Supporting Information

The origin of recombination losses in solution processed Cu₂SnS₃ films based solar cells

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Film characterization details: Crystal structure is determined by X-ray diffraction (Bruker D8 Advance with CuK α radiation; step size 0.02° at room temperature ~23 °C) with quantitative Rietveld refinement analysis (Fullprof suite³⁸) and Raman spectroscopy (Renishaw inVia spectrometer with 514 nm Spectra physics laser). Scanning electron microscopy (Jeol iT300) featuring an Oxford X-max (80 mm²) detector for energy dispersive analysis of X-rays (EDAX) were used for investigating the topography and composition of the films. Surface composition was obtained from X-ray photoelectron spectroscopy XPS (VSW Scientific XPS spectrophotometer employing Al K α radiation of 1,486.6 eV). Diffuse reflectance spectrum between wavelengths 300-1200 nm is acquired against BaSO₄ as the reference with a Shimadzu-2600 spectrophotometer.



Fig. S1 Thermogravimetric analysis of dry precursor powder.



Fig. S2 Cu_2SnS_3 unit cell derived from the Rietveld refinement of the film XRD.

Table S1 Summary of the main PV metric of 24 CTS solar cells with the structure: glass/Mo/CIS/CdS/i-ZnO/ZnO:Al/Ni-Al, and total area of 0.5 cm². AM1.5G illumination was employed at 23°C.

	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	ղ (%)
Best cell	202	27.6	34.5	1.92
mean	142.20	18.0	30.53	1.35
Std. dev.	33.92	4.23	2.52	0.34

Impedance Spectroscopy of the CTS cells at various temperatures

Fig. S3a shows three equivalent circuits were used for the systematic analysis of the impedance spectra of CTS devices. **Fig. S3b** and **c** show an example of the fits obtained for the impedance spectrum recorded at 300 K. Circuit 1 is a basic circuit with one resistance, representing a series resistance, connected to a parallel R_jC_j loop associated with the shunt resistance and junction capacitance. It is clearly seen that Circuit 1 can only fit half of the spectrum. Circuit 2 includes an additional parallel R_bC_b loop linked to the non-Ohmic back contact barrier originating from partially sulfurized Mo layer. The simulated responses of Circuit 2 could only fit the frequency response below 5 kHz and above 50 kHz. The phase and magnitude components exhibt of multiple time constants which are commonly associated with defect states. The impedance spectra over the entire frequency range can be satisfactorily fitted by inclusion of two series RC loops as shown in Circuit 3, with the net error converging below 3%. Circuit 3 has been used in a number of studies, [42,43,46–48] with the time constants R_1C_1 and R_2C_2 linked to defect states. **Fig. S4** shows the variations of these time constants with temperatures between 80 to 370 K.



Fig. S3. Equivalent circuits used for the systematic analysis of the device impedance spectra between 0.5 Hz to 1 MHz (a). Frequency dependence of the impedance modulus (b) and phase (c) measured at 300 K. Circuit 3 (referred as the equivalent circuit in the manuscript) leads to the most consistent fit over the entire frequency range.



Fig. S4. Temperature dependence of the RC elements associated with the two defect states.