Electronic supplementary information for

Sputtering process highly efficient Cu₂ZnSn(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*,**}

^aOptoelectronic Convergence Research Center, Department of Materials Science and Engineering Chonnam National University, 300 Yongbong-Dong, Puk-Gu, Gwangju 500-757, South Korea ^bCenter for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 305-701, Korea ^cPhotovoltaic 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 μ m 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 °C 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 °C/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 A1 top grid and MgF₂ anti-reflection layers were deposited

using the thermal evaporation technique. The active area of the fabricated TFSCs was 0.43 cm². 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 μ 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 μ 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/cm², 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_o, and R_s for CZTSe and CZTSSe TFSCs, the *J-V* behavior using the one-diode model according to equation (1S) was employed [S1]:

$$J - J_L = J_0 \exp\left[\frac{q}{AkT}(V - R_s J)\right] + \frac{V}{G_{sh}}$$
 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_o 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 AkT/q that can be calculated from Eq. (2S) [S1].

$$\frac{dV}{dJ} = R_s + \frac{AkT}{q}(J+J_L)^{-1}$$
Eq. (2S)

Method	Institute	J _{sc} (mA/cm²)	V _{oc} (mV)	FF (%)	η (%)	Precursor	Post treatment	Remark	Ref.
Sputtering	CNU	32.14	454.6	63.29	9.24	Metallic stacked precursor	Soft annealing 540 °C for 10 min.	Se and S powders	This work
Sputtering	IMEC	38.9	408	61.4	9.7	Metallic stacked precursor	460 °C for 15 min.	H ₂ Se gas	[82]
Sputtering	DIGST	36.1	410	54.62	8.06	S contained and stacked precursor	570 °C for 20 min.	Se powders	[83]
Sputtering	IREC	32.4	392	64.4	8.2	Metallic stacked precursor	450 °C for 45 min.	Se pellet Sn powder	[84]
Sputtering	AQT solar	28.3	520		9.3	Se contained and co- sputtering precursor	590 °C for 10 min.	Se and SnS powders	[85]
Sputtering	Solar Frontier	33.5	502	64.0	10.8	Metallic precursor	550~590 °C for 10 ~30 min.	H ₂ Se and H ₂ S gas	[86]
Co- evaporation	NREL	37.4	377	64.9	9.15	Se contained precursor			[87]
Co- evaporation	IBM	40.6	423	67.3	11.6	Se contained precursor	590 °C for 10 min. and introduction of NaF and TiN interlayer	Se pellet	[88]
Nanoparticle based	IBM	38.9	466	69.8	12.7	S and Se contained precusor	500 °C for 10- 30 min.	Se and S powders.	[89]
Electro- deposition	Osaka Univ.	17.7	719	62.9	8	Metallic stacked precursor	Soft annealing 590 °C for 10 min.	S powder	[S10]
Electro- deposition	KIST	32.4	390	58	8	Metallic stacked precursor	Soft annealing 580 °C for 15 min.	Se pellet	[\$11]

Table S1 Summarized experimental conditions, the institutes involved, and the reported performances of CZTSSe-based solar cells

Table S2 List of experimental conditions and compositional ratio measured by XRF of the samples.

Sample	Soft annealed conditions	S or Se vapor pressure (Torr)	Ratio of S/(S+Se) vapor pressure (Torr)	Cu/(Zn+Sn)	Cu/Sn	Zn/Sn	S/(S+Se)
Precursor				0.65	2.06	2.17	•
Precursor 200 °C	200 °C for 10 min			0.71	1.98	1.80	
Precursor	300 °C			0.67	1.98	1.95	
Precursor	400 °C			0.67	1.90	1.89	
Precursor	500 °C			0.62	1.87	1.87	
CZTSe-1	for 10 min.	11.5 (Se)		0.67	2.18	2.23	
CZTSe-2	200 °C for 10 min	11.5 (Se)		0.67	1.86	0.94	
CZTSe-3	300 °C	11.5 (Se)		0.69	1.96	0.89	
CZTSe-4	400 °C	11.5 (Se)		0.68	1.97	0.96	
CZTSe-5	500 °C	11.5 (Se)		0.68	1.97	0.98	
CZTSSe-1	300 °C	11.5 (Se) 12 (S)	0.51	0.71	2.16	0.94	0.24
CZTSSe-2	300 °C	11.5 (Se) 25 (S)	0.68	0.68	2.19	0.91	0.32
CZTSSe-3	300 °C	11.5 (Se)	0.78	0.66	2.19	0.92	0.41
CZTSSe-4	300 °C for 10 min.	40 (S) 11.5 (Se) 53 (S)	0.82	0.66	2.16	1.06	0.49



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.





Fig. 7S Certificated conversion efficiency (9.24 %) of the CZTSSe solar cell with the best performance described in the manuscript.



P1 : Mo scribing, P2 : CZTS absorber, CdS and i-ZnO layers scribing, P3 : AZO scribing



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

- S1. S.S. Hegedus, W.N, Shafarman, Prog. Photovolt.: Res. Appl., 12 (2004) 155-176, DOI:10.1002/pip518.
- S2. G. Brammertz, M. Buffière, S. Oueslati, H. ElAnzeery, K. Ben Messaoud, S. Sahayaraj, C. Köble, M. Meuris and J. Poortmans, Appl. Phys. Lett., 103, (2013) 163904.
- S3. G.Y. Kim, A.R. Jeong, J.R. Kim, W. Jo, D.H. Son, D.H. Kim, J.K. Kang, Sol. Energy Mater. Sol. Cells 127 (2014) 129-135
- S4. M. Neuschitzer, Y. Sanchez, S. Lopez-Marino, H. Xei, A. Fairbrother, M. Placidi, S. Haass, V. Izquierdo-Roca, A. Perez-Rodriguez and E. Sauecedo, Prog. Photovolt.: Res. Appl.,(2015) DOI:10.1002/pip2589.
- S5. Chawla, V., and Clemens, B. (2012). 38th IEEE Photovoltaic Specialists Conference (PVSC)
- S6. T. Kato, H. Hiroi, N. Sakai, H. Sugimoto, 28'h Eur. Photovolt. Sol. Energy Conf., 2013, pp. 2125-2127
- S7. I. Repins, C. Beall, N. Vora, C. DeHart, D. Kuciauskas, P. Dippo, B. To, J. Mann, W.C. Hsu, A. Goodrich and R. Noufi, Sol. Energy Mater. Sol. Cells, 101 (2012) 154-159
- S8. B. Shin, Y. Zhu, N. A. Bojarczuk, S. Jay Chey and S. Guha, Appl. Phys. Lett., 101 (2012) 053903.
- S9. J. H. Kim, H. Hiroi, T.K. Todorov, O. Gunawan, M. Kuwahara, T. Gokmen, D. Nair, M. Hopstaken, B. Shin, Y.S. Lee, W. Wang, H. Sugimoto, D.B. Mitzi, Adv. Mater., 26 (2014) 7427-7431
- S10. F.Jiang, S. Ikeda, T. Harada, and M. Matsumura, Adv. Energy Mater. 4 (2014) 1301381
- S11. J.O. Jeon, K. D. Lee, L. Seul Oh, S.W. Seo, D.K. Lee, H. Kim, J.H. Jeong, M. J. Ko, B. Kim, H. J. Son and J. Y. Kim, Chem. Sus. Chem., 7 (2014) 1073-1077.