COMMUNICATION

Interface stoichiometry control to improve device voltage and modify band alignment in ZnO/Cu₂O heterojunction solar cells

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The interface stoichiometry of cuprous oxide (Cu_2O) was controlled by adjusting the O_2 and Zn partial pressures during ZnO sputter deposition and measured by high-resolution X-ray photoelectron spectroscopy of ultrathin (<3 nm) ZnO films on Cu_2O. Open-circuit voltage measurements for ZnO/Cu_2O heterojunctions under AM1.5 illumination were measured and it was found that a stoichiometric interface can achieve the voltage entitlement dictated by the band alignment, whereas the non-stoichiometric interface showed large open-circuit voltage deficits. These results highlight not only the need for stoichiometric interfaces in Cu_2O devices, but also a reproducible experimental method for achieving stoichiometric interfaces that could be applied to any potential heterojunction partner. Additionally, valence-band offset measurements indicated changing the interface stoichiometry shifted the band alignment between Cu_2O and ZnO, which accounts for the variation in previously reported band offset values.

Broader context

Cuprous oxide (Cu_2O) is a candidate material for photovoltaic and photoelectrochemical device applications due to its suitable band gap and low processing cost. Furthermore, due to the natural abundance of its component elements in the atmosphere and crust, it is a candidate for terawatt scale solar energy production. Given the electronic band gap of Cu_2O is 2.1 eV, the detailed balance energy conversion efficiency limit is 20%. However, the efficiency record for Cu_2O stands at 5.38%. Currently, device efficiencies are limited in part because there is no method for creating a reproducible, stoichiometric interface between Cu_2O and heterojunction partners. Cu_2O is a uniquely reactive semiconductor due to its low enthalpy of formation (-168.7 kJ mol^{-1}) and the existence of multiple stable Cu oxidation states. The present work presents a method for the controlled modification of the chemical state of Cu at the interface of Cu_2O/ZnO by modifying the O_2 partial pressure during emitter deposition. It was determined that stoichiometric interfaces had open circuit voltages approaching the thermodynamic limit set by the band offset of the heterojunction, and thus are necessary for optimal device performance.

Introduction

Cuprous oxide (Cu_2O) is a promising alternative to traditional thin-film photovoltaic materials (CIGS, CdTe, a-Si, etc.) because of its low materials cost, the abundance of its component elements in the earth's crust,[1] and its uniquely straightforward processing.[2–4] Crystalline wafers of Cu_2O can be fabricated directly by thermal oxidation of Cu foils, making manufacturing high quality photovoltaic materials possible through low-cost processing.[2,5] Furthermore, Cu_2O has an electronic band gap of 2.1 eV which gives it a detailed balance efficiency of ~20% for a homojunction solar cell and also the potential for an independently connected Cu_2O/Si tandem device with an efficiency of ~43%.[2,3,6,7] It is an intrinsic p-type semiconductor with relatively

high absorbance in the visible region above the gap.[2] Finally, minority carrier diffusion lengths of 10 μm and hole mobilities of up to 100 cm^2 V^{-1} s^{-1} have also been reported for Cu_2O made by thermal oxidation.[2,5,6,8]

Despite band gap and minority carrier properties that are favorable for achieving a high energy conversion efficiency, the highest efficiency achieved in a photovoltaic device with a Cu_2O absorber layer is 5.38%.[9] There are several challenges to making a Cu_2O photovoltaic device, including an inability to dope the material,[2,10] its relatively low chemical stability compared to other oxides,[11] and a lack of suitable heterojunction partners due to an unusually small electron affinity.[12] We have focused on the low chemical stability, namely the fact that Cu_2O is an especially reactive oxide due to its low enthalpy of formation ($\Delta H_f^o = -168.7$ kJ mol^{-1}). The low value of the heat of formation means Cu_2O will be reduced when in contact with nearly any elemental material. Cu forms a low barrier Schottky diode with Cu_2O, thus the presence of interfacial Cu lowers the photovoltaic cell's built-in voltage. The effect of interfacial Cu on device performance has been well characterized for Cu_2O Schottky

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devices.[2,13] However Cu is not the only species that may reactively form at the interface as copper has another stable oxide, CuO.[14] The effect of interfacial CuO has not been studied explicitly in Cu_2O heterojunctions, and its specific impact on device performance is unknown.

We have chosen to study the ZnO/Cu_2O interface because it has been the most widely studied Cu_2O based heterostructure, and until recently, the most efficient heterojunction system as well.[2,3,15–22] In this manuscript, we describe the controlled modification of ZnO/Cu_2O heterostructures to yield stoichiometric interfaces as well as nonstoichiometric interfaces with Cu and CuO present. We also show that stoichiometric interfaces are necessary for achieving large device voltages. The ZnO/Cu_2O interface stoichiometry and valence-band alignments were measured experimentally by high-resolution X-ray photoelectron spectroscopy (XPS). Finally, in order to quantify the effect of local deviations in interface stoichiometry, ZnO/Cu_2O photovoltaic devices of varying interface composition were tested under AM1.5 1-sun solar illumination.

Results and discussion

a.   Determination of ZnO/Cu_2O and Zn/Cu_2O interface stoichiometry by X-ray photoelectron spectroscopy

In order to measure the interface stoichiometry, we performed XPS on thin heterointerfaces (Fig. 1). Due to the surface sensitivity of XPS, film thicknesses were constrained to less than the escape depth of photo-excited electrons ($\sim$3 nm). This allowed analysis of the heterojunction stoichiometry without the need for sputter depth profiling, leaving pristine interfaces free of crystalline damage.

X-ray photoelectron spectroscopy is a particularly powerful technique for Cu_2O stoichiometry determination because CuO,
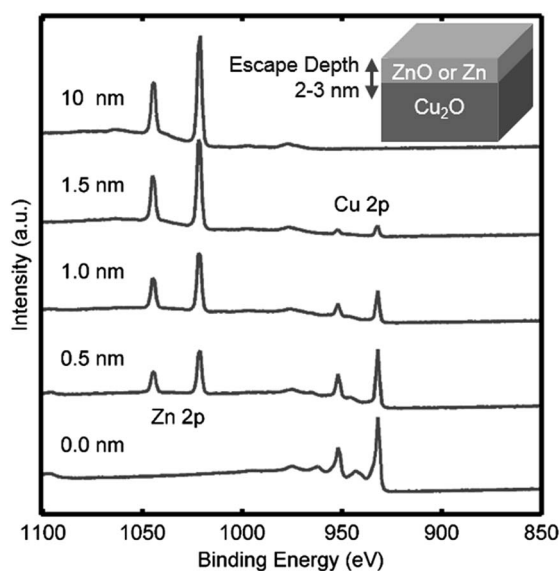

Fig. 1   X-ray photoelectron spectroscopy of Zn-rich ZnO/Cu_2O heterojunctions for indicated thickness of ZnO. Both Cu and Zn peaks are visible meaning the interface is being effectively probed.

Cu_2O and elemental Cu can be differentiated by analyzing high-resolution XPS spectra of the Cu $2p_{3/2}$ (Cu 2p) and Cu Auger (Cu a) peaks.[23] If Cu is bound as CuO, the Cu $2p_{3/2}$ peak shifts to slightly higher binding energy. However this one peak is not sufficient to understand the oxidation state of the Cu at the interface since Cu_2O and elemental Cu have the same Cu $2p_{3/2}$ peak position. Elemental Cu can be differentiated from Cu_2O by looking for peak shifts in the Cu Auger peak. Cu shifts to lower binding energies in the Auger peak while Cu_2O and CuO have the same peak position.

High-resolution XPS spectra (Fig. 2) were collected for different thicknesses of Cu_2O heterojunctions made with (Fig. 2a) O-rich ZnO, (Fig. 2b) Zn-rich ZnO, or (Fig. 2c) elemental Zn. The XPS spectra for the bare Cu_2O wafer (0.0 nm) shows a shoulder in the Cu 2p peak in all samples, indicating there is CuO on the surface of the wafer. This surface oxide forms when Cu_2O is exposed to atmosphere because CuO is the stable phase of copper oxide at room temperature and pressure.[14] When O-rich ZnO is deposited onto the slightly oxidized Cu_2O surface (Fig. 2a), the shoulder in the Cu 2p peak continues through all thicknesses of ZnO. This result is expected since O-rich ZnO should have no elemental Zn available to react with the surface of the Cu_2O. Thus by depositing O-rich ZnO directly onto the slightly oxidized Cu_2O surface, we can produce a mixed phase surface with both CuO and Cu_2O.

When Zn-rich ZnO is deposited instead of O-rich ZnO (Fig. 2b) we expect the wafer surface to be reduced due to the availability of elemental Zn. The data shows that as Zn-rich ZnO is deposited onto Cu_2O the shoulder in the Cu 2p peak disappears, indicating that the CuO layer is reduced. Furthermore, analysis of the Cu Auger peak shows no Cu_2O is reduced since no low binding energy peak is present, thus the reaction terminates at the Cu_2O surface. The reaction appears to be highly selective, which could be due to the slightly higher formation enthalpy (ΔH_f^o) of Cu_2O versus CuO.[11] This reaction was also found to be highly reproducible and all deposited thicknesses showed the same trend. Thus depositing Zn-rich ZnO onto a slightly oxidized Cu_2O surface yields a stoichiometric ZnO/Cu_2O interface.

Elemental Cu was formed at the interface by sputtering elemental Zn onto Cu_2O (Fig. 2c) because it was found to be impossible to reduce Cu_2O to Cu by sputtering ZnO alone. This is probably due to the low thermodynamic driving force for Zn to reduce Cu_2O, as ZnO also has a fairly low enthalpy of formation.[11] The Cu 2p data shows that Zn, similarly to Zn-rich ZnO, reduces the CuO on the surface. However, the Cu Auger peak shows a second lower binding energy peak indicating Cu is forming at the interface. Therefore, solely by altering the partial pressures of Zn and O_2 during deposition, we were able to create Cu_2O heterointerfaces that were stoichiometric, or had elemental Cu or CuO present at the interface.

b.   Measurement of valence-band offsets

The valence-band offset for the ZnO/Cu_2O heterojunction has been widely studied with published values ranging from 1.7 to 2.8 eV.[18–22] However, little attempt has been made to correlate
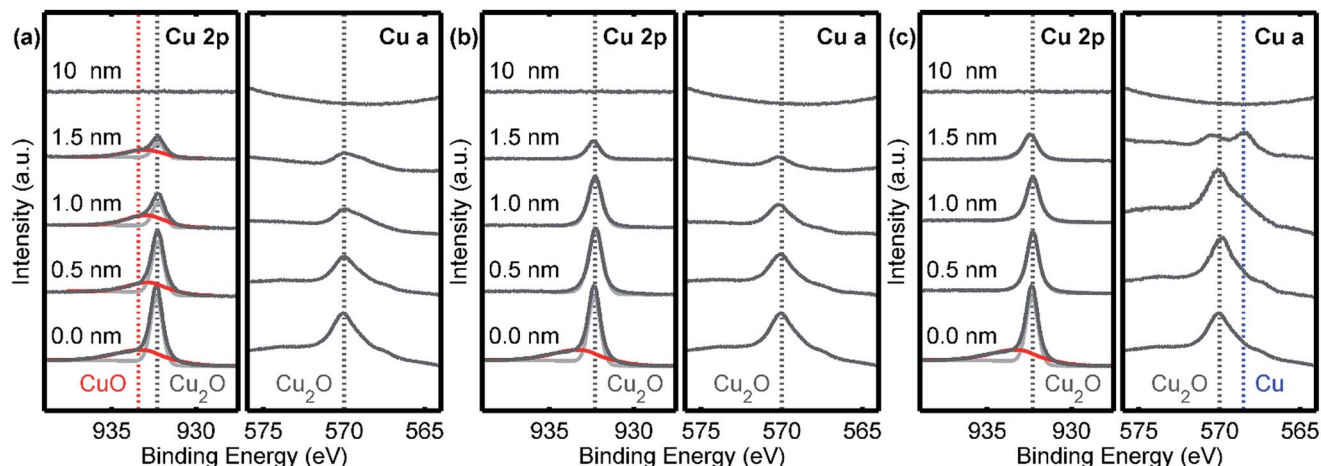
Fig. 2 High-resolution X-ray photoelectron spectroscopy of the Cu $2p_{3/2}$ and main Cu Auger peak for Cu_2O heterointerfaces made with (a) O-rich ZnO, (b) Zn-rich ZnO and (c) elemental Zn. The thickness of the deposited ZnO or Zn is indicated. The heterojunctions made with Zn-rich ZnO have a stoichiometric interface while the samples made with O-rich ZnO and Zn have CuO and Cu present, respectively.

the observed variation in the offset with deviations in interface stoichiometry. The ZnO/Cu_2O valence-band offsets were determined for the stoichiometric and CuO-containing interfaces *via* the Kraut method using XPS.[24] In short, the binding energy difference between the Cu 3s and Zn 3s core-levels was observed for thin ZnO/Cu_2O interfaces. The bulk core-level to valence-band maximum energy differences for Cu_2O and ZnO were determined by fitting the valence-band region of the respective photoelectron spectrum to an instrument-convolved valence-band density of states calculated by density functional theory. The details of this procedure have been reported previously to successfully determine the band alignment of II–VI materials with other earth abundant PV absorbers.[25]
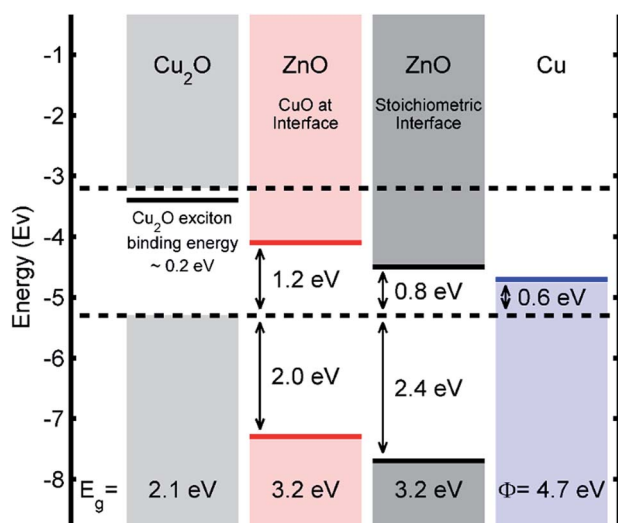

Fig. 3 Band structure and valence band offset measurements derived from X-ray photoelectron spectroscopy measurements of Zn-rich ZnO/Cu_2O (stoichiometric interface) and O-rich ZnO/Cu_2O (CuO at interface) samples. The Cu work function is also indicated.

We found the stoichiometric interface and the interface with CuO precipitates had valence-band offsets of 2.4 ± 0.1 eV and 2.0 ± 0.1 eV respectively (Fig. 3). This indicates that the presence of a CuO interfacial species changes the band energetics between Cu_2O and ZnO. The modification of heterojunction band alignment with the insertion of an interfacial layer has been observed previously in III–V and II–VI material systems.[26] The dependence of the band offset on interface composition, which in turn is dependent on the ZnO deposition conditions, is likely responsible for the large variation in reported offset values and emphasizes the need for improved control and understanding of the interface stoichiometry.

c. Open-circuit voltage of ZnO/Cu_2O photovoltaic devices with different interface species

The open-circuit voltage of photovoltaic devices (Table 1) was used to evaluate the relationship between the interface stoichiometry and the electronic quality of ZnO/Cu_2O heterojunctions. *J–V* measurements were performed for devices made with a stoichiometric interface, with CuO at the interface, and with Cu present at the interface. The data was collected under simulated AM1.5 1-sun solar illumination. We focused our analysis on device open-circuit voltage because it is more sensitive to interfacial and bulk defects than other *J–V* characteristics and is thus considered an appropriate measure of interface quality. The reported open-circuit photovoltages were averaged over a minimum of 9 tested devices. The device with the stoichiometric interface demonstrated the highest open-circuit voltages of 530 ± 4 mV. The devices fabricated with CuO and Cu inclusions at the interface had substantially lower average open-circuit voltages of 109 ± 11 mV and 347 ± 30 mV, respectively. The short-circuit current densities and efficiencies of all of the devices were limited by the resistivity ($\rho > 1500$ Ω cm) and thickness ($\sim$1 mm) of the Cu_2O substrate, as indicated by the large slopes of the *J–V* curves near the open-circuit voltage (R_{OC}).

Table 1 Current–voltage parameters for illuminated devices, with open-circuit photovoltages highlighted. The devices with stoichiometric interfaces showed the largest open-circuit photovoltages despite having less ideal band offsets. All values are averaged over a minimum of 9 devices

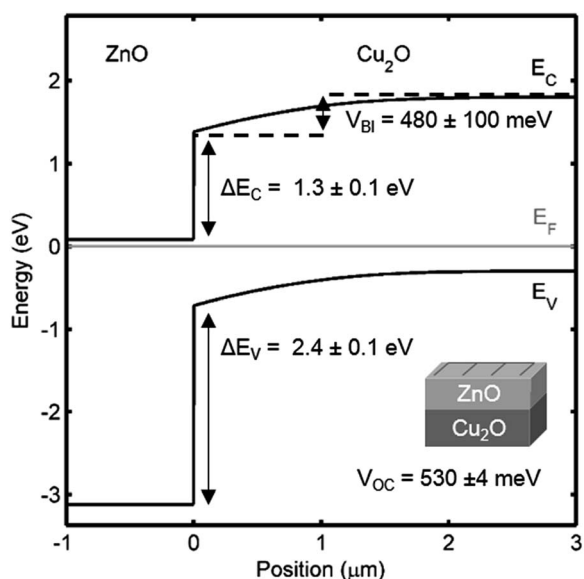| Photovoltaic device structure	Open-circuit voltage	Short-circuit current	Fill factor	Slope around open-circuit voltage (R_{OC})
ZnO/Cu$_2$O	530 ± 4 meV	0.69 ± 0.47 mA cm^{-2}	30.4 ± 3.85%	$1.1 \times 10^5 \pm 1.8 \times 10^5$ Ω
ZnO/CuO/Cu$_2$O	109 ± 11 meV	0.46 ± 0.21 mA cm^{-2}	25.5 ± 3.85%	$1.2 \times 10^4 \pm 6.9 \times 10^3$ Ω
ZnO/Cu/Cu$_2$O	347 ± 30 meV	1.41 ± 0.54 mA cm^{-2}	26.0 ± 0.56%	$7.05 \times 10^3 \pm 2.3 \times 10^3$ Ω

Fig. 4 The 1-D Poisson equations were solved for a ZnO/Cu$_2$O junction in order to determine the voltage limits of the device. That the ideal built-in voltage and the measured open-circuit voltage are so similar indicates the formation of a near perfect interface.

In order to understand the voltage limits of the stoichiometric devices we modeled the band bending at the ZnO/Cu$_2$O interface by solving the 1-D Poisson equations (Fig. 4). For this model we choose a Cu$_2$O doping level of 10^{14} cm^{-3} to reflect the majority carrier concentration of our thermally oxidized Cu$_2$O wafers under illumination.[27] To calculate the carrier concentration in the ZnO, we made a conservative estimate of mobility in the sputtered thin film of 1 cm^2 V^{-1} s^{-1}. We then used the measured resistivity of ~1 Ω cm to calculate a carrier concentration of 10^{18} cm^{-3}. Solving the Poisson equation, we calculated a built-in voltage of 480 ± 100 meV. The error in the estimation comes from the error in the band offset calculation, which has a much larger effect than error in the doping estimates. The built-in voltage is the voltage drop across the space charge region at equilibrium and thus is the maximum achievable open-circuit voltage in an ideal device. That the open-circuit voltage and the built-in voltage are so close shows that the stoichiometric interface is approaching its voltage entitlement, meaning the interface is behaving ideally. Thus the stoichiometric device performance is limited solely by the heterojunction offset, and the large series resistance contribution

of the undoped Cu$_2$O substrate. If stoichiometry is maintained at the interface and an emitter with a more favorable offset is found, we believe large voltages and high efficiencies are achievable in a Cu$_2$O device.

The open-circuit voltage observed for the Cu interface is in agreement with the expectation that a Cu/Cu$_2$O Schottky barrier is formed at the interface. The reactively formed Cu/Cu$_2$O interface has been explored previously, and the device photovoltages align well with the work of Olsen et al. and Assimos et al.[2,4] It is well understood that the device voltage is limited by the small work function difference between Cu$_2$O and Cu metal, and our photovoltages are identical to those previously achieved in Cu/Cu$_2$O Schottky devices.[4,13]

Analysis of the ZnO/CuO/Cu$_2$O devices is slightly less obvious, because according to the valence-band offset measurements, these devices should have a larger built-in voltage and open-circuit voltage than the stoichiometric interface devices. However, the opposite trend was observed from the device measurements. There are several possible reasons for this including increased recombination at the interface and Fermi level pinning due either to the low band gap of CuO (~1.2 eV) or an increased density of interface states. However, we believe the lower observed open-circuit voltage for the device with CuO at the interface is most likely due to the degenerate nature of CuO. It is difficult to make a rectifying contact to CuO, and its presence would make contact at the junction nearly ohmic.[28] These results show the importance of controlling the emitter deposition conditions in order to control the heterojunction interfacial composition. Clearly, a stoichiometric Cu$_2$O interface is desirable for obtaining improved PV device performance.

Conclusions

We have demonstrated the ability to tune the Cu oxidation state between CuO, Cu$_2$O, and Cu at the ZnO/Cu$_2$O interface with careful modification of the emitter deposition conditions. High-resolution XPS was used to accurately probe the interface stoichiometry as well as the band alignment between the two semiconductors. It was found that the presence of CuO at the interface causes a 0.4 eV shift in the valence-band offset between Cu$_2$O and ZnO, which could help explain the variation in literature values of the ZnO/Cu$_2$O valence-band offset. Furthermore, photovoltaic device performance of ZnO/Cu$_2$O heterojunctions was observed to depend strongly on interfacial composition. Stoichiometric interfaces demonstrated

significantly larger photovoltages under AM1.5 1-sun illumination. The control of interfacial chemistry demonstrated herein is directly transferable to other heterojunction systems incorporating a Cu_2O absorber and should result in further improvements in solar conversion efficiency.

Experimental

The Cu_2O wafers used in these experiments were grown by thermal oxidation of 500 μm copper foils (99.9999%, Alfa Aesar) in a tube furnace. The Cu foils were hung vertically from Cu wires on a quartz substrate holder during oxidation. The Cu substrates were heated to 950 °C under N_2 flow and then oxidized for 24 hours at 1 Torr O_2. The temperature and pressure were chosen because they are within the stability range of the Cu_2O phase in the Cu–O phase diagram.[14] The substrates were then cooled to room temperature under a N_2 flow resulting in ~1 mm thick, phase pure Cu_2O wafers with a lateral grain size on the order of ~1 mm^2.

Heterostructures for XPS studies were fabricated by radio-frequency magnetron sputter deposition of Zn or ZnO directly onto an untreated Cu_2O surface at room temperature. A compound ZnO target and a pure Zn metal target were used as sputtering sources. Zn or ZnO films were deposited at 100 W substrate power and a sputtering pressure of 5 mTorr. ZnO was sputtered under both a pure Ar atmosphere and a 0.25 mTorr partial pressure of O_2 in Ar. The ZnO sputtered with O_2 was O-rich as indicated by its resistivity (ρ > 1000 Ω cm), while the ZnO sputtered in pure Ar was Zn-rich ($\rho \sim$ 1 Ω cm). Zn was sputtered only under a pure Ar atmosphere. For XPS samples, the thickness of deposited films ranged from 0.5–10 nm.

For photovoltaic device fabrication, each of the three interface types was made by depositing ~2 nm of ZnO or Zn, which were sputtered according to the three conditions outlined above, onto a ~1 mm thick, untreated Cu_2O wafer. An additional 10 nm of ZnO sputtered in Ar was deposited onto all the samples and capped with 50 nm of sputtered Al-doped ZnO (AZO) followed by 100 nm of Sn-doped In_2O_3 (ITO) as a top electrical contact. A thick Au film was deposited on the Cu_2O as a back electrical contact. Device area was approximately 3 mm^2.

The surface stoichiometry and interface stoichiometry of thin ZnO/Cu_2O samples were measured using a Kratos Ultra XPS system. The Al Kα line (1486.6 eV) was used as a monochromatic X-ray source and the excited photoelectrons were collected by a hemispherical analyzer at 0° from the surface normal. Low-resolution survey spectra were acquired between binding energies (B.E.) of 1–1200 eV. Higher-resolution, detailed scans (detection line width of <0.26 eV), were collected on individual XPS features of interest. The sample chamber was maintained at <2 × 10^{-9} Torr. Finally, current density *vs.* potential (*J–V*) measurements on the full PV devices were performed under AM1.5 1-sun illumination.

Acknowledgements

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