Engineering Schottky Contacts in Open-Air Fabricated Heterojunction Solar Cells to Enable High Performance and Ohmic Charge Transport

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ABSTRACT: The efficiencies of open-air processed Cu$_2$O/Zn$_{1-x}$Mg$_x$O heterojunction solar cells are doubled by reducing the effect of the Schottky barrier between Zn$_{1-x}$Mg$_x$O and the indium tin oxide (ITO) top contact. By depositing Zn$_{1-x}$Mg$_x$O with a long band-tail, charge flows through the Zn$_{1-x}$Mg$_x$O/ITO Schottky barrier without rectification by hopping between the sub-bandgap states. High current densities are obtained by controlling the Zn$_{1-x}$Mg$_x$O thickness to ensure that the Schottky barrier is spatially removed from the $p$–$n$ junction, allowing the full built-in potential to form, in addition to taking advantage of the increased electrical conductivity of the Zn$_{1-x}$Mg$_x$O films with increasing thickness. This work therefore shows that the Zn$_{1-x}$Mg$_x$O window layer sub-bandgap state density and thickness are critical parameters that can be engineered to minimize the effect of Schottky barriers on device performance. More generally, these findings show how to improve the performance of other photovoltaic system reliant on transparent top contacts, e.g., CZTS and CIGS.

KEYWORDS: Schottky barrier, Cu$_2$O solar cells, electrochemical deposition, spatial atmospheric atomic layer deposition, zinc magnesium oxide

INTRODUCTION

Ideally, heterojunction solar cells should be designed with ohmic contacts at all charge extraction interfaces so that all power losses due to series resistance are minimized, and current densities and fill factors maximized. Avoiding Schottky barrier formation is a particularly important consideration in the selection of transparent conducting electrodes (TCE) for the top contacts of solar cells. TCEs admit light to the active layer and conduct charge away, ideally forming an ohmic contact with the semiconductor in order to do so most efficiently. However, other design requirements of TCEs include transparency to visible light, low bulk electrical resistivity and chemical stability. Materials properties and fabrication limitations typically restrict the ability to fulfill all design requirements simultaneously. TCEs are commonly oxides (transparent conducting oxides or TCOs), such as indium tin oxide (ITO) and aluminum-doped zinc oxide (AZO). Zinc oxide (ZnO) is a common $n$-type metal oxide employed to form a $p$–$n$ junction or act as an electron-selective transport layer in a wide variety of solar cells, including Cu$_2$O–ZnO quantum dot, dye-sensitized and hybrid solar cells. Although AZO forms an ohmic contact with ZnO (whereas ITO tends to form a Schottky barrier), AZO tends to be less stable than ITO due to the reactive Al dopant, and can be less conductive than ITO. As a result, despite the limitations of the presence of the Schottky barrier, ITO is often deposited on top of ZnO as the transparent top contact layer, such as in CIGS and CZTS solar cells. Understanding and finding a means of overcoming the limitations imposed by top contact Schottky barriers is an important challenge that can improve the performance and commercial applicability of the wide variety of solar cells employing these contacts, and is more feasible than finding a new TCO that simultaneously fulfills all design requirements.

In this work, we identify the critical parameters for overcoming the negative effects of Schottky barriers by examining the top contact Schottky interface between zinc magnesium oxide (Zn$_{1-x}$Mg$_x$O) and ITO in Cu$_2$O–Zn$_{1-x}$Mg$_x$O heterojunction solar cells. Cu$_2$O solar cells are appealing because they have the potential to reach 20%
Adjusting the amount of Mg incorporated into ZnO allows us to perform our studies on a system with high performance. Instead of ZnO was used in our devices so that we could examine how charge can be transported through a Schottky barrier without rectiﬁcation. Cu2O is a stable, nontoxic, earth-abundant material.15 Because it is challenging to dope Cu2O to make it n-type, much research has been focused on heterojunction architectures, namely Cu2O/ZnO.15 ZnO/ITO Schottky barriers are prevalent in these devices,9,15 making it an ideal system to study Schottky interfaces. Zn1−xMgO instead of ZnO was used in our devices so that we could perform our studies on a system with high performance. Adjusting the amount of Mg incorporated into ZnO allows us to tune the conduction band offset with the Cu2O absorber and therefore optimize the Voc to maximize the efﬁciency by reducing Voc losses due to interfacial recombination.8,14 The ZnO conduction band can also be raised by forming Zn1−xTiOx,17 but Zn1−xMgO is advantageous because the ZnO conduction band position can be tuned over a wide range.8 After ﬁrst optimizing the deposition of Zn1−xMgO onto Cu2O, we examine how charge can be transported through a Schottky barrier without rectiﬁcation (like an ohmic contact), before elucidating how the Schottky barrier controls photocurrent densities.

**EXPERIMENTAL SECTION**

**Device Synthesis.** The ITO/glass substrates (Colorado Concepts LLC) were roughened by scrubbing with 10 vol % HCl using a cotton bud. These substrates were then cleaned by ultrasonication for 15 min in deionized water, toluene and isopropyl alcohol sequentially. Film characterization. Films were sputtered with Ar pressure of 7.4 × 10−3 mbar. During sputtering, the power used was 20 W, Ar pressure ~2.55 Pa. 5 min of sputtering was employed to deposit ~60 nm ITO (measured using cross-sectional scanning electron microscopy, SEM). A shadow mask was employed so that the overlap between the top and bottom ITO contacts was ~6 mm².

Al-doped ZnO (AZO) was also deposited at room temperature by DC magnetron sputtering from a ceramic target (ZnO; 1 wt % Al). Films were sputtered with flowing argon (35 mL min⁻¹, operating pressure of 7.4 × 10⁻³ mbar). The maximum base pressure was 3 × 10⁻⁸ mbar.

**Device Characterization.** Solar simulations were performed using an Oriel 92250A solar simulator under AM 1.5G illumination, corrected for spectral mismatch. A Keithley 2623A source-measure unit was employed to sweep through the applied biases and measure the current from the cells. Each cell was masked to 4 mm² to prevent edge effects. At least ﬁve samples were employed for each averaged parameter.

**Film Characterization.** Cross-sectional scanning electron microscopy (SEM) was performed using a LEO VP-1530 instrument. Impedance spectroscopy was performed using an Agilent 4294 Precision Impedance Analyzer. An oscillating voltage with an amplitude of 0.02 V and a speciﬁed series of DC biases was applied from a frequency of 40 Hz to 10 MHz. The impedance magnitude and argument were measured with 201 data points per sweep and recorded using custom-made Labview software. The Nyquist plots were fitted

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**Figure 1.** Optimization of 60 nm thick SAALD Zn1−xMgO composition and deposition temperature. (a) Cross-sectional SEM image of a typical glass/ITO/Cu2O/SAALD Zn1−xMgO/sputtered ITO device structure employed in this work. The dashed white line is to indicate the 60 nm thick Zn1−xMgO layer. A close-up on the Zn1−xMgO (layer boundaries indicated by the pair of dashed white lines to guide the eye) is shown inset. (b) Efficiency (PCE) and open-circuit voltage (Voc) of SAALD Zn1−xMgO deposited at 150 °C vs Mg composition (x). (c) PCE vs SAALD Zn1−xMgO deposition temperature. (d) X-ray diffraction patterns of SAALD Zn1−xMgO deposited at 80 °C vs 150 °C.
numerically with the Voigt model to determine the equivalent circuit parameters.

The absorption spectra of the films were obtained using UV-visible spectrophotometry above the bandgap and photothermal deflection spectroscopy (PDS) below the bandgap. The Zn$_{1-x}$Mg$_x$O films were deposited onto a quartz substrate. UV-visible spectra were obtained using an Agilent/HP 8453 UV-visible spectrometer. Because interference patterns obscure the sub-bandgap absorption, PDS was employed to measure the film absorption coefficients that were not convoluted with interference patterns. PDS spectra were obtained by immersing the quartz-mounted sample in Fluorinert FC-72. The deflection of a fixed wavelength (670 nm) probe laser beam was measured using a position sensing detector and lock-in detector to measure the absorption at that particular wavelength.

Conductivity measurements on zinc magnesium oxide and Hall measurements on AZO were performed using the van der Pauw method on the metal oxide films deposited on Corning glass using an H-50 and Kepco Bipolar Power Supply Unit from MMR Technologies Inc. The magnetic fields applied during measurements were 0.1 and 0.2 T. The films were deposited on glass square substrates and had indium contacts applied at the four corners after cleaning in isopropyl alcohol and ethanol.

For the ITO films, Hall measurements were also performed using the van der Pauw method, but using a magnetic field of 1 T. The ITO films on borosilicate glass were electrically contacted using silver paste. A Keithley 6220 Precision Current Source was used to apply current to the van der Pauw method, but using a magnetic field of 1 T. The ITO films were deposited onto a quartz substrate. UV−visible spectroscopy (PDS) below the bandgap. The Zn$_{1-x}$Mg$_x$O devices were obtained using photothermal deflection spectroscopy (PDS). For comparison, the PDS absorption spectrum of Zn$_{1-x}$Mg$_x$O deposited at 80 °C was also shown along with the respective Urbach energies obtained by fitting the band-tail. (d) Band diagram illustrating the hopping mechanism for electron transport through the Schottky barrier via states in the conduction band-tail of Zn$_{1-x}$Mg$_x$O deposited at 80 °C to the conduction band of ITO.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Electron transport through the Zn$_{1-x}$Mg$_x$O/TCO contact. (a) Nyquist plot comparing Zn$_{0.8}$Mg$_{0.2}$O/(60 nm) ITO with Zn$_{0.8}$Mg$_{0.2}$O/(30 nm) AZO/(60 nm) ITO with Zn$_{0.8}$Mg$_{0.2}$O/(70 nm) AZO. Ca/Ag was used to form an ohmic contact with Zn$_{1-x}$Mg$_x$O in these measurements. (b) J−V plot of Zn$_{0.8}$Mg$_{0.2}$O/ITO. (c) Absorption spectra for Zn$_{0.8}$Mg$_{0.2}$O deposited at 80 °C obtained using photothermal deflection spectroscopy (PDS). (d) Energy band diagram illustrating the hopping mechanism for electron transport through the Schottky barrier via states in the conduction band-tail of Zn$_{1-x}$Mg$_x$O deposited at 80 °C to the conduction band of ITO.

In this study, the heterojunction was fabricated using two scalable open-air techniques in order to be highly relevant to the ultimate goal of implementing these solar cells on a commercial scale. Electrodeposition was employed for fabricating Cu$_2$O and spatial atmospheric atomic layer deposition (SAALD) for ZnO. The SAALD ZnO was conformally coated onto 2.5 μm thick Cu$_2$O electrodeposited on ITO (Figure 1a).

First, we optimized the deposition conditions to achieve high performance and record open-circuit voltages. Although this inverted architecture (as opposed to Cu$_2$O being deposited on ZnO) has the advantage of greater light absorption due to the highly textured Cu$_2$O layer, it is limited by the formation of thermodynamically unstable CuO on the surface of Cu$_2$O, which can degrade device performances. To minimize CuO formation, we (i) lowered the deposition temperature of SAALD Zn$_{1-x}$Mg$_x$O from the typical 150 °C to 80 °C (Figure 1c) and (ii) scanned the Cu$_2$O under flowing vapors of the organometallic precursors from the SAALD gas manifold for five cycles before flowing the oxidant (Figure S1, Supporting Information.). These improved the efficiencies from 0.8% to 1.5%. Also, X-ray diffraction measurements show that even when the SAALD Zn$_{1-x}$Mg$_x$O deposition temperature was reduced from 150 to 80 °C, the films remained polycrystalline (Figure 1d). We also incorporated Mg into ZnO because the band-alignment of ZnO with Cu$_2$O is not optimal, which produces a “cliff” in the conduction band offset between the two materials that encourages interfacial recombination and reduces open-circuit voltages ($V_{OC}$). By raising the ZnO conduction band through Mg incorporation, the $V_{OC}$ of Cu$_2$O−Zn$_{1-x}$Mg$_x$O devices was increased up to 0.66 V (Figure 1b), which, to our knowledge, is the highest for open-air fabricated heterojunctions based on electrodeposited Cu$_2$O.22−24 That the $V_{OC}$ increase was due to a reduction in recombination can be seen from the reduction in the reverse bias saturation current densities (Figure S2a, Supporting Information), which, to our knowledge, is the highest for open-air fabricated heterojunctions based on electrodeposited Cu$_2$O.22−24 That the $V_{OC}$ increase was due to a reduction in recombination can be seen from the reduction in the reverse bias saturation current densities (Figure S2a, Supporting Information) with increasing Mg contents. The highest efficiencies were obtained with 20 at. % Mg incorporation in the ZnO (Figure S2b, Supporting Information) because higher Mg contents leads to reduced current-densities, which offset the increase in the $V_{OC}$.8

Second, we examined how charge can be transported through a Schottky barrier without rectification like an ohmic contact. Using impedance spectroscopy, the Zn$_{1-x}$Mg$_x$O/ITO interface was found to form a Schottky barrier, as is evident from the large parallel resistance in its Nyquist plot in Figure 1a. It should follow that if electrons need to overcome a Schottky barrier in order to be injected from the Zn$_{0.8}$Mg$_{0.2}$O to the ITO, the current density−voltage ($J−V$) curve should display rectifying behavior. Unexpectedly, this rectification is absent, with a linear $J−V$ plot (Figure 2b) exhibited. A linear $J−V$ curve in the presence of a Schottky barrier may be due to (i) the Zn$_{0.8}$Mg$_{0.2}$O Fermi level being pinned by surface states, leading to no band-bending, or (ii) the potential difference between Zn$_{0.8}$Mg$_{0.2}$O and ITO being screened as a result of surface dipoles introduced by localized surface states or (iii) charge tunneling through the Schottky barrier, either directly or via trap states extending below the band-edge of the Zn$_{0.8}$Mg$_{0.2}$O. Fermi level pinning is unlikely because there is a large parallel resistance at the Zn$_{0.8}$Mg$_{0.2}$O/ITO junction observed from impedance spectroscopy. Likewise, it is unlikely that surface dipoles are reducing the effective Schottky barrier since the Schottky barrier height between Zn$_{0.8}$Mg$_{0.2}$O and ITO was measured to be 0.9 eV (Figure S3, Supporting Information) and this correlates well with the expected energy
level offset between Zn$_{0.8}$Mg$_{0.2}$O (conduction band minimum at $\sim-3.5$ eV) and ITO (workfunction of $\sim-4.4$ eV). The Schottky barrier width between Zn$_{0.8}$Mg$_{0.2}$O and ITO was calculated to range over 20–50 nm (or an average of 30 nm, and is calculated in Section S3 of the Supporting Information) and current cannot tunnel through a Schottky barrier of such height and width to a magnitude that is consistent with the photocurrent observed in these devices. Transport via a tunneling process may be possible if there exists a sufficient density of sub-bandgap states in the Schottky barrier depletion width that electrons can tunnel (hop) between. Accordingly, absorption measurements of Zn$_{0.8}$Mg$_{0.2}$O deposited at 80 °C show the presence of a high density of sub-bandgap states in the metal oxide film (Figure S2), which would be due to a high level of disorder, as can be seen from the high.

Figure 3. Variation in device performance with SAALD Zn$_{0.8}$Mg$_{0.2}$O thickness. (a) Short-circuit current density ($J_{SC}$), (b) open-circuit voltage ($V_{OC}$), (c) efficiency (PCE) and (d) fill-factor (FF) vs SAALD Zn$_{0.8}$Mg$_{0.2}$O thickness in devices with only ITO top contacts. Each data point is the average of at least five samples (highest measured values also shown). All devices were measured 1 day after fabrication.

Figure 4. (a) Variation in the conductivity of SAALD Zn$_{0.8}$Mg$_{0.2}$O films with thickness measured by four-point measurements. (b) Short-circuit current density ($J_{SC}$) vs SAALD Zn$_{0.8}$Mg$_{0.2}$O thickness for devices with a 30 nm Al-doped ZnO (AZO) layer between the Zn$_{0.8}$Mg$_{0.2}$O and ITO. Each data point is the average of 5–11 devices and measurements were performed on the same day as fabrication. (c) Built-in potential of the Cu$_2$O/ Zn$_{0.8}$Mg$_{0.2}$O p–n junction for devices with ITO-only top contacts) estimated from light and dark $J$–$V$ curves. (d) Light $J$–$V$ curves of glass/ITO/ (2.5 μm) Cu$_2$O/(90 nm) SAALD Zn$_{0.8}$Mg$_{0.2}$O/TCO devices measured under AM 1.5G illumination corrected for spectral mismatch. The TCOs compared are 60 nm ITO, 70 nm AZO, and 30 nm AZO with 60 nm ITO. Devices were measured immediately after fabrication.
The spacing between absorption centers in the Γ-points of the Brillouin zones, because ZnO is a direct bandgap semiconductor with the bandgap transition at the Fermi level, was estimated to be 0.3 nm based on the spacing between the I-β points of the Brillouin zones, where ZnO is a direct bandgap semiconductor with the bandgap transition at the Fermi level. Sub-bandgap states were present in the ZnO.31 We also note that Cu2O/Zn0.8Mg0.2O/ITO devices reported here through tunneling, the tunneling barrier must be approximately 5 nm (Figure S6, Supporting Information). However, it can be seen through a comparison of Figures 4a and 3a that this AZO layer forms an ohmic contact with Zn0.8Mg0.2O deposited at 80 °C (Figure 2c), and this correlates with a trap spacing of ~4 nm (Figure S6, Supporting Information). The spacing of sub-bandgap states extending up to 1 eV beneath the band-edge is therefore small enough for electrons to tunnel (hop) between adjacent states. Sub-bandgap states thus offer an alternative pathway for electrons to be transported through the Zn0.8Mg0.2O/ITO Schottky barrier and be directly injected into the ITO conduction band, as illustrated in Figure 2d.

This trap-facilitated method of charge transport through a Schottky barrier is similar to that found for ZnO/Au, in which the I–V curves changed from showing a Schottky junction to showing a junction behaving like an ohmic contact when defect states were present in the ZnO.31 We also note that Cu2O electrodeposited on ITO forms a Schottky interface, but behaves like an ohmic contact because Cu2O has a high density of sub-bandgap states, allowing a similar hopping mechanism as discussed above for Zn0.8Mg0.2O (Figure S7, Supporting Information). Whereas in our previous work we showed that metal oxide band-tails at heterojunctions limit open-circuit photo-current densities, this work shows that those band-tails are needed at Schottky interfaces to allow charge transport without rectification. Engineering the band-tail length to achieve a balance between the two effects is an important consideration for the future design of metal oxide solar cells.

Finally, to better understand the influence of the Zn0.8Mg0.2O/ITO Schottky barrier on device performance, we varied the Zn0.8Mg0.2O thickness and found that the Jsc’s and efficiencies were strongly thickness-dependent for films thinner than 90 nm (Figures 3a,c). This effect may be due to (i) the electrical conductivity of Zn0.8Mg0.2O increasing with thickness or (ii) the Schottky barrier reducing charge flow or (iii) the optical spacer effect.32 These are separately examined in turn.

Using four-point measurements, we found that the conductivity of the SAALD Zn0.8Mg0.2O films increased with thickness for films >60 nm (Figure 4a). This would lead to increased Jsc’s due to a decreasing series resistance. Photoluminescence measurements suggest that the increase in conductivity with film thickness is not fully accounted for by a carrier concentration change and we therefore deduce it to be mainly due to an increase in electron mobility, especially for films thicker than 60 nm (Figures S8 and S9, Supporting Information). However, it can be seen through a comparison of Figures 4a and 3a that a changing Zn0.8Mg0.2O conductivity does not account for all of the observed Jsc change with thickness because the conductivities do not change for films thinner than 60 nm, whereas the Jsc’s change significantly.

To examine whether the Zn0.8Mg0.2O/ITO Schottky barrier influences the Jsc’s, a new measurement was made with 30 nm AZO inserted between the Zn0.8Mg0.2O and ITO. It can be seen from the Nyquish plot in Figure 2a that this AZO layer forms an ohmic contact with Zn0.8Mg0.2O. Figure 4b shows that with an ohmic contact, the trend in Jsc with increasing SAALD Zn0.8Mg0.2O thickness follows the trend in film conductivity but, importantly, the Jsc’s do not drop off for films thinner than 30 nm. This strongly suggests that the decrease in Jsc for films thinner than 30 nm is a result of the Schottky barrier.
For such a claim that the Schottky barrier is influencing the current densities to hold true, the Schottky barrier width must be at or near the 30 nm cutoff point. The barrier width can be estimated from the Poisson equation, where full carrier depletion is assumed, and is estimated to be between 20 and 50 nm (see the Supporting Information, Section S3). Thus, when the films are 30 nm or thinner, the band-bending due to the Schottky barrier should overlap with the band-bending at the p–n junction and therefore reduce the built-in potential (Figure 5a). To verify this concept, the built-in potentials \( V_{BI} \) were estimated from the voltage at which the light and dark current densities are equal (Figure 4c). It can be seen that there was an increase in the \( V_{BI} \) from the 10 to 30 nm thick films. The series resistance of the devices was 20–40 \( \Omega \cdot \text{cm}^2 \), from which a 0.04 V increase in the \( V_{BI} \) corresponds to a maximum increase of 1.3 mA-cm\(^{-2}\) in the \( J_{SC} \) (calculation given in Section S3 of the Supporting Information), which more than accounts for the increase in \( J_{SC} \) that occurred (Figure 3a). Thus, spacing the Schottky barrier away from the p–n junction allows a larger built-in potential to form at the heterojunction (Figure 5b), producing a larger driving force for electrons to overcome the series resistance of the device. The \( V_{BI} \) change is not large enough compared to the factors governing the \( V_{OC} \) loss mechanisms to lead to a significant change in the \( V_{OC} \) in Figure 3b.

Finally, to evaluate whether the optical spacer effect accounts for the \( J_{SC} \) changing with thickness, a transfer matrix model was employed to calculate the maximum \( J_{SC} \) from the solar cells. It was found that the modeled change in the \( J_{SC} \) with thickness is less than 0.5 mA-cm\(^{-2}\) (Figure S10a, Supporting Information), which does not account for the \( >1 \) mA-cm\(^{-2}\) change in \( J_{SC} \) observed.

The change in fill factors (FFs) in Figure 3d relates to the influence of the Schottky barrier, \( Zn_{0.8}Mg_{0.2}O \) conductivity and device fabrication on recombination. When the Schottky barrier is closer to the heterojunction than its depletion width (\( <30 \) nm thick \( Zn_{0.8}Mg_{0.2}O \)), it opposes electron-injection, which therefore increases interfacial recombination and decreases FFs. On the other hand, the increasing film conductivity for devices with \( Zn_{0.8}Mg_{0.2}O \) thicker than \( 30 \) nm (with reducing series resistance) allows a greater fraction of injected charges to be extracted before they recombine in the bulk of the \( Zn_{0.8}Mg_{0.2}O \) window layer. For thicknesses of \( Zn_{0.8}Mg_{0.2}O \) larger than \( 90 \) nm, a decrease in FF is observed in Figure 3d. The reason for this is likely related to the prolonged heating of the Cu\( _2 \)O at 80 °C due to the longer deposition time required to produce thicker metal oxide films. This could have two effects: (i) creation of a thicker surface layer of Cu\( _2 \)O, which can enhance interfacial recombination or (ii) the creation of microcracks in Cu\( _2 \)O arising from the different thermal expansion of the Cu\( _2 \)O across its thickness. If these microcracks are introduced, they can act as shunt pathways that increase recombination and reduce FFs.

Overall, ITO-only top contacts led to better performance than devices with AZO. By mitigating the effects of the \( Zn_{0.8}Mg_{0.2}O \) Schottky barrier, an efficiency of 1.6% (Figure 4d) was achieved. This is double that obtained using a 70 nm AZO TCO, and is also 50% higher than the efficiency of 1.07% obtained using a (30 nm) AZO/(60 nm) ITO top transparent contact. The main reason for these improved performances is a higher \( J_{SC} \) arising from the low resistivity of ITO (\( (7 \pm 1) \times 10^{-4} \text{\Omega} \cdot \text{cm} \)) compared with AZO (0.8 \( \Omega \cdot \text{cm} \)), which is consistent with reports in the literature. The \( J_{SC} \) of ~6.2 mA-cm\(^{-2}\) obtained using ITO as the top contact is higher than \( J_{SC} \)’s typically obtained using a bilayer device with electrochemically deposited Cu\( _2 \)O with the p–n junction fabricated in open-air (3.8–4.5 mA-cm\(^{-2}\)). We also note that 1.6% is the highest efficiency obtained from an electrochemically deposited Cu\( _2 \)O device with a p–n junction fabricated using open-air techniques.

## CONCLUSION

In summary, we have shown that it is possible to overcome the performance-reducing effects of Schottky barriers between \( Zn_{1-x}Mg_{x}O \) and ITO, allowing higher current densities to be obtained and efficiencies that were double those obtained using ohmic AZO contacts. Charge transport through the \( Zn_{1-x}Mg_{x}O \) Schottky barrier without rectification (like an ohmic contact) was found to occur via charge hopping through states in the \( Zn_{1-x}Mg_{x}O \) band-tail. The extent to which the \( Zn_{1-x}Mg_{x}O \) Schottky barrier limits current densities is minimized by spacing it away from the p–n junction to allow the full built-in potential to form while simultaneously increasing the conductivity of the films. By showing that transparent conducting electrodes do not need to have matching Fermi levels with the metal oxides they are in contact with, this work has important implications for the design of new generation solar cells, thus providing greater flexibility in the selection of electrode materials.

## ASSOCIATED CONTENT

### Supporting Information

Photovoltaic measurements for the optimization of SAALD \( Zn_{1-x}Mg_{x}O \) composition and deposition conditions onto Cu\( _2 \)O, analysis of \( Zn_{1-x}Mg_{x}O \)/ITO and Cu\( _2 \)O/ITO interfaces to determine how charge can be transported through a Schottky barrier without rectification, supporting measurements for the analysis of the reasons for the change in current density of Cu\( _2 \)O–Zn\( _{0.8} \)Mg\( _{0.2} \)O devices with \( Zn_{0.8}Mg_{0.2}O \) thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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