Formation of Cu-rich and Sn-poor CZTSSe via $Cu_3Sn(S,Se)_4$-ZnS Solid-Solution as the Intermediate

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Supporting Information

Experimental Section

Fabrication of CZTSSe precursor films: Nanoparticle inks were prepared by weighing out the desired amount of stock Cu_2SnS_3, ZnS and SnS nanopowders and dispersing in a mixture of butanethiol and toluene solution. The composition of the nanoparticle inks was varied by simply changing the relatively amount of the binary and ternary nanopowders used. All precursor films were prepared by bar-coating on Mo-coated soda-lime-glass substrates. After each coating, the films were soft-baked at 350 ^{o}C for 2 minutes unless specified otherwise. The soft-baked nanoparticle films were then stored in a nitrogen-filled desiccator box prior to selenization.

Annealing process: The routine selenization process used in the fabrication of CZTSSe thin films is based on a graphite-box design. The nanoparticle precursor films and elemental selenium pellets were placed inside a graphite box which is heated to high temperatures using a rapid thermal processing (RTP) furnace. The standard annealing temperature profiles consists of

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two steps which are 350 ^{o}C/15 mins and then 560 ^{o}C/10 minutes at atmospheric pressure. For the growth mechanism studies, the samples were annealed using the Flow-Se furnace at atmospheric pressure (see the schematic in Figure S4). In the Fow-Se annealing process, elemental Se evaporates from an independently heated source and is then carried down-stream using Argon as the carrier gas. An independently heated Se source ensures a steady and controllable concentration of Se vapor throughout the entire annealing run. For the flow-Se annealing process, a two-step temperature profile shown in Figure S4 was used. The two-step temperature profile was chosen to mimic the temperature profile used in the conventional graphite-box selenization process. The Se source was typically heated to 550^{o}C with an Ar flow of 100 sccm. For the extended annealing time series, the Se source was lowered 450 ^{o}C to ensure the Se loading was sufficient to last through the long annealing runs. The estimated Se vapor pressure at the evaporation source temperature of 450 ^{o}C and 550 ^{o}C are 16.2 torr and 110 torr respectively. At the end of annealing runs, the samples were cooled down rapidly by opening the furnaces.

Characterization and Analysis: Transmission mode Fourier transformed infrared spectra were collected using a Nicolet Nexus 870 spectrometer. X-ray diffraction (XRD) data of CZTSSe films were obtained with a Philips X'PERT automated powder diffractometer, Model 3040. The diffractometer is equipped with automatic variable anti-scatter and divergence slits, X'Celerator RTMS detector, and Ni filter. The radiation is Cu Kα) (45 kV, 40 mA). Data were collected at room temperature from 4 to 80 degrees 2θ; using a continuous scan with an equivalent step size of 0.02 degree; and a count time of 80 seconds per step in theta-theta geometry. Plan-view and cross-sectional scanning electron microscopy (SEM) images obtained using a Hitachi S4700 electron microscope.

Device cross-sections roughly 100 nm in thickness and 15 microns in length for transmission electron microscopy (TEM) analysis were prepared using a Ga ion focused-ion beam (FIB) in a Zeiss Auriga 60 scanning electron microscope (SEM). For comparative study, a thin TEM specimen was also prepared by microtomy. For microtomy, the CZTSSe film was peeled off the substrate using epoxy and was then ultra-microtomed under cryogenic conditions using a Reichert Ultracut UCT. The thin section was nominally 70 to 80-nm thick to enable effective electron beam transmission and was placed on a holey-carbon coated Ni-grid to minimize any elemental interference with the constituent elements in CZTSSe. The microstructure of the thin sections was analyzed by high-resolution transmission electron microscopy (TEM) and its associated elemental analysis by energy dispersive X-ray spectroscopy (EDS) using a Tecnai F-20 scanning transmission electron microscope (STEM) equipped with a field-emission electron source. The microscope was operated at an accelerating voltage of 200 kV. The elemental analysis was accomplished with an Oxford Instruments INCA x-sight EDS system attached to the microscope column and capable of identifying elements as light as boron. The EDS system has a Li-doped Si detector and an ATW ultra-thin window.

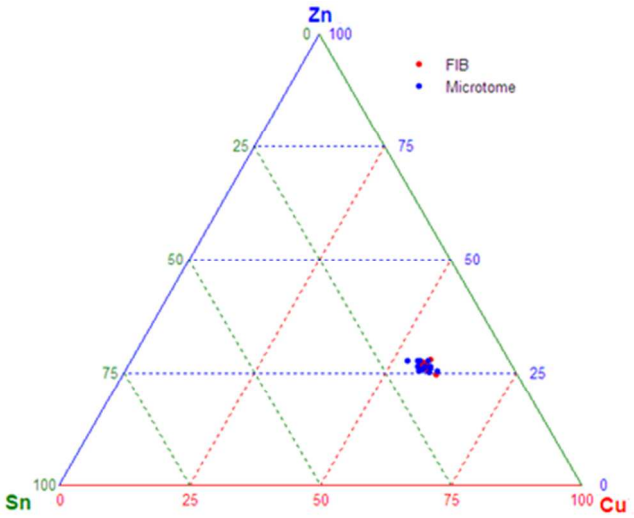

Figure S1. An excellent agreement between compositions determined using STEM-EDS from ten different locations within the large-grain layer of specimen prepared by FIB and microtome respectively.

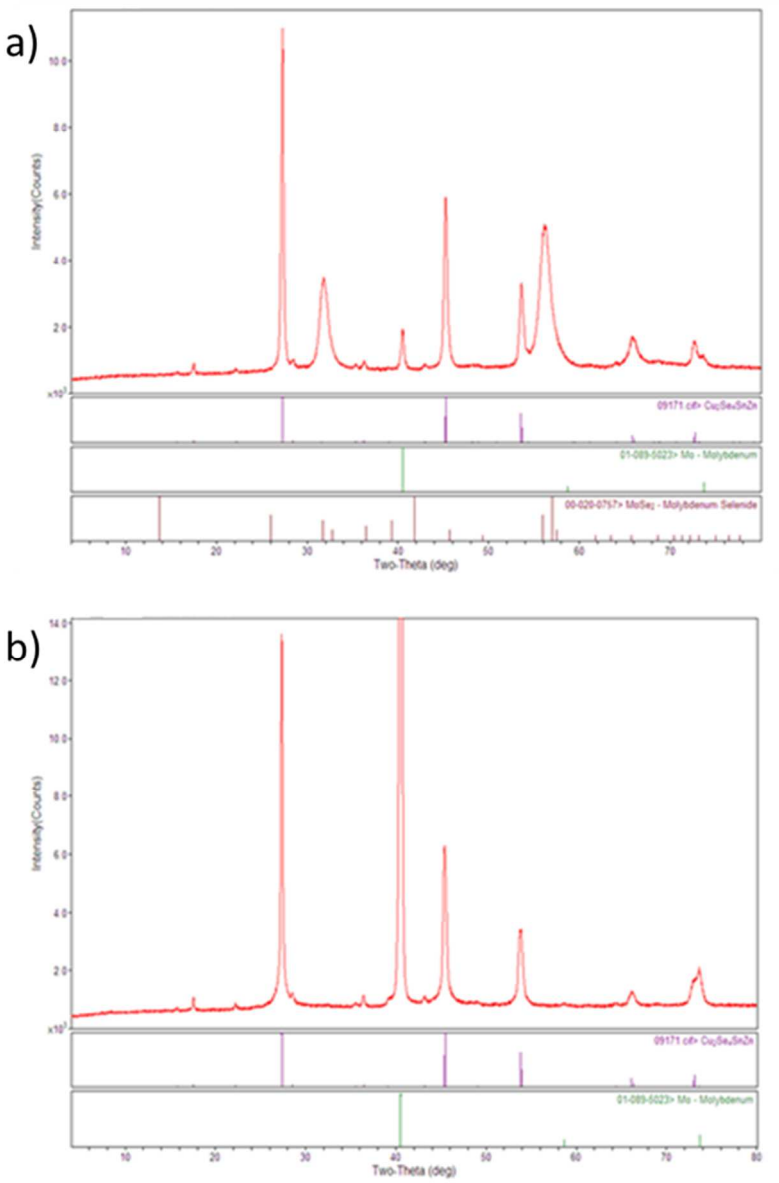

Figure S2. XRD patterns of CZTSSe films obtained after selenization using nanoparticle precursor films soft-baked in air at a) 200 ^{o}C for 15 mins and b) 300 ^{o}C for 5 mins.

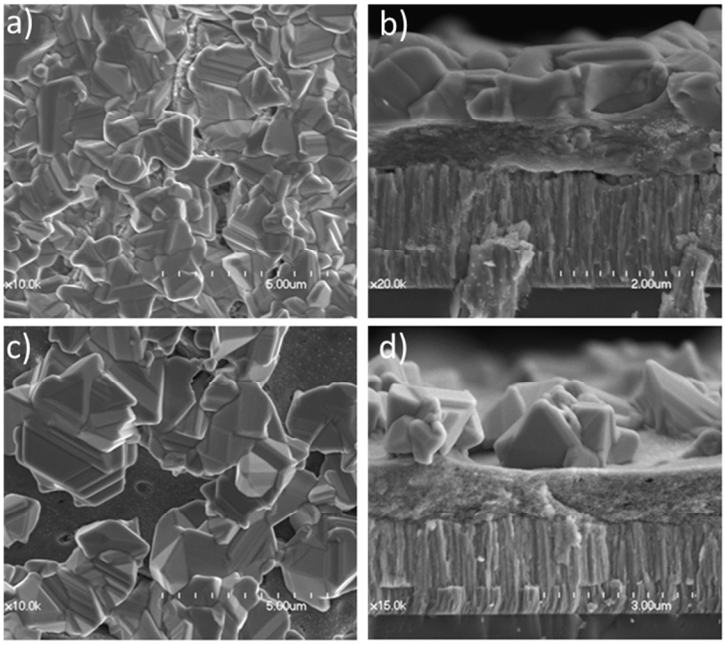

Figure S3. a) Plan-view and b) cross-sectional SEM images of CZTSSe films obtained by RTP selenization of nanoparticle precursors soft-baked in air at 350 ^{o}C for 2 minutes. c) Plan-view and d) cross-sectional SEM images of CZTSSe films obtained by RTP selenization of nanoparticle precursors soft-baked in Ar at 375 ^{o}C for 30 minutes. Note the large-grain layer in the sample derived from the precursor film soft-baked in Ar is not continuous.

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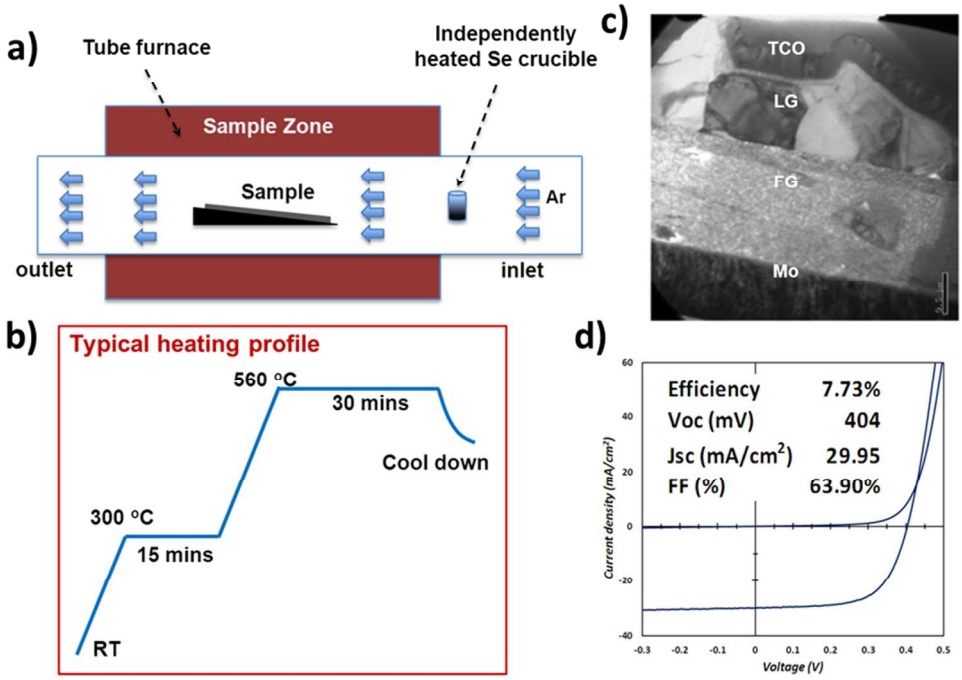
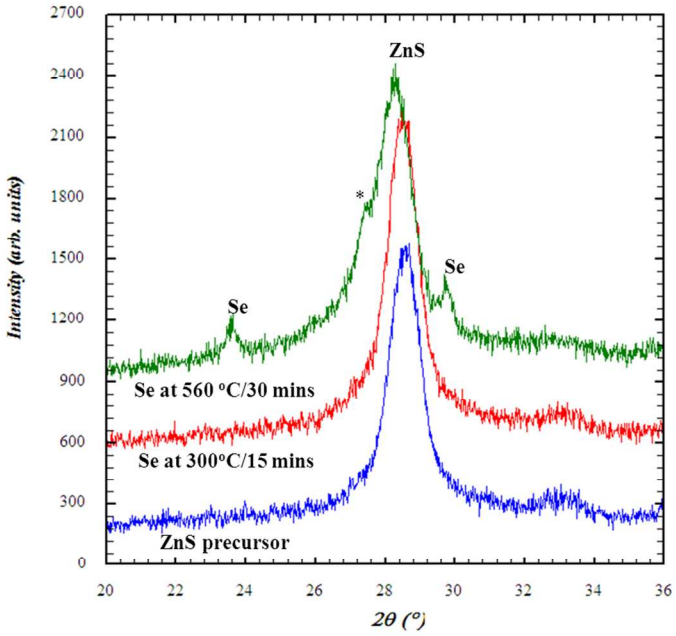


Figure S4. a) Schematic drawing of the Flow-Se annealing furnace, and b) the two-step annealing temperature profile used in the growth mechanism study. Using the Flowing-Se furnace, CZTSSe thin films with c) microstructure and d) device performance are comparable to the graphite-box based process.



b)

	As coated	Se at 300 °C For 30 mins	Se at 560 °C for 30 mins
Peak 1 position	28.56	28.50	28.23
Peak 1 FWHM	1.05	1.01	1.03
Peak 2 position	N/A	N/A	27.36
Peak 2 FWHM	N/A	N/A	1.03

Figure S5. a) XRD patterns of ZnS nanoparticle films before and after selenization at different temperatures. At 560 °C, a new peak (*) is formed indicating the formation of a Se-rich Zn(S,Se). Table 1 b) summarizes the peak positions and FWHM's of the ZnSSe diffraction peaks. The shift in the ZnS peak position is very small suggesting a high chemical stability of ZnS nanoparticles. In addition, the crystalline size of the ZnS nanoparticles did not change significantly indicating no grain growth.

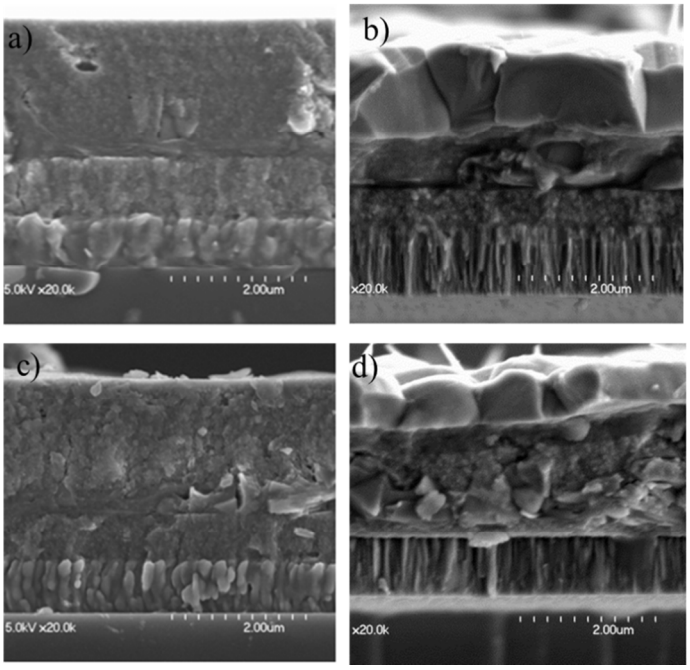


Figure S6. Cross-sectional SEM images of the precursor films shown in Figure 10a a) before and b) after selenization. Similarly, c) and d) are the SEM images for precursor film shown in Figure 10b before and after selenization respectively.