Electronic Supplementary Material (ESI) for Energy & Environmental Science.


# Supporting information

## Cd-free $Cu_2ZnSnS_4$ solar cell with an efficiency greater than 10 % enabled by $Al_2O_3$ passivation layers

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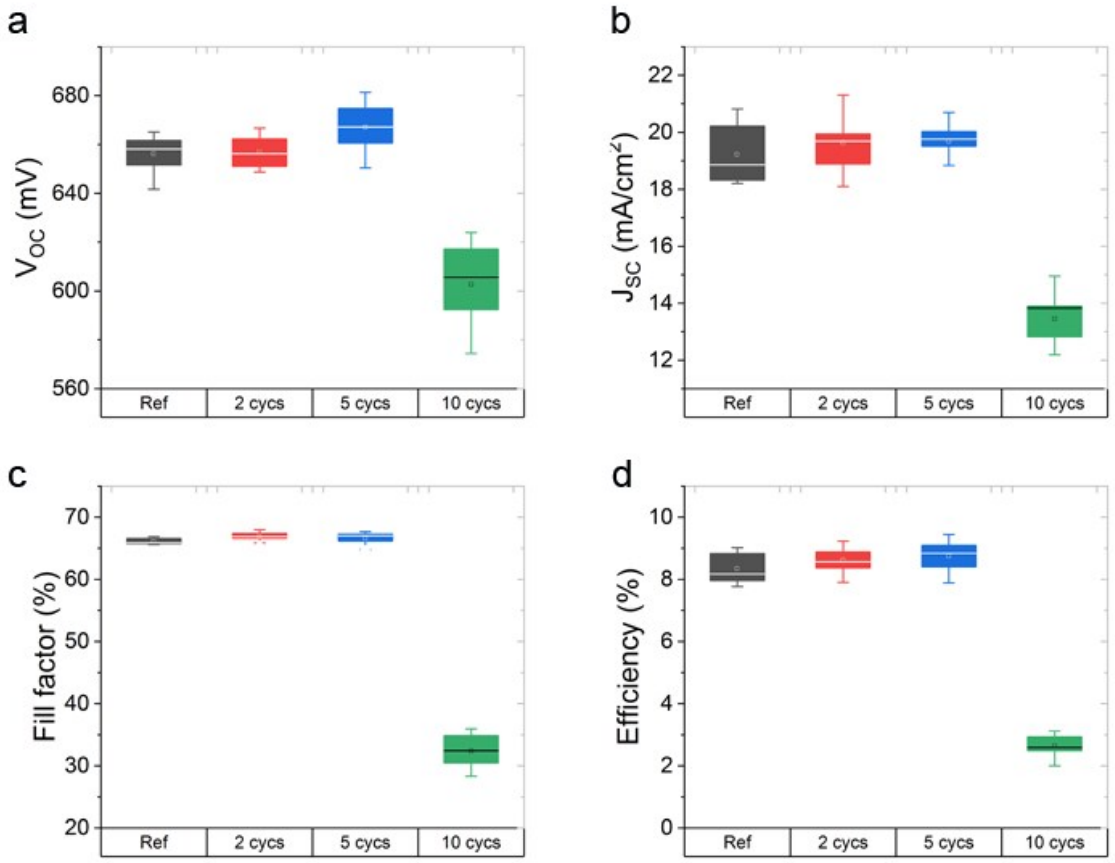

**Figure S1.** a-d) Box-plot diagram of the one-sun solar cell parameters of CZTS cells as a function of the number of ALD cycles used for the $Al_2O_3$ passivation layer. 10 CZTS solar cells were fabricated per experimental condition. The box, horizontal bars, and point symbols indicate the 25/75 percentile, min/max and mean values, respectively.

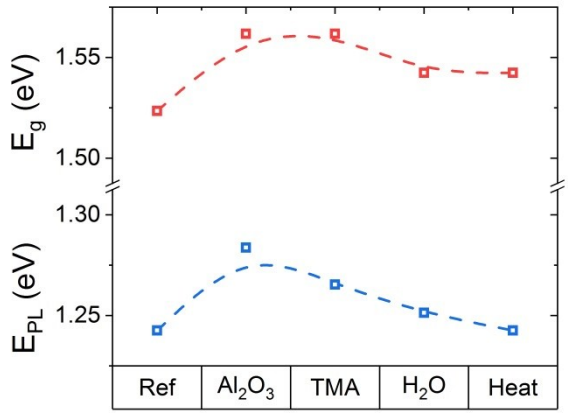


**Figure S2.** Bandgap values extracted from the EQE measurements and PL peak position for devices with various ALD treatment. The inflection point of the EQE was used to determine the bandgap ($E_g$), Dash lines are plotted for guiding purpose.

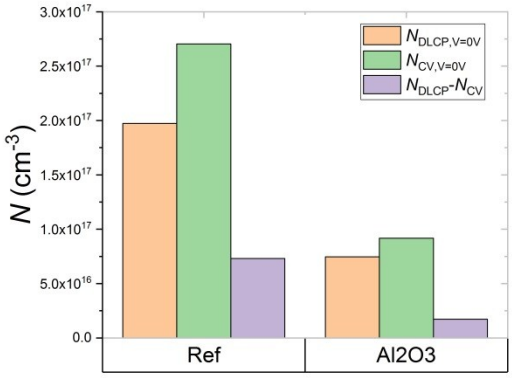


**Figure S3.** Defect density $N_{DLCP}$ and $N_{CV}$ at $V_{dc}$ = 0 derived from *C-V* and DLCP measurements of devices with different ALD treatment, respectively.

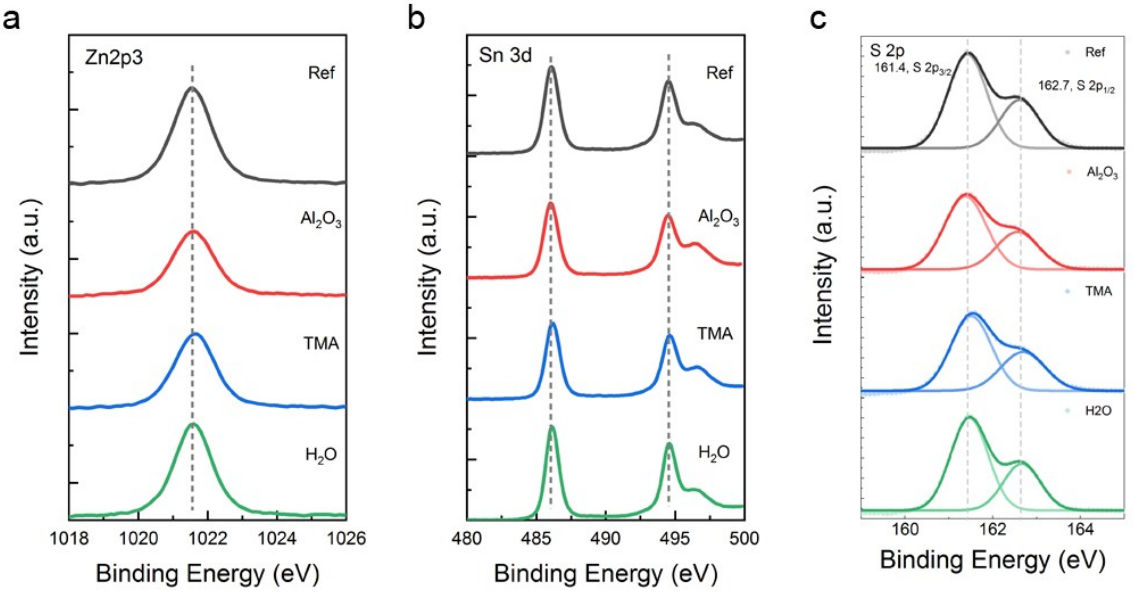


**Figure S4.** a-c) XPS peak of Zn 2p3, Sn 3d, S 2p, respectively, obtained from the surface of CZTS absorbers with no treatment (Ref), $Al_2O_3$ treatment, TMA treatment, and $H_2O$ treatment.

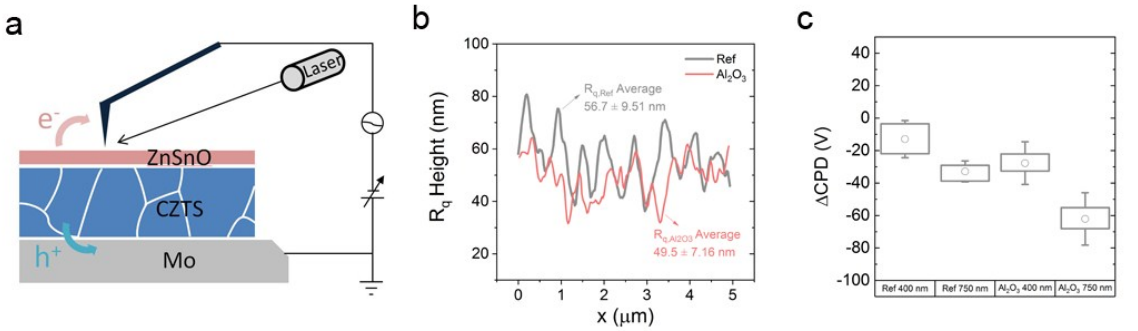


**Figure S5.** a) KPFM set up under illumination. b) Root-mean-square (RMS) roughness ($R_q$) distribution profile across the captured images in Figure 5a,e. c) Average CPD values difference between dark and light at an illumination intensities of 894 mW/cm$^2$ (400 nm) and 12000 mW/cm$^2$ (750 nm) for the reference and $Al_2O_3$ treatment samples. Measurements were taken at a wavelength of 400 nm and 750 nm.

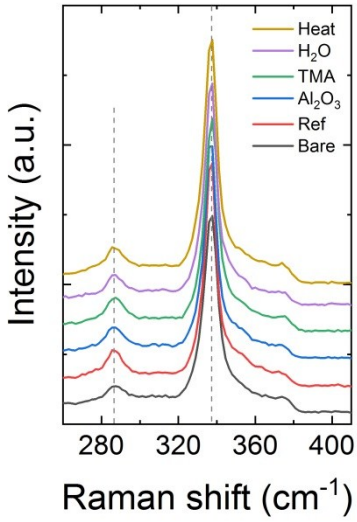


**Figure S6.** Raman spectra for bare CZTS absorbers and CZTS/ZnSnO after different ALD treatment. An excitation wavelength of 514 nm was used for the measurements.

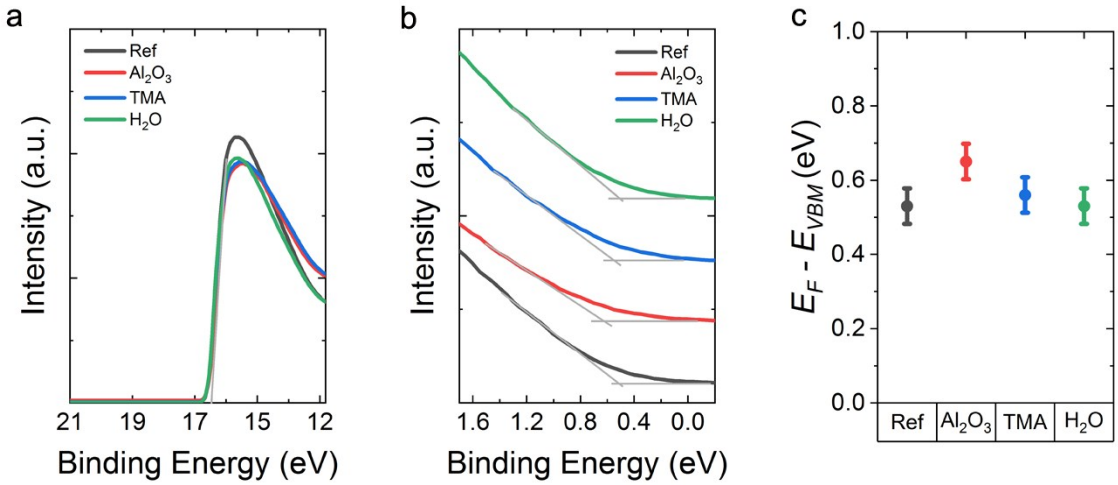


**Figure S7.** a, b) UPS spectra of the CZTS absorbers with different ALD treatment. c) Energy band positions for CZTS absorbers of valance band maximum with respect to Fermi level energy, $E_F$.