

Eliminating S-Kink to Maximize the Performance of MgZnO/CdTe Solar Cells

*Deng-Bing Li, Zhaoning Song, Rasha A. Awni, Sandip S. Bista, Niraj Shrestha, Corey R. Grice,
Lei Chen, Geethika K. Liyanage, Mohammed A. Razooqi, Adam B. Phillips, Michael J. Heben,
Randy J. Ellingson, and Yanfa Yan**

Department of Physics and Astronomy, and Wright Center for Photovoltaics Innovation and
Commercialization (PVIC), University of Toledo, Toledo, OH 43606, USA.

KEYWORDS:cadmium telluride, CdTe,magnesium doped zinc oxide, ZMO, S-kink

ABSTRACT:Comparing to the traditional CdS buffer layer, magnesium zinc oxide (ZMO) offers the following advantages for CdTe-based thin-film solar cells: it introduces a spike to conduction band offset, which reduces interface recombination that is beneficial for increasing open-circuit voltage (V_{OC}), and decreases parasitic optical absorption of the buffer layer that is favorable for enhancing short-circuit current (J_{SC}). However, ZMO/CdTe thin-film solar cells often show the so-called S-kink behavior in their current-voltage curves, making it difficult to reproduce the expected benefits. Here, we show that S-kink can be successfully eliminated, and improved V_{OC} and J_{SC} can be simultaneously achieved if the $CdCl_2$ treatment process is

conducted in oxygen-free atmosphere. As a result, the device efficiencies increased from 9.2% to 16.1%. Our device characterization and simulation reveal that a sufficiently high electron density of the ZMO buffer layer is critical to eliminate the S-kink, which is achievable through an oxygen-free CdCl_2 treatment.

INTRODUCTION

CdTe solar cells are gathering more attention due to the significant efficiency improvement from 16% to over 22% in the past six years.¹ This dramatical improvement is mainly attributed to the replacement of the traditional CdS buffer layer by a wider band gap buffer layer as well as the use of $\text{Cd}(\text{Te}_{1-x}\text{Se}_x)$ absorber layer that together result in increased short circuit current density (J_{SC}).²⁻⁴ Magnesium zinc oxide (ZMO) has been considered as an alternate buffer to replace CdS. Device simulation has shown that ZMO can introduce a spike to the conduction band offset (CBO), which can help reduce carrier recombination at the ZMO/CdTe interface.⁵⁻⁶ [ENREF 4](#) A systematical simulation by Ablekim et. al has revealed that ZMO/ $\text{Cd}(\text{Te}_{1-x}\text{Se}_x)$ solar cells are capable of achieving power conversion efficiencies up to 25% with open circuit voltage (V_{OC}) exceeding 1 V.⁶ This prediction has been experimentally confirmed by Sites, Sampath and co-workers who have demonstrated ZMO/CdTe solar cells with efficiencies exceeding 18% and ZMO/ $\text{Cd}(\text{Te}_{1-x}\text{Se}_x)$ solar cells with efficiencies over 19%, surpassing the performance of CdS/CdTe solar cells.^{3, 7-8}

However, the success of fabricating high efficiency ZMO/CdTe solar cells has not been reproduced by other research groups, though significant efforts have been paid.⁹⁻¹² Bittau et. al improved their CdS/CdTe solar cell performance from 8.2% to 10.5% when ZMO was deposited prior to the CdS layer.⁹ [ENREF 8](#) [ENREF 5](#) Wang et. al obtained an efficiency of 13.1% and

14.7% for ZMO/CdS/CdTe and ZMO/CdS/CdSe/CdTe stack, respectively.¹⁰ Menossi et. al improved the efficiency of CdS/CdTe devices to 16.2% with ZMO as high resistive transparent layer.¹³ [ENREF_5](#) In all the studies, ZMO was used as high resistive transparent layer rather than a buffer layer to improve their device performance. In 2017, Delahoy et. al reported the fabrication of ZMO/CdTe solar cells, but the devices showed unsatisfactory efficiencies (~10.5%) accompanied with low fill factors (FF) due to the existence of S-kink in the current density-voltage (J - V) curves.¹¹ In 2018, Bittau et. al reported ZMO/CdTe solar cells, but their best-performing cell showed an efficiency of 13.5% with a low FF around 65%.¹²

[ENREF_11](#) S-kink in J - V curves has been observed in other solar cells including organic,¹⁴ copper indium gallium selenide (CIGS, without blue photons),¹⁵ and crystalline silicon¹⁶ [ENREF_13](#) cells. The S-kink is often attributed to the poor charge extract at the absorber/buffer interfaces.¹⁵⁻¹⁷ For ZMO/CdTe solar cells, it is generally attributed to the high CBO spike at ZMO/CdTe interface.^{11, 18} [ENREF_10](#) [ENREF_17](#) Device modeling has shown that high CBO spike, large interface recombination velocity, and low doping density in absorber and buffer layers can induce a significant barrier at the ZMO/CdTe interface that blocks electrons transferring from CdTe into fluorine doped tin oxide (FTO) electrode, causing S-kink in the J - V curves.⁶ However, keeping CBO spike small and fully realizing the benefits of the CBO spike are challenging. If the spike is too small, its impact on the reduction of interface recombination and consequently the improvement in V_{OC} can be negligible. If the CBO spike is too large, it may cause an S-kink, leading to poor FF and low J_{SC} , and, therefore, low performance. For these reasons, most reported ZMO/CdTe devices showed lower efficiencies than CdS/CdTe devices and most CdTe works published in recent years were still focused on CdS/CdTe devices.¹⁹⁻²¹

Here, we show that the S-kink in ZMO/CdTe devices can be successfully eliminated, and improved V_{OC} and J_{SC} can be simultaneously achieved if the CdCl_2 treatment process is conducted in oxygen-free atmosphere. The best-performing cell using CdCl_2 treatment in dry air showed a V_{OC} of 0.882 V, a J_{SC} of 23.2 mA/cm^2 , and a FF of 44.8%, yielding an efficiency of 9.2%. However, the best-performing cell using CdCl_2 treatment in helium (He) showed a V_{OC} of 0.866 V, J_{SC} of 25.5 mA/cm^2 and a FF of 72.9%, yielding an efficiency of 16.1%. Our device characterization and simulation reveal that S-kink seen in J - V curves is attributed to the large CBO spike at ZMO/CdTe interface and the low electrical conductivity of ZMO buffer layer. Since a larger CBO spike is preferred for better interface passivation, achieving a sufficiently high electron density of the ZMO buffer layer is preferred to eliminate the S-kink. Our work shows that utilizing an oxygen-free CdCl_2 annealing is critical to achieve high ZMO electron density and eliminate the S-kink behavior.

RESULTS AND DISCUSSIONS

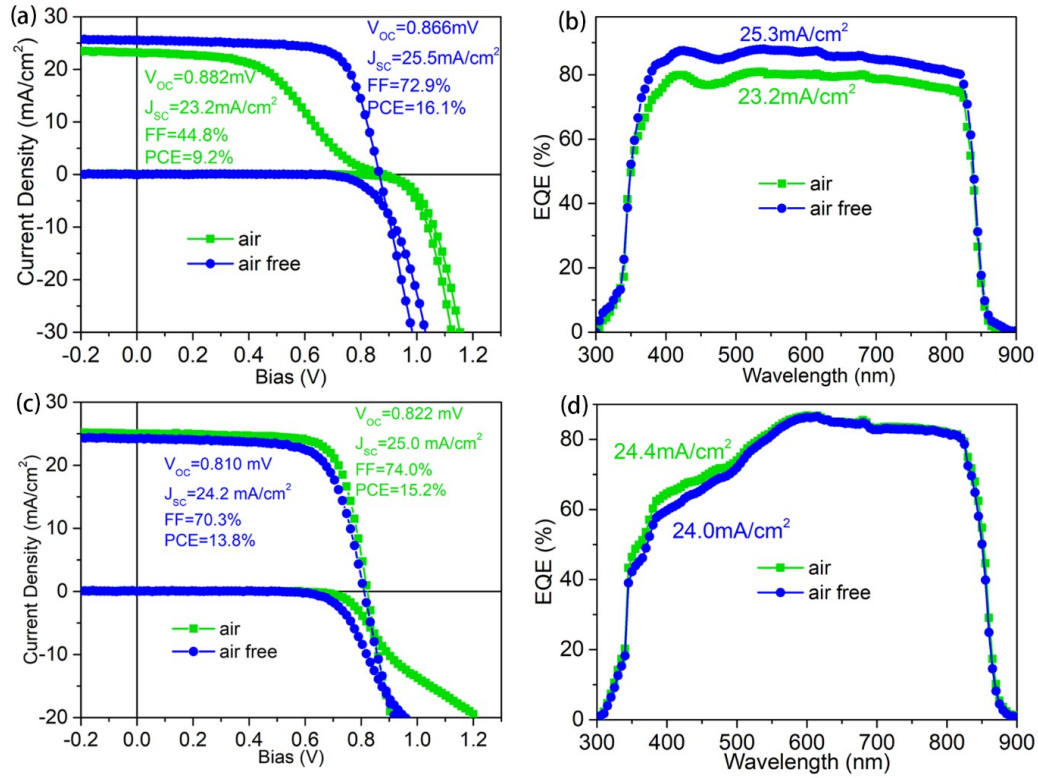


Figure 1. (a) J - V and (b) EQE curves of ZMO/CdTe-air and ZMO/CdTe-air free devices. (c) J - V and (d) EQE curves of CdS/CdTe-air and CdS/CdTe-air free devices.

The statistics of device performance parameters of 20 ZMO/CdTe solar cells with CdCl₂ treatment in dry air (named ZMO/CdTe-air hereafter) and He (named ZMO/CdTe-air free hereafter) are shown in Figure S1. The ZMO/CdTe-air free cells outperform the ZMO/CdTe-air cells. The J - V curves of the best-performing ZMO/CdTe-air and ZMO/CdTe-air free cells are shown in Figure 1a. For the ZMO/CdTe-air cell, the J - V curve shows clear S-kink (or S-shape) with an V_{OC} of 0.882 V, a J_{SC} of 23.2 mA/cm², and a FF of 44.8%, yielding an efficiency of 9.2%. In contrast, the ZMO/CdTe-air free cell shows no obvious S-kink, with an V_{OC} of 0.866 mV, a J_{SC} of 25.3 mA/cm² and a FF of 72.9%, yielding an efficiency of 16.1%, which is among

the highest efficiency CdTe solar cells without Se incorporation reported in literature.⁷⁻⁸ The CdCl₂ treatment in air-free atmosphere significantly improves the J_{SC} and FF , but with a slightly lower V_{OC} . The improvement of J_{SC} is confirmed by external quantum efficiency (EQE) measured without external bias as shown in Figure 1b. The ZMO/CdTe-air free device shows high quantum efficiencies around 85% for most wavelengths with a flat plateau in the wavelength range from 370 to 830 nm, indicating high electronic quality of the absorber layer and the interfaces. On the other hand, the EQE curve of ZMO/CdTe-air cell shows much lower values over the whole absorption wavelength range, which is attributed to higher recombination rate at front or back junction and inefficient carrier extraction. The integrated current density over the AM1.5 solar spectrum is 23.2 mA/cm² for the ZMO/CdTe-air cell and 25.3 mA/cm² for the ZMO/CdTe-air free cell. It is worth noting that from ZMO/CdTe-air cell to ZMO/CdTe-air free cell, the FF is increased from 44.8% to 72.9% due to the elimination of the S-kink.

CdCl₂ treatment in dry air has been widely used in CdS/CdTe solar cell fabrications.²²⁻²³ Besides the benefit of grain boundary passivation by chloride²⁴, oxygen in the dry air also plays an important role in improving p-type doping through the formation of shallow acceptor-like defects in CdTe as well as the improvement of CdTe crystalline quality and grain size.²⁵⁻²⁸ [ENREF 25](#)

We have also fabricated CdS/CdTe solar cells with CdCl₂ treatment in dry air and He. As shown in Figure 1c and Figure S2, the CdS/CdTe-air cells show higher performance in all parameters than the CdS/CdTe-air free cells. The best-performing CdS/CdTe-air cell shows an efficiency of 15.2%, with an V_{OC} of 0.822 mV, a J_{SC} of 25.0 mA/cm² and a FF of 74.0%. In contrast, the best-performing CdS/CdTe-air free cell shows an efficiency of 13.8% with an V_{OC} of 0.810 mV, a J_{SC} of 24.2 mA/cm², and a FF of 70.3%. The trend is opposite to the ZMO/CdTe cells discussed above. The above results draw our attention to the roles of oxygen in these solar cells. Oxygen

might have different effects on CdS and ZMO buffer layers. The EQE results of CdS/CdTe cells shown in Figure 1d provide some insights. The EQE curves for these cells show visible differences in the wavelength range from 350 to ~525 nm. The EQE improvement in this range for CdS/CdTe-air cell indicates that the CdS buffer layer is partially oxidized during the CdCl₂ treatment in air, demonstrating that oxygen can diffuse through 3 μm CdTe films to the front junction. The accumulation of oxygen at the CdS/CdTe interface due to the annealing ambient has also been proven by other researchers through transmission electron microscopy method.²⁹ The oxidization of CdS would increase the band gap and permit more light absorption in CdTe. Therefore, it is reasonable to expect that in our ZMO/CdTe devices with 2.8 μm CdTe films, oxygen can also pass through CdTe films and reach the ZMO/CdTe interface, which may reduce the density of oxygen vacancies and consequently lower the electron density in ZMO buffer layer. This reduction of electron density is responsible for the S-kink in the J - V curves as discussed below.

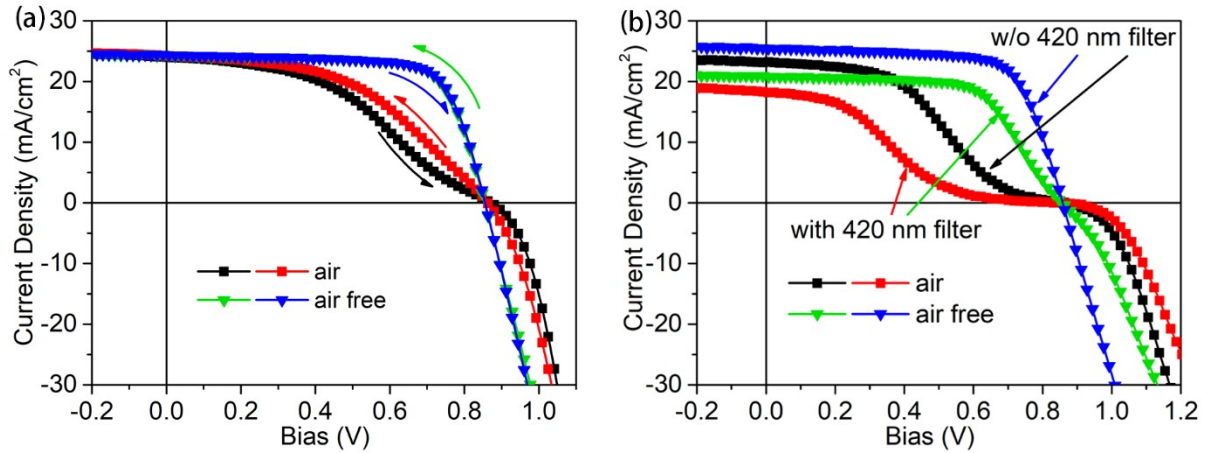


Figure 2. J - V curves of ZMO/CdTe-air and ZMO/CdTe-air free devices measured (a) in different scan directions and (b) with or without UV filter (420 nm).

We find that ZMO/CdTe-air shows J - V hysteresis, i.e., the J - V curve measured by scanning the bias from positive to negative bias (reverse scan) is different from the J - V curve measured by scanning bias from negative to positive bias (forward scan), as shown in Figure 2a and Table S1. The forward scan shows a lower FF (41.1% vs 47.0%), a higher V_{OC} (872 mV vs 863 mV), and similar J_{SC} , and, therefore a much lower performance (8.61% vs 9.83%) than reverse scan. The J - V hysteretic effect has been widely investigated in hybrid perovskite solar cells³⁰⁻³², CIGS (with In(OH,S) as buffer layer)³³, multijunction solar cells (high flux)³⁴ and some CdS/CdTe solar cells³⁵⁻³⁶. There are some primary mechanisms to explain the origin of hysteresis: transient capacitive current, ion migration, ferroelectric polarization, dynamic charge carrier trapping and detrapping.³⁰⁻³³ [ENREF 29](#) In our ZMO/CdTe devices, hysteresis only happens when S-kink shows up. The large CBO spike and poor conductivity of ZMO could be the causes of the J - V hysteresis. The ZMO/CdTe-air free device shows no J - V hysteresis, indicating the absence of barrier to the carrier transfer. It is noted that the ZMO films for both devices were deposited in an identical condition. In addition, the composition of the ZMO film is not expected to change during the device fabrication, because both magnesium and zinc have low saturated vapor pressure. Furthermore, the bandgap of ZMO (~3.66 eV) should not be affected by the oxygen vacancy concentration as shown in Figure S3. Thus, the same band gap for ZMO (Figure S4) and CBO for interfaces should be expected in both devices. It has been reported that ZnO film has a bandgap of about 3.3 eV³⁷⁻³⁸ and it has a zero CBO with CdTe¹⁸. We estimate that the CBO between our ZMO film and CdTe is about 0.4 eV.³⁹⁻⁴⁰ The different device behavior is likely due to the different conductivity of the ZMO buffer layers. Figure 2b and Table S2 show the J - V curves of ZMO/CdTe-air and ZMO/CdTe-air free cells measured under AM1.5 illumination with and without a UV filter (420 nm). When the UV filter is applied, ZMO/CdTe-air cell shows a

lower FF (25% vs 38.5%) due to the severe S-kink. This change mainly results from the dramatical increase in series resistance from $108 \Omega \text{ cm}^2$ to $364 \Omega \text{ cm}^2$. The ZMO/CdTe-air free cell shows apparent S-kink in the J - V curve when a UV filter is applied. The FF is decreased from 70% to 64%, due to the increase of series resistance from about 5 to $11 \Omega \text{ cm}^2$. These results are likely attributed to the photoconductivity of ZMO. The conductivity of ZMO can be increased by many orders of magnitudes under illumination, which has been widely used in photodetectors.⁴¹⁻⁴² We deposited a $\sim 100 \text{ nm}$ thick ZMO film on FTO-coated glass. Our photoconductivity measurement confirmed the significant improvement (~ 3 orders of magnitudes) of the ZMO conductivity under UV illumination as shown in Figure S5.

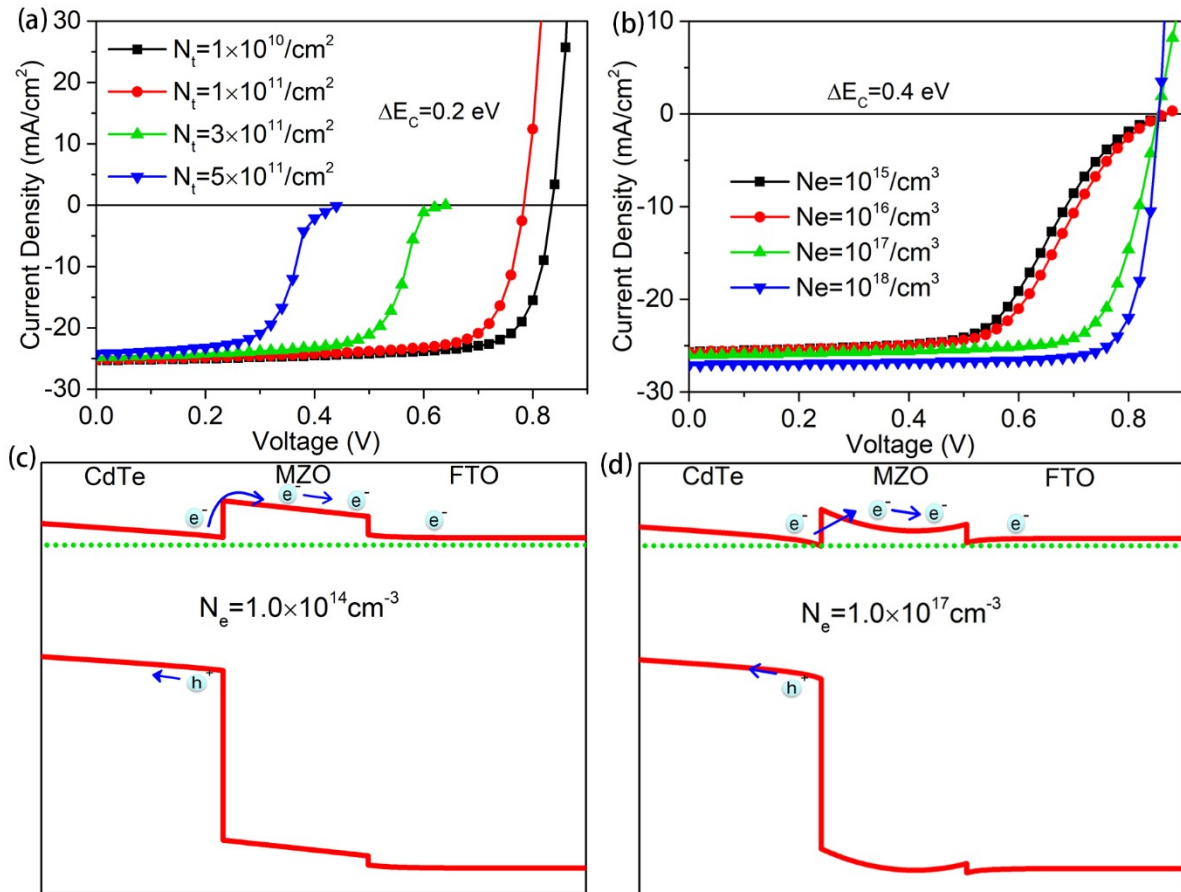


Figure 3. SCAPS simulation of J - V curves for ZMO/CdTe cells with different (a) acceptor-like trap densities (N_t) while the CBO is 0.2 eV and (b) ZMO doping densities while the CBO is 0.4

eV. (c) and (d) are simulated band diagrams of ZMO/CdTe cells with different electron density in ZMO.

Since there is no suitable method to directly measure the electron density of the ZMO buffer layer in the devices, we conducted device simulation using SCAPS⁴³ to examine the effects of electron density in ZMO on J - V curve, along with other selected device properties, such as back-barrier height, CBO value, and the density of interface trap states on J - V behavior of ZMO/CdTe devices. Parameters used for the SCAPS simulation are adopted from the literature^{5, 44-46} and are tabulated in Table S3. The results show that back-barrier height does not result in S-kink in J - V curves, as shown in Figure S6a, even when a very high back-barrier height, 0.7 eV, is considered. The high back-barrier height only causes severe rollover and reduction in V_{OC} , which are consistent with the results seen in CdS/CdTe devices with an inappropriate back barrier height, due to the back contact work function misalignment (e.g., direct CdTe/Au contact)⁴³ or impurities on the back surface (e.g., oxides and chlorides formed during the CdCl₂ treatment in dry air).⁴⁷ [ENREF_33](#) Our SCAPS simulation (Figure S6b) shows no S-kink in the J - V curve if the CBO spike is 0.2 eV, but the S-kink is clearly present in the J - V curve if the CBO spike is 0.4 eV. Besides CBO spike, the density of acceptor-like trap states at the ZMO/CdTe interface also significantly affects the J - V curve. As shown in Figure 3a, when the CBO is small (0.2 eV), the high density of acceptor-like defects at the ZMO/CdTe interface can cause severe S-kink accompanying with a rapid decrease of V_{OC} . In contrast, devices with a high CBO (e.g., 0.4 eV), as shown in Figure S6c, tolerate a much higher trap density without sacrificing V_{OC} . However, the devices always suffer from S-kink and low FF even when the interface trap density is low (Figure S6b), which is consistent with results reported in the literature.⁶ For our ZMO/CdTe-air devices, both S-kink and higher V_{OC} are observed, as shown in Figure 1a, indicating that

interface recombination caused by deep trap states is not responsible to the S-kink in our ZMO/CdTe-air devices.

J - V curve simulations with different ZMO carrier concentrations (N_e) were performed for two CBO spike values of 0.2 and 0.4 eV (Figure 3b and Figure S6d). When the CBO spike is 0.2 eV, no S-kink is observed in a large range of electron density of ZMO (Figure S6d). However, when the CBO spike is 0.4 eV, the S-kink in the J - V is eliminated when increasing the electron density in ZMO to 10^{17} cm^{-3} or higher. These results reveal that the S-kink seen in our ZMO/CdTe solar cells is caused by the large CBO spike (larger than 0.2 eV) and the insufficient electron density (electrical conductivity) in the ZMO buffer layer. It is noted that a higher CB spike leads to a better interface defect tolerance and, therefore, a higher V_{OC} . To maintain the high V_{OC} and avoid S-kink, a sufficiently high electron density in the ZMO buffer layer is necessary. The formation and elimination of S-kink in the J - V curves for CBO spike of 0.4 eV can be understood from the band diagrams shown in Figures 3c and d. When the electron density of ZMO is low, e.g., $10^{14}/\text{cm}^3$, the 0.4 eV spike can effectively block photogenerated electrons from transferring from the CdTe absorber into FTO electrode (Figure. 3c). This inevitably leads to poor carrier extraction, which results in S-kink in the J - V curve. If the electron density is high, e.g., $10^{17}/\text{cm}^3$, the depletion width in ZMO is significantly reduced. Therefore, photogenerated electrons have much higher probability of tunneling through the barrier and being transferred into the FTO electrode. As a result, there is no severe barrier for extracting photogenerated electrons and, therefore, no S-kink in the J - V curve. These results confirm that ZMO/CdTe cells should be processed in oxygen-free atmosphere to avoid detrimental oxygen diffusion into ZMO layer during the fabrication processes.

SCAPS simulation has shown that a higher electron density in ZMO layer should lead to a reduced carrier recombination rate at ZMO/CdTe interface.⁵ Therefore, we performed PL measurements to reveal the recombination properties in ZMO/CdTe-air and ZMO/CdTe-air free samples (no copper and Au layers were deposited). For both samples, PL spectra with emission peak centered at 1.54 eV are observed when these are excited through glass and CdTe sides as shown in Figure 4a.⁴⁸ For both samples, stronger PL signals are observed when the excitation is excited from the glass side than from the CdTe side, suggesting a noticeable interface passivation by ZMO buffer layer. The PL intensity excited from the glass side is higher for the ZMO/CdTe-air free sample than for the ZMO/CdTe-air sample, suggesting a higher charge recombination rate at the ZMO/CdTe interface in the ZMO/CdTe-air sample than in the ZMO/CdTe-air free sample. This result can be explained using the band diagram analysis (Figures 3c and d). The ZMO film in ZMO/CdTe-air free sample should have a higher electron density than the ZMO/CdTe-air sample, which results in a stronger band bending in the CdTe, depleting holes at the ZMO/CdTe interface and effectively reducing the interface recombination.⁵ The more the interface recombination is suppressed, the stronger the radiative recombination in the bulk and the more intense PL signal. TRPL decay curves (Figure 4b) confirm these conclusions. The mean carrier lifetime measured from the CdTe side is short (< 1 ns) for both samples due to surface-induced high carrier recombination. The mean carrier lifetime measured from the glass side is longer, suggesting passivation effects by the ZMO layer. The lifetime (~ 3.0 ns) of the ZMO/CdTe-air free sample is longer than the lifetime (~ 2.3 ns) of the ZMO/CdTe-air sample, suggesting less charge recombination in the ZMO/CdTe-air free sample. Therefore, combining J-V, PL, and TRPL measurements and SCAPS device simulation, we conclude that the removal of oxygen during the CdCl_2 treatment can lead to higher electron concentration in the ZMO

layer, which results in more favorable junction barrier and reduced charge recombination at the ZMO/CdTe interface.

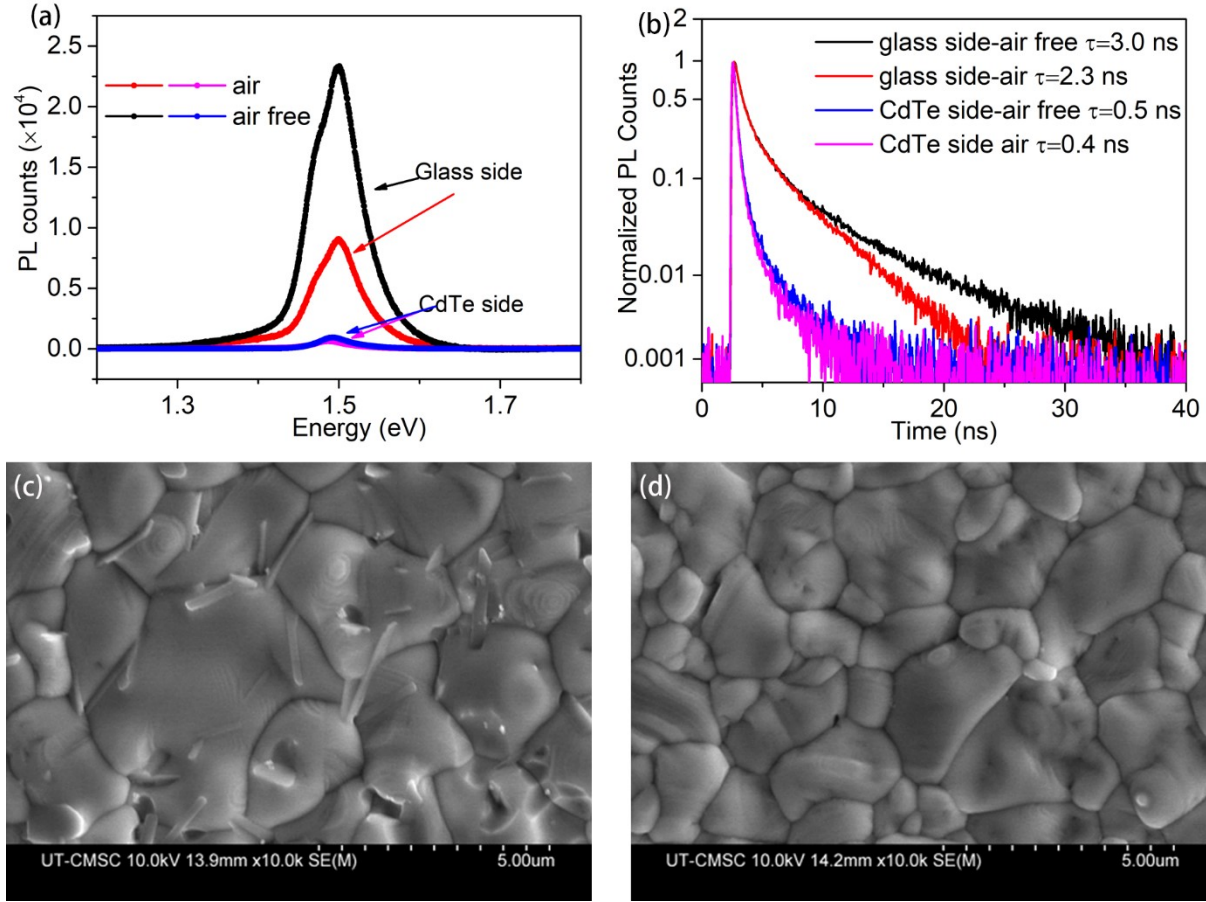


Figure 4. (a) PL spectra and (b) PL decays of CdTe films with CdCl_2 treatment in dry air and He with excitation from both glass and CdTe sides. Top view SEM images of CdTe film with CdCl_2 treatment in (c) dry air and (d) He atmosphere.

The oxygen-free fabrication process has another benefit for CdTe solar cells. We find that the surface morphology of CdTe films treated in dry air and He is different. As shown in Figure 4c and d, the CdTe film treated in dry air shows a larger average grain size than the film treated in He, indicating the beneficial effect of oxygen on the recrystallization of CdTe grain during the CdCl_2 treatment, which is consistent with results reported by others.^{25-28, 49} However, the CdTe

film treated in dry air contains many small particles on the surface, while the film treated in He shows a cleaner surface. EDS analysis indicates that these small particles are oxides and chlorides, as shown in Figure S7 and Table S3. The formation of such oxides and chlorides is inevitable when the CdCl_2 treatment is performed in dry air, and these impurity particles are difficult to remove completely without chemical etching.⁵⁰⁻⁵¹ These oxides and chlorides can cause a poor contact between CdTe and the metal electrode, leading to high recombination at the back surface of CdTe. Our recent study has shown that a clean surface is beneficial for reducing the back-barrier height and, therefore, for improving FF and efficiency of CdS/CdTe solar cells.⁴⁷ We performed current density-voltage-temperature (J - V - T) (Figure S8) measurements under an AM1.5 illumination. Figure S9 shows Arrhenius plots of J - V - T curves and the extracted back-contact barrier heights for ZMO/CdTe-air and ZMO/CdTe-air free cells. For ZMO/CdTe-air cell, the back-barrier height is 0.604 ± 0.020 eV, while for ZMO/CdTe-air free cells, it is 0.339 ± 0.013 eV. The ZMO/CdTe-air free cell shows a much lower back barrier height than the ZMO/CdTe-air cell, likely due to clean and impurity-free back surface for air-free CdCl_2 treatment.⁴⁷ [ENREF 36](#)

Till now, we have demonstrated the S-kink can be eliminated by performing the CdCl_2 -treatment in an air-free environment and proposed mechanisms to explain the origin and elimination of S-kink. Although our best-performing ZMO/CdTe solar cells have achieved efficiency of over 16%, the performance is still unsatisfactory compared with the state-of-art ZMO/CdTe cells with efficiencies of 18.3%.⁷ Our J - V - T results reveal that the large back-barrier height (0.339 ± 0.013 eV), which is still significantly higher compared to the state-of-art devices employing a thin tellurium layer as back contact to eliminate the back-barrier height, [ENREF 39](#)⁵² is the main factor limiting the performance of our ZMO/CdTe solar cells.

CONCLUSION

In conclusion, we have fabricated and characterized ZMO/CdTe thin film solar cells with CdCl₂ treatment in dry air and He atmospheres. We found that with identical ZMO buffer layers, the ZMO/CdTe-air free cells showed no obvious S-kink in the J - V curves, but ZMO/CdTe-air cells showed severe S-kinks. Detailed characterization and device simulation suggested that the appearance of S-kinks in J - V curves is attributed to the large conduction band spike between ZMO and CdTe and the low electrical conductivity of the ZMO buffer layer. For ZMO/CdTe cells fabricated with CdCl₂ treatment in dry air, oxygen is expected to diffuse through CdTe, reach the ZMO, and reduce the electron density of ZMO by filling oxygen vacancies. With the elimination of S-kink, our best performing ZMO/CdTe cell has achieved an efficiency of 16.1% with an V_{OC} of 0.866 V. Our results provide important insights for improving the performance of ZMO/CdTe solar cells.

EXPERIMENTAL METHODS

Device Fabrication. For ZMO/CdTe devices, FTO-coated glass (TEC 12; Pilkington NA) was used as the substrates. The substrates were first cleaned sequentially with Micro-90 detergent in an ultrasonic bath in hot water (~ 70 °C) for an hour and then in de-ionized water for 30 min for 4 times, then rinsed with de-ionized water and dried with nitrogen. 80 nm ZMO layer was deposited on FTO at ambient temperature by radio-frequency (RF) sputtering using a ZMO target with 8 wt% magnesium oxide (MgO) under mixed flow gas of 3% oxygen and 97% argon. Then a ~ 2.8 μ m CdTe film was deposited by close space sublimation (CSS) with a source

temperature of 560 °C and a substrate temperature of 495 °C at 1 Torr. For CdS/CdTe devices, the CdS layer was deposited on FTO coated glass (TEC 15M; Pilkington NA) using a procedure reported in the literature¹. Then a ~3 μm CdTe film was deposited by CSS with a source temperature of 660 °C and a substrate temperature of 595 °C at 10 Torr. CdCl₂ treatment was performed with a saturated CdCl₂ in methanol solution on CdTe surfaces dropwise and heated at 390 °C (CdS/CdTe) or 420 °C (ZMO/CdTe) for 20 min with a 500 sccm He or dry air flow at 400 Torr. After the samples cooled to room temperature, excess CdCl₂ was removed by rinsing with methanol. After that, copper chloride (CuCl) solution was dropped on the CdTe surface and annealed in nitrogen at 175 °C to promote Cu doping in CdTe. Then Au (40 nm) electrodes were deposited by thermal evaporation via a shadow mask with an individual cell area of 0.08 cm². [ENREF 17](#)

Measurement and Characterization. The morphology of the CdTe films was characterized by high resolution field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) equipped with X-ray energy dispersive spectroscopy (EDS). Solar cell performance was characterized by measuring J - V curves under AM1.5G illumination using a solar simulator (PV Measurements Inc.) and a source meter (Keithley 2400) with a scanning speed of 1.17 V/s. External quantum efficiency (EQE) spectra were performed on a QE system (PV Measurements Inc.). The photoconductivity measurement of the ZMO film was performed by depositing a 100 nm thick ZMO film on FTO-coated glass. Before ZMO deposition, we used a laser to scribe a channel with a width of about 150 μm. I-V measurement was carried out with a voltage swept from -10 to 10 V in dark and under UV illumination. Temperature dependent light current voltage (J - V - T) was performed using a Solartron Modulab potentiostat with light supplied by a halogen lamp with voltage swept from -0.4 to 1.5 V. A liquid nitrogen cooling cryo-system

(Janis VPF-100 system) was used to carry out all the temperature dependent (140 to 310K with a step size of 10 K) measurements. The temperature was controlled by a temperature controller (Lakeshore 330). A sensor was mounted on the top of the device directly to ensure that the recorded temperature is the device temperature. Photoluminescence (PL) characteristics of FTO/ZMO/CdTe samples after CdCl_2 treatment were investigated utilizing steady-state and time-resolved PL (TRPL). PL measurements were performed separately through glass and CdTe sides. A 633 nm laser wavelength at 2.86 Wcm^{-2} and $1.38 \times 10^{10} \text{ photon pulse}^{-1}\text{cm}^{-2}$ were used for steady-state and TRPL respectively. Steady-state PL signal was detected by a symphony-II CCD detector (from Horriba) while TRPL signal was collected via a hybrid APD/PMT module (Hamamatsu R10467U-50).

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

- Performance statistics of 20 ZMO/CdTe-air and ZMO/CdTe-air free devices
- Performance statistics of 20 CdS/CdTe-air and CdS/CdTe-air free devices
- Performance parameters in different scan directions of ZMO/CdTe-air and ZMO/CdTe-air free devices
- Transmittance spectra of ZMO film deposited in different oxygen concentration atmosphere on TEC12 glass

- Performance parameters measured with or without UV filter (420 nm) of devices ZMO/CdTe-air and ZMO/CdTe-air free devices
- Parameters used for SCAPS 1D Simulation
- SCAPS simulation of J - V curves for CdTe cells with different back barrier heights, CBO, acceptor-like trap densities (N_t) at ZMO/CdTe interface with CBO 0.4 eV and ZMO doping densities with CBO 0.2 eV
- SEM image and energy dispersive spectroscopy (EDS) spectra of CdTe film with CdCl₂ treatment in dry air taken from an oxide and/or chloride particle and a CdTe grain
- EDS results of CdTe film with CdCl₂ treatment in dry air taken from an oxide and/or chloride particle and a CdTe grain
- Temperature dependent J - V curves of ZMO/CdTe-air and ZMO/CdTe-air free devices, with their and corresponding $(J+J_{SC})$ - V curves in semi-exponential axis
- Arrhenius plots of light J - V - T curves with the extracted back-contact barrier heights

AUTHOR INFORMATION

Corresponding Author

*E-mail: yanfa.yan@utoledo.edu

ORCIDList

Dengbing Li:0000-0003-4555-4894

Zhaoning Song: 0000-0002-6677-0994

Rasha A. Awni:0000-0002-5971-0934

Sandip S. Bista:0000-0003-0162-8468

Niraj Shrestha: 0000-0001-5702-2938

Corey R. Grice:0000-0002-0841-5943

Lei Chen:0000-0003-2206-9140

Geethika K. Liyanage: 0000-0003-4000-0729

Mohammed A. Razooqi:0000-0001-5567-5927

Adam B. Phillips: 0000-0002-2675-5052

Michael J. Heben:0000-0002-3788-3471

Randy J. Ellingson: 0000-0001-9520-6586

Yanfa Yan: 0000-0003-3977-5789

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work is supported by Air Force Research Laboratory, Space Vehicles Directorate (contract # FA9453-11-C-0253) and National Science Foundation under contract no. 1711534 and the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under Solar Energy Technologies Office (SETO) Agreement Number DE-EE0007541. We thank Dr. David Strickler from Pilkington North America Inc. for supplying us FTO coated substrates.

REFERENCES

- (1) NREL Research Cell Record Efficiency Chart. <https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.201812171.pdf> (Accessed: January 2019).
- (2) Paudel, N. R.; Yan, Y., Enhancing the Photo-Currents of CdTe Thin-Film Solar Cells in Both Short and Long Wavelength Regions. *Appl. Phys. Lett.* **2014**,*105*, 183510.
- (3) Munshi, A. H.; Kephart, J.; Abbas, A.; Raguse, J.; Beaudry, J.; Barth, K.; Sites, J.; Walls, J.; Sampath, W., Polycrystalline CdSeTe/CdTe Absorber Cells with 28 mA/cm² Short-Circuit Current. *IEEE J. Photovolt.* **2018**,*8*, 310-314.
- (4) Gloeckler, M.; Sankin, I.; Zhao, Z., CdTe Solar Cells at the Threshold to 20% Efficiency. *IEEE J. Photovolt.* **2013**,*3*, 1389-1393.
- (5) Song, T.; Kanevce, A.; Sites, J. R., Emitter/Absorber Interface of CdTe Solar Cells. *J. Appl. Phys.* **2016**,*119*, 233104.
- (6) Ablekim, T.; Colegrove, E.; Metzger, W. K., Interface Engineering for 25% CdTe Solar Cells. *ACS Appl. Energ. Mater.* **2018**,*1*, 5135-5139.
- (7) Sites, J.; Munshi, A.; Kephart, J.; Swanson, D.; Sampath, W. S., Progress and Challenges with CdTe Cell Efficiency, In *IEEE 43th Photovolt. Spec. Conf.* **2016**; p 3632-3635.
- (8) Munshi, A. H.; Kephart, J. M.; Abbas, A.; Shimpi, T. M.; Barth, K.; Walls, J. M.; Sampath, W. S., Effect of Varying Deposition and Substrate Temperature on Sublimated CdTe Thin-Film Photovoltaics, In *IEEE 43th Photovolt. Spec. Conf.* **2016**; p 0465-0469.

- (9) Bittau, F.; Artegiani, E.; Abbas, A.; Menossi, D.; Romeo, A.; Bowers, J. W.; Walls, J. M., Magnesium-Doped Zinc Oxide as a High Resistance Transparent Layer for Thin Film CdS/CdTe Solar Cells, In *IEEE 44th Photovolt. Spec. Conf.* **2017**; p 752-756.
- (10) Wang, T.; Ren, S.; Li, C.; Li, W.; Liu, C.; Zhang, J.; Wu, L.; Li, B.; Zeng, G., Exploring Window Buffer Layer Technology to Enhance CdTe Solar Cell Performance. *Sol. Energy* **2018**, *164*, 180-186.
- (11) Delahoy, A. E.; Peng, S.; Patra, P.; Manda, S.; Saraf, A.; Chen, Y.; Tan, X.; Chin, K. K., Cadmium Tin Oxide and Zinc Magnesium Oxide Prepared by Hollow Cathode Sputtering for CdTe Photovoltaics. *MRS Adv.* **2017**, *2*, 3203-3214.
- (12) Bittau, F.; Potamialis, C.; Togay, M.; Abbas, A.; Isherwood, P. J. M.; Bowers, J. W.; Walls, J. M., Analysis and Optimisation of the Glass/TCO/ZMO Stack for Thin Film CdTe Solar Cells. *Sol. Energ. Mat. Sol. Cell* **2018**, *187*, 15-22.
- (13) Menossi, D.; Artegiani, E.; Bittau, F.; Barbato, M.; Meneghini, M.; Meneghesso, G.; Bowers, J. W.; Walls, J. M.; Piccinelli, F.; Romeo, A., High Efficiency CdTe Solar Cells by Low Temperature Deposition with MgZnO HRT Layer, In *33th Eur. Photvolt. Sol. Energ. Conf. & Exhibition* **2017**; p 1027 - 1030.
- (14) Krebs, F. C.; Norrman, K., Analysis of the Failure Mechanism for a Stable Organic Photovoltaic During 10000 H of Testing. *Prog. Photovolt: Res. Appl.* **2007**, *15*, 697-712.
- (15) Pudov, A. O.; Sites, J. R.; Contreras, M. A.; Nakada, T.; Schock, H. W., CIGS J-V Distortion in the Absence of Blue Photons. *Thin Solid Films* **2005**, *480-481*, 273-278.

- (16) Rath, J. K., Electrical Characterization of HIT Type Solar Cells. In *Physics and Technology of Amorphous-Crystalline Heterostructure Silicon Solar Cells*, van Sark, W. G. J. H. M.; Korte, L.; Roca, F., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, **2012**; pp 377-404.
- (17) Vogel, M.; Doka, S.; Breyer, C.; Lux-Steiner, M. C.; Fostiropoulos, K., On the Function of a Bathocuproine Buffer Layer in Organic Photovoltaic Cells. *Appl. Phys. Lett.* **2006**,*89*, 163501.
- (18) Kephart, J. M.; McCamy, J. W.; Ma, Z.; Ganjoo, A.; Alamgir, F. M.; Sampath, W. S., Band Alignment of Front Contact Layers for High-Efficiency CdTe Solar Cells. *Sol. Energ. Mat. Sol. Cell* **2016**,*157*, 266-275.
- (19) Romeo, A.; Artegiani, E.; Menossi, D., Low Substrate Temperature CdTe Solar Cells: A Review. *Sol. Energy* **2018**,*175*, 9-15.
- (20) Hossain, M. S.; Rahman, K. S.; Islam, M. A.; Akhtaruzzaman, M.; Misran, H.; Alghoul, M. A.; Amin, N., Growth Optimization of $Zn_xCd_{1-x}S$ Films on ITO and FTO Coated Glass for Alternative Buffer Application in CdTe Thin Film Solar Cells. *Opt. Mater.* **2018**,*86*, 270-277.
- (21) Bosio, A.; Rosa, G.; Romeo, N., Past, Present and Future of the Thin Film CdTe/CdS Solar Cells. *Sol. Energy* **2018**,*175*, 31-43.
- (22) Paudel, N. R.; Grice, C. R.; Xiao, C.; Yan, Y., High Temperature Cds Processed CdTe Solar Cells on Commercial $SnO_2:F/SnO_2$ Coated Soda-Lime Glass Substrates. *J. Mater. Sci-mater. El.* **2015**,*26*, 4708-4715.

- (23) Paudel, N. R.; Yan, Y., Fabrication and Characterization of High-Efficiency CdTe-Based Thin-Film Solar Cells on Commercial SnO₂:F-Coated Soda-Lime Glass Substrates. *Thin Solid Films* **2013**,*549*, 30-35.
- (24) Li, C.; Wu, Y.; Poplawsky, J.; Pennycook, T. J.; Paudel, N.; Yin, W.; Haigh, S. J.; Oxley, M. P.; Lupini, A. R.; Al-Jassim, M.; Pennycook, S. J.; Yan, Y., Grain-Boundary-Enhanced Carrier Collection in CdTe Solar Cells. *Phys. Rev. Lett.* **2014**,*112* (15), 156103.
- (25) Hsu, T. M.; Jih, R. J.; Lin, P. C.; Ueng, H. Y.; Hsu, Y. J.; Hwang, H. L., Oxygen Doping in Close - Spaced - Sublimed CdTe Thin Films for Photovoltaic Cells. *J. Appl. Phys.* **1986**,*59*, 3607-3609.
- (26) Du, M.-H.; Takenaka, H.; Singh, D. J., Native Defects and Oxygen and Hydrogen-Related Defect Complexes in CdTe: Density Functional Calculations. *J. Appl. Phys.* **2008**,*104*, 093521.
- (27) Hasaneen, M. F.; Mohamed, W. S., Effect of CdCl₂ Heat Treatment in (Ar + O₂) Atmosphere on Structural and Optical Properties of CdTe Thin Films. *Optik* **2018**,*160*, 307-321.
- (28) Regalado-Pérez, E.; Reyes-Banda, M. G.; Mathew, X., Influence of Oxygen Concentration in the CdCl₂ Treatment Process on the Photovoltaic Properties of CdTe/CdS Solar Cells. *Thin Solid Films* **2015**,*582*, 134-138.
- (29) Terheggen, M.; Heinrich, H.; Kostorz, G.; Romeo, A.; Baetzner, D.; Tiwari, A. N.; Bosio, A.; Romeo, N., Structural and Chemical Interface Characterization of CdTe Solar Cells by Transmission Electron Microscopy. *Thin Solid Films* **2003**,*431-432*, 262-266.

- (30) Wang, C.; Xiao, C.; Yu, Y.; Zhao, D.; Awni, R. A.; Grice, C. R.; Ghimire, K.; Constantinou, I.; Liao, W.; Cimaroli, A. J.; Liu, P.; Chen, J.; Podraza, N. J.; Jiang, C.-S.; Al-Jassim, M. M.; Zhao, X.; Yan, Y., Understanding and Eliminating Hysteresis for Highly Efficient Planar Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1700414.
- (31) Snaith, H. J.; Abate, A.; Ball, J. M.; Eperon, G. E.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.-W.; Wojciechowski, K.; Zhang, W., Anomalous Hysteresis in Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2014**, *5*, 1511-1515.
- (32) Zheng, X.; Chen, H.; Wei, Z.; Yang, Y.; Lin, H.; Yang, S., High-performance, Stable and Low-cost Mesoscopic Perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) Solar Cells Based on Poly(3-hexylthiophene)-Modified Carbon Nanotube Cathodes. *Front. Optoelectron.* **2016**, *9*, 71-80.
- (33) Huang, C. H.; Li, S. S.; Shafarman, W. N.; Chang, C. H.; Lambers, E. S.; Rieth, L.; Johnson, J. W.; Kim, S.; Stanbery, B. J.; Anderson, T. J.; Holloway, P. H., Study of Cd-Free Buffer Layers Using $\text{In}_x(\text{OH},\text{S})_y$ on CIGS Solar Cells. *Sol. Energ. Mat. Sol. Cell* **2001**, *69*, 131-137.
- (34) Gordon, J. M.; Katz, E. A.; Tassew, W.; Feuermann, D., Photovoltaic Hysteresis and Its Ramifications for Concentrator Solar Cell Design and Diagnostics. *Appl. Phys. Lett.* **2005**, *86*, 073508.
- (35) Albin, D. S.; Dhere, R. G.; Glynn, S. C.; A. del Cueto, J.; Metzger, W. K., Degradation and Capacitance: Voltage Hysteresis in CdTe Devices. *Proc. SPIE* **2009**, *7412*, 74120I.
- (36) Albin, D. S.; A. del Cueto, J., Effect of Hysteresis on Measurements of Thin-Film Cell Performances. *Proc. SPIE* **2010**, *7773*, 77730N-1.

- (37) Wang, L.; Li, D.-B.; Li, K.; Chen, C.; Deng, H.-X.; Gao, L.; Zhao, Y.; Jiang, F.; Li, L.; Huang, F.; He, Y.; Song, H.; Niu, G.; Tang, J., Stable 6%-Efficient Sb_2Se_3 Solar Cells with a ZnO Buffer Layer. *Nat. Energy***2017**, *2*, 17046.
- (38) Adamopoulos, G.; Bashir, A.; Gillin, W. P.; Georgakopoulos, S.; Shkunov, M.; Baklar, M. A.; Stingelin, N.; Bradley, D. D. C.; Anthopoulos, T. D., Structural and Electrical Characterization of ZnO Films Grown by Spray Pyrolysis and Their Application in Thin-Film Transistors. *Adv. Funct. Mater.***2011**, *21*, 525-531.
- (39) Minemoto, T.; Hashimoto, Y.; Satoh, T.; Negami, T.; Takakura, H.; Hamakawa, Y., Cu(In,Ga)Se₂ Solar Cells with Controlled Conduction Band Offset of Window/Cu(in,Ga)Se₂ Layers. *J. Appl. Phys.***2001**, *89*, 8327-8330.
- (40) Hu, L.; Li, D.-B.; Gao, L.; Tan, H.; Chen, C.; Li, K.; Li, M.; Han, J.-B.; Song, H.; Liu, H.; Tang, J., Graphene Doping Improved Device Performance of ZnMgO/PbS Colloidal Quantum Dot Photovoltaics. *Adv. Funct. Mater.***2016**, *26*, 1899-1907.
- (41) Kind, H.; Yan, H.; Messer, B.; Law, M.; Yang, P., Nanowire Ultraviolet Photodetectors and Optical Switches. *Adv. Mater.* **2002**,*14*, 158-160.
- (42) Li, Y.; Feng, S.; Yang, J.; Zhang, Y.; Xie, X.; Lü, C.; Lu, Y., Photoresponse of ZnO Single Crystal Films. *Front. Optoelectron.* **2008**, *1*, 309-312.
- (43) Burgelman, M.; Nollet, P.; Degraeve, S., Modelling Polycrystalline Semiconductor Solar Cells. *Thin Solid Films* **2000**,*361-362*, 527-532.
- (44) Phillips, A. B.; Khanal, R. R.; Song, Z.; Zartman, R. M.; DeWitt, J. L.; Stone, J. M.; Roland, P. J.; Plotnikov, V. V.; Carter, C. W.; Stayancho, J. M.; Ellingson, R. J.; Compaan, A.

D.; Heben, M. J., Wiring-up Carbon Single Wall Nanotubes to Polycrystalline Inorganic Semiconductor Thin Films: Low-Barrier, Copper-Free Back Contact to CdTe Solar Cells. *Nano Lett.* **2013**, *13*, 5224-5232.

(45) Liyanage, G. K.; Phillips, A. B.; Heben, M. J., Role of Band Alignment at the Transparent Front Contact/Emitter Interface in the Performance of Wide Bandgap Thin Film Solar Cells. *APL Materials* **2018**, *6* (10), 101104.

(46) Roland, P. J.; Bhandari, K. P.; Ellingson, R. J., Electronic Circuit Model for Evaluating S-Kink Distorted Current-Voltage Curves, In *IEEE 43th Photovolt. Spec. Conf.* **2016**; p 3091-3094.

(47) Awni, R. A.; Li, D.-B.; Grice, C. R.; Song, Z.; Razooqi, M. A.; Phillips, A. B.; Bista, S. S.; Roland, P. J.; Alfadhili, F. K.; Ellingson, R. J.; Heben, M. J.; Li, J. V.; Yan, Y., The Effects of Hydrogen Iodide Back Surface Treatment on CdTe Solar Cells. *Solar RRL* **2018**, *0*, 1800304.

(48) Roland, P. J.; Paudel, N. R.; Chuanxiao, X.; Yan, Y.; Ellingson, R. J., Photoluminescence Spectroscopy of Cadmium Telluride Deep Defects, In *IEEE 40th Photovolt. Spec. Conf.* **2014**; p 3266-3271.

(49) Hiie, J., CdTe: CdCl₂: O₂ Annealing, *Thin Solid Films* **2003**, *431-432*, 90-93.

(50) Wathage, S. C.; Phillips, A. B.; Liyanage, G. K.; Song, Z.; Gibbs, J. M.; Alfadhili, F. K.; Alkhayat, R. B.; Ahangharnejhad, R. H.; Almutawah, Z. S.; Bhandari, K. P.; Ellingson, R. J.; Heben, M. J., Selective Cd Removal from CdTe for High-Efficiency Te Back-Contact Formation. *IEEE J. Photovolt.* **2018**, *8*, 1125-1131.

(51) Niles, D. W.; Waters, D.; Rose, D., Chemical Reaction of CdCl_2 Wet-Deposited on CdTe Films Studied by X-ray Photoelectron Spectroscopy. *Appl. Surf. Sci.* **1998**, *136*, 221-229.

(52) Song, T.; Moore, A.; Sites, J. R., Te Layer to Reduce the CdTe Back-Contact Barrier. *IEEE J. Photovolt.* **2018**, *8*, 293-298.

Table of Contents

