Supporting Information For

Alkali-metal-enhanced grain growth in Cu₂ZnSnS₄ thin films

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KEYWORDS: Copper zinc tin sulfide, Sodium, Solar cells, Secondary ion mass spectrometry, Compositional depth profiles.

Detailed description of the time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements

Time-of-flight secondary ion mass spectrometry (TOF SIMS) depth profiling was conducted in single-beam mode in SARISA, S11, S12 a custom designed analytical instrument capable of operating as a laser post-ionization secondary neutral mass spectrometer (LPI SNMS) and as TOF SIMS. The 10 keV Ar⁺ beam was used in a sequence of alternating cycles, that consisted of milling in a direct-current (dc) raster-scanned mode followed by elemental TOF SIMS analysis in a pulsed mode without raster scanning. The Ar⁺ ion beam was produced by an Atomika WF421 ion gun equipped with a Wien filter, two pairs of electrostatic deflectors for scanning, and another pair for pulsing. The ion gun was pointed at the sample at 60° from the sample surface normal. Pulse duration was set to 200 ns, the shortest duration possible with SARISA's pulsing electronics. Even though 200 ns pulse may result in decreased mass resolution in most TOF SIMS instruments, this was not the case in SARISA, which was designed to operate with long primary ion pulses (\approx 1µs, typical for LPI SNMS) and maintain high mass resolving power.^{SI3} When performing sputter depth profiling analysis with primary ions of inert gases, a long primary ion pulse was followed with delayed extraction of secondary ions thus enabling high sensitivity to secondary ions such as O^+ and S^+ . A 500×500 μ m² surface area was ion milled in the raster-scanned mode. Elemental composition information was collected from a $\approx 30 \ \mu m$ spot in the center of the 500×500 μ m² crater. This estimate of the analytical spot size (30 μ m) corresponds to the width of the Gaussian-shaped ion beam profile close to its base. The analytical beam size (at 10 keV energy and 60 nA dc current) was found to have a symmetric Gaussian distribution with a FWHM of $\sim 15 \mu m$ by burning dents in silicon and profiling the dents using white light interferometry (WLI).^{S14} Including the primary ions within the tails of the analytical beam profile averages the secondary ion intensity over a larger area and across many CZTS grains. Averaging over a 30 µm spot was necessary because CZTS grains were several microns in some films. The size of the beam was controlled *in situ* using a Schwarzschild type microscope and measured before and after depth profiling.^{S13} WLI was also used to measure some of the craters within the CZTS films after depth profiling to confirm both the lateral size and depth of the crater from which material was removed. All profiles were measured with a 60

nA dc current beam, a current high enough to mill through a $\sim 2 \mu m$ thick sample in a reasonable amount of time and to have sufficient dynamic range for detecting secondary ion species within broad mass range (from ¹⁰B to ¹²²Sn). The ion beam current was measured *in situ* by a custom graphite Faraday cup consisting of an internal pin (60°, 250 µm diameter inlet hole) and the external surface. This design provides coarse control over the ion beam focusing conditions by measuring internal and external components of the ion current. The Faraday cup could be positioned accurately and reproducibly at the same location as the sample surface with respect to the ion optics of the mass spectrometer and the Atomika ion gun. Each film was depth profiled at least twice at different locations to ensure the reproducibility of the results.

Quantification of the impurity concentrations using Saha-Eggert analysis

The Na, K and Ca SIMS intensities were converted to their respective atomic concentrations, using the Saha-Eggert approach. The Saha-Eggert method does not require calibration standards. Instead, it relies on the correlation between the secondary ion yields and the ionization potentials of elements to quantify trace amounts of low concentration species (*e.g.*, impurities) with respect to the composition of a host matrix with known stoichiometry (*e.g.*, Cu₂ZnSnS₄). It was first introduced for SIMS analysis with oxygen as the primary ions^{S15} and expanded later to SIMS analysis with Ar ions.^{S16} Central to this analysis is the Saha-Eggert ionization plot which correlates the SIMS intensity of an element *i* to its ionization potential, I_{pi} , by assuming that its secondary ion emission yield, γ_{b} from a multinary solid host is given by

$$\gamma_i \propto \exp\left(-\frac{I_{pi} - \delta\varepsilon}{kT}\right) \tag{1}$$

where k is the Boltzmann's constant, T is the temperature and $\delta \varepsilon$ is an adjustable parameter that accounts for the work function and the lowering of energy barriers on the surface due to plasma effects. Assuming the SIMS intensity to be proportional to the secondary ion yield and the atomic concentration of species *i*, i.e.,

$$S_i \propto \gamma_i x_i,$$
 (2)

a semi-logarithmic plot of the weighted SIMS intensity, S_i/x_i , vs. the ionization potential, I_{pi} should be linear. Such a line can be generated from the known stoichiometry of the host (*e.g.*, Cu, Zn, Sn and S concentrations in CZTS) and then used to infer the unknown concentrations of impurities. For example, Figure S1 shows this Saha-Eggert plot for CZTS. Figure S1 was generated by plotting the SIMS intensities of Cu, Zn, Sn and S divided by their concentrations as measured by EDS (Table 2) versus their respective ionization potentials. The dotted line is the best fit to the data and represents the dependence expected from equation 1. Intensity of any other impurity element lying on the dotted line would mean that its relative concentration is on the order of the four matrix elements, i.e. ≈ 10 at%. Thus, the atomic concentration of an impurity, *i*, can be calculated from

$$x_i = \frac{S_i}{\left(S/x\right)|_{Ipi}},\tag{3}$$

where S_i is the measured SIMS signal intensity and $(S/x)|_{I_{pi}}$ is the value of the weighted SIMS signal intensity at the ionization potential of the species *i*, on the dashed line in Figure S1.

Saha-Eggert analysis to determine the Na, K, Ca and Si concentrations must be done with care because matrix effects can lead to errors. The Saha-Eggert analysis rests on the assumption that the matrix is in fact CZTS. We compared the Si concentrations determined by the Saha-Eggert

analysis to independent measurements to explore the limitations of this approach for our films. This comparison showed that the Saha-Eggert analysis gives reasonable order-of-magnitude estimates provided that only the data below $d/d_o \le 0.4$ is used. For example, when only the data below $d/d_0 \le 0.4$ is used, Si⁺ SIMS intensity of ~0.1 corresponds to ~1 at. % Si within the film, approximately the same as that obtained, independently and reproducibly, from EDS measurements. If we include the data from depths $d/d_0 > 0.4$ in our analysis, the calculated Si concentration in CZTS exceeds 100 at%, which is not physically possible. The data from depths $d/d_0 > 0.4$ includes secondary ions not only from the CZTS film but also from the substrate through the pinholes in the film. The assumptions of the Saha-Eggert analysis fail for $d/d_0 > 0.4$ because the Si ionization efficiency (and therefore the SIMS intensity) in SiO₂ is more than 100 times that in CZTS. To avoid these matrix effects, our analysis was done for all elements using only the data for $d/d_0 \le 0.4$. The ionization potential for Si is in the range covered by the ionization potentials of Cu, Zn, Sn and S. However, an extrapolation is necessary for K, Na and Ca. The average (between the surface and $d/d_o \le 0.4$) atomic concentrations of Si, Na, K, and Ca in the CZTS films synthesized on various substrates were calculated and the results are listed in Table 3.



Figure S1. The Saha-Eggert semi-*log* plot for the CZTS films. Red solid line is the fit to the data for Cu, Zn, Sn and S, Red dashed line is extrapolation of this line to the region of the ionization potentials for Ca, K and Na.



Figure S2. The SIMS intensity depth profiles for Cu, Zn, Sn and S in CZTS films synthesized on soda lime glass (SLG), Pyrex (P) and quartz (Q), with (P+SLG, Q+SLG) and without (P, Q) a bare SLG present in the sulfidation ampoule.

Additional characterization data for CZTS films synthesized with Ca(OH)₂, KOH and NaOH in the sulfidation ampoules



Figure S3. XRD from films sulfidized on quartz at 600 °C in an ampoule whose inside walls were coated with 50 µmol of Ca(OH)₂, 0.1 µmol of KOH, and 1 µmol of NaOH (top panel). The bottom panel shows the expected powder diffraction patterns from CZTS. All films were synthesized on nominally impurity free quartz. Crystalline quartz substrates were used for films synthesized with NaOH and Ca(OH)₂, while amorphous quartz (fused silica) was used for the film grown with KOH. The amorphous background between $2\theta = 20$ and 30° in the XRD of the film synthesized with KOH is due to fused silica.



Figure S4. Raman spectra collected from films sulfidized on quartz at 600 °C in an ampoule whose inside walls were coated with 50 μ mol of Ca(OH)₂, 0.1 μ mol of KOH, and 1 μ mol of NaOH (top panel). The most intense peak, near 334 cm⁻¹, is consistent with CZTS.



Figure S5. SEM images of films sulfidized on quartz at 600 °C in an ampoule whose inside walls were coated with different concentrations of NaOH and KOH. The moles of NaOH or KOH charged into the ampoule is shown in the upper right corner of each image. The films shown in (a) and (d) were comprised of many discontinuous large grains of CZTS along with large domains (10 - 20 μ m) of impurity phases containing Na and K respectively.

Supporting Information References:

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