Electronic supplementary information

Effect of Solid-H_2S gas reactions on CZTSSe Thin Film Growth and the Photovoltaic Properties of a 12.62% Efficiency Device

Dae-Ho Son, Seung-Hyun Kim, Se-Yun Kim, Young-Ill Kim, Jun-Hyung Sim, Si-Nae Park, Dong-Hwan Jeon, Dae-Kue Hwang, Shi-Joon Sung, Jin-Kyu Kang, Kee-Jeong Yang and Dae-Hwan Kim**

Convergence Division of Energy Technology, Daegu Gyeongbuk Institute of Science & Technology, 333 Techno jungang-daero, Hyeonpung-eup, Dalseong-gun, Daegu 42988, Republic of Korea

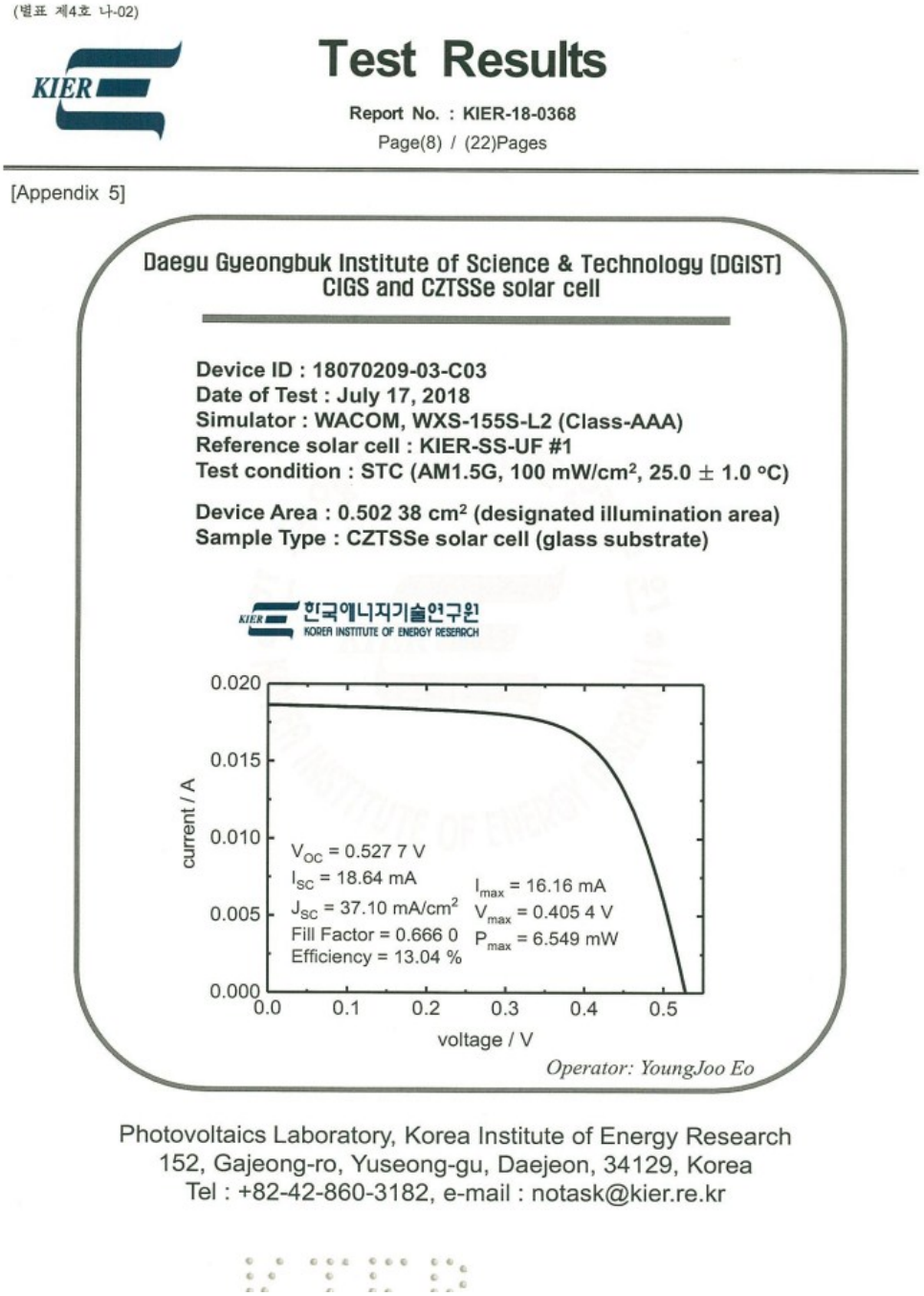
Keywords: CZTSSe, thin film solar cell, kesterites, photovoltaic devices

Corresponding Author

Dae-Hwan Kim : monolith@dgist.ac.kr

Kee-Jeong Yang : kjyang@dgist.ac.kr

Supplementary material – 1: Certificates showing the performance of the 13.04% CZTSSe solar cell


(별표 제4호 나-02)

KIER

Test Results

Report No. : KIER-18-0368

Page(8) / (22)Pages

[Appendix 5]

Daegu Gyeongbuk Institute of Science & Technology [DGIST]
CIGS and CZTSSe solar cell

Device ID : 18070209-03-C03
Date of Test : July 17, 2018
Simulator : WACOM, WXS-155S-L2 (Class-AAA)
Reference solar cell : KIER-SS-UF #1
Test condition : STC (AM1.5G, 100 mW/cm², 25.0 ± 1.0 °C)

Device Area : 0.502 38 cm² (designated illumination area)
Sample Type : CZTSSe solar cell (glass substrate)

KIER 한국에너지기술연구원 KOREA INSTITUTE OF ENERGY RESEARCH

Operator: YoungJoo Eo

Photovoltaics Laboratory, Korea Institute of Energy Research
152, Gajeong-ro, Yuseong-gu, Daejeon, 34129, Korea
Tel : +82-42-860-3182, e-mail : notask@kier.re.kr

Figure S1. Independent certification of the 13.04% CZTSSe device with an area of 0.50238 cm^2.

Supplementary material – 2: The sample box system

Figure S2 shows a photograph of the sample box system used in the heat treatment process. The boat and cover were made of quartz. The sample holder was made of SiC-coated graphite. Several Se shots were placed on the bottom of the quartz boat, and the sample holder was placed between the boat and the cover. The Se shots were a product of Sigma-Aldrich, Inc., and approximately 0.2 g was used for selenization. The quartz cover served to contain vapourized gas from the lower selenium shots. Figure S2 shows nine SLG-Mo/Zn/Cu/Sn stack structure samples placed on the sample holder. Small holes were designed on the four sides of the sample holder. Through these holes, the selenium vapour was brought to the top of the sample.

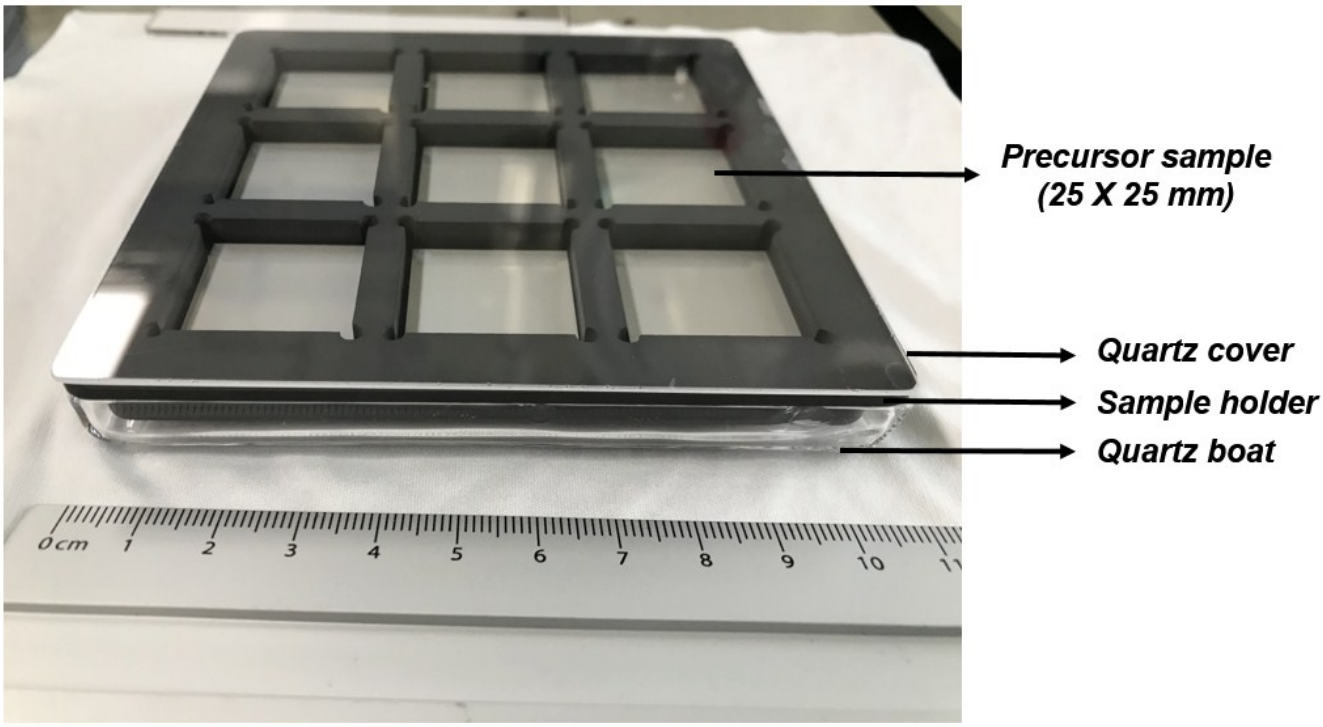


Figure S2. Picture of the sample box system.

Supplementary material – 3: Temperature profile

The temperature profile of our reference process is depicted in Figure S3. The heating profile consisted of two stages, in which the temperature was increased in the first stage from room temperature to 300 °C. The final stage aimed to form a CZTSSe phase by maintaining the temperature at 480 °C, followed by natural cooling to room temperature. The holding time for the first stage was 15 min, and the applied heating rate was 0.5 °C/sec. The holding time for the final stage was 10 min, and the applied heating rate was 0.1 °C/sec.

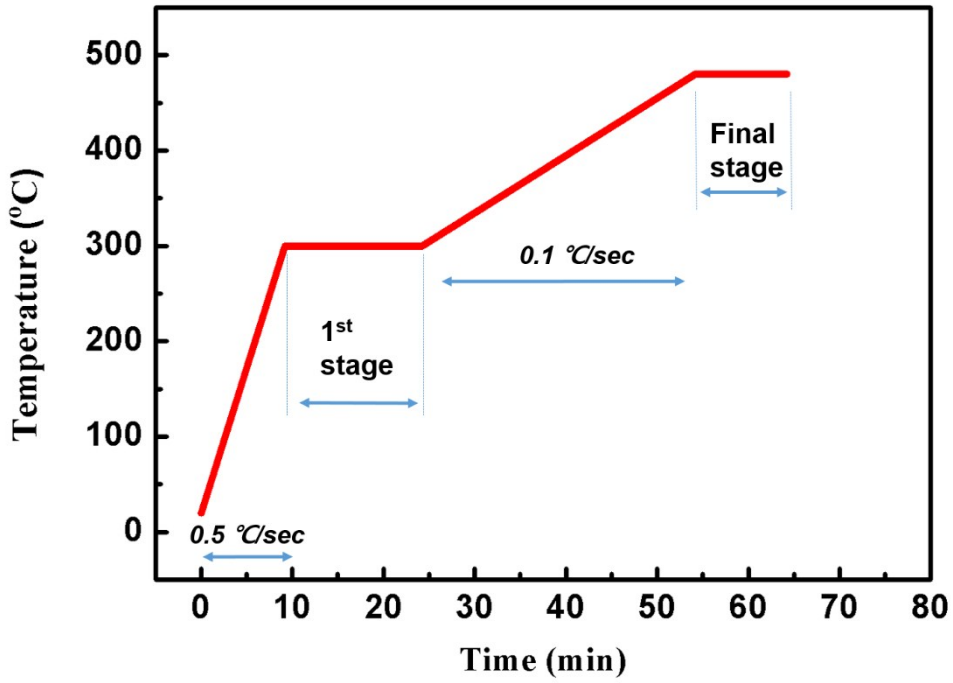


Figure S3. Internal heating profile.

Supplementary material – 4: Nanowire growth in the sample

Supplementary material Figure S4 depicts the Zn volatilization phenomenon with photographs of a sample and a quartz cover. Evidence of volatilization can be confirmed by photographs of the heat treatment process stage. Figure S4-1 is a photograph of a quartz cover and a sample formed by holding at 300 °C for 15 min and then stopping the process and cooling to room temperature. Interestingly, a yellow material is deposited on the quartz cover; the yellow pattern exactly matches the colour gradient area on the sample. According to EDS analysis, the yellow substance deposited on the quartz plate is a Zn-Se compound (not shown here). Analysis of the colour gradient region of the sample surface shows that nanowires are densely formed on the surface of the thin film. In other words, the nanowire region formed on the thin film and the region where the Zn-Se material is attached to the upper quartz cover face each other. The area where the Zn-Se nanowires are formed on the surface of the sample is blacker, and the colour of the area on the quartz cover facing the Zn-Se nanowires is darker. A relatively large number of Zn-Se nanowires were formed in the dark black region of the sample. A dark yellow colour is also observed on the quartz cover area that faces the many nanowire area. This result means that more Zn-Se nanowires are formed in the region where Zn is highly volatile, and the volatilized Zn material reacts with Se and is deposited on the quartz cover.

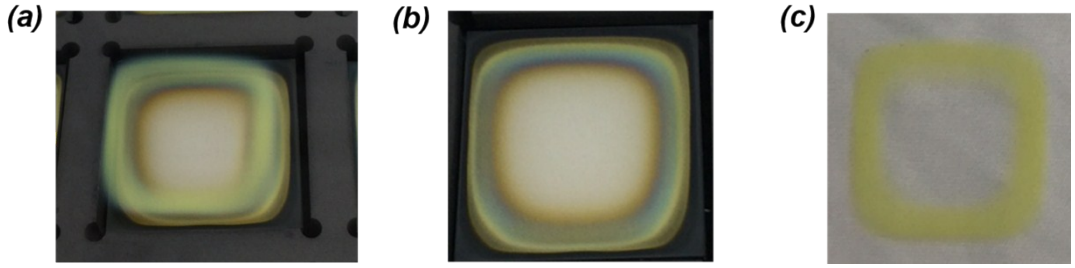


Figure S4-1. Photo of the sample box and a sample annealed at 300 °C for 15 min. (a) An annealed sample is placed in the sample holder, and a quartz plate cover is placed on top. (b) Sample surface photograph, and (c) quartz plate photograph.

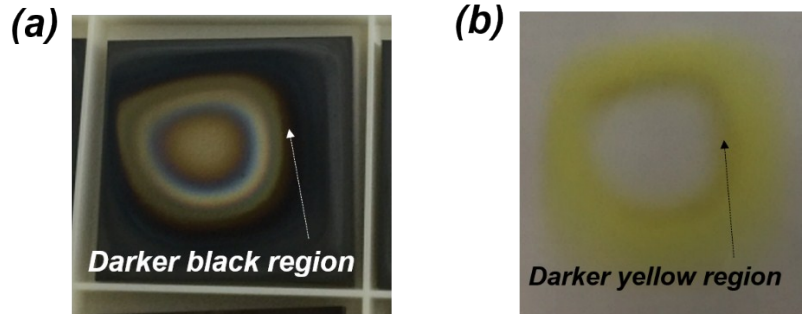


Figure S4-2. Photo of a sample made at 360 °C. (a) Sample surface photograph, and (b) quartz plate cover photograph.

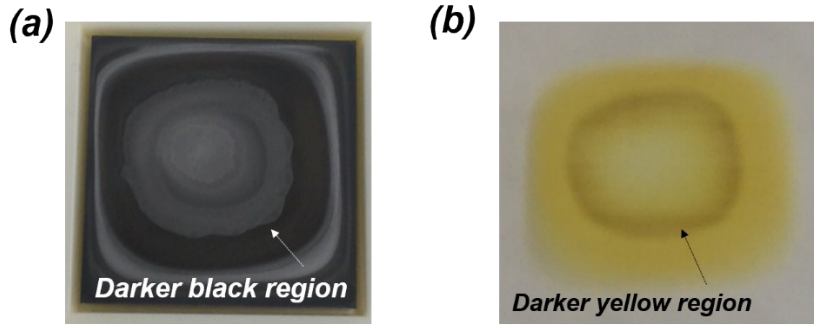


Figure S4-3. Photo of a sample made at 420 °C. (a) Sample surface photograph, and (b) quartz plate cover photograph.

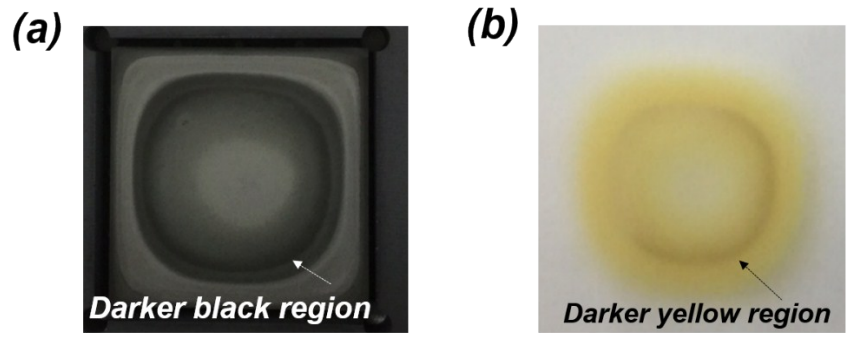


Figure S4-4. Photo of a sample made at 480 °C for 10 min. (a) Sample surface photograph, and (b) quartz plate cover photograph.

Supplementary material – 5: composition of ZnSe nanowires

The components of the nanowires were analysed by excluding the EDX components of background 1 region from the EDX analysis results of region 2 where nanowires were formed. The nanowires were roughly composed of Zn:Se at a ratio of 2:1.

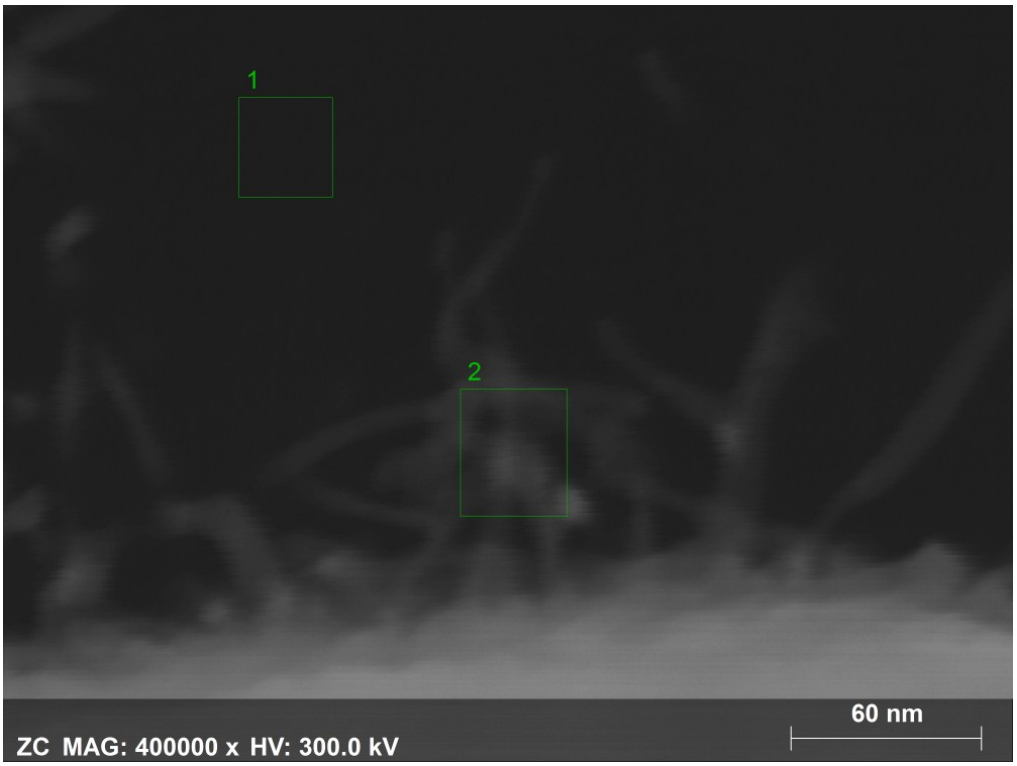


Figure S5. STEM image of nanowires.

Supplementary material – 6: Depth analysis of CZTSSe thin films

To understand the element dispersion, STEM-EDX line scan of Figure 6, time of flight secondary ion mass spectrometry (TOF-SIMS) and Auger electron spectroscopy (AES) depth analyses were employed for the sister cell of the champion device.

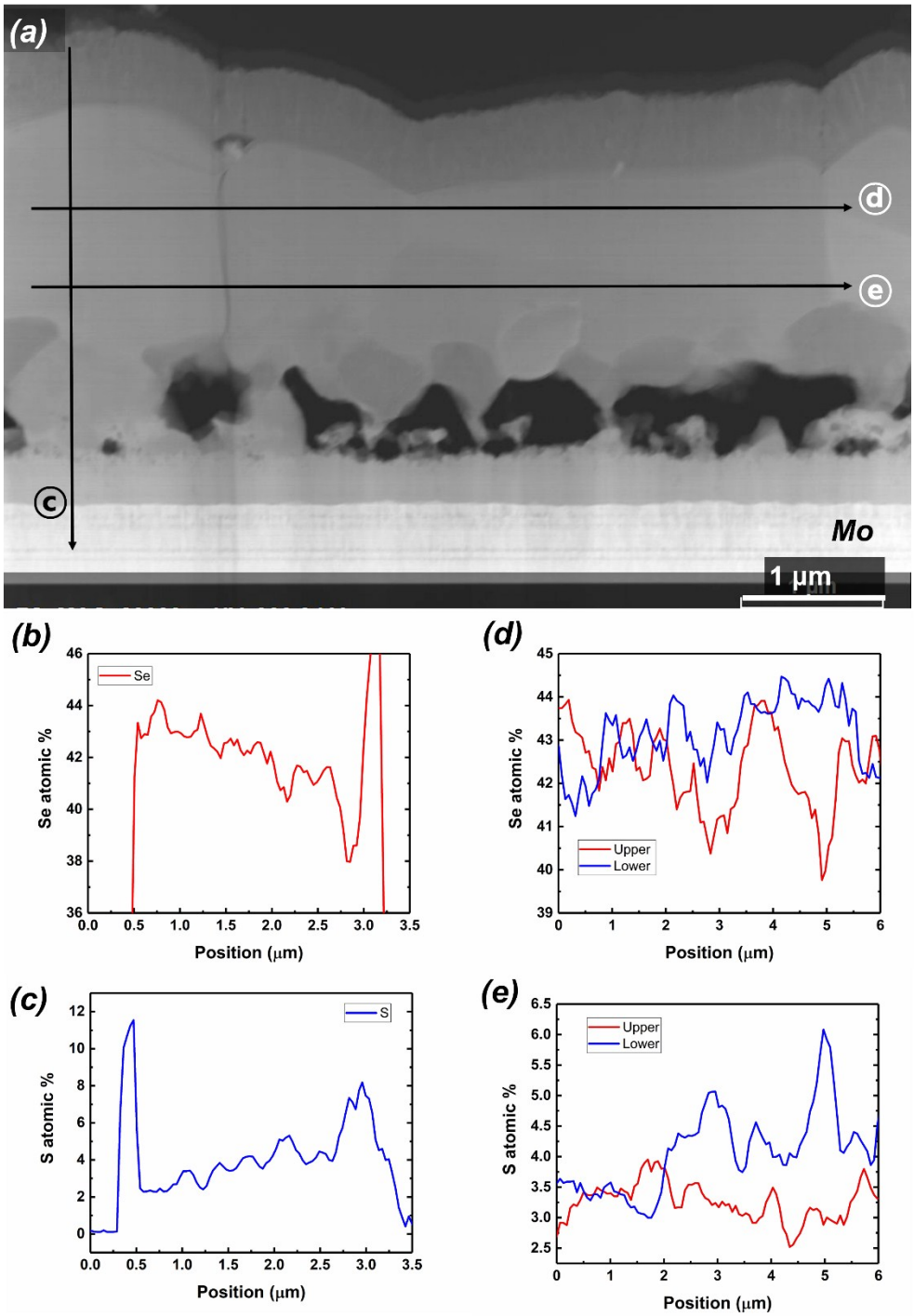


Figure S6-1. In the cross-sectional STEM image (a) of Figure 6 in the articel, the line composition profile of S and Se. The scanning direction of (b) and (c) is the same as arrow

direction ⓒ in (a). As shown in (b) and (c) in the figure, Se decreases by arrow direction ⓒ, and S increases. Figures (d) and (e) are comparative data of Se and S elements in the upper and lower regions of the CZTSSe absorption layer, respectively. It can be seen that S is higher at the bottom of Se than at the bottom.

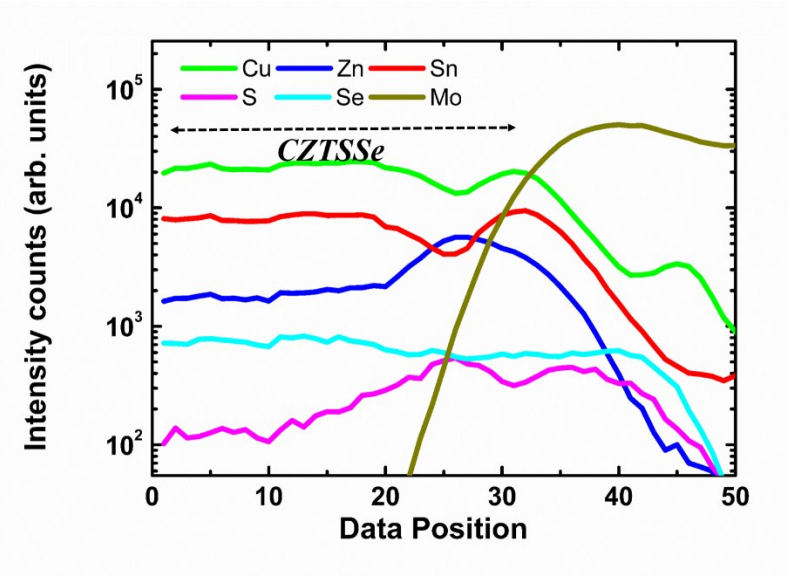


Figure S6-2. TOF-SIMS depth profiles of Cu, Zn, Sn, S, Se and Mo in a CZTSSe thin film. It can be seen that the composition ratios of Se and S are different in the direction of the rear electrode Mo of the absorption layer.

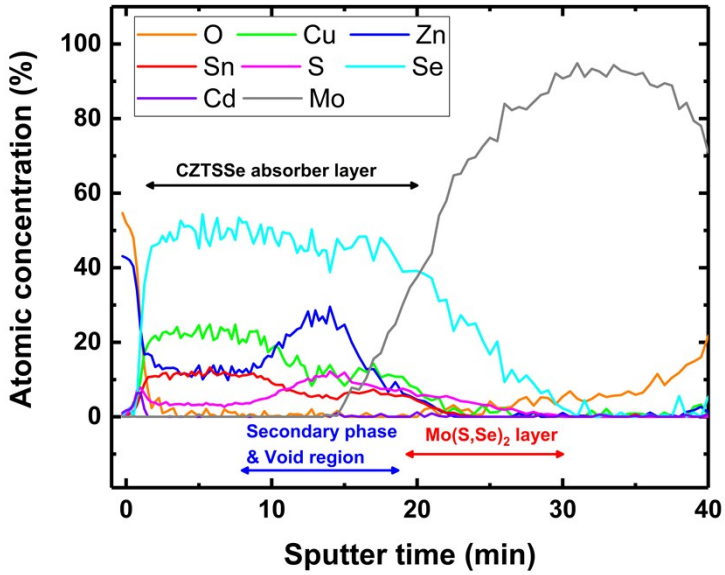
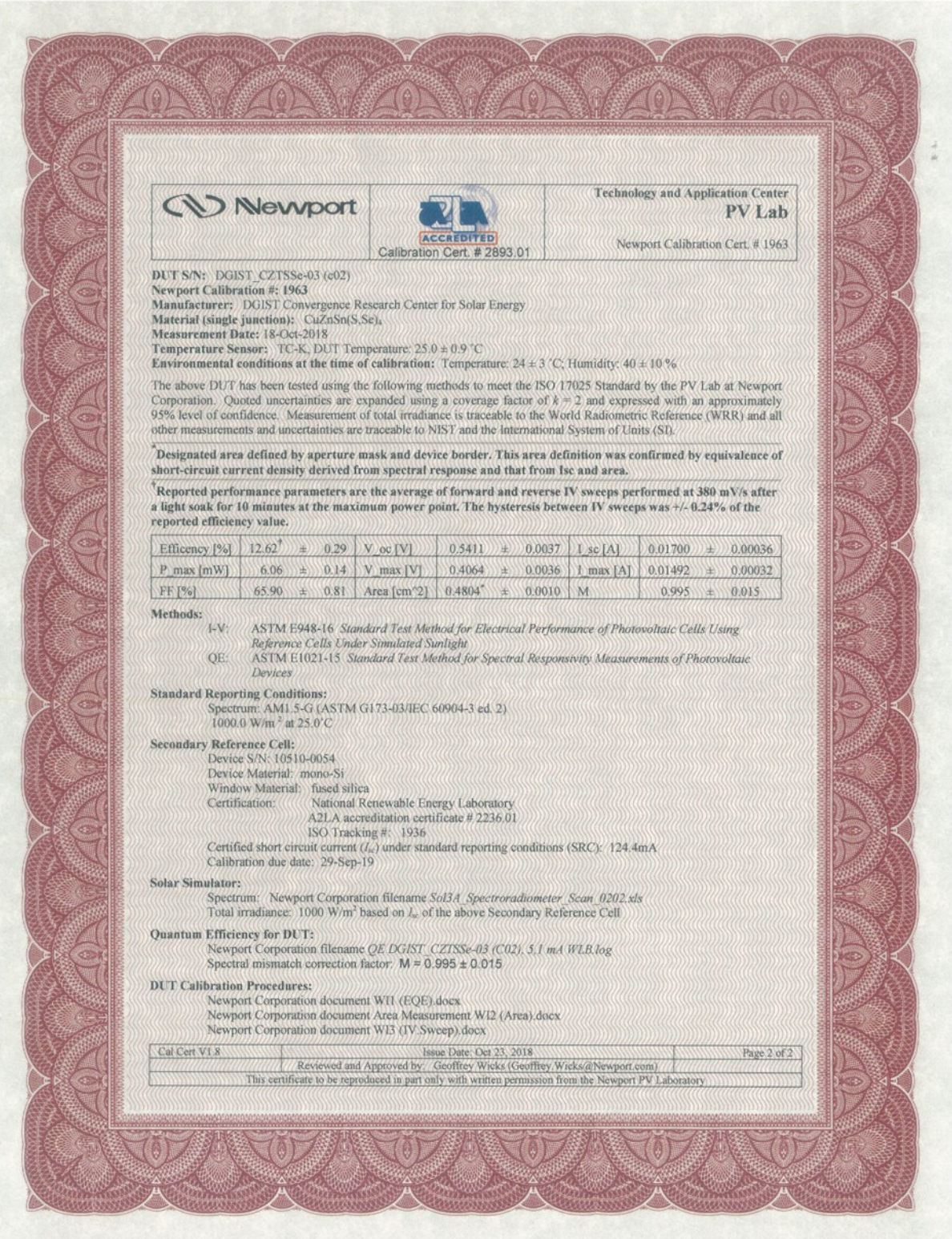


Figure S6-3. AES depth profiles of Cu, Zn, Sn, S, Se, O, Cd and Mo in a CZTSSe solar cell. AES depth profile results are also identical to the depth profiles results of STEM-line and TOF-SIMS.

Supplementary material – 7: Certificates showing the performance of CZTSSe solar cells



Newport

ACCREDITED
Calibration Cert. # 2893.01

Technology and Application Center
PV Lab
Newport Calibration Cert. # 1963

DUT S/N: DGIST_CZTSSe-03 (c02)
Newport Calibration #: 1963
Manufacturer: DGIST Convergence Research Center for Solar Energy
Material (single junction): $Cu_2ZnSn(S,Se)_4$
Measurement Date: 18-Oct-2018
Temperature Sensor: TC-K, DUT Temperature: 25.0 ± 0.9 °C
Environmental conditions at the time of calibration: Temperature: 24 ± 3 °C; Humidity: 40 ± 10 %

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 NIST and the International System of Units (SI).

*Designated area defined by aperture mask and device border. This area definition was confirmed by equivalence of short-circuit current density derived from spectral response and that from Isc and area.

†Reported performance parameters are the average of forward and reverse IV sweeps performed at 380 mV/s after a light soak for 10 minutes at the maximum power point. The hysteresis between IV sweeps was +/- 0.24% of the reported efficiency value.

Efficency [%]	12.62†	±	0.29	V_oc [V]	0.5411	±	0.0037	I_sc [A]	0.01700	±	0.00036
P_max [mW]	6.06	±	0.14	V_max [V]	0.4064	±	0.0036	I_max [A]	0.01492	±	0.00032
FF [%]	65.90	±	0.81	Area [cm^2]	0.4804*	±	0.0010	M	0.995	±	0.015

Methods:
I-V: ASTM E948-16 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-15 *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/m² at 25.0°C

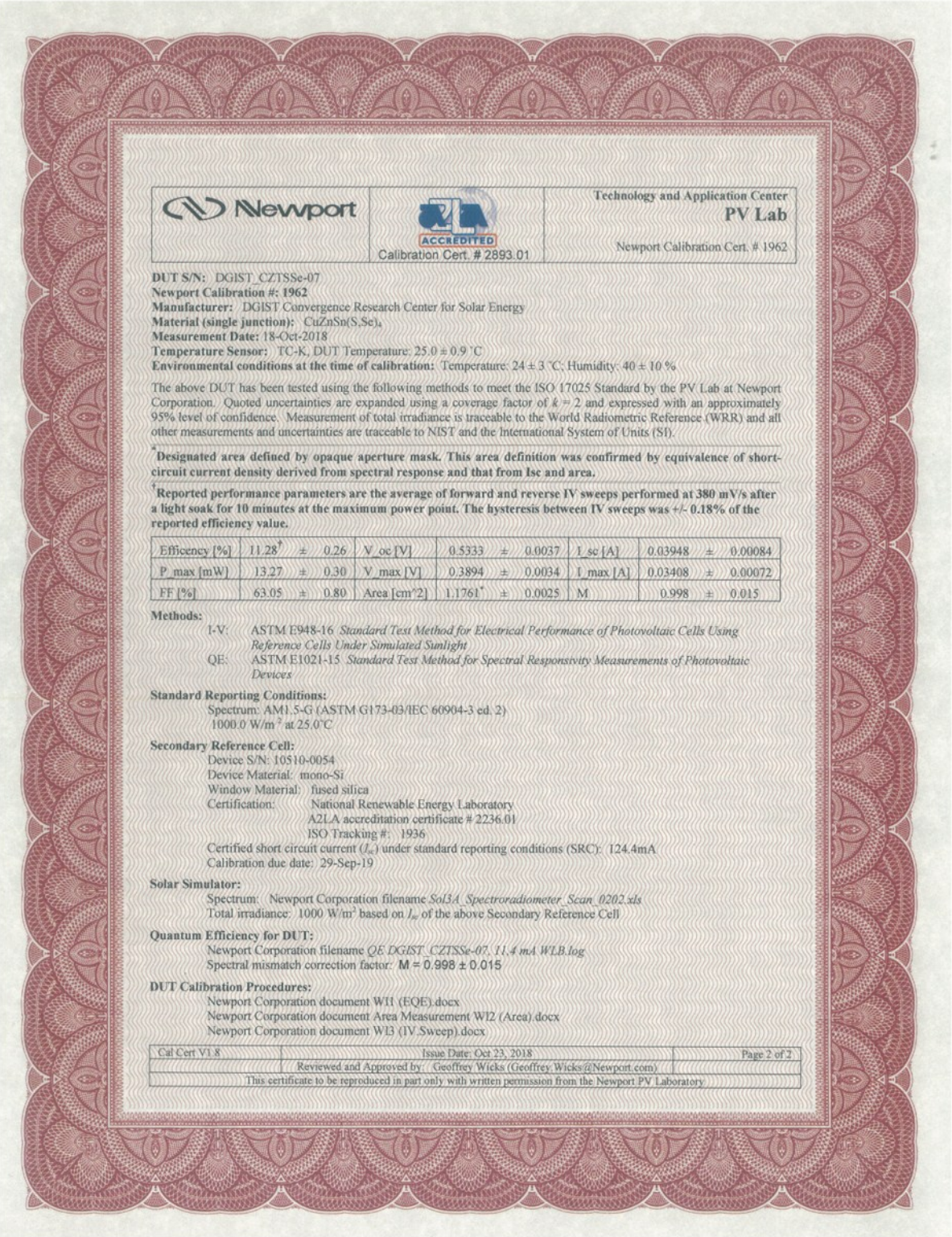
Secondary Reference Cell:
Device S/N: 10510-0054
Device Material: mono-Si
Window Material: fused silica
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 1936
Certified short circuit current (I_{sc}) under standard reporting conditions (SRC): 124.4mA
Calibration due date: 29-Sep-19

Solar Simulator:
Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer_Scan_0202.xls*
Total irradiance: 1000 W/m² based on I_{sc} of the above Secondary Reference Cell

Quantum Efficiency for DUT:
Newport Corporation filename *QE DGIST_CZTSSe-03 (C02), 5.1 mA WLB.log*
Spectral mismatch correction factor: M = 0.995 ± 0.015

DUT Calibration Procedures:
Newport Corporation document WI1 (EQE).docx
Newport Corporation document Area Measurement WI2 (Area).docx
Newport Corporation document WI3 (IV Sweep).docx

Figure S7-1. Independent certification of the 12.62% CZTSSe device with an area of 0.4804 cm^2.



Newport

ACCREDITED
Calibration Cert. # 2893.01

Technology and Application Center
PV Lab
Newport Calibration Cert. # 1962

DUT S/N: DGIST_CZTSSe-07
Newport Calibration #: 1962
Manufacturer: DGIST Convergence Research Center for Solar Energy
Material (single junction): CuZnSn(S,Se)$_4$
Measurement Date: 18-Oct-2018
Temperature Sensor: TC-K, DUT Temperature: 25.0 ± 0.9 °C
Environmental conditions at the time of calibration: Temperature: 24 ± 3 °C; Humidity: 40 ± 10 %

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 NIST and the International System of Units (SI).

*Designated area defined by opaque aperture mask. This area definition was confirmed by equivalence of short-circuit current density derived from spectral response and that from Isc and area.

†Reported performance parameters are the average of forward and reverse IV sweeps performed at 380 mV/s after a light soak for 10 minutes at the maximum power point. The hysteresis between IV sweeps was +/- 0.18% of the reported efficiency value.

Efficiency [%]	11.28†	±	0.26	V_oc [V]	0.5333	±	0.0037	I_sc [A]	0.03948	±	0.00084
P_max [mW]	13.27	±	0.30	V_max [V]	0.3894	±	0.0034	I_max [A]	0.03408	±	0.00072
FF [%]	63.05	±	0.80	Area [cm^2]	1.1761*	±	0.0025	M	0.998	±	0.015

Methods:
I-V: ASTM E948-16 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-15 *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: 10510-0054
Device Material: mono-Si
Window Material: fused silica
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 1936
Certified short circuit current (I_{sc}) under standard reporting conditions (SRC): 124.4mA
Calibration due date: 29-Sep-19

Solar Simulator:
Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer_Scan_0202.xls*
Total irradiance: 1000 W/m^2 based on I_{sc} of the above Secondary Reference Cell

Quantum Efficiency for DUT:
Newport Corporation filename *QE DGIST_CZTSSe-07, 11.4 mA WLB.log*
Spectral mismatch correction factor: M = 0.998 ± 0.015

DUT Calibration Procedures:
Newport Corporation document WI1 (EQE).docx
Newport Corporation document Area Measurement WI2 (Area).docx
Newport Corporation document WI3 (IV Sweep).docx

Cal Cert V1.8	Issue Date: Oct 23, 2018	Page 2 of 2
	Reviewed and Approved by: Geoffrey Wicks (Geoffrey.Wicks@Newport.com)	
This certificate to be reproduced in part only with written permission from the Newport PV Laboratory		

Figure S7-2. Independent certification of the 11.28% CZTSSe device with an area of 1.1761 cm^2.

Supplementary material – 8: External quantum efficiency of certified 12.62% CZTSSe (DGIST)

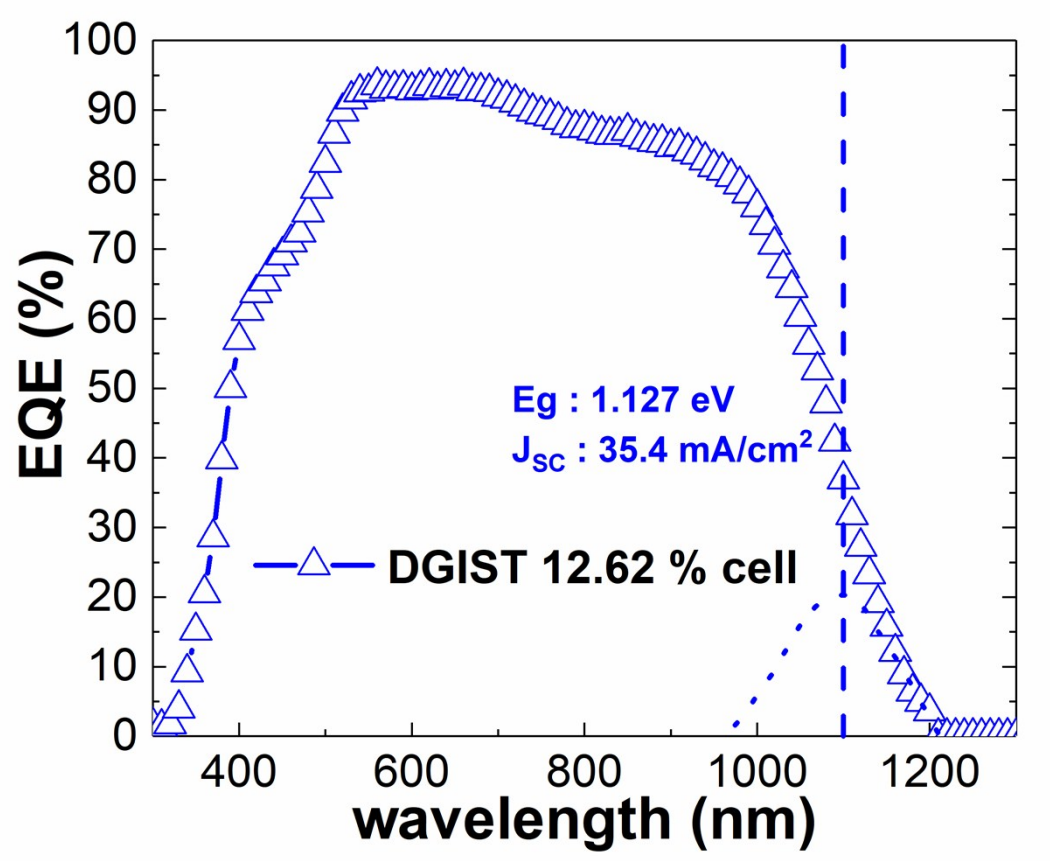


Figure S8. EQE characteristic curves and extracted band gap characteristics of 12.62% certified devices (EQE data was measured with Newport's certification.)