Electronic Supplementary Information

Relationship between the intermediate phases of sputtered Zn(O, S) buffer layer and the conduction band offset in Cd-free Cu(In,Ga)Se_2 solar cells

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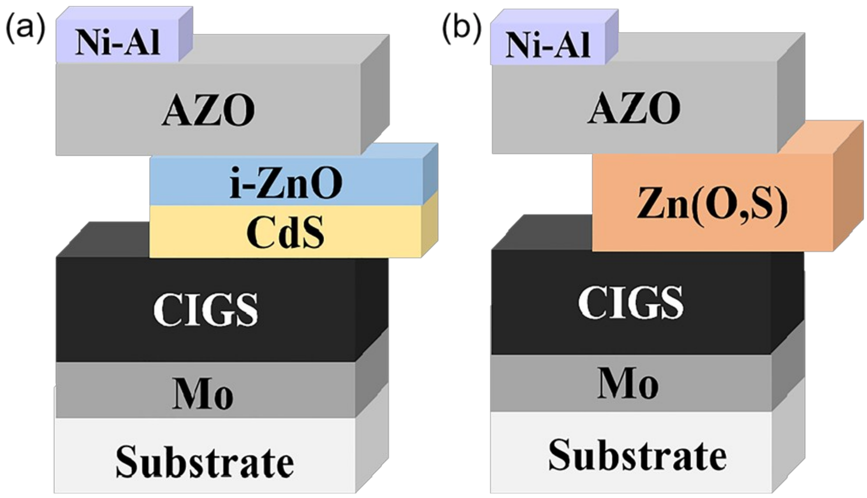

Figure S1. (a) The configurations of conventional CdS-based CIGS solar cells and (b) Zn(O,S)-based CIGS solar cells.

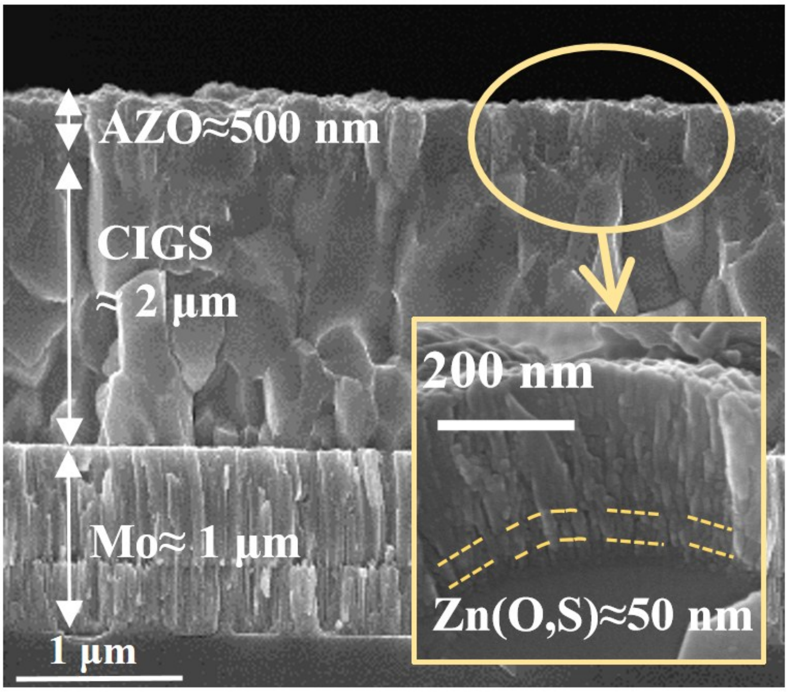

Figure S2. The configuration of cross-sectional SEM image of Zn(O,S)/CIGS heterojunction solar cells. The amplified part in the white circle is the Zn(O,S) buffer layer of 50 nm approximately.

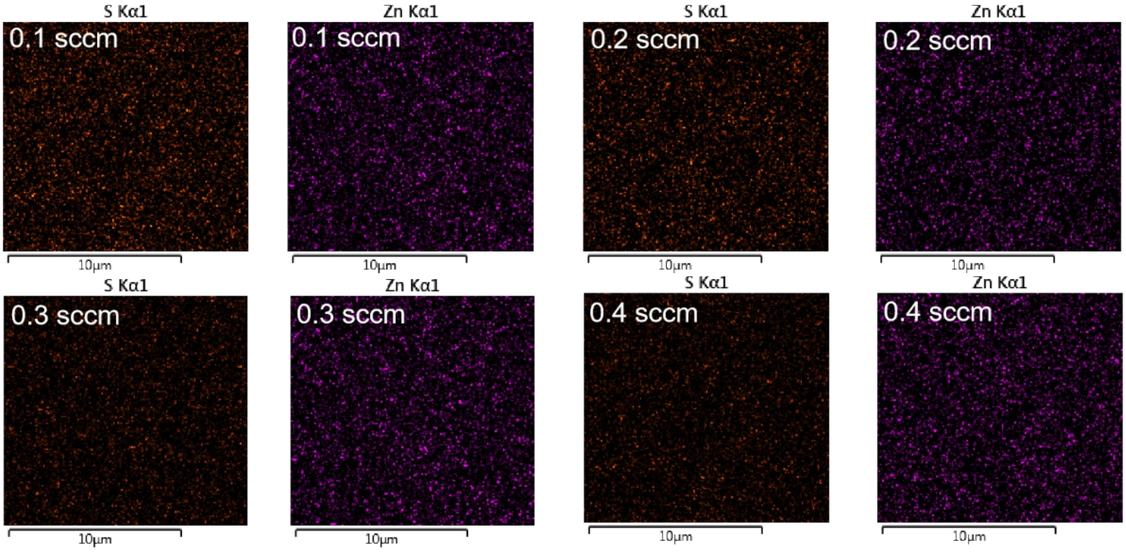

Figure S3. The EDS results of S and Zn elements distribution in the Zn(O,S) thin films with different oxygen fluxes (from 0.1 sccm to 0.4 sccm).

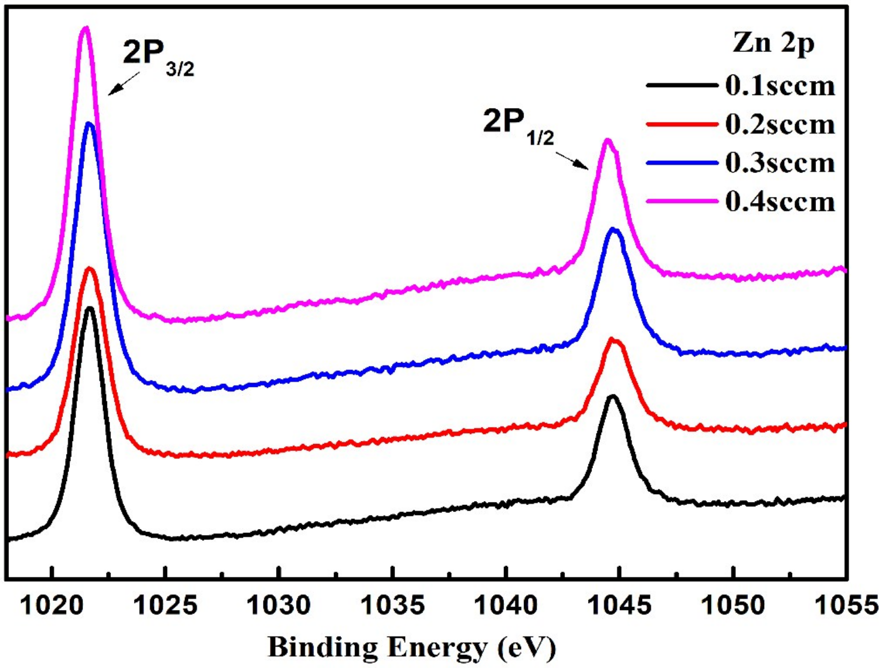

Figure S4. The XPS result of Zn 2p spectra in Zn(O,S) thin films with the various oxygen flux. The peak centered at 1022.3 eV is Zn $2p_{3/2}$ and the peak positioned at 1044.9 eV is Zn $2p_{1/2}$.

Table S1. The variation of S content in Zn(O,S) thin films with the different oxygen fluxes based on XRF results.

Oxygen flux (sccm)	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**
S content based on XRF result	0.58	0.54	0.28	0.27	0.27	0.26

Table S2. GIXRD Peak position of thin films under different oxygen fluxes based on XRD results.

Oxygen flux (sccm)	Crystal orientation 2θ (°)		
	（100）	（002）	（101）
0.1	30.33	N/A	N/A
0.2	30.88	N/A	N/A
0.3	31.17	33.36	35.47
0.4	31.44	33.82	35.85

Table S3. The variation of S content in Zn(O,S) thin films with the different oxygen fluxes based on XRF and XPS results.

Oxygen flux (sccm)	0.1	0.2	0.3	0.4
S content based on XRF result	0.58	0.54	0.28	0.27
S content based on XPS result	0.63	0.57	0.28	0.23

Table S4. Peak area of O1s under the different oxygen fluxes

Oxygen flux (sccm)	Peak area		
	O-A	**O-B**	**O-C**
0.1	4268.1	14094.9	7866.0
0.2	4235.9	14302.6	6960.1
0.3	4762.0	19674.6	9624.4
0.4	4591.2	19820.6	10789.9

Table S5. The simulation parameters of the Zn(O,S)/CIGS solar cells

	Al-ZnO	**CdS**	**Zn(O,S)**	**CIGS**
Thickness (nm)	350	50	50	~2000
Permittivity	9	10	13.6	13.6
Eg(eV)	3.3	2.4	variable	variable
Electron affinity	4.6	4.2	variable	variable
Nc (cm^{-3})	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}
Nv (cm^{-3})	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}
μ_e ($cm^2/V*s$)	100	100	75	40
μ_h ($cm^2/V*s$)	30	20	20	10
Nd (cm^{-3})	1.0×10^{18}	1.0×10^{18}	1.0×10^{12}	~
Na (cm^{-3})	~	~	~	2.0×10^{16}

Table S6. Performance of $Cu(In,Ga)Se_2$ (CIGS) solar cells based on the samples with different oxygen fluxes and the samples with CdS buffer layer.

Cells	Cell number	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF [%]	Eff [%]
0.1 sccm	**#1**	**478**	**27.13**	**41.32**	**5.4**
	#2	430	27.79	35.71	4.3
	#3	490	26.70	38.45	5.04
	#4	484	24.60	29.85	3.56
	#5	482	27.32	39.87	5.25
	#6	476	27.45	41.18	5.38
	#7	473	27.21	41.10	5.29
	#8	489	27.03	40.25	5.32
0.2 sccm	**#1**	**538**	**34.04**	**59.43**	**10.89**
	#2	508	28.8	66.95	9.8
	#3	466	28.5	55.74	7.39
	#4	562	26.18	61.09	8.9
	#5	554	32.31	58.78	10.52
	#6	539	33.94	56.52	10.34
	#7	542	28.57	56.77	8.79
	#8	546	30.92	58.40	9.86
0.3 sccm	**#1**	**592**	**31.63**	**71.24**	**13.34**
	#2	580	32.7	70.12	13.3
	#3	556	33.53	69.66	12.99
	#4	538	32.57	65.83	11.53
	#5	584	32.32	70.20	13.25
	#6	581	32.69	69.03	13.11
	#7	569	33.41	67.72	12.87
	#8	552	31.55	65.98	11.49
0.4 sccm	**#1**	**574**	**25.11**	**66.11**	**9.54**
	#2	512	29.34	57.58	8.65
	#3	550	26.03	51.93	7.43

	#4	557	28.43	59.42	9.41
	#5	542	28.69	57.36	8.92
	#6	554	27.64	61.78	9.46
	#7	561	29.11	57.20	9.34
	#8	549	28.34	54.77	8.52
CdS/CIGS	**#1**	**616**	**30.73**	**76.06**	**14.4**
	#2	658	32.16	67.06	14.19
	#3	634	29.18	69.99	12.95
	#4	640	29.96	69.83	13.39
	#5	647	30.55	72.15	14.26
	#6	635	31.67	68.97	13.87
	#7	638	32.15	66.74	13.69
	#8	641	30.76	72.22	14.24

Table S7. Performance of $Cu(In,Ga)Se_2$ (CIGS) solar cells based on the samples with different oxygen fluxes and the samples with CdS buffer layer after a half year.

Cells	Cell number	Voc [mV]	Jsc [mA cm^{-2}]	FF [%]	Eff [%]
0.1 sccm	#1	477	26.52	41.15	5.21
	#2	428	27.82	35.43	4.22
	#3	491	26.54	38.79	5.05
	#4	480	24.48	29.39	3.42
	#5	482	27.17	39.56	5.18
	#6	477	26.98	41.01	5.28
	#7	471	27.19	39.86	5.14
	#8	483	26.75	40.17	5.20
0.2 sccm	#1	539	33.91	59.22	10.82
	#2	501	28.81	66.24	9.56
	#3	465	28.34	55.12	7.26
	#4	557	25.96	60.74	8.78
	#5	546	31.99	57.32	10.01
	#6	528	33.67	56.66	10.07
	#7	543	27.74	54.57	8.22
	#8	546	30.12	58.23	9.58
0.3 sccm	#1	590	31.52	70.83	13.17
	#2	572	32.25	69.34	12.79
	#3	554	33.29	69.47	12.81
	#4	529	32.33	65.26	11.16
	#5	585	32.24	70.03	13.21
	#6	580	32.42	68.69	12.92
	#7	562	32.89	67.36	12.45
	#8	548	30.74	65.21	10.98
0.4 sccm	#1	573	25.12	66.08	9.51
	#2	510	29.25	57.46	8.57
	#3	543	25.58	50.69	7.04

	#4	557	28.38	59.25	9.37
	#5	541	28.43	56.99	8.77
	#6	555	27.63	61.74	9.47
	#7	559	29.10	57.12	9.29
	#8	547	28.19	54.53	8.41
CdS/CIGS	#1	612	30.37	75.98	14.12
	#2	658	32.09	66.84	14.11
	#3	630	29.17	69.75	12.82
	#4	640	29.81	69.48	13.26
	#5	644	30.13	71.87	13.95
	#6	631	31.55	68.62	13.66
	#7	638	32.14	66.75	13.69
	#8	642	30.58	72.19	14.17