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Supplemental Information

The matrix method for calculating the optical properties of an *N*+2 layer stack

Optical modeling is performed using scattering-matrix formalism to describe transmission and reflection at interfaces as well as propagation through absorbing media (see reference 11). The forward- and reverse-propagating waves on both sides of each interface are related by the continuity equations for the tangential electric and magnetic fields. For N layers (of thickness d_1, d_2, … d_N) arranged between a semi-infinite ambient and substrate (designated layers 0 and N+1, respectively), the transmission T and reflection R coefficients at each wavelength λ are related by:

$$\begin{bmatrix} T \\ 0 \end{bmatrix} = \overline{\beta} \cdot \overline{V}_N \overline{V}_{N-1} \cdots \overline{V}_2 \overline{V}_1 \begin{bmatrix} 1 \\ R \end{bmatrix} \qquad \text{(SI.1)}$$

We omit the explicit dependence of each term on incident wavelength λ for clarity; this dependence enters through the wavelength-dependent complex index of refraction $\tilde{n}$ (introduced below). The 2x2 matrix $\overline{V}_i$ describes the reflection/transmission at interface i (which separates layers i and i–1) as well as the propagation through layer i to interface i +1. The matrices $\overline{V}_i$ are given by:

$$\overline{V}_i = \frac{1}{2}(1+p_i) \begin{bmatrix} \exp(-jk_z^i d_i) & 0 \\ 0 & \exp(jk_z^i d_i) \end{bmatrix} \cdot \begin{bmatrix} 1 & \Gamma_i \\ \Gamma_i & 1 \end{bmatrix} \qquad \text{(SI.2)}$$

where $p_i = Z_i / Z_{i-1}$ is the ratio of the wave impedances Z in layers i and i-1, and $\Gamma_i = (1 - p_i)/(1 + p_i)$ is the reflection coefficient at the interface between the layers i and i – 1. In this form, we have explicitly separated the terms describing propagation through the distance d_i of layer i (the

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first matrix) from reflection and transmission at the interface (the second matrix). For non-magnetic materials, the wave impedance of a medium differs depending on the polarization of the incident light:

$$Z_i^{TE} = \sqrt{\frac{\mu_0}{\varepsilon_0}} \frac{1}{\tilde{n}_i \cos(\theta_i)} \qquad \text{SI.3}$$

$$Z_i^{TM} = \sqrt{\frac{\mu_0}{\varepsilon_0}} \frac{\cos(\theta_i)}{\tilde{n}_i} \qquad \text{SI.4}$$

Where μ_0 and ε_0 are the permeability and permittivity of vacuum, $\tilde{n}_i$ is the complex index of refraction of layer i — which is generally wavelength dependent — and θ_i is the angle of propagation through layer i, which can be found by iteratively applying Snell's law ($\tilde{n}_i \sin(\theta_i) = \tilde{n}_{i-1} \sin(\theta_{i-1})$), beginning with the initial angle of incidence θ_0 at the interface between the ambient and layer 1. The final interface between layer N and the substrate is described by the 2x2 matrix $\overline{\beta}$, which is equivalent to $\overline{V_{N+1}}$ under the condition $d_{N+1} = 0$.

The transmittance t and reflectance r are related to T and R by:

$$r = |R|^2 \qquad \text{SI.5}$$

$$t = |T|^2 \frac{Z_0}{\mathrm{Re}[Z_{N+1}^*]} \qquad \text{SI.6}$$

For all modeling performed in the text, the spectrally-dependent complex index of refraction $\tilde{n}(\lambda)$ is used in equations SI.1 – SI.4 (see Figure SI.1). To model a mirror-like back interface underneath the CZTSSe, we used a purely imaginary index ($\tilde{n} = i$) for all wavelengths.

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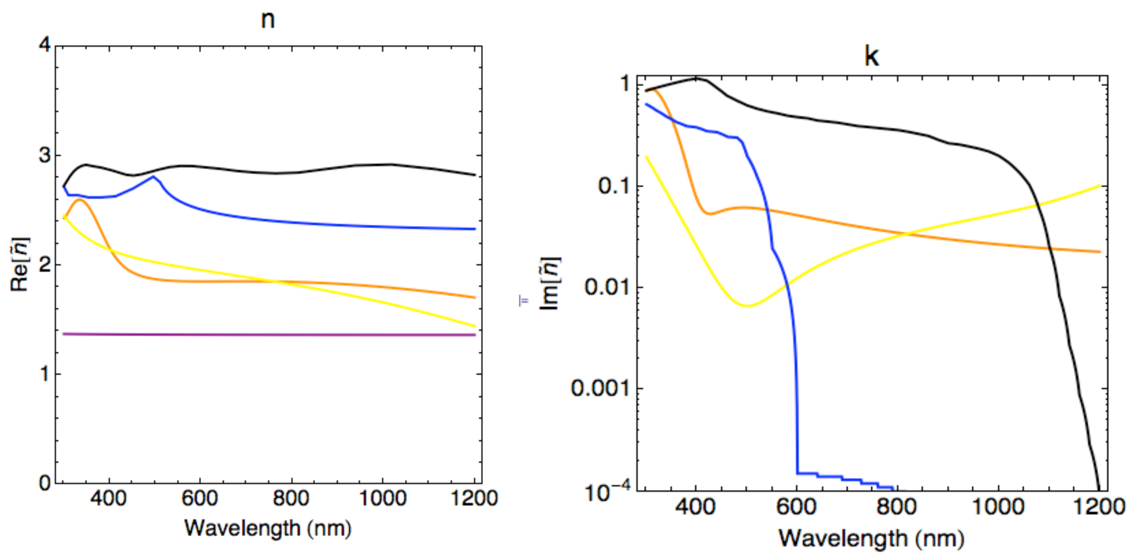

Figure SI.1 – Index of refraction for optical modeling. The n- and k-values used for the analytical optical modeling of CZTS (black), CdS (blue), ZnO (orange), ITO (yellow), and MgF_2 (purple). For ITO and ZnO, these values were measured by spectroscopic ellipsometry of thin films on Si wafers; for MgF_2, fits to broadband reflectivity were used in the same geometry. Surface roughness prevented measurements of CdS and CZTSSe; values from literature were therefore used.

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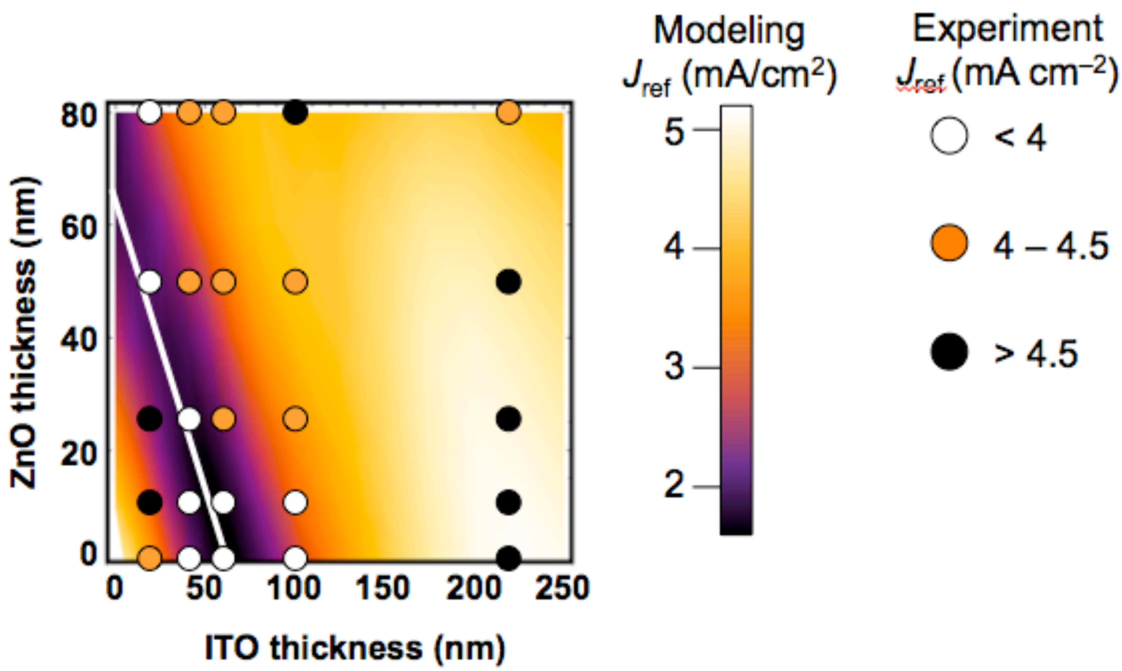

Figure SI.2 – Reflectivity for varying TCO combinations. The total reflected photon current is shown for both analytical modeling (density plot, see text) and experiment (overlaid points); reflected-photon current values are obtained by integrating the spectrally-dependent reflectivity against the AM1.5G spectrum between 300 — 1200 nm. Experiment and modeling confirm that, to a good approximation, reflectivity is a function of the total ITO and ZnO thickness due to their similar indices of refraction. The white line is a line of constant thickness ($d_{TCO} = d_{ITO} + d_{ZnO} =$ 60 nm).

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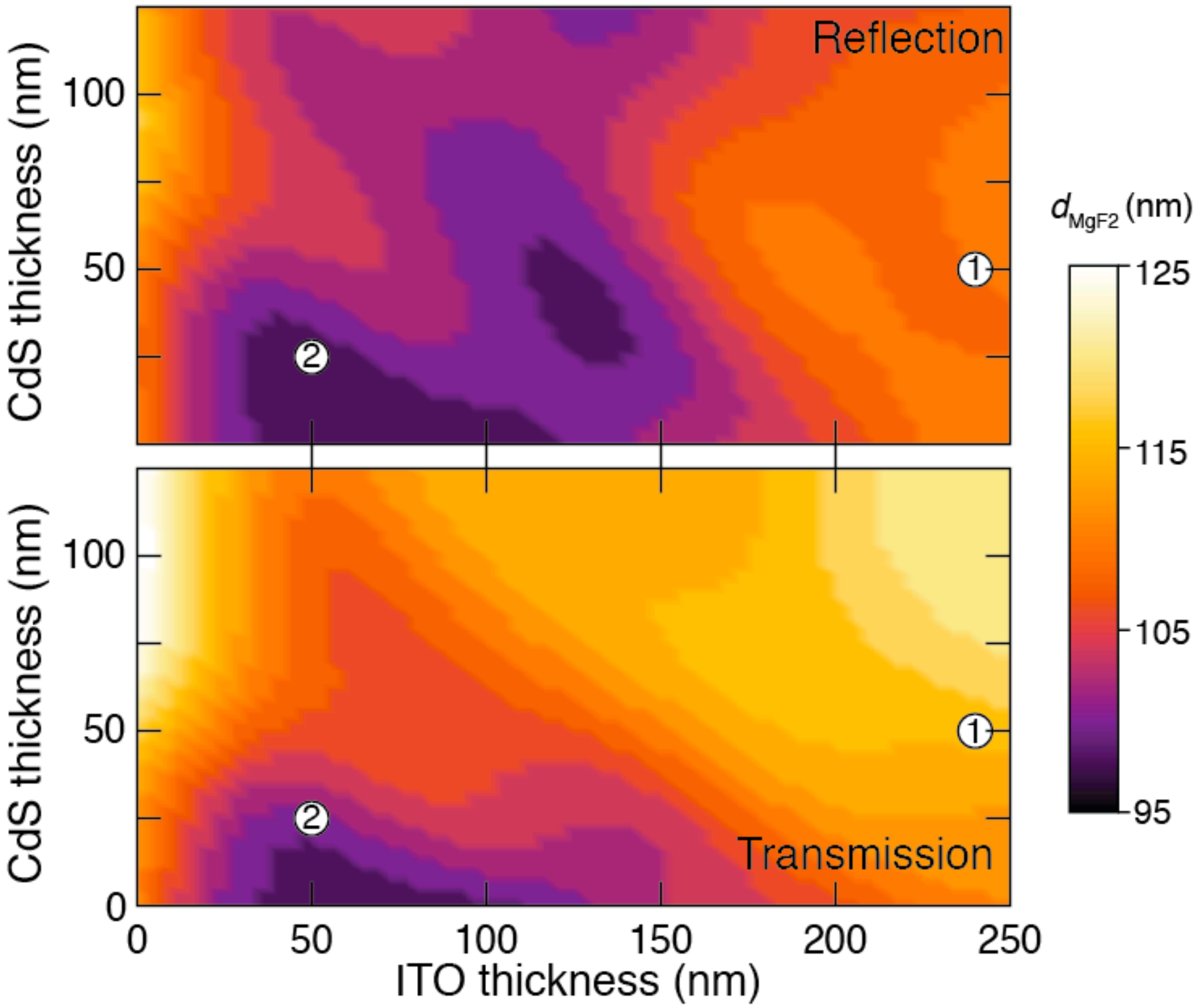

Figure SI.3 – Optimal thickness of MgF_2 for the architectures studied in the paper. Figure 2 in the main text showed total reflected (J_R) and transmitted (J_T) currents for a wide range of TCO and CdS-layer thicknesses. At each point in Figure 2, J_R and J_T were chosen for the optimal value of MgF_2 thickness. This figure shows that the optimal MgF_2 thickness ranges from 95 – 125 nm when optimizing *(top)* reflection and (*bottom)* transmission.

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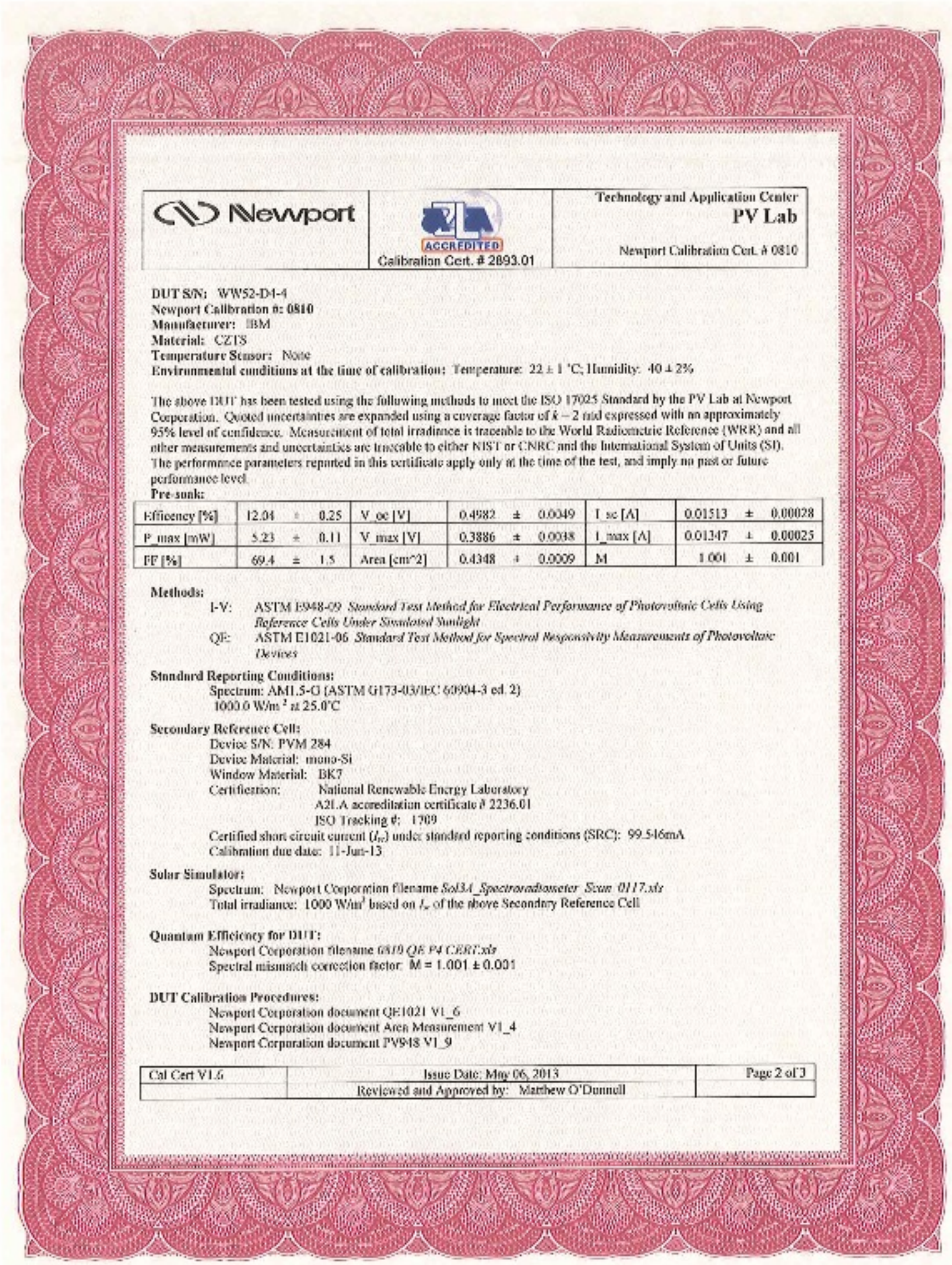

Newport	ACCREDITED Calibration Cert. # 2893.01	Technology and Application Center PV Lab Newport Calibration Cert. # 0810

DUT S/N: WW52-D4-4
Newport Calibration #: 0810
Manufacturer: IBM
Material: CZTS
Temperature Sensor: None
Environmental conditions at the time of calibration: Temperature: 22 ± 1 °C; Humidity: 40 ± 2%

The above DUT has been tested using the following methods to meet the ISO 17025 Standard by the PV Lab at Newport Corporation. Quoted uncertainties are expanded using a coverage factor of *k* = 2 and expressed with an approximately 95% level of confidence. Measurement of total irradiance is traceable to the World Radiometric Reference (WRR) and all other measurements and uncertainties are traceable to either NIST or CNRC and the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test, and imply no past or future performance level.

Pre-soak:

Efficency [%]	12.04	±	0.25	V_oc [V]	0.4982	±	0.0049	I_sc [A]	0.01513	±	0.00028
P_max [mW]	5.23	±	0.11	V_max [V]	0.3886	±	0.0038	I_max [A]	0.01347	±	0.00025
FF [%]	69.4	±	1.5	Area [cm^2]	0.4348	±	0.0009	M	1.001	±	0.001

Methods:
I-V: ASTM E948-09 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-06 *Standard Test Method for Spectral Responsivity Measurements of Photovoltaic Devices*

Standard Reporting Conditions:
Spectrum: AM1.5-G (ASTM G173-03/IEC 60904-3 ed. 2)
1000.0 W/m ^{2} at 25.0°C

Secondary Reference Cell:
Device S/N: PVM 284
Device Material: mono-Si
Window Material: BK7
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 1709
Certified short circuit current (I_{sc}) under standard reporting conditions (SRC): 99.516mA
Calibration due date: 11-Jun-13

Solar Simulator:
Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer Scan 0117.xls*
Total irradiance: 1000 W/m^2 based on I_{sc} of the above Secondary Reference Cell

Quantum Efficiency for DUT:
Newport Corporation filename *0810 QE P4 CERT.xls*
Spectral mismatch correction factor: M = 1.001 ± 0.001

DUT Calibration Procedures:
Newport Corporation document QE1021 V1_6
Newport Corporation document Area Measurement V1_4
Newport Corporation document PV948 V1_9

Cal Cert V1.6	Issue Date: May 06, 2013	Page 2 of 3
	Reviewed and Approved by: Matthew O'Donnell	

Figure SI.4 – Newport calibration certificate. Certificate 0810, documenting the efficiency (12.0%) of the champion CZTS solar cell described in the main text.

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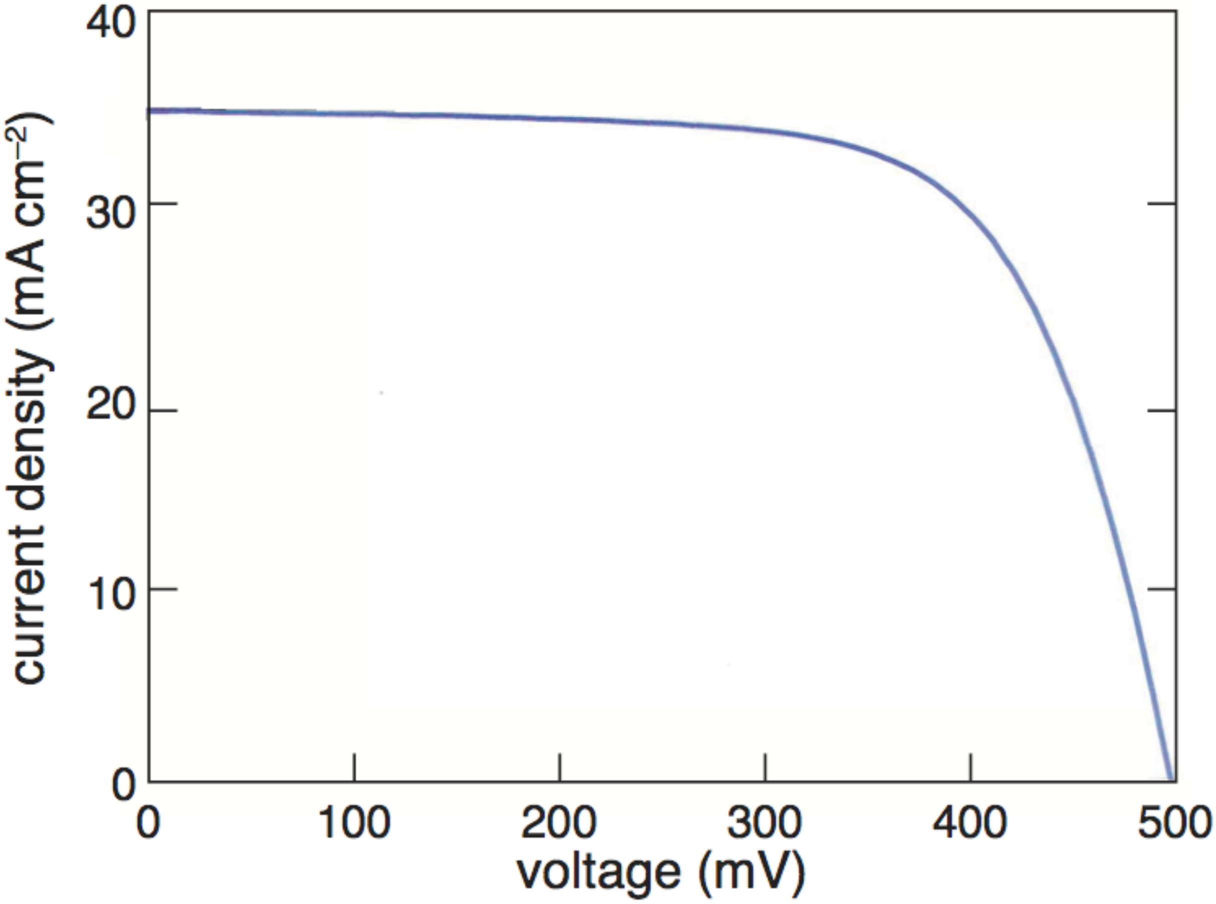

Figure SI.5 – Calibrated J-V Certificate 0810, documenting the efficiency (12.0%) of the champion CZTS solar cell described in the main text.