Ultrathin amorphous zinc-tin-oxide buffer layer for enhancing heterojunction interface quality in metal-oxide solar cells

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Supporting Information

1. Optical absorption of a-ZTO thin-films

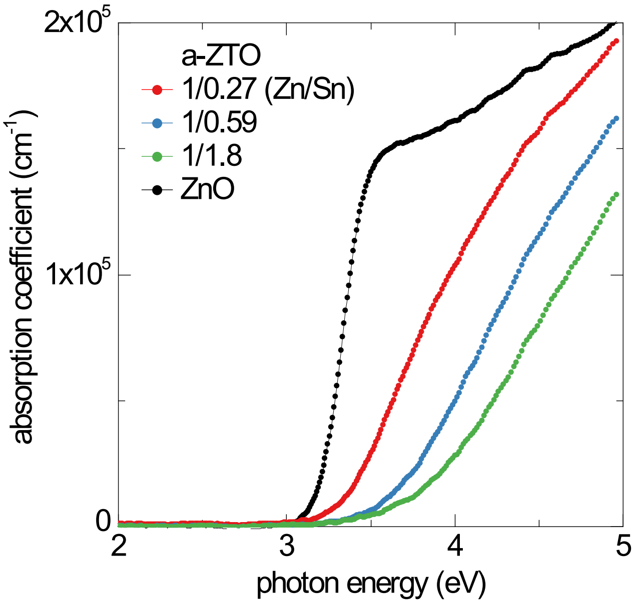

Figure S1. Optical absorption coefficient of atomic layer deposited a-ZTO and ZnO thin-films (sample thickness: ~ 40 nm). Increasing Sn content in a-ZTO films reduces high energy photon absorption.

2. Band offset measurement

The valence band offset (ΔE_{VB}) at the heterojunction was calculated by using the following equation:

$$\Delta E_{VB} = (E_{Cu2p}^{a-ZTO/Cu_2O} - E_{Zn2p}^{a-ZTO/Cu_2O}) + (E_{Zn2p}^{a-ZTO} - E_{VBM}^{a-ZTO}) - (E_{Cu2p}^{Cu_2O} - E_{VBM}^{Cu_2O}), \quad \text{(S1)}$$

where $(E_{Cu2p}^{a-ZTO/Cu_2O} - E_{Zn2p}^{a-ZTO/Cu_2O})$ is the binding energy difference between the Cu-2*p* and Zn-2*p* core levels measured at the Cu_2O/a-ZTO interface. $(E_{Zn2p}^{a-ZTO} - E_{VBM}^{a-ZTO})$ and $(E_{Cu2p}^{Cu_2O} - E_{VBE}^{Cu_2O})$ are the positions of the core level peaks referenced to the valence band maximum (VBM). Subsequently, the conduction band offset (ΔE_{CB}) can be determined by using the following relation:

$$\Delta E_{CB} = \Delta E_{VB} - (E_g^{a-ZTO} - E_g^{Cu_2O}), \quad \text{(S2)}$$

where $E_g^{Cu_2O}$ and E_g^{a-ZTO} are the bandgaps of Cu_2O and a-ZTO, respectively.

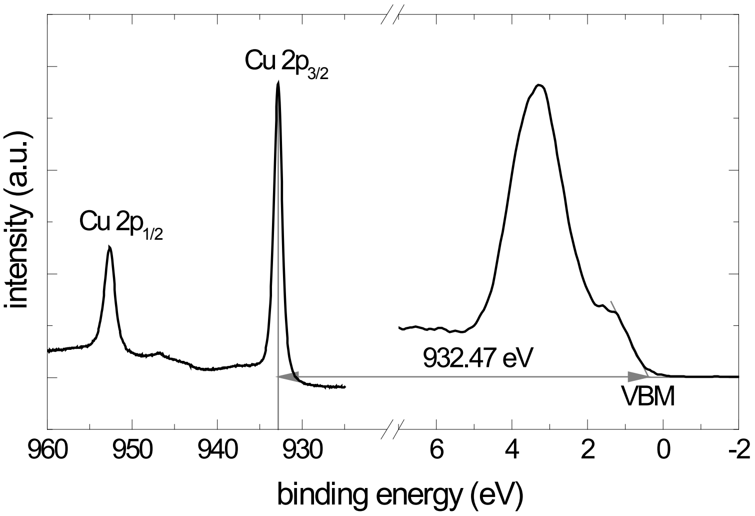

Figure S2. XPS spectra of electrochemically deposited Cu_2O thin-films. The films show only Cu^{1+} state for Cu_2O. The characteristic peaks of CuO (Cu^{2+} state) at 940 – 945 eV[1] were not detected. Cu $2p_{3/2}$ core level spectra show a relative energy level of 932.47 eV reference to VBE.

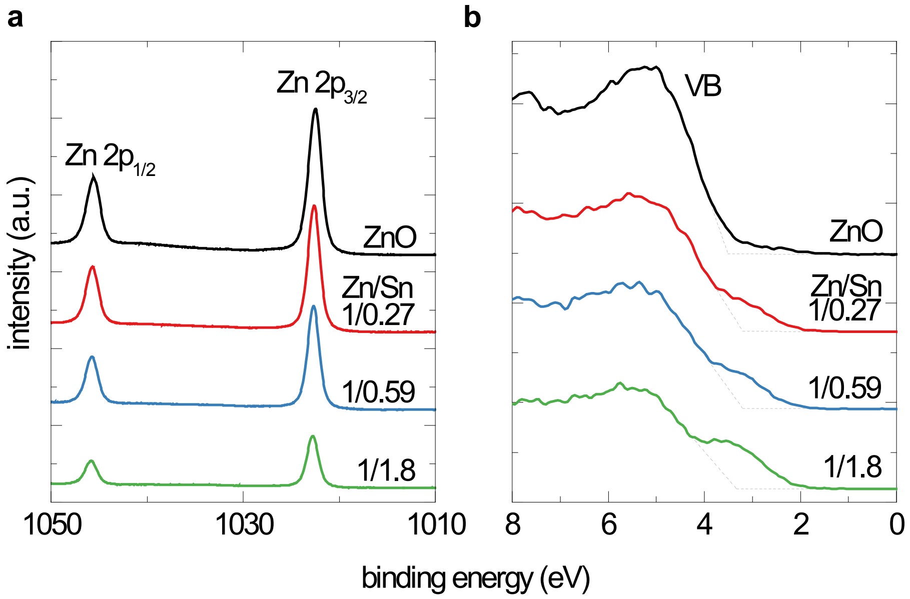

Figure S3. XPS spectra of (a) Zn core level and (b) valence band for atomic layer deposited a-ZTO and ZnO thin-films. Zn 2p$_{3/2}$ core level peaks of ZnO and a-ZTO with a Zn/Sn ratio of 1/0.27, 1/0.59 and 1/1.8 exhibit relative energy levels of 1019.02, 1019.44, 1019.57, 1019.47 eV in reference to their VBEs, respectively. In this analysis, small humps near the valence band edges of a-ZTO are attributed to tail states in the bandgap[2] which originate from increased SnO_2 content. The hump near the VBE of SnO_2 is often observed in photoelectron spectroscopy when a high energy photon source is used[3], though the states are not expected from theoretical calculations[4, 5]. The valence band edge is also measured by UPS to investigate the band tail states (Figure S4).

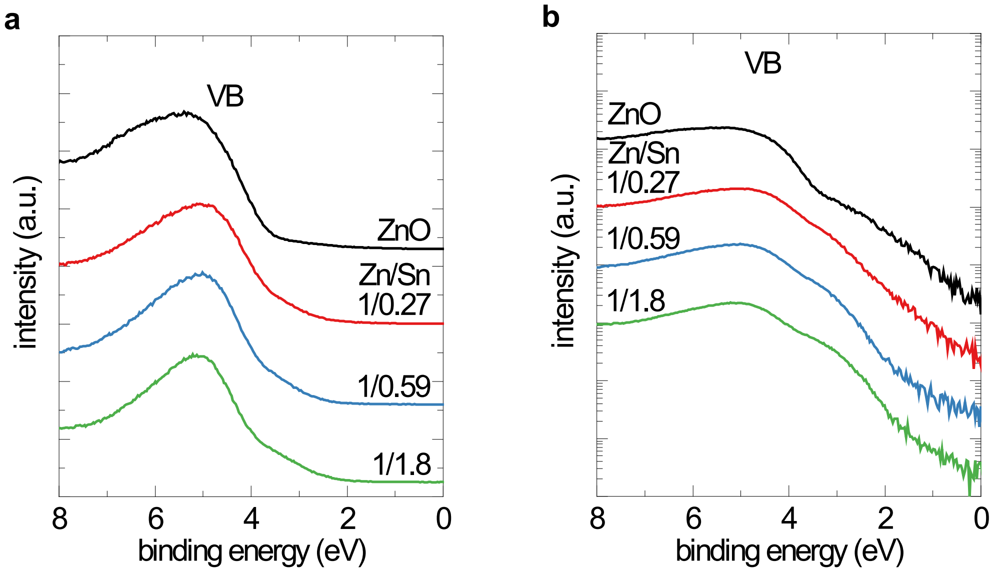

Figure S4. UPS spectra of valence band on (a) a linear scale and (b) a semi-log scale for atomic layer deposited a-ZTO and ZnO thin-films measured by using a He-I photon source ($h\nu$ = 21.2 eV). The intensities of small humps near the valence band edges of a-ZTO are smaller than the spectra from XPS. The signal intensity from the hump near the valence band edge of the a-ZTO films increases as the Sn content increases in the films, indicating an increased density of tail states.

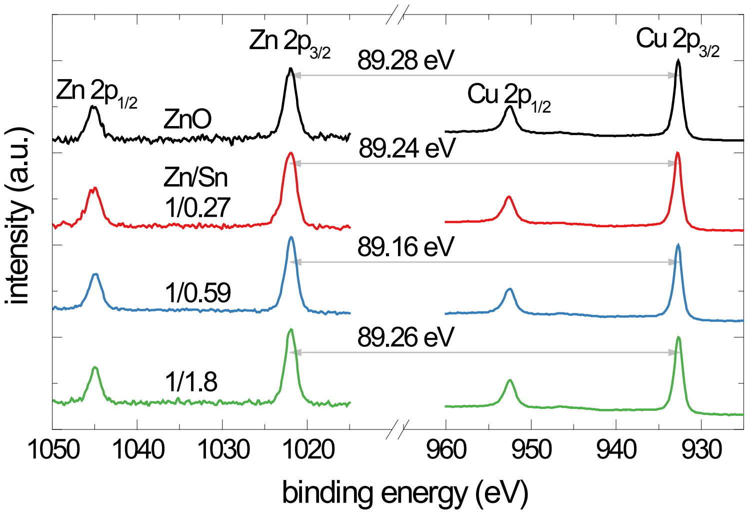

Figure S5. XPS spectra of Zn and Cu core levels from 2-nm-thick ZnO and a-ZTO films on Cu_2O thin-films.

3. QE simulation

In the FDTD simulation, we modelled the device as a textured 2-dimensional layer stack. The Cu_2O texture was characterized using an AFM and had a feature size of approximately 1 μm. To properly incorporate the randomness of this texture, the FDTD simulation area was chosen to be 10 μm wide. Incident light with TM polarization was then used to simulate the light propagation with 300 – 650 nm wavelength range within this structure. We used FDTD Solutions software (Ver. 7.5, Lumerical, Inc.) to calculate the electromagnetic field profile inside the Cu_2O as a function of space and frequency. Using this electromagnetic field profile, we calculated the divergence of the Poynting vector to obtain the power absorption per unit volume as a function of space and frequency inside the Cu_2O. We further simulated the EQE of the device using this optical absorption profile. We modelled a collection probability function for photo-generated carriers as shown in **Figure S6**. EQE was calculated using the equation:

$$EQE(\lambda) = \frac{\iint P_{ABS}(x, y, \lambda) CP(x, y)\, dx\, dy}{P_{TOTAL}(\lambda)} \qquad \text{(S3)}$$

, where $P_{\mathrm{ABS}}(x, y, \lambda)$ is the spatial profile for power absorption per unit volume for a specific wavelength, $CP(x, y)$ is the spatial profile for carrier collection, and $P_{\mathrm{TOTAL}}(\lambda)$ is the total incident power per unit length for a specific wavelength.

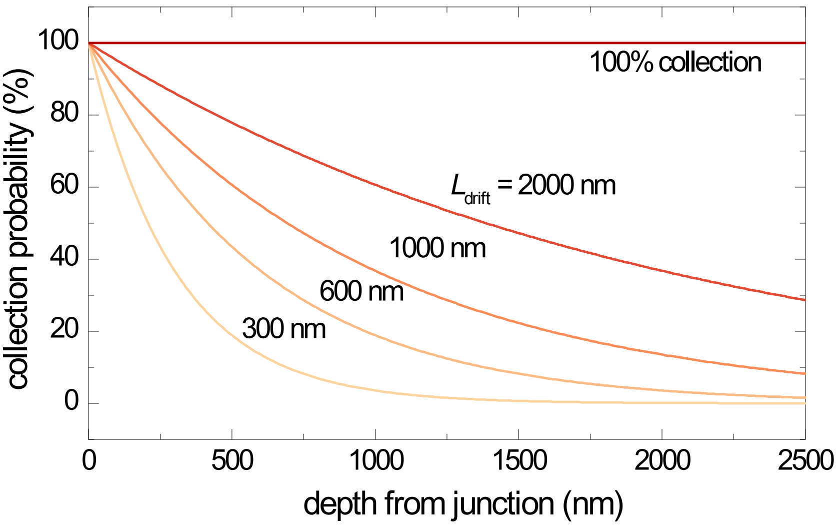

Figure S6. Modelled collection probability profiles for photo-generated carriers in the Cu_2O layer.

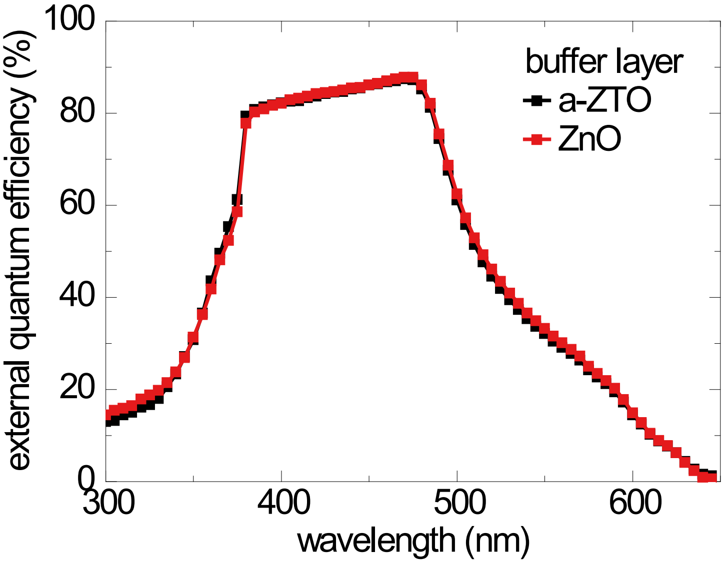

Figure S7. Measured external quantum efficiencies of the devices with a-ZTO (Zn/Sn = 1/0.27) and undoped ZnO buffer layers at zero bias condition.

Reference

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