achieved with no device optimization, suggesting optimization may yield further improvement.

This investigation motivates follow-up research on incorporation of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ as a back contact for CdTe solar cells and on the bilayer contact formation. First, a more in-depth exploration of $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thickness, Cu concentration, deposition temperature, and synthesis method should be pursued to investigate whether the ternary can be thermodynamically stabilized. Alloying in the Zn(S,Se,Te) phase space could also be explored as a possibility to tune barrier height and increase passivation. Second, device modeling and experimental analysis using XPS can be performed to assess band edges, determine interfacial band-bending, and inform optimal growth conditions. Third, further interfacial characterization is recommended to understand the role of diffusion, the physics of the interfacial layer(s), grain boundary segregation, hole transport at the interface, and so forth. Stress testing and temperature-dependent performance should be assessed. It is also of interest to investigate whether the interfacial bilayer

indeed forms at different Cu concentrations, and to intentionally grow and optimize a bilayer back contact.

More broadly, because such high performance is achieved upon the first try, this study should also inspire research to incorporate underexplored semi-transparent p-type materials as back contacts, such as those outlined in our most recent review article,¹⁸ in both single-layer and bilayer configurations. Many new compounds are becoming available to the scientific community as a result of high-throughput computational and experimental searches for wide band gap p-type semiconductors. In particular, the use of combinatorial synthesis coupled to device optimization has been demonstrated as a promising avenue to rapidly explore phase space and optimize such new contact materials.⁷⁸ Perhaps, the incorporation of one of these underexplored materials such as $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ in a well-optimized configuration will enable elimination of voltage losses at the back interface and push CdTe solar cell efficiencies toward their 30% theoretical detailed balance limit.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.0c00413>.

Materials properties; device properties; interfacial reaction calculations; and experimental details (PDF)

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Notes

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