

Electronic Supplementary Information for:

Co-electrodeposited Cu₂ZnSnS₄ thin-film solar cells with over 7% efficiency fabricated via fine-tuning of the Zn content in absorber layers

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Experimental

CdS thin films preparation

The CdS buffer layers were prepared in a radio frequency (RF) magnetron sputtering system. A sintered ceramic CdS target (99.999% purity, 2 inches diameter) was employed as source material. The separation between target and substrate was about 6 cm in the on-axis geometry. The base pressure of the deposition system was 4×10^{-5} Pa and the growth pressure was fixed at 2.7 Pa. The sputtering power was fixed at 30 W. The deposition was carried out in pure argon gas (99.999%) at a constant substrate temperature of 200 °C during 25 min after 5 min of pre-sputtering.

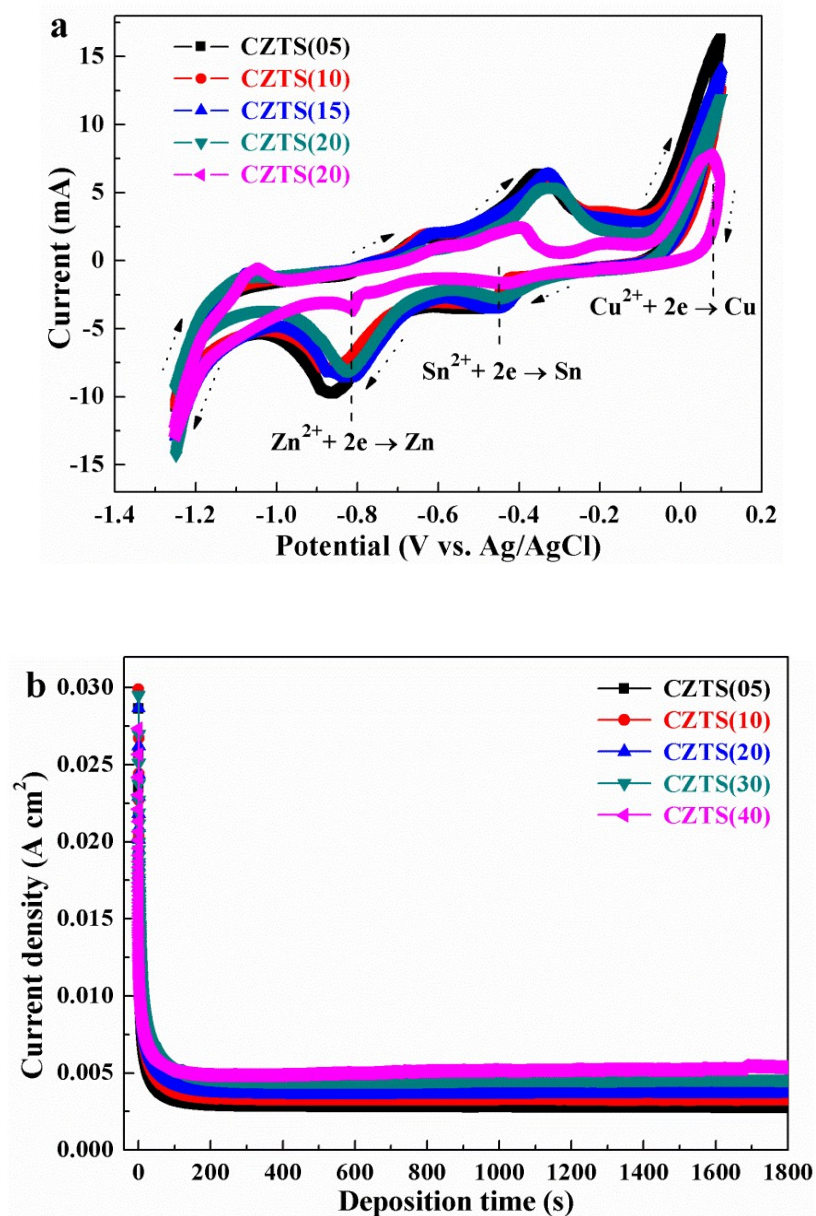


Figure S1. (a) Cyclic-voltammetry diagrams of aqueous electrolyte solutions with different Zn(II) concentrations used for co-electroplated Cu–Zn–Sn–S precursors on Mo/glass electrodes, scanned from 0.2 to –1.3 V at a scan rate of 10 mV s^{–1}. Arrows indicate scan directions. (b) The corresponding chronoamperograms during co-electrodeposition with constant potential at –1.15 V (vs. Ag/AgCl) for 30 min.

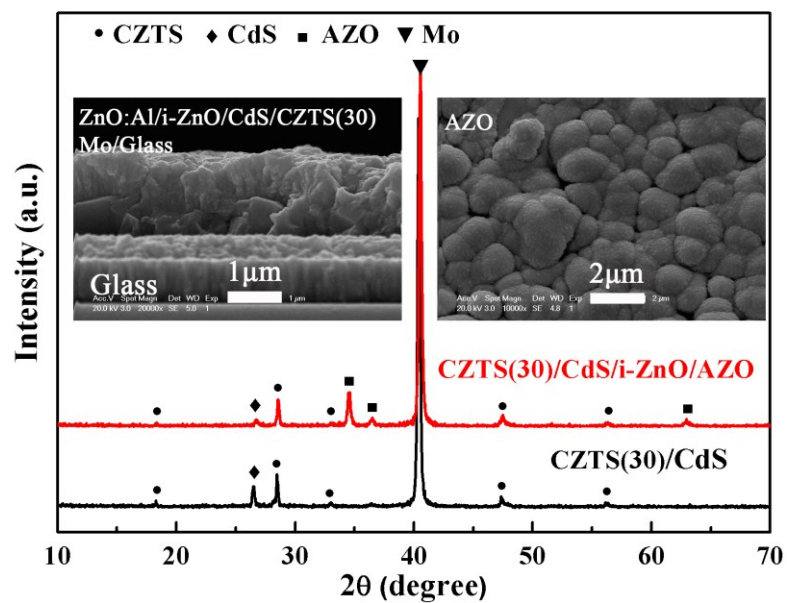


Figure S2. XRD pattern of a CdS thin film deposited on the CZTS(30)/Mo/glass substrate and then an AZO film successively deposited on CdS/CZTS(30)/Mo/glass substrate by RF magnetron sputtering. Inset cross-sectional SEM image of the CZTS thin-film solar cell, displaying the device structure of AZO/ZnO/CdS/CZTS/Mo/Glass.

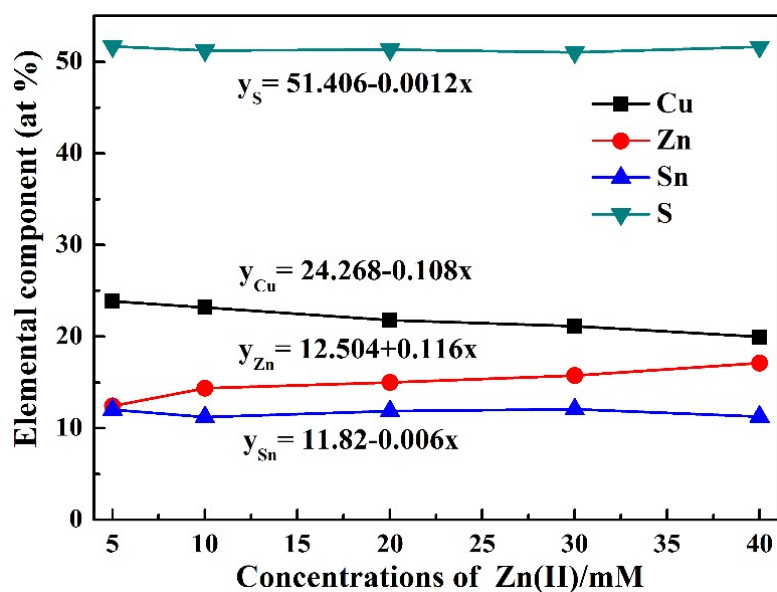


Figure S3. Dependence of Cu, Zn, Sn and S content in the sulfurized CZTS thin films as a function of different concentrations of Zn(II) concentrations in the electrolyte solutions.

Table S1. Chemical compositions of the precursor films as a function of the concentration of Zn(II) in electrolyte solutions.

| Sample ID | Elemental component (at %) | | | | Composition ratio | | |
|-----------|----------------------------|-------|-------|-------|-------------------|-------|---------|
| | Cu | Zn | Sn | S | Cu/(Zn+Sn) | Zn/Sn | S/Metal |
| CZTS(05) | 39.76 | 21.91 | 21.87 | 16.46 | 0.91 | 1.00 | 0.20 |
| CZTS(10) | 39.01 | 23.27 | 21.57 | 16.15 | 0.87 | 1.08 | 0.19 |
| CZTS(20) | 38.89 | 23.94 | 21.06 | 16.11 | 0.86 | 1.14 | 0.19 |
| CZTS(30) | 38.21 | 24.51 | 21.25 | 16.03 | 0.84 | 1.15 | 0.19 |
| CZTS(40) | 38.07 | 24.98 | 20.69 | 16.26 | 0.83 | 1.21 | 0.19 |

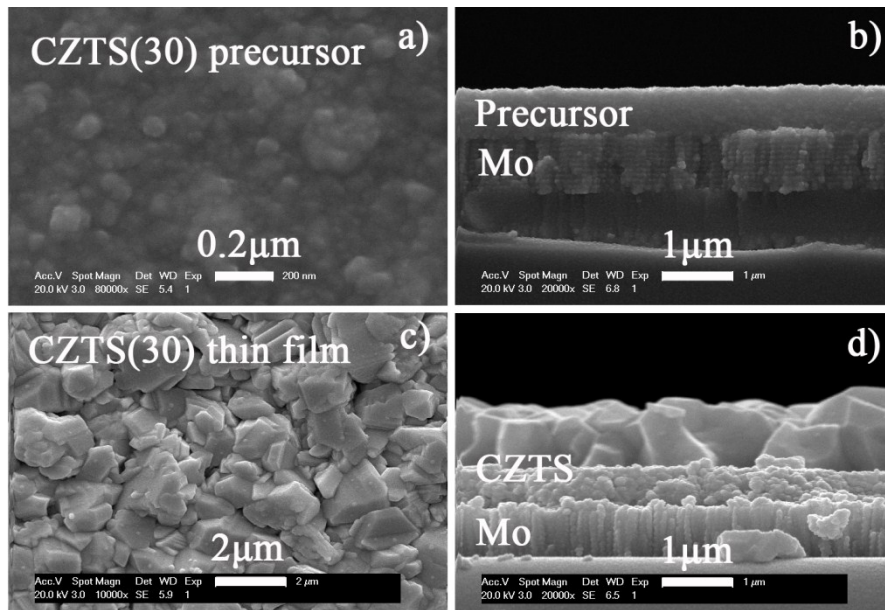


Figure S4. Surface and cross-sectional SEM images of (a and b) CZTS(30) precursor and (c and d) CZTS(30) thin film.

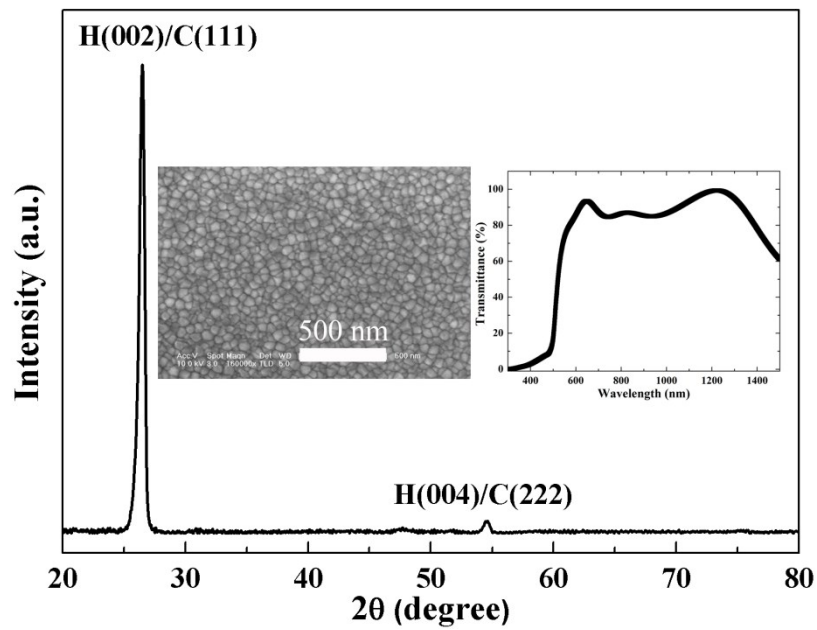


Figure S5. The XRD spectra of the sputtered CdS thin film deposited on a glass substrate. Inset SEM image and optical transmittance spectra of the sputtered CdS thin film on a glass substrate, respectively.

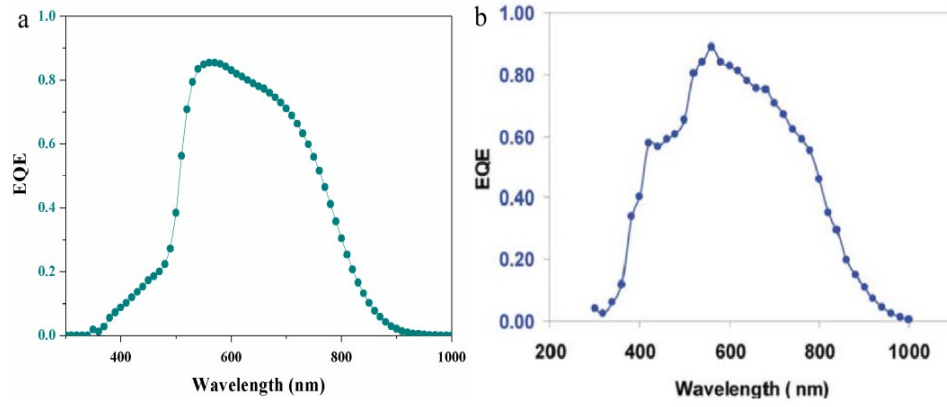


Figure S6. EQE measurements of the CZTS solar cells; (a) this work (CZTS(30) solar cell, PCE=7.23%, J_{sc} =19.2 mA cm⁻²) and (b) Ref (PCE=7.3%, J_{sc} =22 mA cm⁻²).¹

- 1 S. Ahmed, K.B. Reuter, O. Gunawan, L. Guo, L.T. Romankiw and H. Deligianni, Adv. Energy Mater., 2012, 2, 253–259.

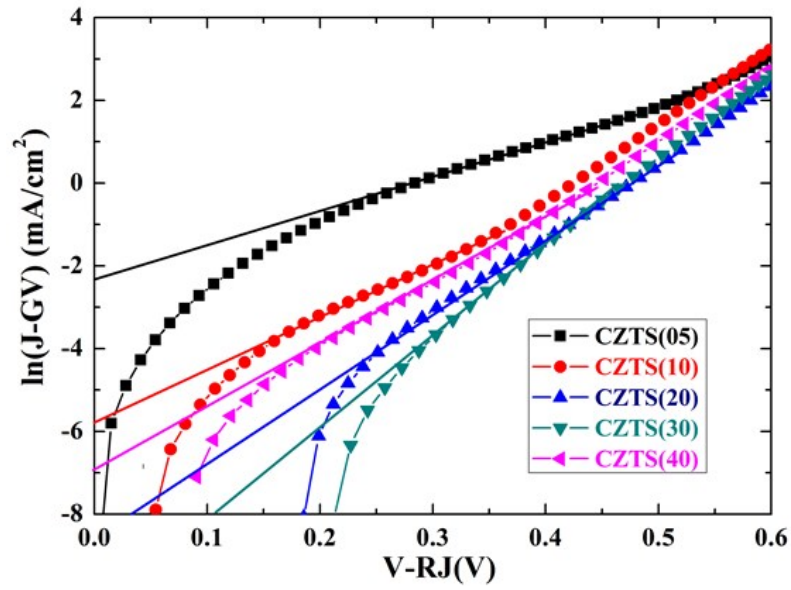


Figure S7 $\ln(J-GV)$ versus $V-RJ$ with fit used to determine the reverse saturation current density (J_0) for CZTS solar cells.