Supplementary Information for

Self-regulation of Cu/Sn ratio in the synthesis of Cu_2ZnSnS_4 films

Melissa C. Johnson, Cody Wrasman, Xin Zhang, Michael Manno, C. Leighton*, Eray S. Aydil*

Department of Chemical Engineering & Materials Science, 421 Washington Avenue, University of Minnesota, Minneapolis, Minnesota 55455, United States of America

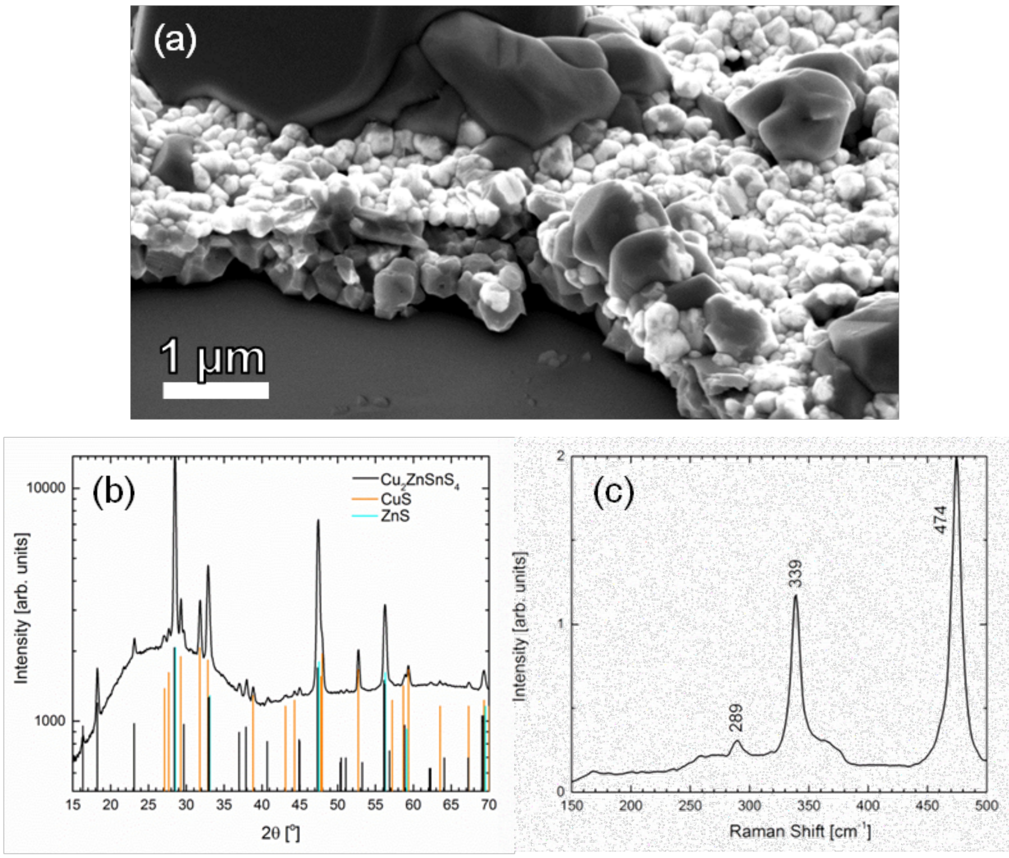

Figure S1. (a) SEM image of a very Sn-poor (51% Cu, 38% Zn, 11% Sn, Cu/Sn = 4.6) precursor film after sulfidation at 600 ^{o}C with 1 mg of Sn charged to the ampoule. The final elemental composition of the sulfidized film was 24% Cu, 19% Zn, 6% Sn, and 51% S. The large darkest features on the surface of the film are domains of CuS, which sit atop a layer of ZnS, which appears brighter because ZnS is insulating. The darker layer between this ZnS layer and the substrate is a layer of CZTS. These morphological features were identified from the local compositions determined by EDS. Structural characterization, using (b) XRD and (c) Raman spectroscopy, confirms the presence of CZTS and CuS.

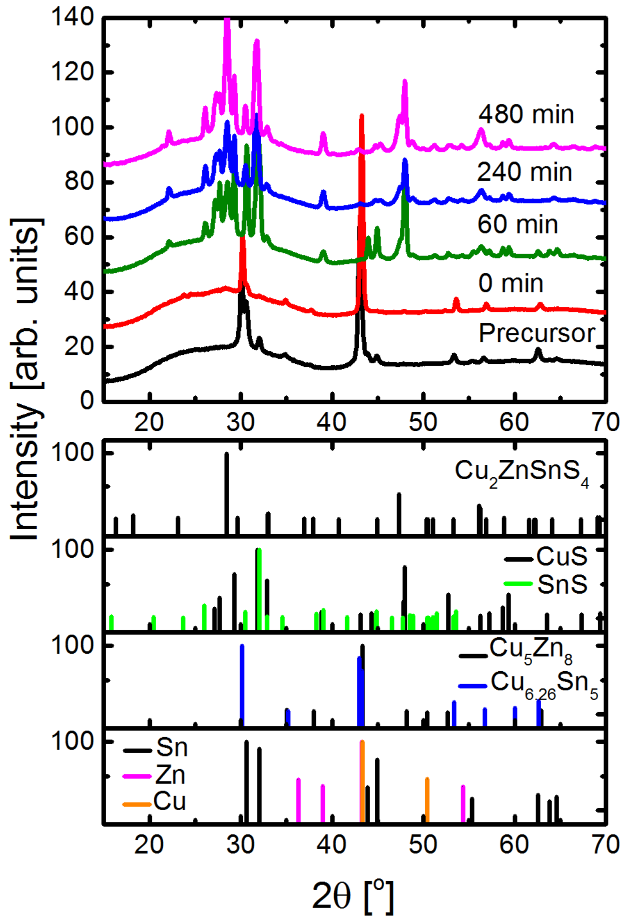

Figure S2. The top panel displays the XRD patterns collected from films before and after sulfidation at 300 °C for 0, 60, 240, and 480 minutes. The precursor film is Sn-rich and slightly Zn-poor such that Cu/Sn = 1.6 and Cu/Zn = 2.3. The bottom panel displays the expected powder diffraction patterns for Cu_2ZnSnS_4, CuS, SnS, Cu_5Zn_8, Sn, Zn, and Cu.

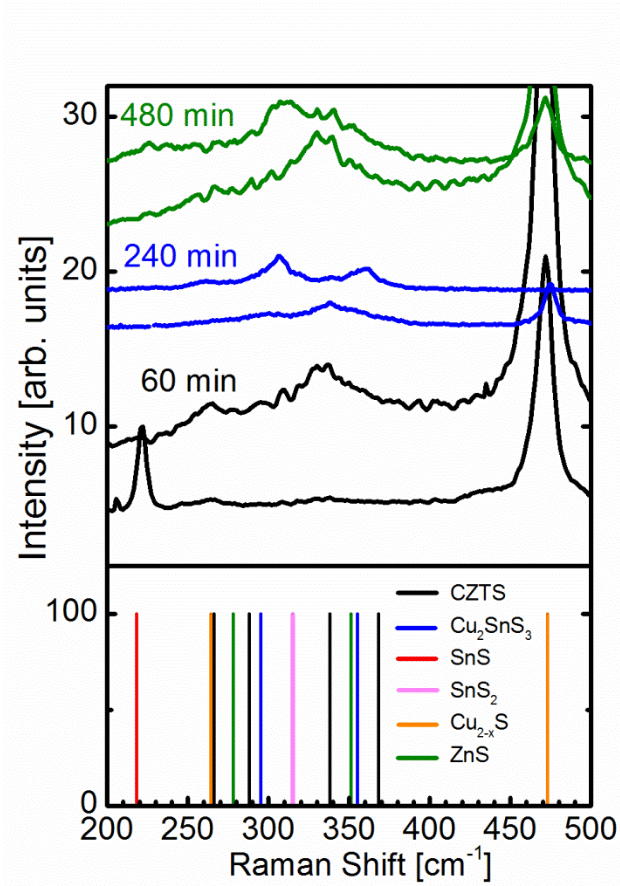

Figure S3. The top panel displays Raman spectra collected from films sulfidized at 300 °C for 60, 240, and 480 minutes. A confocal Raman microscope was used to examine different locations on the films. Two representative spectra taken from different locations on each film are shown. The spectra were selected to show the presence of different phases within the film, and are not representative of the *quantity* of a given phase within the film. The bottom panel shows the expected peak locations of various phases for comparison.

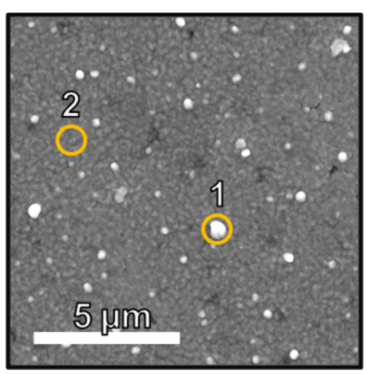

Figure S4. An SEM image of a CZTS film sulfidized for 0 minutes at 300 °C. The cation composition found by EDS for the white insulating features (point 1) is 44% Cu, 27% Zn, and 29% Sn. The composition of the rest of the film (point 2) is 49% Cu, 23% Zn, and 28% Sn. We surmise that these white insulating features are small domains of ZnS.

Table S1. Thermodynamic data for the formation of binary sulfides and alloys.

Reaction	ΔG_f (kJ/mol) @ 300 °C	Reference
$2Cu + S_2\,(g) \rightarrow 2CuS$	-146.02	S1
$2Sn + S_2\,(g) \rightarrow 2SnS$	-243.04	S1
$2Zn + S_2(g) \rightarrow 2ZnS$	-427.88	S1
$6Cu + 5Sn \rightarrow Cu_6Sn_5$	-7.42	S2
$5Cu + 8Zn \rightarrow Cu_5Zn_8$	-12.34	S2

References

(S1) Vaughan, D.; Craig, J. *Mineral Chemistry of Metal Sulfides*; Cambridge University Press: London, UK, 1978.

(S2) Yu, S.; Wang, M.; Hon, M. *J. Mater. Res.* **2001**, *16*, 76-82.