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SCHOLARSHIP AT HARVARD**Improved Cu<sub>2</sub>O-Based Solar Cells Using Atomic Layer Deposition to Control the Cu Oxidation State at the p-n Junction**

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## **Improved Cu<sub>2</sub>O-based solar cells using atomic layer deposition to control the Cu oxidation state at the *p-n* junction**

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Recombination at a defect-rich interface is one of the major efficiency-loss mechanisms in polycrystalline heterojunction thin-film solar cells.<sup>[1, 2]</sup> Cuprous oxide (Cu<sub>2</sub>O) is considered a promising Earth-abundant semiconductor for thin-film solar cells compatible with terawatt-level deployment.<sup>[3-5]</sup> However, the power conversion efficiency (PCE) of Cu<sub>2</sub>O-based solar cells has remained significantly lower than the theoretical single-junction maximum efficiency of > 20%, often due to low open-circuit voltages ( $V_{OC}$ ) resulting from rapid interfacial recombination.<sup>[6-8]</sup> This interfacial recombination is believed to originate mostly from (i) non-ideal band-alignment with an adjacent *n*-type transparent conductive oxide (TCO) layer (*e.g.* Al-doped ZnO or indium-tin-oxide) and (ii) a high density of trap states in the region near the heterojunction interface. Various buffer layers including Ga<sub>2</sub>O<sub>3</sub>,

TiO<sub>2</sub>, and amorphous zinc-tin-oxide (a-ZTO) have been applied at the junction interface to provide more ideal band alignment.<sup>[6, 9, 10]</sup>

To reduce the interfacial trap density and further enhance heterojunction quality, any defects at the heterojunction interface should be minimized.<sup>[11]</sup> In particular, a cupric oxide (CuO) layer on the Cu<sub>2</sub>O surface is highly undesirable since it has a smaller bandgap ( $E_g = \sim 1.4$  eV) than Cu<sub>2</sub>O ( $E_g = \sim 2$  eV) and its conduction band energy near 4 eV from the vacuum level can create deep states at the interface, enhancing interfacial recombination.<sup>[3, 12-14]</sup> A CuO layer is formed readily on a Cu<sub>2</sub>O or Cu surface during quenching and/or exposure to an oxygen-rich ambient.<sup>[7, 15]</sup> Similar surface chemistry changes are common for many thin-film solar cell materials including copper indium gallium selenide (CIGS).<sup>[16]</sup> In the past, chemical treatments have been employed to modify the surface chemistry of air-exposed CIGS films.<sup>[16, 17]</sup> For Cu<sub>2</sub>O prepared by a thermal oxidation method, similar methods for Cu<sub>2</sub>O surface modification, including wet etching, heat treatments, and a catalyst layer, have been introduced to remove the CuO surface layers, resulting in enhancements of solar cell performance.<sup>[5, 7, 18]</sup> However, even if the surface treatments remove the CuO layer completely, a nanometer-scale-thick CuO layer can re-grow when the surface is exposed to air thereafter.<sup>[15]</sup> Thus, a surface modification process with high controllability should be performed *in situ* immediately prior to overlayer deposition during solar cell fabrication (*e.g.* buffer layer deposition) to achieve higher PCE. Recently, Wilson *et al.*, proposed a method to control interface stoichiometry of Cu<sub>2</sub>O *in situ* by controlling the oxygen partial pressure during sputtering of a ZnO over-layer.<sup>[14]</sup>

In this communication, we demonstrate a method to tune the chemical state of the interfacial layer of Cu<sub>2</sub>O absorbers by chemical means, by engineering the atomic layer deposition (ALD) reaction conditions of an a-ZTO buffer layer in an all-oxide thin-film solar cell device architecture (ZnO:Al/a-ZTO/Cu<sub>2</sub>O). During the past decade, ALD has demonstrated utility in a range of photovoltaic device-processing applications, including

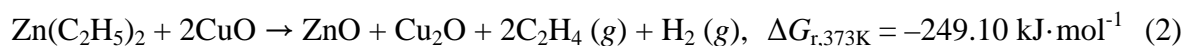
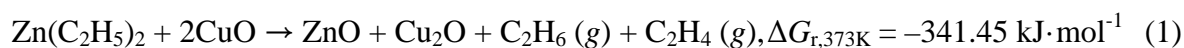
buffer-layer deposition and surface passivation.<sup>[19, 20]</sup> The discrete nature of the ALD process enables a high degree of tunability of the layer properties as well as an excellent uniformity over large-scale substrates.<sup>[19-21]</sup>

We exploit the fact that ALD can involve highly reactive metal-precursors and oxidizers, which can also affect surface chemistry of substrates. We utilize the thermodynamics of the half-cycle reaction in the ALD sequence of a-ZTO buffer layer deposition to control the surface chemistry of as-grown Cu<sub>2</sub>O thin-film, and describe how this approach could be generalized to other buffer-layer materials. The CuO (Cu<sup>2+</sup> state) interfacial layer at a-ZTO/Cu<sub>2</sub>O can be reduced to Cu<sub>2</sub>O (Cu<sup>1+</sup> state) by pulsing a Zn precursor, and additional oxidation of Cu<sub>2</sub>O surface by an oxidant pulse can be suppressed by lowering the ALD reaction temperature. By engineering the surface chemistry associated with the ALD reaction temperature, the chemical state of Cu at the interface can be controlled and a high-quality heterojunction can be formed. We demonstrate the enhanced performance of Cu<sub>2</sub>O-based solar cells by controlling interface chemistry, resulting in an improved  $V_{OC}$ .

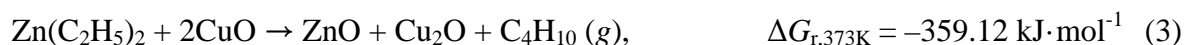
A nanometer-scale-thick surface layer of CuO phase is normally formed on Cu<sub>2</sub>O films grown by electrochemical deposition. **Figure 1** shows XPS spectra of the Cu-2*p* core levels for an as-grown Cu<sub>2</sub>O film surface and a Cu<sub>2</sub>O surface sputtered by argon ions at 1 keV *in situ*. Peaks at 932.2 and 934.2 eV indicate Cu<sup>1+</sup> and Cu<sup>2+</sup> states, respectively.<sup>[22, 23]</sup> Broad satellite peaks near 940 – 945 eV originate from the CuO phase, which is a characteristic of materials having a  $d^9$  configuration in the ground state.<sup>[23]</sup> Thus, the existence of the satellite peaks is an evidence of formation of the CuO phase in addition to the peak assigned to the Cu<sup>2+</sup> state at ~934 eV. After sputtering the sample surface for 1 min, the signals from the CuO phase disappear and only signals from the Cu<sub>2</sub>O phase are observed. The XPS spectra with depth profiling suggest that the CuO forms only at the near-surface region of the Cu<sub>2</sub>O. The CuO is likely due to exposure of the sample to ambient atmosphere, in which an abundance of oxygen can promote the complete oxidation of copper cations to Cu<sup>2+</sup> (CuO).<sup>[23, 24]</sup>

Considering the electron escape depth of ~5 nm and the XPS signal intensity of CuO phase relative to Cu<sub>2</sub>O phase, the surface CuO layer is expected to have an approximate thickness of only 1 nm, perhaps suggesting that the formation of a thicker surface layer is limited by oxygen diffusion through CuO.

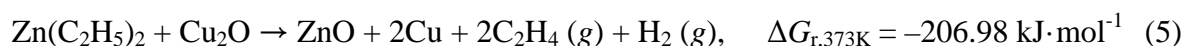
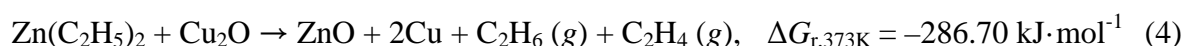
To remove the surface CuO layer and create a high-quality a-ZTO/Cu<sub>2</sub>O interface, the thermodynamics of the a-ZTO ALD reaction are investigated. The optimized a-ZTO ALD consists of ZnO and SnO<sub>2</sub> deposition reactions with a pulse ratio of 3:1.<sup>[9, 25]</sup> The starting sequence is a pulse of diethylzinc (DEZ) as a Zn precursor, followed by a pulse of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidizer. It has been reported that the injection of ALD metal precursors can reduce an underlying layer if the reactions are energetically favorable.<sup>[26, 27]</sup> The Gibbs free energy of reaction ( $\Delta G_r$ ) can predict whether the surface reactions in a-ZTO ALD are spontaneous. Plausible reactions of DEZ with CuO and their  $\Delta G_r$  at 373 K are the following:<sup>[28]</sup>



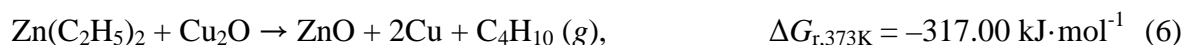
or



In addition, the reduction of Cu<sub>2</sub>O to metallic Cu by DEZ is also possible by the following reactions:



or



On the other hand, the H<sub>2</sub>O<sub>2</sub> sequence after the DEZ pulse can oxidize Cu<sub>2</sub>O to CuO by the following reaction:



All reactions have negative  $\Delta G_r$  at 373 K, indicating that both reduction and oxidation reactions are thermodynamically favorable in the presence of reducing and oxidizing precursors, respectively.

As the thermodynamic analysis predicts, the Zn precursor in the a-ZTO ALD process is experimentally observed to reduce the CuO surface layer to Cu<sub>2</sub>O. **Figure 2a** shows normalized XPS spectra of Cu-2*p* at the Cu<sub>2</sub>O surface after DEZ and an Sn(II) precursor (1,3-bis(1,1-dimethylethyl)-4,5-dimethyl-(4*R*,5*R*)-1,3,2-diazastannolidin-2-ylidene) were pulsed on Cu<sub>2</sub>O films with CuO surface layers. Here, nine super-cycles (three DEZ pulses and one Sn(II) precursor pulse per one super-cycle) of metal precursor injections were used, skipping the injection of H<sub>2</sub>O<sub>2</sub>. Two reaction temperatures of 90 and 170 °C were investigated. At both temperatures, the intensities of the CuO peaks decreased after the injection of metal precursors, which indicates that the CuO layer was partially reduced to Cu<sub>2</sub>O or Cu. The similar decrease in the intensity of the CuO peak for both temperatures suggests that the reduction rate is rapid at both temperatures. A control experiment was performed (the Cu<sub>2</sub>O samples were kept in the chamber without doing any ALD treatment), which showed negligible change of XPS spectra as shown in **Figure S1**.

When only Sn(II) precursor pulses were introduced to the Cu<sub>2</sub>O film while not injecting DEZ or H<sub>2</sub>O<sub>2</sub> with the same conditions mentioned above, negligible reduction of the CuO layer was observed. In contrast, the injection of DEZ without any Sn(II) precursor or H<sub>2</sub>O<sub>2</sub> significantly decreased the size of the CuO peak. Thus, the reduction of the CuO layer is mainly driven by DEZ, forming a stable ZnO without the aid of the oxidant (**Figure 2b**). The reduction of Cu<sub>2</sub>O by the Sn(II) precursor is thermodynamically or kinetically unfavorable.

Interestingly, the reduction of CuO is most effective when only DEZ was introduced without any Sn(II) precursor, which suggests the surface-adsorbed Sn(II) precursor inhibits further adsorption of DEZ. The reduction of CuO is possible by the reactions of DEZ to form ZnO as described in Reactions 1 – 6. Figure 2b shows the XPS spectra of Zn-2*p* core levels after only DEZ molecules were introduced to the Cu<sub>2</sub>O film at 90 °C. The Zn peak at 1021.6 eV (Zn-2*p*<sub>3/2</sub>) corresponds to the peak of a reference ALD ZnO film grown by DEZ and H<sub>2</sub>O<sub>2</sub>. The thickness of the ZnO layer formed after the DEZ pulse to the Cu<sub>2</sub>O film is estimated to be about 1 nm thick. Based on these observations, we conclude that starting the a-ZTO ALD process with the DEZ sequence is more effective to reduce the CuO surface layer than the process starting with the Sn(II) precursor sequence.

Although both reduction reactions to Cu<sub>2</sub>O and metallic Cu are thermodynamically possible, metallic Cu is not detected after the metal precursor injections. It is difficult to distinguish Cu<sup>1+</sup> from metallic Cu by XPS, because the peak positions of Cu-2*p* from the both states are close.<sup>[22]</sup> Instead, Cu<sub>2</sub>O and Cu metal can be distinguished from the Cu-*LMM* Auger transition kinetic energy.<sup>[24]</sup> The Cu-*LMM* kinetic energies from Cu<sub>2</sub>O and metallic Cu have been reported to be 916.5 and 918.4 eV, respectively, with an Al-K $\alpha$  radiation when the peaks were referenced to the C-1*s* binding energy at 284.6 eV.<sup>[24]</sup> As shown in **Figure 2c**, the kinetic energy of 916.9 eV is observed when the CuO phase was reduced by the DEZ during the a-ZTO ALD process. Both the peak position and shape are closer to the signal from Cu<sub>2</sub>O than from metallic Cu. To compare with the signal from the metallic Cu phase, a 20-nm-thick metallic Cu film was deposited by e-beam evaporation at room temperature and an a-ZTO film was grown on the Cu film. Obviously, the metallic Cu is observed at 919 eV, as well as a peak from the Cu<sub>2</sub>O phase (formed by air exposure of Cu film after the growth) at 917 eV. The metallic Cu phase was detected successfully by XPS in the a-ZTO/Cu sample, owing to the a-ZTO layer protecting the Cu surface from the further oxidation by air. However, no metallic Cu phase was observed in the a-ZTO/Cu<sub>2</sub>O sample. This indicates the formation of

Cu may be limited kinetically at the a-ZTO/Cu<sub>2</sub>O sample, although the thermodynamic criteria for the formation of Cu are satisfied according to the Reactions 4 – 6. In addition, we investigated the potential for Cu diffusion through a-ZTO layers, since any trace of metallic Cu is known to pose significant diffusion issues as experienced in Cu-related processes of various semiconductor applications.<sup>[29]</sup> 10-nm-thick a-ZTO films, thicker than an electron escape depth of ~5 nm in XPS, were deposited on Cu<sub>2</sub>O at reaction temperatures between 90 and 170 °C. No signal from Cu is detected by XPS for all temperatures shown in **Figure 2d**. The Auger signal and the Cu-diffusion investigation did not indicate any trace of metallic Cu, which suggests that the reactions by Reaction 4 – 6 are limited by a high activation-energy (slow kinetics).

On the other hand, H<sub>2</sub>O<sub>2</sub> exposure after the DEZ sequence can re-oxidize the Cu<sub>2</sub>O surface layer to the CuO phase. **Figure 3** shows the normalized XPS spectra of Cu-2*p* for three different Cu<sub>2</sub>O samples: as-grown Cu<sub>2</sub>O film and the H<sub>2</sub>O<sub>2</sub>-exposed Cu<sub>2</sub>O films at reaction temperatures of 90 and 170 °C. Here, 36 H<sub>2</sub>O<sub>2</sub> pulses were introduced to the Cu<sub>2</sub>O samples, which is equal to the total H<sub>2</sub>O<sub>2</sub> pulses of nine super-cycles. The increased satellite peak intensities at 940 – 945 eV for both temperatures indicate that the surface of the Cu<sub>2</sub>O film is partly re-oxidized to CuO by H<sub>2</sub>O<sub>2</sub>. As the reaction temperature is raised from 90 to 170 °C, the relative intensity of the Cu<sup>2+</sup> peak at 934 eV to the Cu<sup>1+</sup> peak at 932 eV is increased. This result suggests that more oxidation of Cu<sub>2</sub>O to CuO occurs at higher ALD temperatures.

Since the reduction and oxidation reactions possess different temperature dependences, the surface chemistry of Cu<sub>2</sub>O films can be controlled by changing the reaction temperature. To investigate the chemical state of Cu at the a-ZTO/Cu<sub>2</sub>O interface by XPS, 3-nm-thick a-ZTO films were grown on Cu<sub>2</sub>O films at different reaction temperatures in the range of 90 – 170 °C. **Figure 4a** shows the normalized XPS spectra of Cu-2*p* from the a-ZTO/Cu<sub>2</sub>O samples. The Cu<sup>2+</sup> peak at 934 eV is not detected in samples with ALD reaction temperatures



below 120 °C. This result suggests that the a-ZTO ALD process itself can effectively reduce the detrimental CuO layer to Cu<sub>2</sub>O. However, at the reaction temperature of 170 °C, a small peak shoulder near ~934 eV is observed. The peak shoulder is further investigated by deconvoluting the spectrum into multiple peaks as shown in **Figure 4b**. The peak shoulder is attributed to the Cu<sup>2+</sup> state centering at ~933.7 eV. As discussed in the previous experiments, a higher reaction temperature could increase the oxidation rate by H<sub>2</sub>O<sub>2</sub> significantly, while the reduction rate by DEZ was not affected in the temperature range between 90 and 170 °C.

Thus, it can be concluded that the oxidation reaction by H<sub>2</sub>O<sub>2</sub> competes with the reduction reaction by DEZ in the a-ZTO ALD process. As the reaction temperature increases, the oxidation reaction becomes faster than the reduction reaction, possibly due to different activation energies. It should be noted that the CuO formation by H<sub>2</sub>O<sub>2</sub> is likely diffusion-limited by the a-ZTO layer: the oxidation by H<sub>2</sub>O<sub>2</sub> becomes weaker as the a-ZTO layer gets thicker; thus the a-ZTO layer appears to protect the Cu<sub>2</sub>O layer from further oxidation by H<sub>2</sub>O<sub>2</sub>. The Cu<sup>2+</sup> peak intensities relative to Cu<sup>1+</sup> shown in Figure 4b are much smaller than ones where only H<sub>2</sub>O<sub>2</sub> was injected, as shown in Figure 3. The protection of the substrate surface from the oxygen precursor by growing layers has also been proposed in other ALD processes.<sup>[27, 30]</sup> Our XPS results suggest that a lower reaction temperature for a-ZTO ALD is beneficial for reducing the CuO surface layer to Cu<sub>2</sub>O and preventing further re-oxidation by H<sub>2</sub>O<sub>2</sub>.

To demonstrate the effect of the interface chemistry control on solar cell performance, we fabricated Cu<sub>2</sub>O-based solar cells with a-ZTO ALD reaction temperatures at 50 – 170 °C. **Figure 5a** shows a cross-sectional scanning electron microscopy (SEM) image of the device structure: ZnO:Al TCO (80 nm) / a-ZTO buffer (10 nm) / Cu<sub>2</sub>O absorber (2.5 μm) / Au bottom electrode (200 nm). The ZnO:Al TCO layer was deposited *in situ* at 120 °C after the formation of the a-ZTO buffer layer on electrochemically-deposited Cu<sub>2</sub>O. Here, the first ALD reaction started with the injection of DEZ as discussed. Except for the ALD temperature

of the a-ZTO buffer layer growth, all processing parameters were identical for all devices. Devices with a-ZTO ALD temperatures of 150 and 170 °C showed slightly darker color than other devices, possibly due to a CuO layer formed at interface. The devices were completed by coating Al top-electrode (1  $\mu\text{m}$ ) and MgF<sub>2</sub> anti-reflective layer (95 nm).

As the analysis of ALD reactions predicted, decreasing the ALD temperature enhances the solar-cell device performance. Current-density *vs.* voltage (*J-V*) characteristics of the devices were measured under 1-sun (AM 1.5G, 100  $\text{mW}\cdot\text{cm}^{-2}$ ) illumination conditions as shown in **Figure 5b**. While the short-circuit current densities ( $J_{\text{SC}}$ ) remain between 7 and 8  $\text{mA}\cdot\text{cm}^{-2}$ , the  $V_{\text{OC}}$  shows a strong dependence on the a-ZTO ALD temperature. The changes of  $V_{\text{OC}}$  and PCE of the devices are summarized as a function of the a-ZTO ALD temperature in **Figure 5c**. By decreasing the ALD temperature down to 50 °C,  $V_{\text{OC}}$  increases up to 0.65 V. However, the devices with ALD temperatures over 150 °C show a significant reduction of  $V_{\text{OC}}$  below 0.3 V. This drastic change can be explained by the increase of CuO content at higher ALD temperatures, increasing defect density at the a-ZTO/Cu<sub>2</sub>O interface. The highest PCE of 3.06% is achieved with an a-ZTO ALD temperature of 70 °C. The device with an ALD temperature of 50 °C shows the highest  $V_{\text{OC}}$ , but its reduced fill-factor results in a lower PCE.

The possibility of bulk Cu<sub>2</sub>O thermal degradation was ruled out by an additional experiment. A heat treatment of a Cu<sub>2</sub>O layer at 150 °C before a-ZTO deposition at 70 °C was performed. The heat-treated device showed performance comparable to the device made without the heat treatment (**Figure S2**), suggesting that the high temperature during a-ZTO deposition degrades only the heterojunction interface.

The heterojunction quality of the fabricated devices is further investigated by measuring capacitance *vs.* frequency (*C-f*) characteristics as shown in **Figure 5d**. A direct-current bias of 0 V and an alternating-current bias of 10 mV were applied at room temperature. At high frequencies near 1 MHz, all devices show capacitances converging to 3 – 5  $\text{nF}\cdot\text{cm}^{-2}$ ,

which is close to a simple geometric capacitance ( $C_g \sim 2.7 \text{ nF}\cdot\text{cm}^{-2}$ ) due to dielectric freeze-out. At low frequencies, on the other hand, the capacitances plateau to a depletion capacitance ( $C_d$ ), which is dominated by the energy levels and densities of interfacial and bulk defects in the depleted region.<sup>[31]</sup> As the ALD temperature for a-ZTO decreases from 120 to 70 °C, the capacitance at 1 kHz decreases from 42.7 to 35.9  $\text{nF}\cdot\text{cm}^{-2}$ , which suggests reduced  $\text{Cu}^{2+}$ -related defect densities at the a-ZTO/ $\text{Cu}_2\text{O}$  interface. However, the ALD temperature of 50 °C shows a higher capacitance than that of 70 °C, possibly due to bulk defects in the a-ZTO layer. Too-low ALD reaction temperature often results in increased carbon and nitrogen-related impurities, which might be mitigated with plasma-assisted ALD.<sup>[32, 33]</sup>

The device with the highest efficiency was characterized independently at the National Renewable Energy Laboratory (NREL). The  $J$ - $V$  characteristic of the device under the ASTM G173 global 1-sun illumination is shown in **Figure 6**. The device was measured on a temperature-controlled stage, after a 10-minute light-soak at the maximum power condition (a forward bias of 0.49 V) and a 5-minute cool down. A spectral mismatch correction was applied using a normalized quantum efficiency (QE) spectrum (**Figure S3**) to measure accurate device performance. The device shows a PCE of 2.85%. The  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ , and fill-factor of the device are 622 mV, 7.25  $\text{mA}\cdot\text{cm}^{-2}$ , and 63.1%, respectively. A small discrepancy from the result shown in **Figure 5** is observed, which could be from a spectral mismatch of the light source and a different device temperature during the measurements. The measurement at NREL is the first verified efficiency of  $\text{Cu}_2\text{O}$ -based thin-film solar cells measured independently to date.

In summary, the presence of a deleterious CuO layer at the a-ZTO/ $\text{Cu}_2\text{O}$  interface can be minimized by optimizing the a-ZTO ALD process to reduce this layer to  $\text{Cu}_2\text{O}$ , enhancing the heterojunction open-circuit voltage. In our  $\text{Cu}_2\text{O}$  thin films grown by electrochemical deposition, a nanometer-scale thick CuO surface layer is formed by air exposure. Starting the first ALD sequence with the highly reactive DEZ pulse effectively reduces the CuO surface

layer to Cu<sub>2</sub>O by forming ZnO. As the ALD temperature is increased, re-oxidation of Cu<sub>2</sub>O to CuO by H<sub>2</sub>O<sub>2</sub> becomes a dominant reaction over the reduction of CuO by DEZ. By engineering the Cu<sub>2</sub>O surface chemistry with the a-ZTO ALD temperature, the chemical state of Cu at the interface can be controlled and the formation of a high-quality heterojunction is demonstrated. The controlled interface chemistry increases the V<sub>OC</sub> of a-ZTO/Cu<sub>2</sub>O solar cells, resulting in an independently verified PCE of 2.85%. This approach may also be useful in other material systems that employ ALD overlayers (buffer layers and TCOs), to improve interface quality by engineering cation chemical states locally at the interface.

### Experimental Section

*Atomic layer deposition of a-ZTO thin films:* The a-ZTO thin-films were deposited using a custom-built cylindrical ALD reactor with a sample stage 30 cm long and 3 cm wide, and a chamber volume of 0.627 L. The aluminum substrate stage and the entire wall of ALD chamber were kept at the same ALD reaction temperature inside a Lindberg Blue M tube furnace (Thermo Scientific). Diethylzinc (Sigma Aldrich) and 1,3-bis(1,1-dimethylethyl)-4,5-dimethyl-(4R,5R)-1,3,2-diazastannolidin-2-ylidene were used as Zn and Sn precursors, respectively. The Zn and Sn precursors were kept at constant temperature of 25 and 40 °C, respectively. A H<sub>2</sub>O<sub>2</sub> solution (50 wt.% in H<sub>2</sub>O, Sigma Aldrich) was used as a common oxidant for a-ZTO growth to enable the ALD reaction with the Sn(II) precursor at reaction temperature below 170 °C, which was not possible by using H<sub>2</sub>O. Due to a high vapor pressure of H<sub>2</sub>O<sub>2</sub>, as-received H<sub>2</sub>O<sub>2</sub> solution was placed in a glass container held at 25 °C and it was vaporized into a trap, which is made of stainless steel with a volume of 35 mL, prior to the release into the ALD reactor. One super-cycle of a-ZTO consisted of ZnO and SnO<sub>2</sub> sub-cycles with a ratio of 3:1. During the each sub-cycle, the exposures of diethylzinc, tin precursor, and H<sub>2</sub>O<sub>2</sub> were estimated to be approximately 0.32, 0.033, and 0.027 Torr·s,

respectively. Further details on electrical, structural, and optical properties of a-ZTO films grown by ALD are described elsewhere.<sup>[9,34]</sup>

*Solar Cell Fabrication:* A 200-nm-thick Au bottom-electrode with 5-nm-thick Ti adhesion layer was deposited on a  $1 \times 1$  inch<sup>2</sup> SiO<sub>2</sub> by e-beam evaporation. To define a cell area of  $3 \times 5$  mm<sup>2</sup>, a 2.5- $\mu$ m-thick SiO<sub>2</sub> layer was deposited by plasma-enhanced chemical vapor deposition and areas defined by photolithography were etched by a buffered-oxide-etchant (7:1, J. T. Baker). A 2.5- $\mu$ m-thick Cu<sub>2</sub>O film was deposited on the exposed Au area at 40 °C by the galvanostatic electrochemical method.<sup>[9,35,36]</sup> A lactate-stabilized copper sulfate aqueous solution was prepared with 3 M lactic acid (Sigma Aldrich), 0.2 M cupric sulfate pentahydrate (CuO<sub>4</sub>·5H<sub>2</sub>O, Sigma Aldrich) and de-ionized water (18.3 M $\Omega$ ·cm, Ricca Chemical), and then 2 M sodium hydroxide (NaOH, Sigma Aldrich) aqueous solution was added to adjust the pH of the solution to 12.5. All reagent-grade chemicals were used and the solution was filtered and stirred thoroughly. A constant current density of 0.23 mA·cm<sup>-2</sup> was applied for 2 hours using a Keithley 2400 sourcemeter with a Pt counter electrode to grow the Cu<sub>2</sub>O films. The Cu<sub>2</sub>O film surfaces were rinsed with de-ionized water. The a-ZTO and ZnO:Al thin-films were deposited by ALD as described in detail elsewhere.<sup>[9]</sup> 1- $\mu$ m-thick Al top-electrodes were deposited by e-beam evaporation with a grid spacing of 0.5 mm defined by a lift-off process. A 95-nm-thick MgF<sub>2</sub> film as an anti-reflective layer was deposited by thermal evaporation.

*Characterization:* Surface morphologies of the devices were analyzed using an Ultra 55 FESEM (Zeiss). XPS measurements were performed using a K-alpha XPS (Thermo Scientific). Samples were etched *in situ* by an Ar ion beam for a depth profiling. The *J*-*V* and the *C*-*f* characteristics of the devices were measured by using Agilent 4156C and Keithley 2400 semiconductor characterization systems. The standard 1-sun illumination was generated by a Newport Oriel 91194 solar simulator with a 1600W ozone-free Xe-lamp with a AM1.5G

filter and a Newport Oriel 6895 flux controller calibrated by an NREL-certified Si reference cell equipped with a BG-39 window.

## **Supporting Information**

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

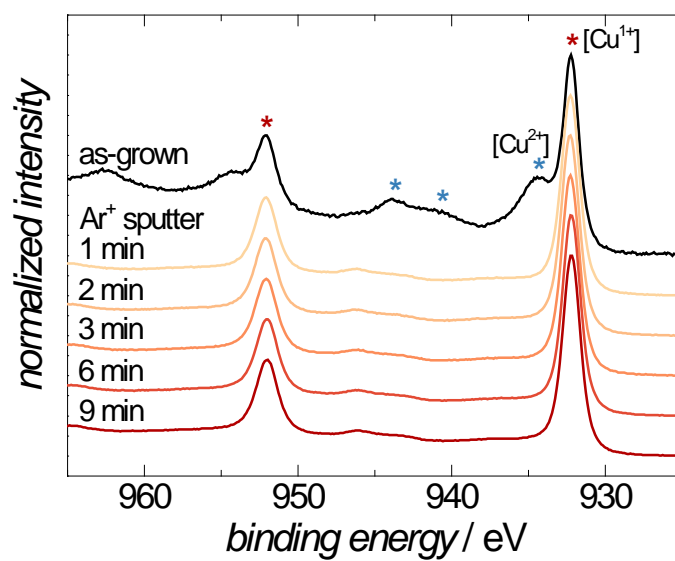
## **Acknowledgements**

We thank P. Cizek and the NREL cell measurement team for assistance with certified cell testing. This work was supported by the Office of Naval Research ONR N00014-10-1-0937, the National Science Foundation (NSF) award CBET-1032955, and NSF CAREER award ECCS-1150878. This work made use of the Center for Nanoscale Systems at Harvard University and the Microsystems Technology Laboratories at MIT supported by NSF awards ECS-0335765 and DMR-0819762, respectively. A Clean Energy Scholarship from NRF Singapore (S.C.S.) and an NSF Graduate Research Fellowship (R.E.B.) are acknowledged.

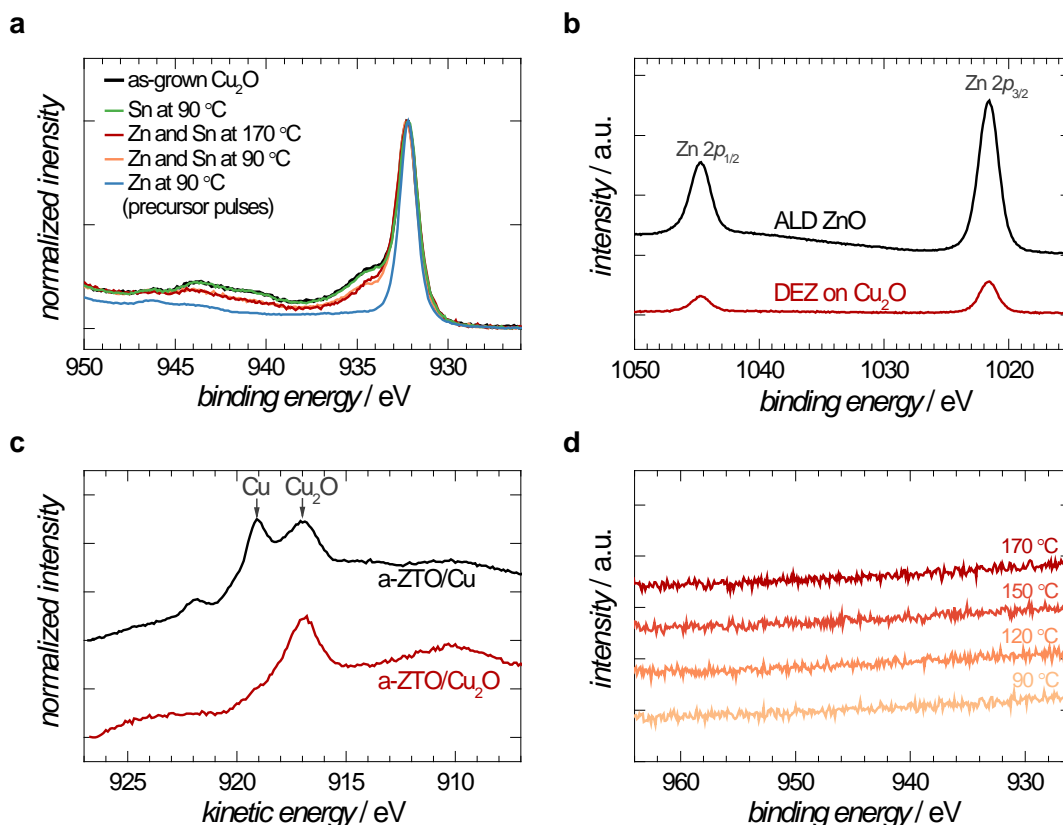
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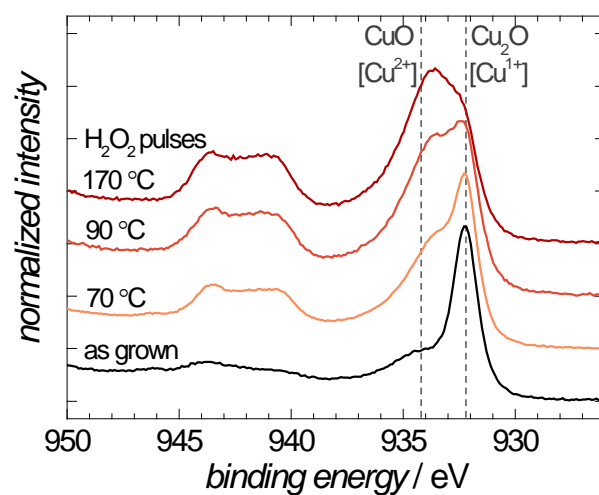


**Figure 1.** XPS spectra of Cu-2p core levels for an as-grown Cu<sub>2</sub>O film surface and sputtered surfaces by Ar-ion at 1 keV *in situ*. The peaks from Cu<sup>1+</sup> and Cu<sup>2+</sup> states are shown in red and blue asterisks respectively. The native CuO surface layer, which is removed by sputtering, is estimated to be 1 nm thin.

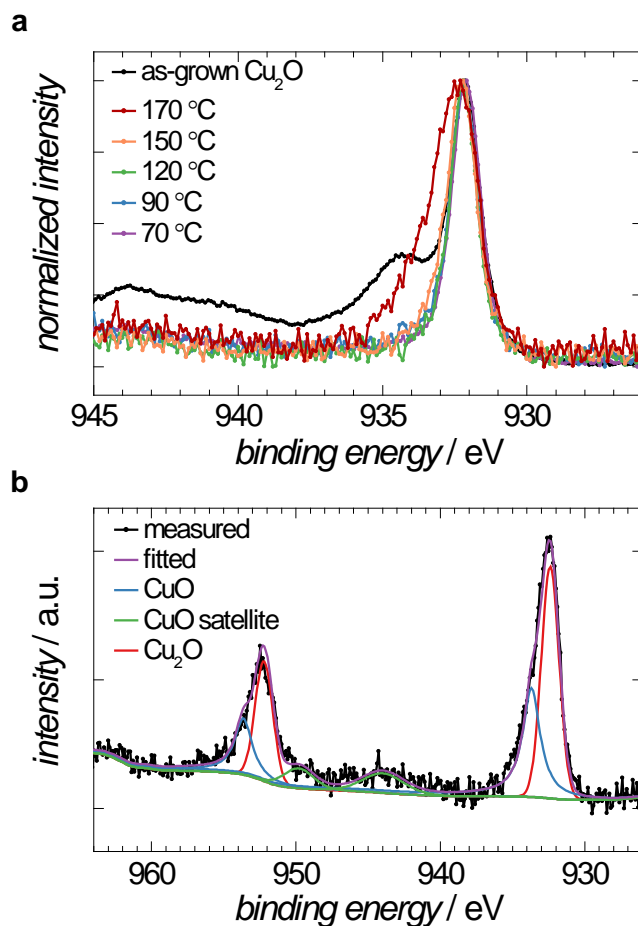


**Figure 2.** The Zn precursor in the a-ZTO ALD process is experimentally observed to reduce the oxidation state of the Cu<sub>2</sub>O absorber's native CuO surface layer to Cu<sub>2</sub>O. **(a)** Normalized XPS spectra of Cu-2*p* of Cu<sub>2</sub>O surface after a pulse of DEZ and Sn(II) molecules on electrochemically-deposited Cu<sub>2</sub>O films having nanometer-scale-thick CuO surface layers. **(b)** XPS spectra of Zn-2*p* core levels after a pulse of only DEZ molecules on the Cu<sub>2</sub>O film at 90 °C, showing same Zn-2*p* core level with ZnO film grown by ALD using DEZ and H<sub>2</sub>O<sub>2</sub>. **(c)** The Cu-LMM kinetic energies from Cu<sub>2</sub>O and metallic Cu after the growth of a-ZTO layer by ALD at 90 °C. (20-nm-thick Cu film was prepared by e-beam evaporation at room temperature for the comparison). **(d)** XPS spectra of Cu-2*p* core levels with 10-nm-thick a-ZTO films deposited on Cu<sub>2</sub>O at reaction temperatures between 90 and 170 °C, showing no signal from elemental Cu for all temperatures, which indicates no Cu diffusion occurred.

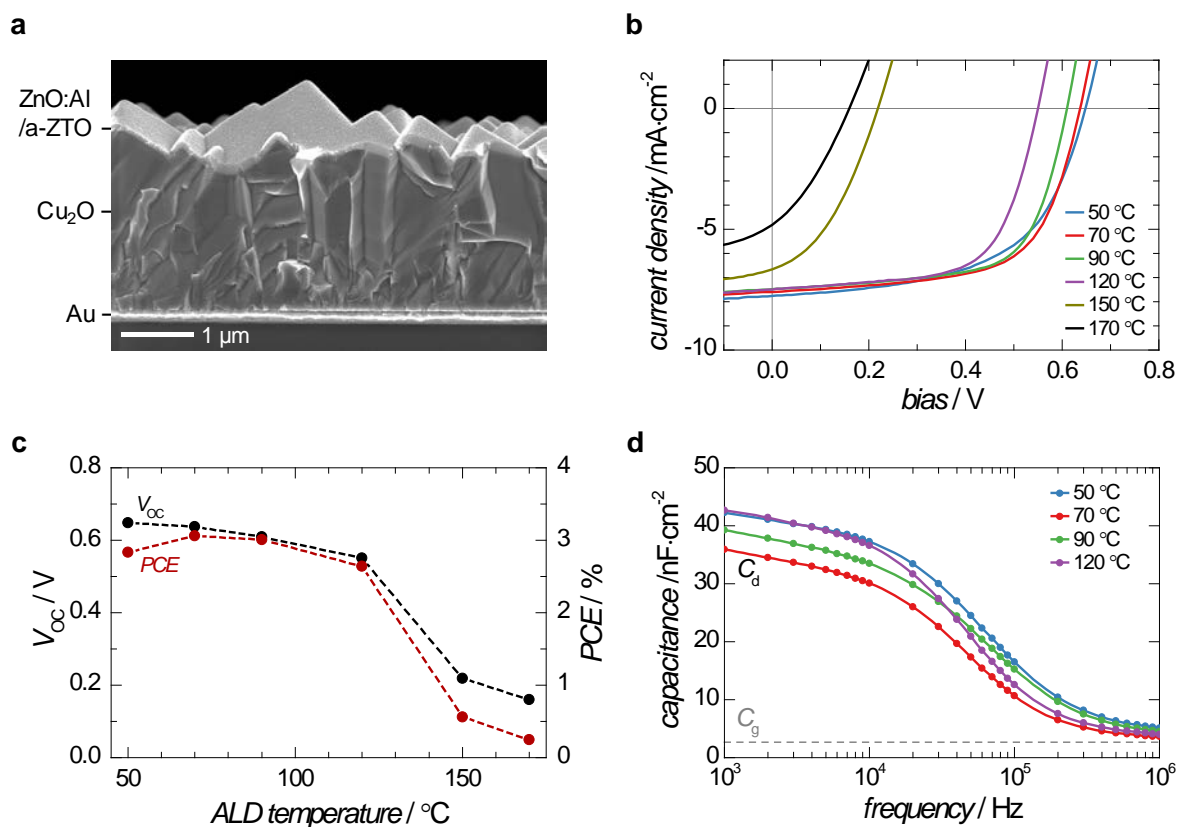




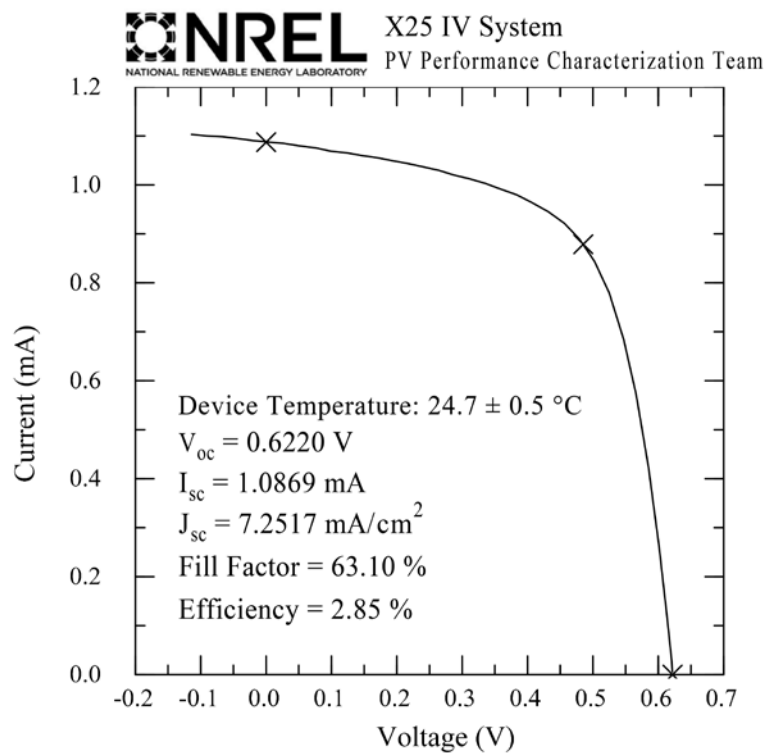
**Figure 3.** H<sub>2</sub>O<sub>2</sub> exposure can re-oxidize the Cu<sub>2</sub>O surface layer to CuO. Shown are normalized XPS spectra of Cu-2p for three different Cu<sub>2</sub>O films. Only H<sub>2</sub>O<sub>2</sub> pulses were injected on Cu<sub>2</sub>O samples at reaction temperatures of 90 and 170 °C.



**Figure 4.** ALD reaction temperature can control the oxidation state of the Cu<sub>2</sub>O surface layer. **(a)** Normalized XPS spectra of Cu-2p from the Cu<sub>2</sub>O samples after the growth of a-ZTO films at reaction temperatures between 90 and 170 °C. **(b)** The deconvoluted XPS spectra of Cu-2p of Cu<sub>2</sub>O surface with a-ZTO film grown at 170 °C, showing a peak shoulder at ~933.7 eV corresponding to the Cu<sup>2+</sup> state.



**Figure 5.** Characteristics of solar cell devices with varying Cu oxidation state at the Cu<sub>2</sub>O/a-ZTO interface controlled by ALD temperature. **(a)** A cross-sectional SEM image of Cu<sub>2</sub>O-based solar cells with the device structure (ZnO:Al / a-ZTO / Cu<sub>2</sub>O / Au). **(b)**  $J-V$  characteristics of the devices under 1-sun (AM 1.5G) illuminated conditions. **(c)** A summary of  $V_{OC}$  and PCE of the devices as a function of the a-ZTO ALD temperature. **(d)**  $C-f$  characteristics of solar cell devices at room temperature with 0 mV and 10 mV for DC and AC bias, with a-ZTO films at reaction temperatures between 50 and 120 °C.



**Figure 6.** NREL certified  $J$ - $V$  characteristics of the best device, with an a-ZTO buffer layer grown at 70 °C, under 1-sun (ASTM G173 global) illumination.

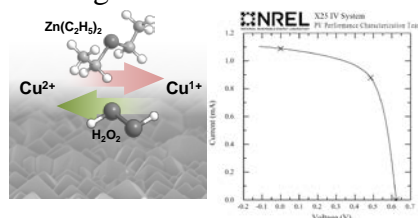
Solar cells are produced by atomic layer deposition (ALD) of *n*-type amorphous zinc-tin-oxide buffer layers on electrochemically-deposited *p*-type cuprous oxide, Cu<sub>2</sub>O, absorber layers. The diethylzinc precursor in the ALD process reduces Cu<sup>2+</sup>-related defects at the heterojunction interface, improving the solar-cell open-circuit voltage. An NREL-certified power conversion efficiency of 2.85% is reported.

**Keywords:** surface modification, solar cells, interface recombination, photovoltaic devices, thin films

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### Improved Cu<sub>2</sub>O-based solar cells using atomic layer deposition to control the Cu oxidation state at the *p-n* junction

ToC figure



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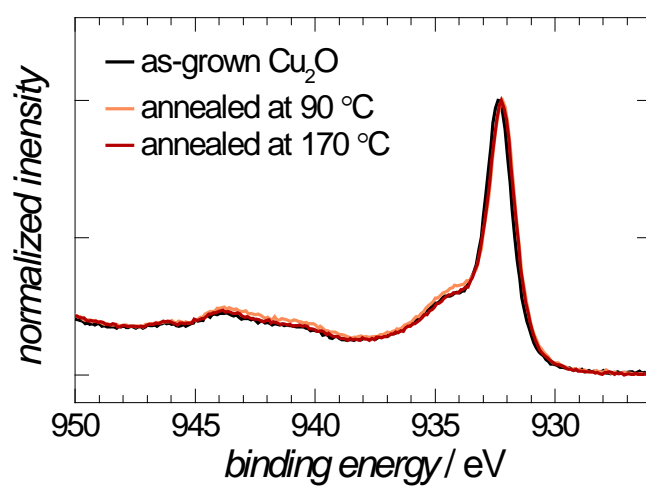
## Supporting Information

**Improved Cu<sub>2</sub>O-based solar cells using atomic layer deposition to control the Cu oxidation state at the *p-n* junction**

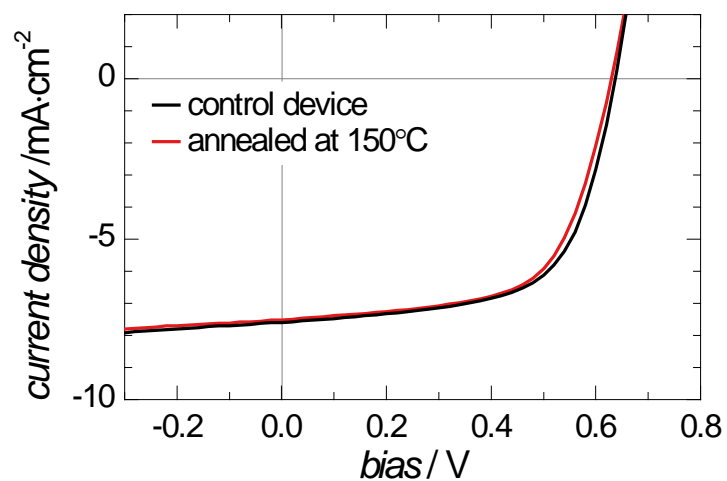
*Sang Woon Lee*<sup>†</sup>, *Yun Seog Lee*<sup>†</sup>, *Jaeyeong Heo*, *Sin Cheng Siah*, *Danny Chua*, *Riley E. Brandt*, *Sang Bok Kim*, *Jonathan P. Mailoa*, *Tonio Buonassisi*<sup>\*</sup>, and *Roy G. Gordon*<sup>\*</sup>

A control experiment was performed to investigate a background influence of ALD chamber on the XPS spectra of Cu-2*p* of Cu<sub>2</sub>O samples. The Cu<sub>2</sub>O samples were kept in the ALD chamber without doing any ALD treatments at 90 and 170 °C for the same duration with the actual ALD process. Negligible change of XPS spectra is noted as shown in **Figure S1**. A possible degradation of Cu<sub>2</sub>O solar cell performance was examined by an intentional heating of Cu<sub>2</sub>O sample at a higher temperature of 150 °C prior to the actual deposition of a-ZTO buffer layer. The Cu<sub>2</sub>O sample was heated at 150 °C for two hours. Then, the deposition of a-ZTO buffer layer was proceeded at 70 °C. *J-V* characteristics of the devices were compared for the cells with and without the intentional heating of Cu<sub>2</sub>O sample. **Figure S2** does not show any degradation by the heating of Cu<sub>2</sub>O sample at 150 °C.

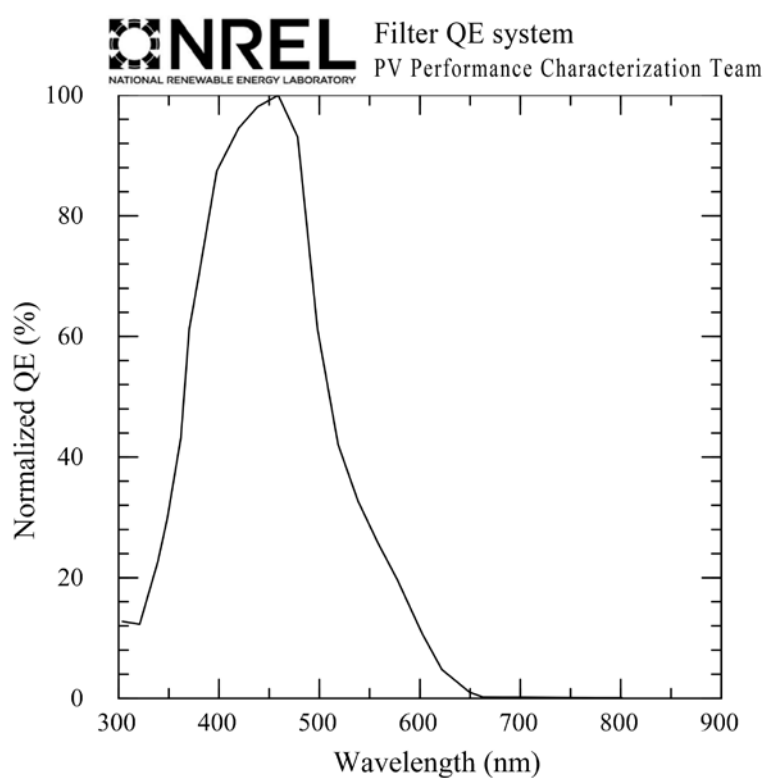




**Figure S1** Normalized XPS spectra of Cu-2*p* of Cu<sub>2</sub>O surfaces before and after heat treatments. As grown Cu<sub>2</sub>O samples were kept in the ALD chamber under vacuum without ALD treatment. The same duration with the ALD treatment was used.



**Figure S2** *J-V* characteristics of the devices under 1-sun (AM 1.5G) illuminated conditions with and without the additional heat treatment of Cu<sub>2</sub>O film at 150 °C for 2 hours under vacuum, before the deposition of a-ZTO buffer layer at 70 °C and ZnO:Al layer at 120 °C.



**Figure S3** Normalized QE spectrum of the device with a-ZTO buffer layer grown at 70 °C. A filtered QE system at NREL was used.