

Electronic Supplementary Material for: **Open-Air, Low-Temperature Deposition of Phase Pure Cu₂O Thin Films as Efficient Hole-Transporting Layers for Silicon Heterojunction solar cells**

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Experimental

SHJ Cell fabrication and characterization

In this work, a high-quality Czochralski (CZ) n-type crystalline Si (<100>, 170 μm thick, 1-5 $\Omega\cdot\text{cm}$) absorber was used for SHJ cell fabrication. The full-sized ($\sim 244.33\text{ cm}^2$) wafers were textured on both sides (KOH solution) and cleaned using an automatic wet bench from AKRION. Thin hydrogenated amorphous silicon (a-Si:H) layers were deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD): an intrinsic (i) a-Si:H layer on the rear side and (i) a-Si:H/(n) a-Si:H stack on the front. The undoped layers allow obtaining good c-Si absorber surface passivation properties while the n-doped layer generates a front surface field for enhanced electron collection. p-doped a-Si:H layers were deposited by PECVD at the rear side of the reference samples to form the typical rear emitter SHJ as reference. All the full-size wafers were cleaved into $5\times 5\text{ cm}^2$ substrates, maximum size compatible with the SALD reactor. Samples without the a-Si:H(p) layer received the Cu_2O deposition using SALD on top of the rear side a-Si:H(i) layer. Front and back Indium Tin Oxide (ITO) transparent electrodes with a thickness of about 75 nm and sheet resistance of about 60 Ω/sq were then deposited by sputtering on an area of $3\times 3\text{ cm}^2$. Finally, for the front and back electrodes, a low-temperature Ag paste was deposited using a screen-printing technique followed by an annealing treatment at 200 $^\circ\text{C}$ for several minutes. Photoluminescence (PL) images were obtained using LIS-R2 equipment from BTI at 1 sun intensity and 0.2 seconds integration time while carrier lifetime measurements were carried out with a WCT-120 tool from Sinton Consulting. Both methods are useful to investigate the homogeneity of the passivation properties and determine implied V_{oc} values prior to cell metallization. Current-Voltage (J-V) curves of all the devices were characterized under AM 1.5G 1 sun spectrum illumination using a designated area of $3\times 3\text{ cm}^2$. External Quantum Efficiency

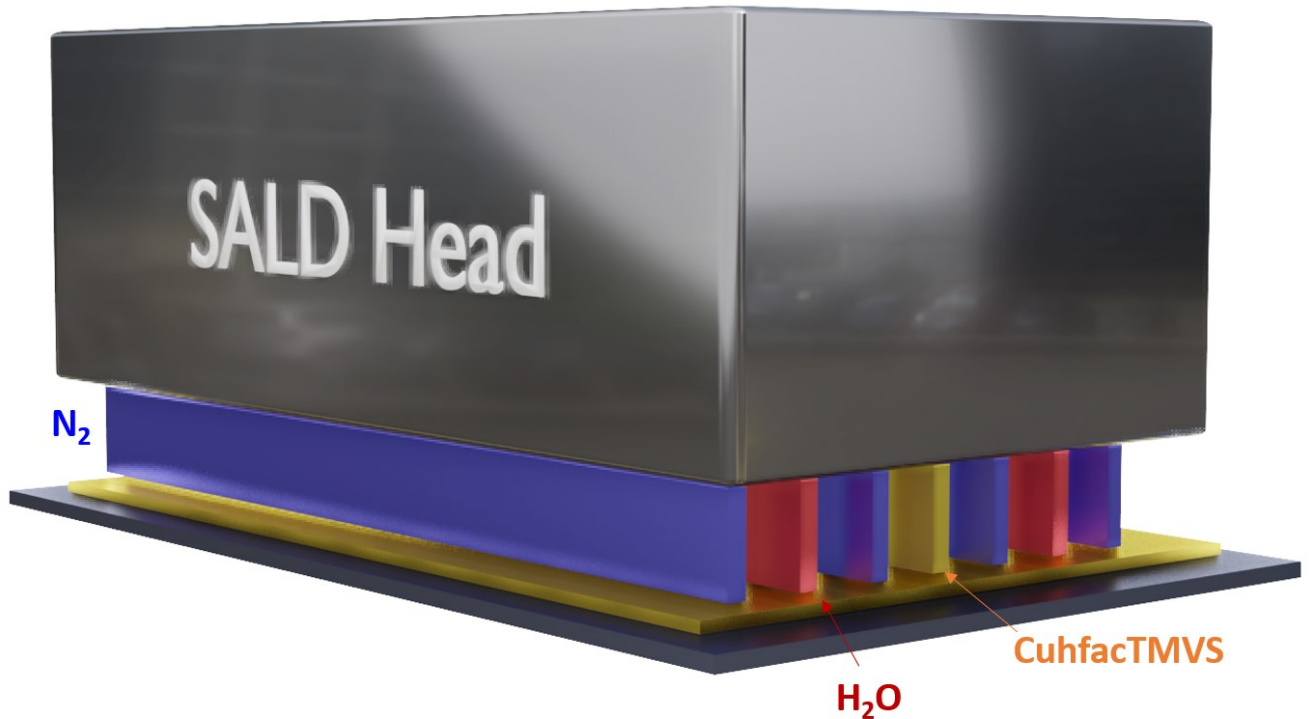
measurements were performed with a large area set up (illumination area of 160x160 mm²) using the same designated area as for J-V testing.

Cu₂O thin film deposition and characterization

The cuprous oxide deposition was done using a home-built atmospheric pressure spatial atomic layer deposition system. Cupraselect® (hexafluoroacetylacetonate)-Cu(I)-(trimethylvinylsilane) was used as Cu precursor.⁴² The deposition temperature was kept at low values (≤ 220 °C) to avoid any degradation of the SHJ based device. The thickness of the Cu₂O films was chosen at 10 nm and 80 nm for 220 °C and kept fixed at 60 nm for films deposited at 200 °C, with a growth rate around 1 ± 0.8 nm/min.

The injection SALD manifold-head, shown in Fig.SI1, contains one metal precursor outlet, separated from the oxidizing agent outlets by inert gas barriers alternatively located in between the reactive gas flows to prevent them from mixing. The Cu precursor was heated at 65 °C and the transport line between the bubbler and the manifold injection head was heated at 70 °C to avoid any condensation of the precursors in the lines. The nitrogen flows bubbled through the precursor with a mass flow of 60 sccm that is diluted in extra nitrogen flow (60 sccm) before being sent to the injection head. Finally, the nitrogen barrier flow was adjusted to obtain a flow of 120 sccm per outlet. The precursor and water are injected continuously from the manifold head onto the substrate that oscillates at a scanning speed of 10 cm/s. Films were deposited on a silicon heterojunction solar cell with a surface area of 10 cm², the cell was covered with a mask to ensure a 9 cm² coating.

Fig S11: Scheme of the close-proximity SALD manifold head used to deposit 9 cm² of Cu₂O on 10 cm² SHJ solar cell



Several physicochemical analyses were used to characterize our samples: SEM-FEG GeminiSEM 300 equipment was used for top view and cross-section imaging of the device. The optical properties were investigated with a lambda 950 spectrophotometer from Perkin Elmer to measure the transmission within the range of 250-2500 nm. The XRD spectra were obtained from an X-ray diffraction Bruker D8 Advance diffractometer equipment in the Bragg-Brentano (θ - 2θ) configuration on the tilted sample by 3 degrees while Raman modes were determined for the cuprous oxide deposited on the a-Si:H samples in the range 50 - 700 cm⁻¹ using a Jobin Yvon/HoribaLabRam Raman microscope with a 488 nm laser excitation. Transmission electron microscopy (TEM) imaging was performed with a JEOL JEM 2010 microscope (model INCA Energy TEM 100 X-Max 65T) operating at 200 kV. X-ray photoelectron spectroscopy (XPS)

spectra were obtained using a K-alpha spectrometer, from ThermoScientific, with an Al K α 1,2 (1486.6 eV) X-ray source. The samples were pretreated with an Ar-etching process for 10 seconds.

Fig SI2: XPS measurements of Cu₂O samples deposited at 150 °C and 250 °C on a glass substrate

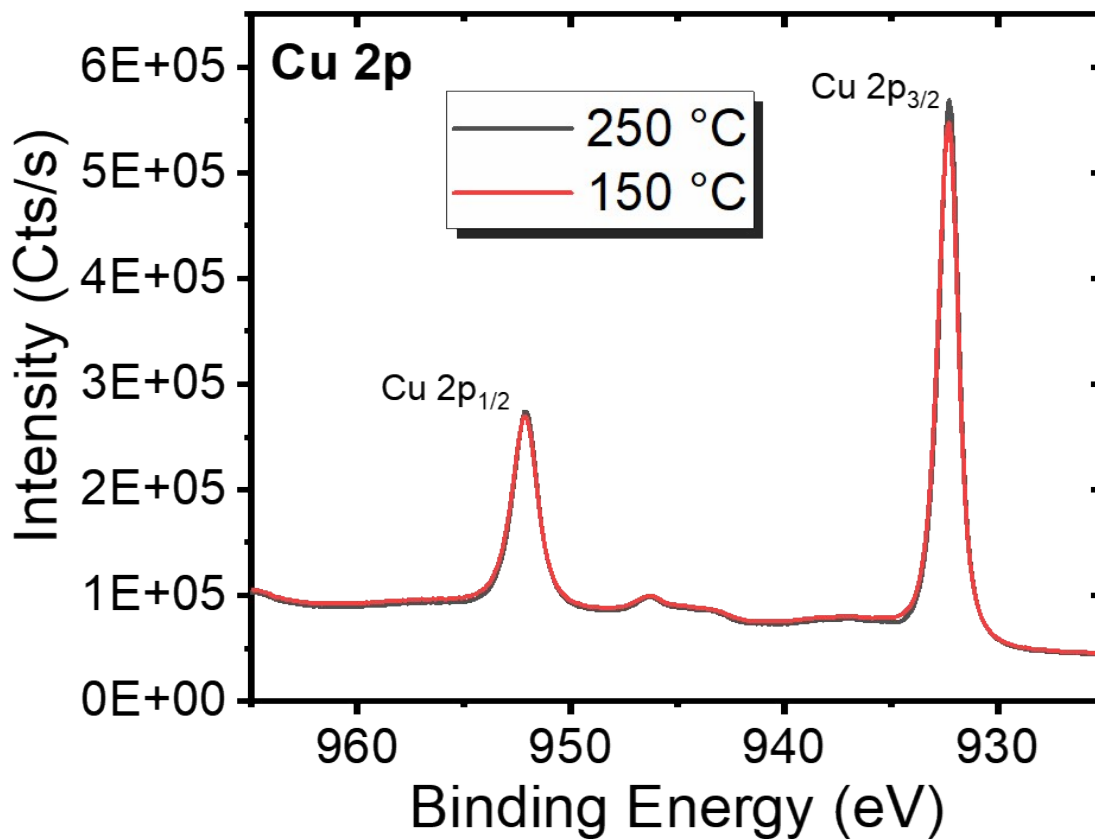


Fig SI3: PL imaging of other Cu_2O SHJ cells. The SHJ cell with a-Si:H(p) deposited using PECVD is much less damaged than the cell with ALD Cu_2O coatings. With the thicker Cu_2O layer (80 nm) (i.e. higher ALD cycling number), there is a more severe loss of the passivation than for the 10 nm thick Cu_2O HTL.

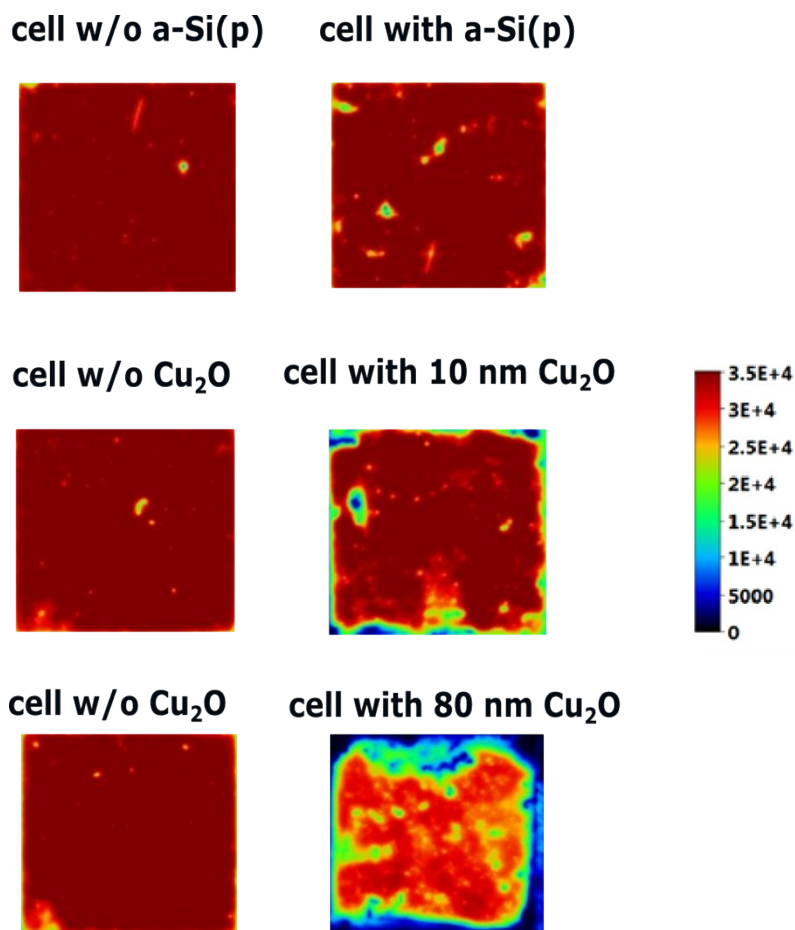


Fig SI4: Comparison of the performances between the SHJ cell with a-Si(p) and with SALD-Cu₂O HTLs. Left: J-V curves, middle: EQE measurement, and right: detail on the cell performances.

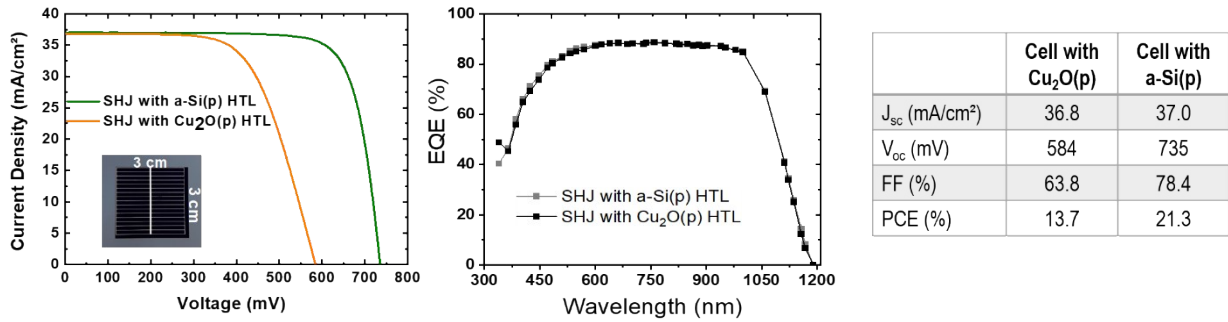


Fig SI5: The equivalent circuit of Cu₂O based SHJ cell for two diode models. R_s and R_{sh} are series and shunt resistance, respectively. J_{ph} is the photogeneration current. D_{SL}^{cell} , D_{def}^{cell} , and E_{rec}^{cell} represent for the Shockley diode, defect diode, and recombination element of the cell.

