Precursor Stack Ordering Effects in $Cu_2ZnSnSe_4$ Thin Films Prepared by Rapid Thermal Processing

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SUPPORTING INFORMATION

Table S1 contains the compositions of the precursor and annealed $Cu_2ZnSnSe_4$ (CZTSe) thin films. These data were used to calculate the Zn- and Sn-loss from annealing presented in Table 1. Specifically, the fraction between precursor and annealed Cu/Zn or Cu/Sn, were used to determine the percentage of each elemental loss. The copper content is used as a reference value, because there is no expected Cu-loss due to the low volatility of Cu and Cu-Se phases when compared to Zn and Sn-Se.

Table S1. Cation composition ratios of metallic precursor and CZTSe films.

Stack order	Prec. Cu/(Zn+Sn)	Ann. Cu/(Zn+Sn)	Prec. Zn/Sn	Ann. Zn/Sn	Prec. Cu/Zn	Ann. Cu/Zn	Prec. Cu/Sn	Ann. Cu/Sn
Zn/Cu/Sn	0.69	0.79	1.07	1.23	1.34	1.44	1.43	1.77
Zn/Sn/Cu	0.75	0.78	1.11	1.15	1.42	1.46	1.58	1.67
Sn/Cu/Zn	0.75	0.82	1.16	1.09	1.39	1.57	1.62	1.71
Sn/Zn/Cu	0.82	0.83	1.28	1.21	1.46	1.51	1.87	1.83
Sn/Cu/Zn/ZnO	0.78	0.86	1.16	1.01	1.45	1.51	1.68	1.73
Sn/Cu/ZnO	0.78	0.93	1.09	1.57	1.50	1.52	1.62	2.39

Figure S1 contains energy-dispersive x-ray spectroscopy (EDX) mappings for Cu, Zn, and Sn of the Zn/Cu/Sn (Figure S1a) and Sn/Cu/Zn (Figure S1b) CZTSe films in cross section. The films containing Zn as the bottom layer (Zn/Cu/Sn and Zn/Sn/Cu) show an accumulation of Zn in the back contact region, consistent with high quantity of the ZnSe phase detected there by Raman spectroscopy. The films containing a Sn bottom layer (Sn/Cu/Zn, Sn/Zn/Cu, and Sn/Cu/Zn/ZnO) show a much more uniform distribution of the elements. While ZnSe and $SnSe_2$ were detected in these films, they appear in much lower amounts than the films with a Zn bottom layer, and the accumulation of Zn is not apparent given the spatial resolution of the EDX mappings.

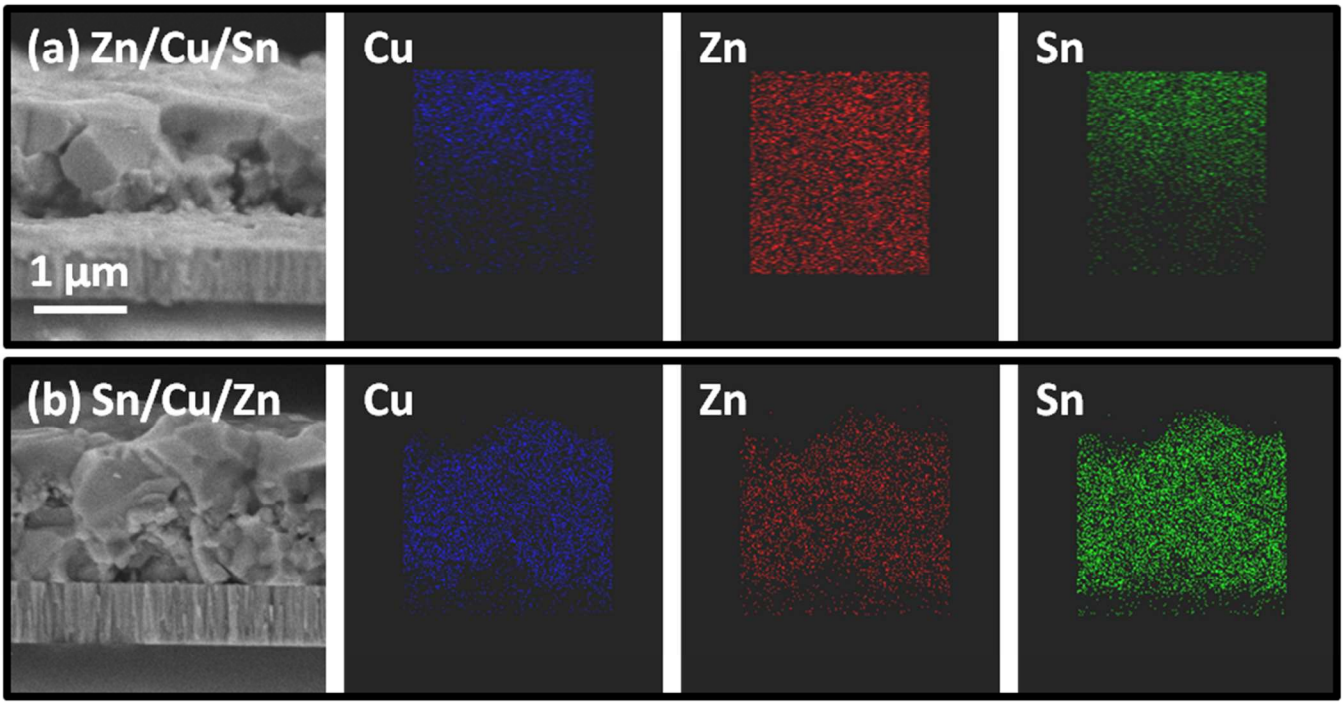

Figure S1. Cross section EDX mapping measurements of Zn/Cu/Sn (a) and Sn/Cu/Zn (b), showing an accumulation of Zn in the back contact region for the first film, and a more uniform distribution of the elements in the latter.

Figure S2 shows the Raman scattering spectra of CZTSe films prepared with the Zn/Sn/Cu (Figure S2a) and Sn/Cu/Zn (Figure S2b) precursor stack orders, which were omitted from the main text because of their similarity to other films. The first is qualitatively similar to the Zn/Cu/Sn sample, and the second to the Sn/Zn/Cu sample. For the Zn/Sn/Cu stack order $SnSe_2$ is detected on the surface, while ZnSe is only detected in the back. For the Sn/Cu/Zn precursor no secondary phases are detected on the surface, but $SnSe_2$ and ZnSe are detected in the back absorber region.

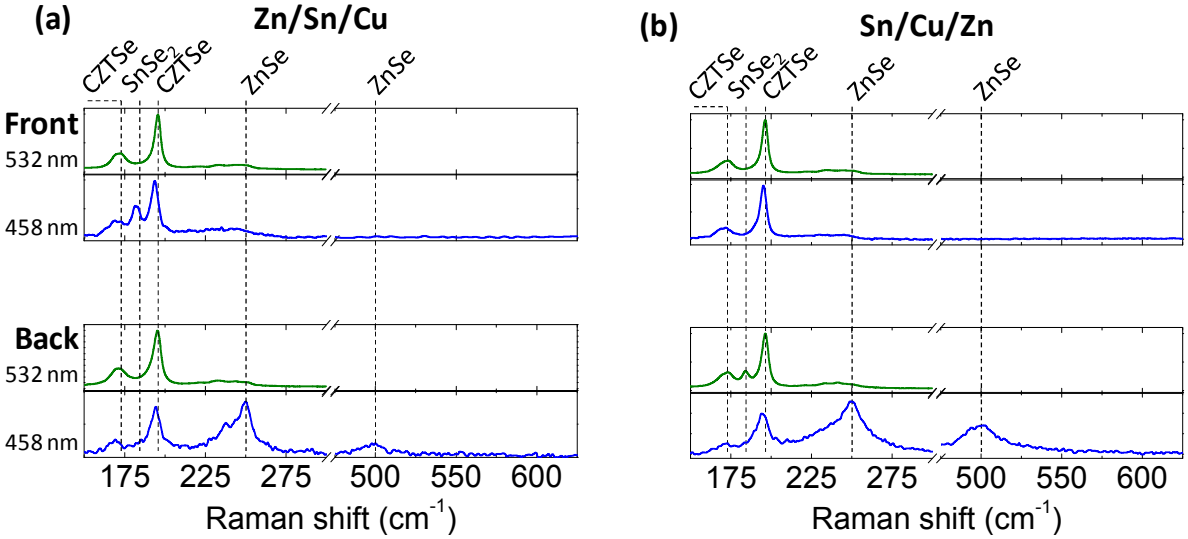

Figure S2. Raman spectra of CZTSe films using different excitation wavelengths (532, 458 nm) made on the front and back of annealed films: (a) Zn/Sn/Cu and (b) Sn/Cu/Zn. Refer to Figure 3 in the main text for films prepared from the other four stack orders.