Electronic Supplemental Information for:

Synthesis of Cu$_2$ZnSnS$_4$ Thin Films Directly onto Conductive Substrates via Selective Thermolysis using Microwave Energy

Theodore. R. Knutson,$^a$ Parker J. Hanson,$^a$ Eray S. Aydil,$^b$ and R. Lee Penn$^{a,c}$

$^a$ Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, USA.  
$^b$ Department of Chemical Engineering and Materials Science, 421 Washington Avenue SE, Minneapolis, Minnesota 55455, USA.  
$^{c}$E-mail: rleepenn@umn.edu.

Description of Characterization Procedure
The films were characterized using a JEOL 6500 scanning electron microscope (SEM) operated either at 5 or 15 keV. Energy-dispersive X-ray spectra (EDS) were collected at 15 keV. X-ray diffraction was performed using a PANalytical X’Pert Pro MPD diffractometer (XRD) equipped with an X’Celerator detector and a Co Ka anode operating at 45 kV and 40 mA. Diffraction patterns were collected using a 0.5° divergent slit, a 1° anti-scattering slit, and a 5.0 mm receiving slit over a 25-70° 2θ range with an effective dwell time and step size of 100 s per step and 0.17° 2θ, respectively, in continuous mode. Films were also characterized using Raman scattering. Raman spectra were collected and recorded using a Witec Alpha300 R confocal Raman microscope equipped with a 514.5 nm argon laser for excitation and a monochromator equipped with an 1800 lines/mm grating. Ultraviolet-visible spectroscopy was performed using an Agilent 8453 UV-Vis spectrometer.

Substrates Preparation
TEC 15 indium tin oxide glass (purchased from Hartford Glass Co. Inc.) was used as received. Molybdenum films were formed by sputtering a Mo metal target onto glass substrates using an AJA-ATC-2000. Molybdenum films were measured by to be ~250 nm thick by profilometry (Dektak 3030 Surface Profiler) and SEM.

Supplemental Figures and Discussion
Figure S1 shows the optical absorption spectra of the precursor solution before microwaving (a) and the solution after microwaving (b). Immediately following microwave synthesis, the solution appears optically clear. Upon cooling, the solution develops a cloudy appearance, and UV-Vis spectra obtained using the cooled solution show evidence of scattering (elevated background). This effect is also seen with precursor solutions that contain no sulfur source and only contain ethylene glycol and the metal salts. This increased absorption and scattering can be reversed re-heating the solution to 150 °C. Thus, it is concluded that solid particles form upon cooling.

![Fig. S1 UV/Vis absorption spectra of the pre-reaction (a) and post-reaction (b) solutions.](image)
The white precipitate was collected by centrifugation (5000 rpm, 5 minutes) and washed with methanol three times. XRD results (Fig. S2) are consistent with the production of zinc and tin oxides, hydroxides, and oxyhydroxides. No evidence for metal sulfides was detected.

![XRD pattern from the aged precursor solution. ZnO (#), Zn(OH)$_2$ (*), Sn$_6$O$_4$(OH)$_4$ (x), and ZnSn(OH)$_6$ (^) have been noted in the pattern.](image)

The film thickness was calculated by cross-sectional measurements at 100 nm intervals. The films were calculated to have an average thickness of 1.4 µm with a maximum and minimum measured thickness of 0.37 µm and 2.5 µm, respectively. The histogram of film thickness is plotted in Fig. S3. The impacts of the surface roughness of these films will be further investigated for its effects on device performance.

![Histogram of film thickness measurements obtained by analyzing calibrated SEM images of cross-section samples. Thickness was measured from SEM images at 100 nm intervals for 200 points along the cross-section.](image)