Supporting Information

Sulfur Alloying Effects on $Cu(In,Ga)(S,Se)_2$ Solar Cell Fabricated by Using Aqueous Spray Pyrolysis

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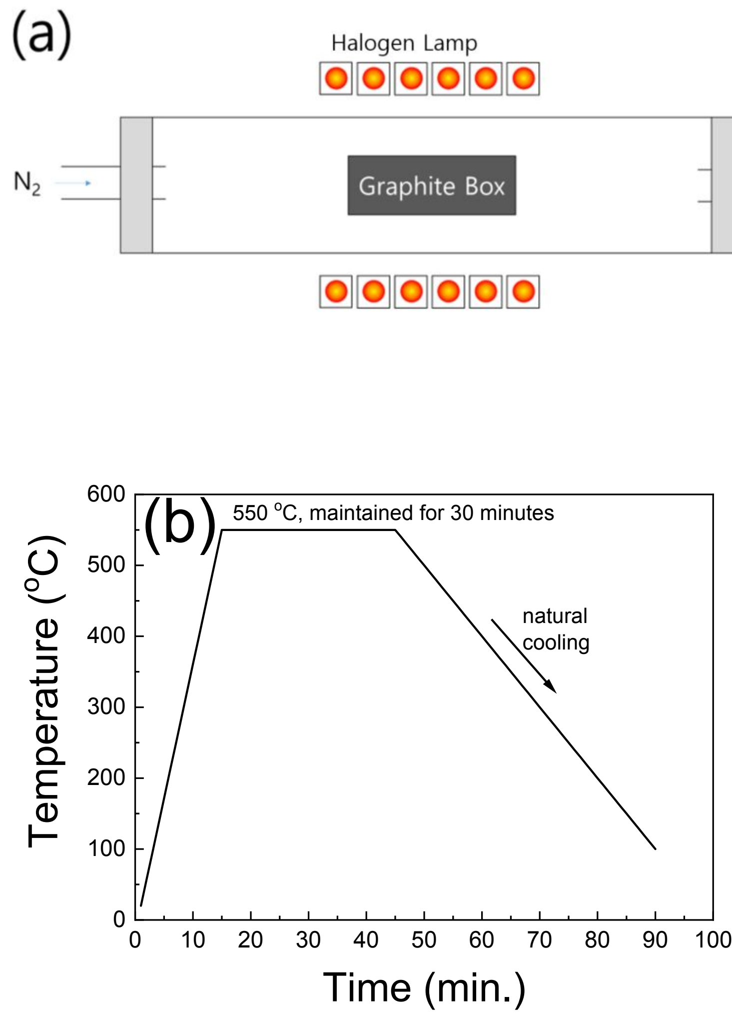

Fig. S1. Schematic of (a) sulfo-selenization furnace and (b) temperature profiling for sulfo-selenization.

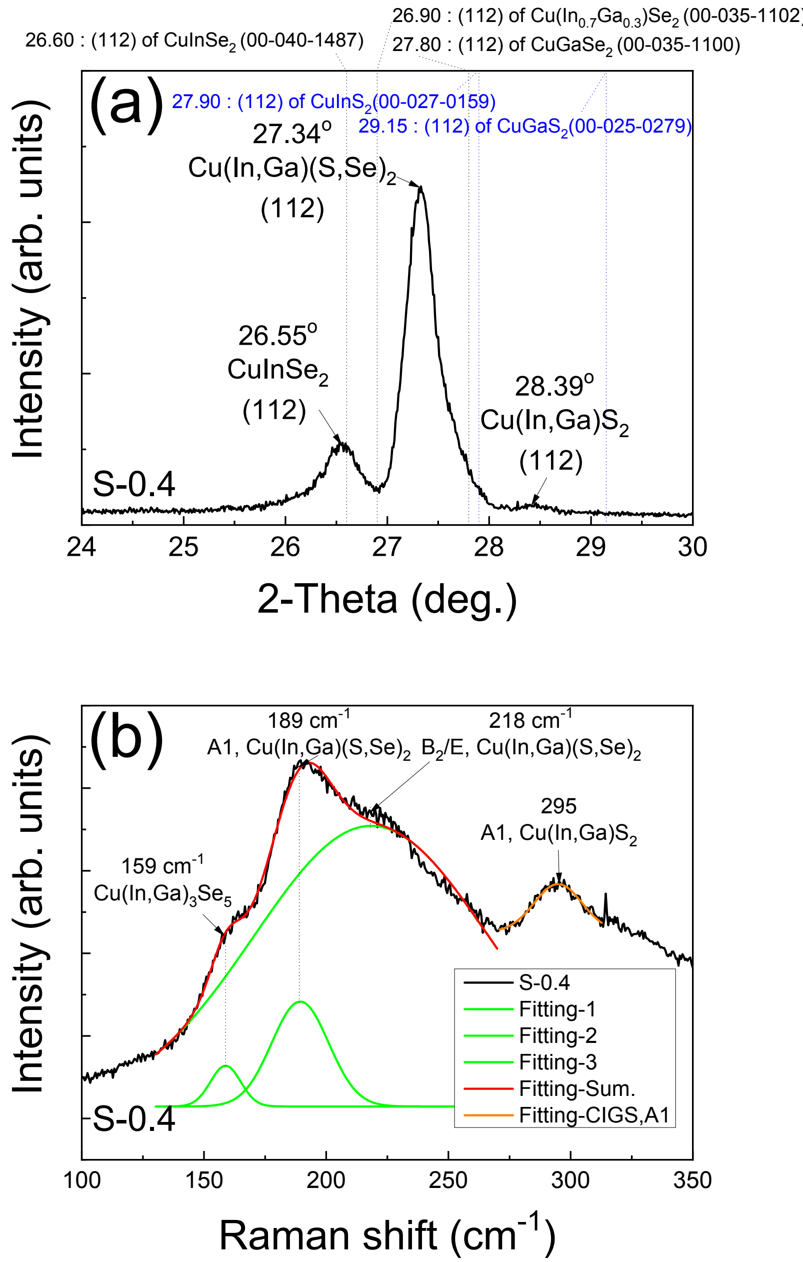

Fig. S2. Detailed analysis of (a) XRD and (b) Raman spectroscopy for S-0.4 CIGSSe thin film. We estimated possible secondary phases referring to JCPDS for XRD and Gaussian fitting for Raman spectroscopy.

Figure S2 shows enlarged graphs of XRD and Raman spectroscopy, which are from Fig. 2 and Fig. 3. In XRD result of Fig. S2(a), no single (112) $Cu(In,Ga)(S,Se)_2$ peak is observed. Three peaks are observed, They can be assigned as (112) of $CuInSe_2$, (112) of $Cu(In,Ga)(S,Se)_2$ and (112) of $Cu(In,Ga)S_2$ (Ref.: 26.60° for (112) of $CuInSe_2$(JCPDS : 00-040-1487), 26.90 ° for (112) of $Cu(In,Ga)(S,Se)_2$ (JCPDS : 00-035-1102), 27.80 ° for (112) of $CuGaSe_2$ (JCPDS : 00-035-1100) , 27.90 for (112) of $CuInS_2$ (JCPDS : 00-027-0159), 29.15 of CuGaS2 (JCPDS : 00-025-0279)). This result indicates that S-0.4 was not grown in single phase. Fig. S2(b) is the enlarged Raman spectrum of Fig. 3. We fitted Raman spectrum in the range of 100 cm^{-1}~ 350 cm^{-1}. The observed spectrum may be composed of A1 mode of $Cu(In,Ga)_3Se_5$ (159 cm^{-1}), A1 mode of $Cu(In,Ga)(S,Se)_2$ (189 cm^{-1}), B2/E mode of $Cu(In,Ga)(S,Se)_2$ (218 cm^{-1}), and A1 mode of $Cu(In,Ga)S_2$ (295 cm^{-1}). Along with XRD result of Fig. S2(a), this result also indicates that S-0.4 absorber was grown in multi phases. From Fig. S(2), it is concluded that the same post sulfo-selenization which was used in the fabrication for S-0, S-0.1,S-0.2 and S-0.4 CIGSSe could not produce S-0.4 CIGSSe absorber in single phase, and for higher S-alloying more than S-0.4 other sulfo-selenization condition is necessary.

Table S1. EDS results of CIGSSe absorbers with S-0.0, S-0.1, S-0.2, S-0.3 and S-0.4.

Atomic (%)	S-0.0	S-0.1	S-0.2	S-0.3	S-0.4
O K	18.06	0	4.58	12.35	5.73
Na K	0	0	0	2.58	0
S K	1.63	13.78	14.9	15.12	20.84
Cu K	15.92	21.15	20.26	17.06	16.81
Ga K	4.44	5.44	5.55	4.49	4.83
Se L	43.06	39.07	35.16	30.9	30.77
In L	16.88	20.57	19.55	17.5	21.02
Cu/(In+Ga)	0.75	0.81	0.81	0.78	0.65
Ga/(In+Ga)	0.21	0.21	0.22	0.2	0.19
S/(S+Se)	0.04	0.26	0.3	0.33	0.4

Table S2. Summary of CIGSSe solar cells made by solution-based deposition

Method	Solution	PCE (%)	MgF_2 anti-reflection coating	Ref.
Spin coating	Hydrazine-based solution	17.3	No	S1
Inkjet	Metal nitrate solution in mixture of 2-propanol and ethylene glycol	11.3	No	S2
Spray pyrolysis	Metal sulfide solution in diamine/dithiol mixture	8	Yes	S3
Spray pyrolysis	Aqueous solution (nitrate-based)	10.7	Yes	S4
Spray pyrolysis	Aqueous solution (chloride-based)	10.5	Yes	S5
Spray pyrolysis	Aqueous solution (chloride-based)	10.89	No	**Our work**

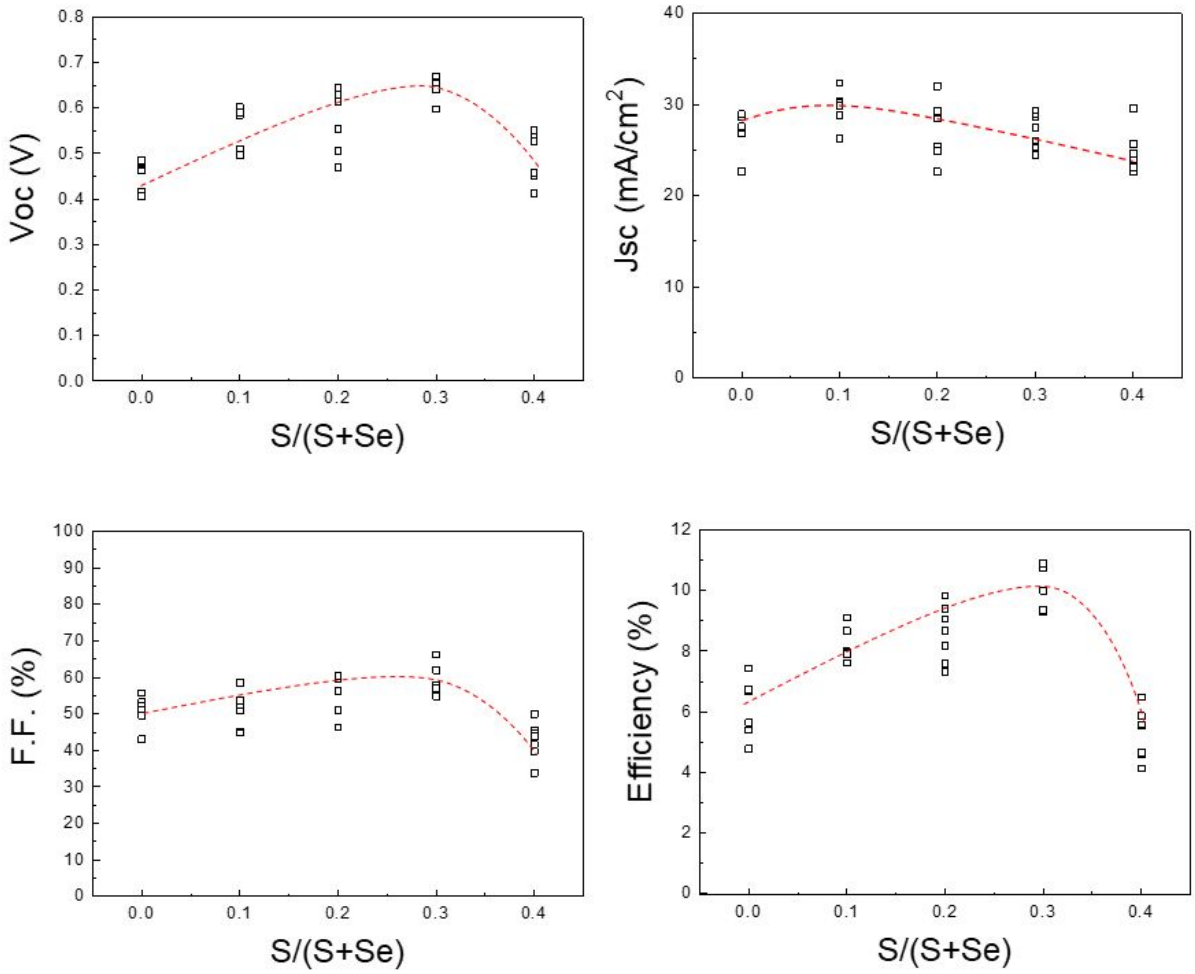

Fig. S3. Statistical data for device parameters of fabricated CIGSSe solar cells. (Seven cells for each S concentration)

Table S3. Table of statistical data for all CIGSSe solar cells (seven cells for each S concentration)

	V_{oc} (V)		J_{sc} (mA/cm^2)		F.F. (%)		PCE (%)	
	average	std. dev.	average	std. dev.	average	std. dev.	average	std. dev.
S-0.0	0.45	0.027	26.90	1.92	50.67	3.63	6.19	0.87
S-0.1	0.56	0.040	29.71	1.73	50.03	4.96	8.33	0.57
S-0.2	0.58	0.063	27.35	2.95	54.95	5.14	8.58	0.86
S-0.3	0.64	0.021	27.15	1.80	58.86	3.60	10.27	0.66
S-0.4	0.5	0.052	24.83	2.15	42.74	4.69	5.26	0.77

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