Electronic supplementary information for

Sputtering process highly efficient Cu$_2$ZnSn(S,Se)$_4$ solar cells by a
low-cost, simple, green, up-scalable approach

Myeng Gil Gang$^{a,*}$, Seung Wook Shin$^{b,**}$, Chang Woo Hong$^a$, K.V. Gurav$^a$, Jihye Gwak$^c$, Jae Ho Yun$^c$, Jeong Yong Lee$^{b,*}$ and Jin Hyeok Kim$^{a,**}$

$^a$Optoelectronic Convergence Research Center, Department of Materials Science and Engineering Chonnam National University, 300 Yongbong-Dong, Pak-Gu, Gwangju 500-757, South Korea
$^b$Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 305-701, Korea
$^c$Photovoltaic Laboratory, Korea Institute of Energy Research, 71-2 Jang-Dong Yuseong-Gu, Daejeon 305-343, South Korea

* Corresponding author: (Jeong Yong Lee)

Email:j.y.lee@kaist.ac.kr

TEL: +82-42-350-4216

FAX: +82-42-350-3310

** Corresponding author: (Jin Hyeok Kim)

Email: jinhyeok@chonnam.ac.kr

TEL: +82-62-530-1709

FAX: +82-62-530-1699

† M.G. Gang and S.W. Shin contributed equally to this work.

‡ Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA
Experimental Section

I. Deposition of the metallic precursor

The metallic precursor stacked with Zn/Sn/Cu was prepared on 1 μm thick Mo coated soda lime glass substrates (0.5 Ω/Sq., sheet resistance) using a direct current (DC) magnetron sputtering technique at room temperature. The 2.5 x 2.5 cm² Mo-coated soda lime glass substrates were ultrasonically cleaned using acetone, methanol, isopropyl alcohol, and deionized water for 10 min, consecutively, and then the substrates were placed in the sputtering chamber. Cu, Zn, and Sn metallic targets of 99.999 % purity (TASCO, USA) were used. The sputtering conditions of each metallic layer were as follows: Cu (0.68 W/cm², 8 mTorr, 2812 seconds), Sn (0.68 W/cm², 8 mTorr, 2215 seconds), and Zn (0.68 W/cm², 8 mTorr, 1806 seconds). The composition of the metallic precursor was Cu-poor and Zn-rich, as measured by X-ray fluorescence. The substrate was cooled using a home-made cooling chuck, and the substrate temperature was maintained at 273 K to improve the morphologies and microstructures of the as-deposited Zn and Sn layers by controlling the growth rate. The substrates were rotated at 5 rpm/min. during the sputtering process.

II. Soft annealing of the metallic precursor

Metallic precursor thin films (2.5 x 2.5 cm²) were prepared using the soft annealing process to obtain the Cu-Zn and Cu-Sn alloys in the metallic precursor at different temperatures from 200 to 500 ºC for 10 min under Ar atmosphere. The pressure of annealing chamber was maintained at approximately 400 Torr. The heating rate of the soft annealing process was 10 ºC/s and then the soft annealed precursor thin films were naturally cooled for 1 h.

III. Selenization and sulfo-selenization of the soft annealed metallic
precursor

Soft annealed precursor thin films were individually annealed to synthesize CZTSe and CZTSSe absorber thin films in the Ar + chalcogenide vapor atmosphere. Chalcogenide powders including S and Se, which were purchased from Sigma Aldrich (99.999 %) and the soft annealed precursor thin films were placed in a graphite box (volume ~ 406 cm³), which was subsequently placed into a chamber type rapid thermal annealing system, which could precisely control chalcogenide vapor pressure during the annealing process (Fig. S2). The annealing process occurred at 540 °C for 10 min, and the heating rate was 10 °C/s. After the annealing process, the annealed thin films were naturally cooled for 1 h. The detailed experimental conditions and compositional ratio of samples are listed in Table S2.

IV. Fabrication of CZTSe and CZTSSe solar cells and CZTSSe submodule.

The CZTSe and CZTSSe TFSCs were fabricated with a multi-layer structure of SLG/Mo/CZTSe/CdS/i-ZnO/AZO/Al/MgF₂. Before deposition of CdS thin films, each CZTSe and CZTSSe thin film was soaked in deionized (DI) water for 300 s, etched with 0.2 M potassium cyanide (KCN) at room temperature for 300 s, and rinsed using DI water for 60 s. The 60 nm-thick CdS buffer layer was deposited onto the CZTSe and CZTSSe absorber layers via the chemical bath deposition method using a precursor solution consisting of 0.2 M CdSO₄, 0.84 M ammonia, and 1.02 M thiourea at 80 °C for 12 min. The highly resistive 50 nm thick i-ZnO thin film was prepared using the RF magnetron sputtering technique at room temperature, with an RF power of 75 W, and at a working pressure of 1 mTorr under Ar and O₂ mixed plasma. The 400 nm-thick AZO layers were deposited using the RF sputtering technique at room temperature, with an RF power of 150 W, and at a working pressure of 1 mTorr under Ar plasma. The Al top grid and MgF₂ anti-reflection layers were deposited
using the thermal evaporation technique. The active area of the fabricated TFSCs was 0.43 cm\(^2\). Three addition integration processes were conducted to fabricate the submodule. A schematic illustration of the CZTSSe submodule structure prepared in this manuscript is shown in Fig. S7 with (i) P1: Mo coated SLG substrate was patterned by a laser scribing process and the width of P1 was 30 \(\mu\text{m}\). (ii) P2: CZTSSe absorber, CdS, and i-ZnO layers separated by mechanical scribing process (iii) P3: After the AZO layer deposition, the AZO layer was fabricated to complete the module structure prepared by mechanical scribing process. The widths of P2 and P3 were 30 ~ 40 \(\mu\text{m}\). Finally, eight cell strings were monolithically integrated on the substrate.

V. Characterizations

X-ray diffraction, Raman, and FE-SEM analyses

The structural properties of thin films were measured by using high-resolution X-ray diffraction (XRD, X’pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 100 mA and analyzed using Raman scattering spectroscopy with a Jobin-Yvon T6400 Raman scattering system with an Olympus microscope equipped with a 100X magnification lens and in the backscattering configuration. The excitation source was an Ar ion laser operating at the wavelength of 514 nm and at a 220 mW output power. The surface morphology of the thin films was characterized by using field emission scanning electron microscopy (FE-SEM, Model: JSM-6700F, Japan).

Transmission electron microscopy (TEM)

The bright-field (BF) transmission electron microscopy (TEM) images of the CZTSSe solar cell were obtained using a JEOL-3010 at an operating voltage of 300 kV. Elemental mapping images and energy-dispersive X-ray spectra were acquired by energy-dispersive X-
ray spectroscopy (EDS), using a Tecnai G2 F30 installed in the scanning transmission electron microscopy (STEM) and equipped with a high-angle annular dark-field (HAADF) unit.

**Solar cell performance**

The conversion efficiency and external quantum efficiency (EQE) for CZTSe and CZTSSe TFSCs were characterized by a class AAA solar simulator (WXS-155S-L2, WACOM, and Japan) satisfying the condition of AM 1.5G, 100 mW/cm$^2$, and 25 °C and with an incident photon conversion efficiency (IPCE) measurement unit (PV measurement, Inc., USA).

**Characterization of Device parameters**

To characterize the device parameters including $G_{sh}$, $A$, $J_0$, and $R_s$ for CZTSe and CZTSSe TFSCs, the $J-V$ behavior using the one-diode model according to equation (1S) was employed [S1]:

$$J - J_L = J_0 \exp \left[ \frac{q}{A k T} (V - R_s J) \right] + \frac{V}{G_{sh}}$$

Eq. (1S)

Where, $J_L$ is the photocurrent, $R_s$ is the series resistance, $G_{sh}$ is the shunt conductance, $A$ is the diode ideal factor, $J_0$ is the saturation current density, $q$ is the electronic charge, and $k$ is Boltzmann’s constant. Hegedus et al. have extracted the diode parameter using the detailed process from Eq. (1S). The derivative $dV/dJ$ vs $(J+J_L)^{-1}$ is plotted. A linear fit to the data gives an intercept of $R_s$ and a slope of $A k T/q$ that can be calculated from Eq. (2S) [S1].

$$\frac{dV}{dJ} = R_s + \frac{A k T}{q} (J + J_L)^{-1}$$

Eq. (2S)
Table S1 Summarized experimental conditions, the institutes involved, and the reported performances of CZTSSe-based solar cells

<table>
<thead>
<tr>
<th>Method</th>
<th>Institute</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Precursor</th>
<th>Post treatment</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>CNU</td>
<td>32.14</td>
<td>454.6</td>
<td>63.29</td>
<td>9.24</td>
<td>Metallic stacked precursor</td>
<td>Soft annealing 540 ºC for 10 min.</td>
<td>Se and S powders</td>
<td>This work</td>
</tr>
<tr>
<td>Sputtering</td>
<td>IMEC</td>
<td>38.9</td>
<td>408</td>
<td>61.4</td>
<td>9.7</td>
<td>Metallic stacked precursor</td>
<td>460 °C for 15 min.</td>
<td>H₂Se gas</td>
<td>[S2]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>DIGST</td>
<td>36.1</td>
<td>410</td>
<td>54.62</td>
<td>8.06</td>
<td>S contained and stacked precursor</td>
<td>570 °C for 20 min.</td>
<td>Se powders</td>
<td>[S3]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>IREC</td>
<td>32.4</td>
<td>392</td>
<td>64.4</td>
<td>8.2</td>
<td>Metallic stacked precursor</td>
<td>450 °C for 45 min.</td>
<td>Se pellet</td>
<td>[S4]</td>
</tr>
<tr>
<td></td>
<td>AQT solar</td>
<td>28.3</td>
<td>520</td>
<td>9.3</td>
<td></td>
<td>Se contained and co-sputtering precursor</td>
<td>590 °C for 10 min.</td>
<td>Se and SnS powders</td>
<td>[S5]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>Solar Frontier</td>
<td>33.5</td>
<td>502</td>
<td>64.0</td>
<td>10.8</td>
<td>Metallic precursor</td>
<td>550–590 °C for 10–30 min.</td>
<td>H₂Se and H₂S gas</td>
<td>[S6]</td>
</tr>
<tr>
<td>Co-evaporation</td>
<td>NREL</td>
<td>37.4</td>
<td>377</td>
<td>64.9</td>
<td>9.15</td>
<td>Se contained precursor</td>
<td>.</td>
<td>.</td>
<td>[S7]</td>
</tr>
<tr>
<td>Co-evaporation</td>
<td>IBM</td>
<td>40.6</td>
<td>423</td>
<td>67.3</td>
<td>11.6</td>
<td>Se contained precursor</td>
<td>590 °C for 10 min. and introduction of NaF and TiN interlayer</td>
<td>Se pellet</td>
<td>[S8]</td>
</tr>
<tr>
<td>Nanoparticle</td>
<td>IBM</td>
<td>38.9</td>
<td>466</td>
<td>69.8</td>
<td>12.7</td>
<td>S and Se contained precursor</td>
<td>500 °C for 10–30 min.</td>
<td>Se and S powders.</td>
<td>[S9]</td>
</tr>
<tr>
<td>Electro-deposition</td>
<td>Osaka Univ.</td>
<td>17.7</td>
<td>719</td>
<td>62.9</td>
<td>8</td>
<td>Metallic stacked precursor</td>
<td>Soft annealing 590 °C for 10 min.</td>
<td>S powder</td>
<td>[S10]</td>
</tr>
<tr>
<td>Electro-deposition</td>
<td>KIST</td>
<td>32.4</td>
<td>390</td>
<td>58</td>
<td>8</td>
<td>Metallic stacked precursor</td>
<td>Soft annealing 580 °C for 15 min.</td>
<td>Se pellet</td>
<td>[S11]</td>
</tr>
</tbody>
</table>
Table S2 List of experimental conditions and compositional ratio measured by XRF of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Soft annealed conditions</th>
<th>S or Se vapor pressure (Torr)</th>
<th>Ratio of S/(S+Se) vapor pressure (Torr)</th>
<th>Cu/(Zn+Sn)</th>
<th>Cu/Sn</th>
<th>Zn/Sn</th>
<th>S/(S+Se)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
<td>2.06</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>Precursor</td>
<td>200 °C for 10 min.</td>
<td>.</td>
<td>.</td>
<td>0.71</td>
<td>1.98</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>Precursor</td>
<td>300 °C for 10 min.</td>
<td>.</td>
<td>.</td>
<td>0.67</td>
<td>1.98</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>Precursor</td>
<td>400 °C for 10 min.</td>
<td>.</td>
<td>.</td>
<td>0.67</td>
<td>1.90</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>Precursor</td>
<td>500 °C for 10 min.</td>
<td>.</td>
<td>.</td>
<td>0.62</td>
<td>1.87</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>CZTSe-1</td>
<td></td>
<td>11.5 (Se)</td>
<td>.</td>
<td>0.67</td>
<td>2.18</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>CZTSe-2</td>
<td>200 °C for 10 min.</td>
<td>11.5 (Se)</td>
<td>.</td>
<td>0.67</td>
<td>1.86</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>CZTSe-3</td>
<td>300 °C for 10 min.</td>
<td>11.5 (Se)</td>
<td>.</td>
<td>0.69</td>
<td>1.96</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>CZTSe-4</td>
<td>400 °C for 10 min.</td>
<td>11.5 (Se)</td>
<td>.</td>
<td>0.68</td>
<td>1.97</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>CZTSe-5</td>
<td>500 °C for 10 min.</td>
<td>11.5 (Se)</td>
<td>.</td>
<td>0.68</td>
<td>1.97</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>CZTSSe-1</td>
<td>300 °C for 10 min.</td>
<td>11.5 (Se)</td>
<td>0.51</td>
<td>0.71</td>
<td>2.16</td>
<td>0.94</td>
<td>0.24</td>
</tr>
<tr>
<td>CZTSSe-2</td>
<td>300 °C for 10 min.</td>
<td>11.5 (Se) 25 (S)</td>
<td>0.68</td>
<td>0.68</td>
<td>2.19</td>
<td>0.91</td>
<td>0.32</td>
</tr>
<tr>
<td>CZTSSe-3</td>
<td>300 °C for 10 min.</td>
<td>11.5 (Se) 40 (S)</td>
<td>0.78</td>
<td>0.66</td>
<td>2.19</td>
<td>0.92</td>
<td>0.41</td>
</tr>
<tr>
<td>CZTSSe-4</td>
<td>300 °C for 10 min.</td>
<td>11.5 (Se) 53 (S)</td>
<td>0.82</td>
<td>0.66</td>
<td>2.16</td>
<td>1.06</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Fig. 1S Photo images of metallic precursor thin films, sulfur, and selenium placed in the graphite box (a), the chamber type RTA system (b), a schematic diagram of the sulfo-selenization process in the RTA (c), and the sulfo-selenized thin film placed in the graphite box (d).
Fig. 2S X-ray diffraction patterns (a) and Raman spectra of (b) of CZTSe absorber layers with different soft annealed samples.
Fig. 4S. X-ray diffraction (a) and Raman spectra (b) of CZTSSe absorber layers with different ratios of S/Se.
Fig. 5S. Band gap energies for CZTSSe absorber layers estimated from EQE graphs with different ratios of S/(S+Se) vapor pressure.
Fig. 6S. Photo (a) and cross sectional FE-SEM images for the best performance of the CZTSSe solar cell.
Chonnam National University
CZTSSe solar cell

Device ID: #1137-2
Date of Test: January 14, 2016
Simulator: WACOM, WXS-1555-L2 (Class AAA)
Spectrum: AM1.5 Global
Irradiance: 100 mW/cm²
Sample type: CZTSSe
Device Area: 5.433 cm² (Active area)
Device Temperature: 20.8 °C

Voltage (V) vs. Current (A)

V_{oc} = 0.454 V
I_{sc} = 12.92 mA
V_{mp} = 0.34 V
I_{mp} = 11.66 mA
Fill Factor = 0.622
Efficiency = 8.345%
P_{max} = 4.04 mW

Operator: Youngsoo Ko

Photovoltaic Research Center, Korea Institute of Energy Research
152, Gajeong-ro, Yuseong-gu, Daejeon 305-343, Korea
Tel: +82-42-850-3182, e-mail: notask@kier.re.kr
Fig. 7S Certificated conversion efficiency (9.24 %) of the CZTSSe solar cell with the best performance described in the manuscript.
Fig. 8S. A schematic illustration (a) of the CZTSSe submodule structure and FE-SEM images for P1, P2, and P3 ((b)–(d)) for each fabrication process of the CZTSSe submodule.
References