Supporting information for:

Understanding quaternary compound $Cu_2ZnSnSe_4$ synthesis by microscopic scale analyses at an identical location

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Synthesis

Step (i) Cu/Sn/Zn thin layer metal stacks were electrodeposited onto inch by inch molybdenum coated glass substrates. The 2 mm thick glass (Thermo Scientific) was sputtered with a 500 nm thick molybdenum (target purity >99.95%, AJA International Inc.). All additional layers were electrodeposited potentiostatically using a rotating disk electrode with the thickness controlled by the charge passed. The potentiostat was an Autolab PGSTAT302N, the reference electrode was a Radiometer analytical calomel reference and the counter electrode was a platinum wire (99.9%, Mateck). A 200 nm Cu layer was electrodeposited from an aqueous electrolyte containing 3 M NaOH (99.99%, Sigma Aldrich), 0.2 M Sorbitol (99%, Sigma Aldrich), 0.1 M Cu (II) sulfate hydrate (99.999%, Alfa Aesar), and 0.932 mM Empigen BB detergent (Sigma Aldrich). A 240 nm Sn layer was electrodeposited from an aqueous electrolyte with 1 M methanesulfonic acid (>99.5%, Sigma Aldrich), 50 mM Sn(II) methane sulfonate (Sigma Aldrich), and 3.6 mM Empigen BB detergent (Sigma Aldrich). Finally a 180 nm Zn layer was electrodeposited from an aqueous solution containing 3 M KCl (99.995%, Alfa Aesar), 50 mM ZnCl2 (99.999%, Alfa Aesar), 1 g pH3 Hydrion buffer (Sigma Aldrich), and 0.2g of Poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized (solution 62 wt. % in H_2O, Sigma Aldrich).

Step (ii) The as-electrodeposited metal stack was soft annealed in vacuum/under nitrogen at 350°C for thirty minutes in a rapid thermal processing oven (Annealsys).

Step (iii) The soft annealed sample was selenized in a tube furnace with a background pressure of 10 mbar of forming gas (10 vol% H_2 in N_2). The sample was placed inside a graphite box with 100 mg of selenium powder (99.999%, Alfa Aesar), 15 mg of tin selenide (99.999%, Alfa Aesar), and was heated to 525°C in approximately 18 minutes and held at this temperature for 30 minutes, and then left to cool naturally to room temperature over a period of four hours.

Marking for identical location

Figure SI1 shows the essential features needed for identical location microscopy on continuous thin films undergoing chemical reactions.
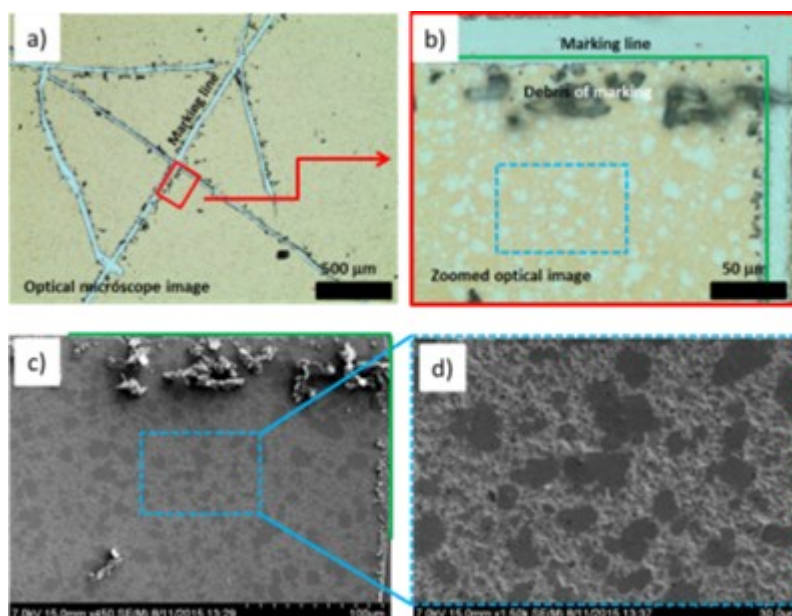

Figure SI1: (a) optical microscope image of a sample scratched with a cross and an additional scratch in three of the quadrants. (b) zoomed optical microscope image of the unscratched quadrant with blue dashed box showing the area of interest. Green lines indicate the unscratched quadrant (c) SEM image of the unscratched quadrant with the blue dashed box showing the area of interest – note the edges of the scratch are lined up with the upper and right edges of the image (indicated by green lines). (d) SEM image of the area of interest obtained zooming to 1500X magnification from the aligned 450X magnification image in (c).

A cross is scratched into the sample with the lines being perpendicular. Into three of the quadrants an additional scratch is done (see figure SI1a) in order to leave one clear identifiable quadrant, by the absence of a scratch. Figure SI1b shows a zoom of (a) with green lines indicating the edges of the scratch and a blue dashed box to indicate the area of interest which will be mapped by EDX, μ-PL, and μ-Raman. Figure SI1c shows an SEM image of the same sample area as the optical image (b) again with green lines and blue dash box indicate the pertinent features. To reproducibly obtain the area of interest, the sample is aligned in the SEM chamber using the x,y rotation stage until the scratches of the unmarked quadrant align on the upper and right edges of the image. Then the magnification is simply increased from 450X to 1500X and the area of interest is obtained. Repeated measurements on a number of samples showed that the area of interest could be reliably found with the image offset +/- 1 μm. This reliability was essential to check and confirm the efficacy of the procedure for the retrieval of the identical location by scanning electron microscopy.

Characterization

Grazing incidence x-ray diffraction (GIXRD) was performed on a Bruker D8 with an incidence angle of 1°. All top view scanning electron microscope (SEM) images were taken using a Hitachi SU-70 with an accelerating voltage of 7.0 kV, and the chemical composition was measured by energy dispersive X-ray spectroscopy (EDS, Oxford Instruments INCAXMAX) with an electron beam of 20 keV. The obtained chemical composition maps were divided into 1.02 x 1 μm^2 corresponding to the interaction area of the electrons penetrating the sample at 20 kV acceleration voltage, which gives each map a total of 64 x 48 points. All molar ratio presented in this study are calculated with Cu_2 to take into account the stoichiometry of the target material $Cu_2ZnSnSe_4$. The molar ratios obtained are colour-coded and binned identically for each of the maps (figures 2(c),(d),(e) and 3(b)) to allow prompt comparison. The zinc, copper and tin molar ratios are respectively defined as $Zn/(Cu_2+Zn+Sn)$, $Cu_2/(Cu_2+Zn+Sn)$ and $Sn/(Cu_2+Zn+Sn)$. Cu_2 is used rather than Cu since this is the standard representation used by the Kesterite community.

Cross section and top view images of figure 1.d were acquired with a dual column focused ion beam microscope (FIB, FEI HeliosNanolab). After SEM imaging of the surface, Pt e-beam deposition was used to define the cutting line on the sample's surface and to prevent damage to the layer during milling. An anion beam with 30 kV acceleration was used to mill and polish the cross section. The cross section was analyzed in the same dual column microscope, with an electron beam of 5 kV energy. The exact position of the cross section on the sample is ensured by the presence of the Pt stripe on the surface. μ-photoluminesence spectra were obtained by means of a Renishaw inVia Micro-Raman spectrometer with an excitation laser wavelength of 633 nm, spot size of 1 μm and a power of about 0.5 mW.

In-depth composition

EDS analyses were performed on the cross section of figure 1.d.ii, in order to confirm the composition of each phase observed in the SEM image. The results are presented in figure SI2.
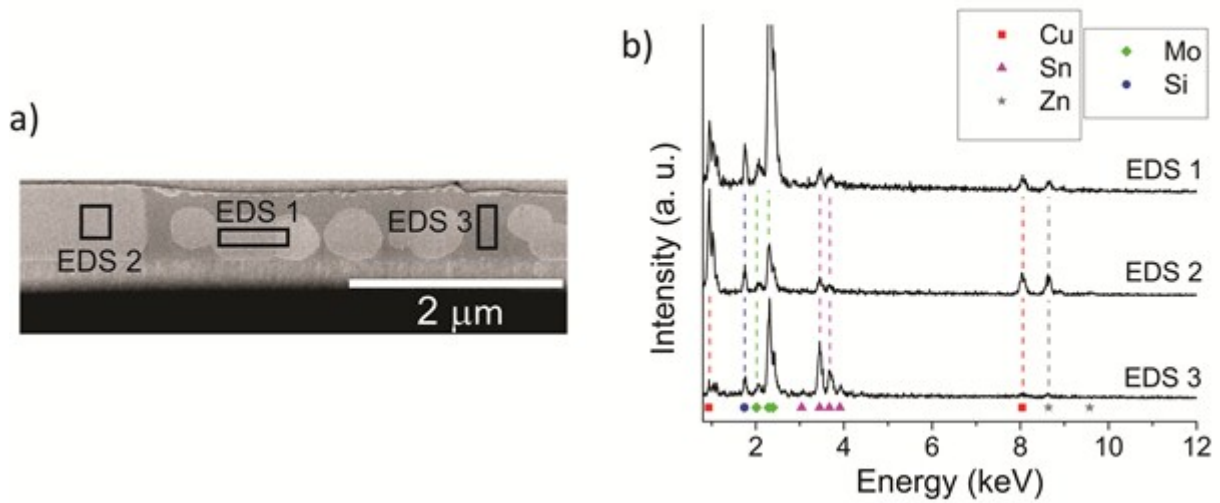

Figure SI2: (a) SEM cross section image of the soft annealed sister sample studied in figure 1.d, this image is identical to figure 1.d.ii of the manuscript. (b) EDS analysis of demarked areas 1, 2 and 3 of figure SI2.a.

In order to observe the EDS signal of zinc, an acceleration voltage of 15 keV was used, at which the electron beam interaction domain has a diameter of about one micrometer. This explains the observation of Mo or Si signals which come from the substrate. Globally, EDS spectra 1 and 2 show much higher zinc and lower tin signals than the spectrum EDS3, which confirms that region 1 of figure 1.d is composed of Cu-Zn, and region 2 is composed of Cu-Sn or Sn phases with inclusions of Cu-Zn.

Chemical maps after selenization

The distributions of molar fractions of copper and tin on the area of interest after selenization are displayed in figure SI3.
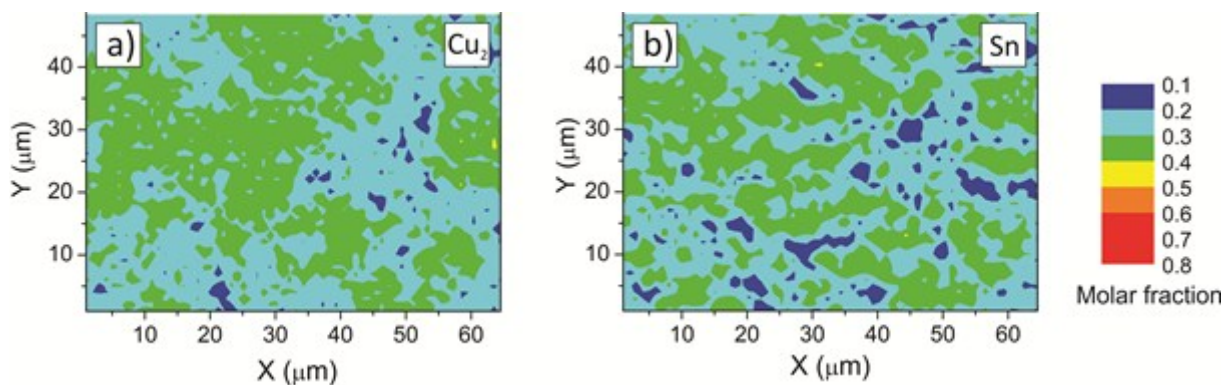

Figure SI3: Chemical map displaying molar fractions of a) Cu_2 and b) Sn on position of interest after selenization.

Position of ZnSe:

The analysis of a cross section of a sample after selenization (figure SI4) shows that surface ZnSe (bright grains) forms a layer of about 500 nm on top of kesterite grains (dark structure).

Figure SI4: SEM cross section image of a sister sample prealloyed and annealed in the same conditions than the reference sample.