Influence of reaction pathway on the defects formation in Cu₂ZnSnSe₄ thin film

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Table S1. The transition of composition ratios before and after annealing process. The composition ratios of precursor and CZTSe films for samples A1–A4 are measured by ICP-OES and EDS, respectively.

	Temp. for LT stage	Temp. for HT stage	[Cu]/[Sn]	[Zn]/[Sn]	[Se]/[Sn]	[Cu]/ ([Zn]+[Sn])	[Se]/ [metals]
Precursor	-	-	1.74	1.39	-	0.73	-
A1	-	490 °C	1.61	1.13	4.38	0.76	1.17
A2	300 °C	490 °C	1.79	1.34	4.73	0.76	1.15
A3	350 °C	490 °C	1.73	1.18	4.56	0.79	1.17
A4	400 °C	490 °C	1.72	1.64	4.91	0.65	1.13



Figure S1. Statistical data of 18 cells per each sample from three series. One series means that all processes – from precursor to Al grid – for a device fabrication are performed at the same time, except annealing process, and one device from one series has 6 cells per samples.



Figure S2. Cross sectional images of A3-p2 sample and composition ratios of each points marked by red and blue circles.



Figure S3. Enlarged view of XRD patterns in range of 42–46 degree for A1-p2, A2-p2, A3-p2 and A4-p2 diffractions from Figure 2a, c, e and g, respectively. By comparison with

diffractions of other samples, it is clear that A4-p2 has $Cu_{2-x}Se$ and Cu_2Zn phases in the film.



Figure S4. Surface (a–d) and cross sectional (e–f) SEM images of CZTSe films for samples A1 (a,e), A2 (b,f), A3 (c,g), and sample A4 (d,f).



Figure S5. Results of a) admittance spectroscopy measured from 300 K (dark red) to 100 K (dark blue), b) spectra for the derivative $(dC(\omega)/d\omega) \cdot (-\omega / kT)$, and c) Arrhenius plots for the samples A1, A2, A3 and A4.^{17–20} Here the maximum of the derivative is the inflection points of capacitance-frequency spectra (Figure S5a). The extracted inflection

points (Figure S5b) by using these spectra are put into the Arrhenius plot (Figure S5c) to calculate the defect energy levels, as described in Figure 5.

Table S2. The assigned defects and other possible intrinsic defects related with the obtained defect levels in this study.⁵

Sample	Obtained	The assigned	The other defects related	
name	defect levels	defect in this study	with the defect energy levels	
A1	86 meV	Zn _{Cu} (0/+)		
	173 meV	Zn _{Sn} (2-/-)	Cu _{Sn} (-/0), V _{Sn} (-/0)	
	211 meV	V _{Zn} (2-/-)	V _{Sn} (2-/-)	
A2	169 meV	Zn _{Sn} (2-/-)	Cu _{Sn} (-/0), V _{Sn} (-/0)	
A3	36 meV	V _{Cu} (-/0)		
	85 meV	Zn _{Cu} (0/+)		
	128 meV	Cu _{Zn} (-/0)		
A4	130 meV	Cu _{Zn} (-/0)		
	168 meV	Zn _{Sn} (2-/-)	Cu _{Sn} (-/0), V _{Sn} (-/0)	



Figure S6. XRD patterns which present the compounded alloys at the points before the formation of CZTSe film per each sample: p1 for A1, p2 for A2, p2 for A3 and p1 for A4 samples. In case of A4 sample, because CZTSe phase is already dominantly formed at point p2 (A4-p2) in the film, XRD pattern for A4-p1 is taken in here.