

Supporting information

for Chemistry of Materials, DOI: <http://dx.doi.org/10.1021/cm504654t>

A Versatile Solution Route to Efficient $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ Thin Film Solar Cells

*Ruihong Zhang[†], Steve M. Szczepaniak[‡], Nathaniel J. Carter[‡], Carol A. Handwerker^{†§}, Rakesh Agrawal^{**‡}*

[†]School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA

[‡]School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA

[§]Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA

Supporting information

A Versatile Solution Route to Efficient $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Thin Film Solar Cells

Ruihong Zhang[†], Steve M. Szczepaniak[‡], Nathaniel J. Carter[‡], Carol A. Handwerker^{†§}, Rakesh Agrawal^{**}

[†]School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA

[‡]School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA

[§]Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA

I. Precursor preparation

Chemicals

Zinc powder, Zn ($\geq 99\%$), copper (I) oxide, Cu_2O ($\geq 99.99\%$), copper (II) chloride, CuCl_2 (99%), copper (I) chloride, CuCl ($\geq 99.99\%$), copper (II) acetate, $\text{Cu}(\text{OAc})_2$ ($\geq 99.99\%$), copper (II) acetylacetonate, $\text{Cu}(\text{acac})_2$ ($\geq 99.99\%$), zinc oxide, ZnO ($\geq 99\%$), zinc chloride, ZnCl_2 ($\geq 99.99\%$), zinc acetate, $\text{Zn}(\text{OAc})_2$ (99.99%), tin (II) chloride, SnCl_2 ($\geq 99.99\%$), tin (IV) biacetylacetonate dichloride, $\text{Sn}(\text{acac})_2\text{Cl}_2$ (98%), hexylamine, $\text{CH}_3(\text{CH}_2)_5\text{NH}_4$ (99%), propanethiol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ (99%), and butylamine, $\text{CH}_3(\text{CH}_2)_4\text{NH}_4$ (99%). All the chemicals were purchased from Sigma Aldrich and used without any further purification.

Solutions

Amine-thiol solvent mixtures can be used to dissolve a variety of cation sources. The examples shown below are solutions prepared at room temperature by dissolving 0.6 mmol Cu_2O , ZnO , CuCl , CuCl_2 , ZnCl_2 , $\text{Cu}(\text{OAc})_2$, $\text{Cu}(\text{acac})_2$, $\text{Zn}(\text{OAc})_2$, SnCl_2 , and $\text{Sn}(\text{acac})_2\text{Cl}_2$ in 2 ml solvent mixture of hexylamine and propanethiol (vol. ratio 4:1) respectively. The metallic Zn solution is prepared by dissolving 1 mmol Zn powder in a 2 ml solvent mixture of butylamine and propanethiol (volume ratio of 1:1). The dissolution process was performed at ambient temperature ($25^\circ\text{C} \pm 2^\circ\text{C}$) in a N_2 glovebox with water and oxygen less than 0.1 ppm.

Based on our current knowledge of this precursor solution route, it is possible to produce optimized solar cells using solutions prepared with any or all of the listed metal sources but the question is how high the efficiency can be for a series of solution conditions, for example, based on varying the type of amine and thiol, cation sources and concentrations, or anion sources and concentrations. Answering this question requires optimization of the deposition, annealing, and selenization conditions for a series of solution conditions. This paper reports on the versatility of the solvent system for preparing precursor solutions, and on the optimization of films from one such solution series with changing cation ratios.

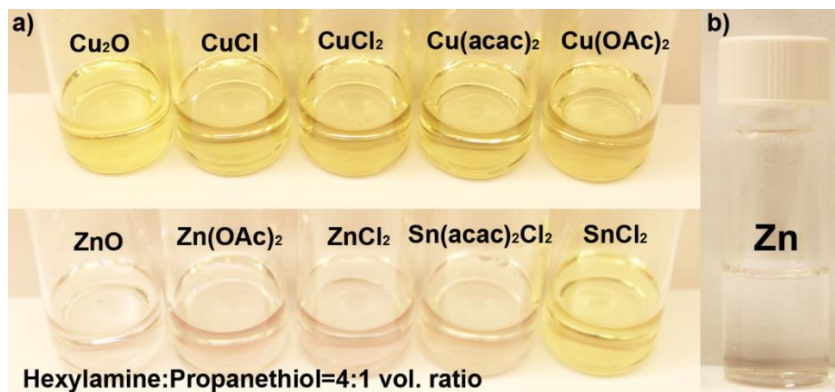


Figure S1. a) Solutions of cation oxides and cation salts dissolved in hexylamine and propanethiol with a volume ratio of 4:1. The concentrations of all solutions are 0.3 M. b) Solution of metallic zinc in butylamine and propanethiol with a volume ratio of 1:1. The concentration of zinc solution is 0.5 M.

II. CZTSSe precursors prepared using other types of amines and thiols

The versatility of the primary amine-monothiol solvent mixture is demonstrated by the following examples as well as the reported solution precursor. Although primary amine/s and monothiol/s with different boiling points can be used as the solvents, the use of relative low boiling point amine/s and thiol/s is necessary, in order to fabricate carbon-free thin films with no fine-grained layer, where “low boiling point” generally means <250°C. The boiling point of the solvent is also important in determining the annealing temperatures and times used for the solvent evaporation/annealing process.

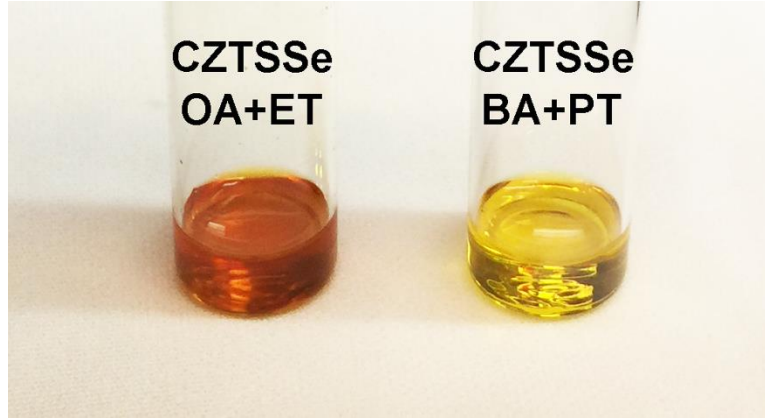


Figure S2. CZTSSe precursors prepared using oleylamine (OA) and ethanethiol (ET) (vol. ratio 1:1) (left) and butylamine (BA) and propanethiol (PT) (vol. ratio 1:1) (right). CZTSSe precursors were prepared using solution recipe 2 list in Table S1.

III. Raman spectrum fitting

A linear superposition of Gaussian and Lorentzian distributions (Equation S1) is used to fit the Raman spectra in this study.

$$I_G(x) = \frac{A}{\omega} \sqrt{\frac{4 \ln(2)}{\pi}} \exp\left(-4 \ln(2) \frac{(x - x_c)^2}{\omega^2}\right)$$
$$I_L(x) = \frac{2A}{\pi} \frac{\omega}{4(x - x_c)^2 + \omega^2} \quad (S1)$$
$$I(x) = gI_G(x) + (1 - g)I_L(x)$$

where A is the peak amplitude, ω is the peak FWHM, x_c is the location of the peak maximum, and g is the weighting factor for the Gaussian contribution. The fitted peaks of the Raman spectra for the precursor and selenized film are shown in Figure S3.

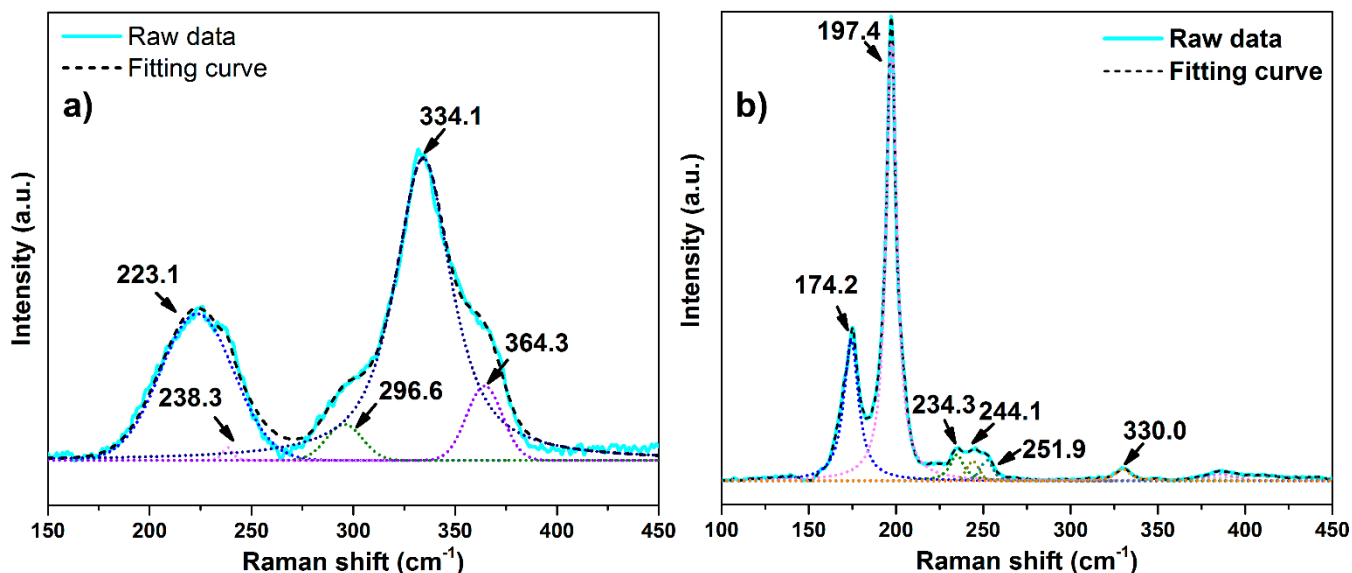


Figure S3. Fitting curves of Raman spectra in Figure 6. a) Raman spectrum of the precursor film and b) Raman spectrum of the selenized film.

IV. SEM-EDX linescan of CZTSSe thin film solar cell

A linescan was performed on the fractured cross-section of the molecular precursor-processed device using an accelerating voltage of 10 keV, as shown in Figure S4. The linescan profile reveals a uniform distribution of Cu, Zn, Sn in the large grain layer of CZTSSe. The concentration of Se is increasing towards the substrate.

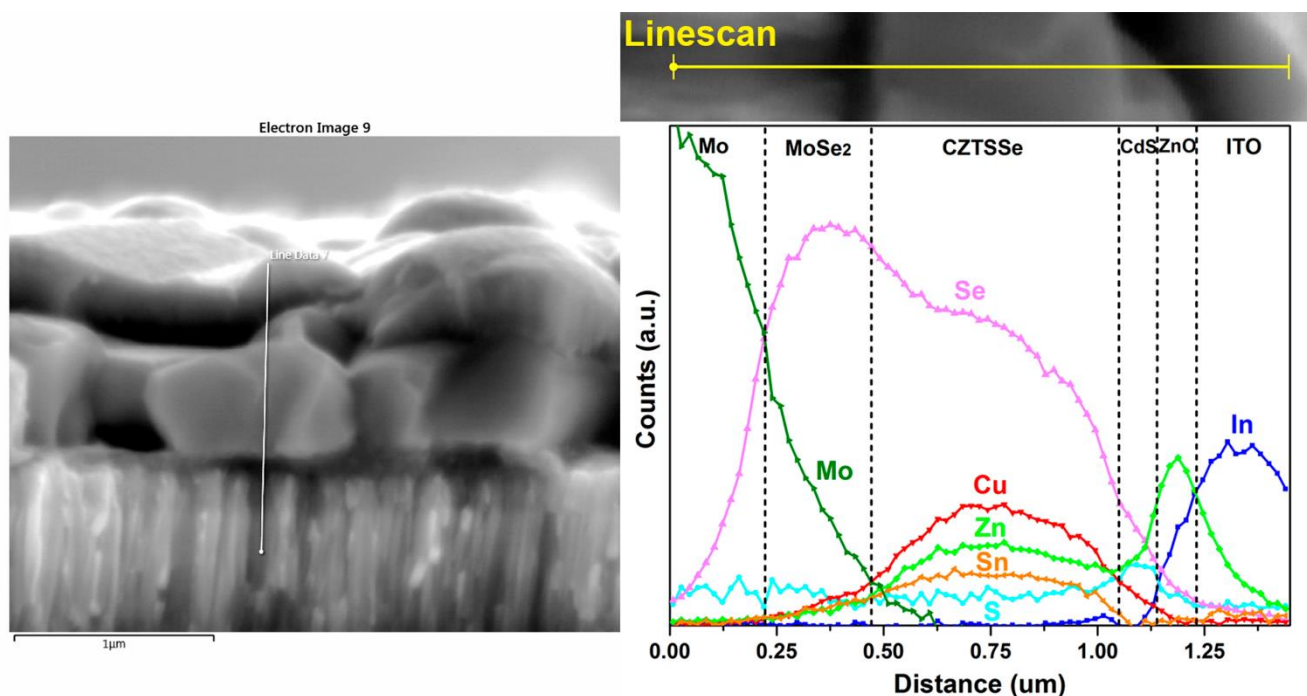


Figure S4. SEM-EDX linescan of fractured cross-section of CTZSSe thin film solar cell.

V. CZTSSe thin film preparation

As described in the article, [Cu]/[Sn] ratio has been adjusted in order to achieve good solar cell efficiencies. Kesterite CZTSSe phase is obtained using different solution recipes. XRD patterns and Raman spectra of the selenized CZTSSe films prepared from different precursor solutions are shown in Figure S5.

Table S1. Recipes of CZTSSe precursor solutions for solar cell fabrication.

Precursor recipe	[Cu]/[Sn]	[Cu]+[Zn]/[Sn]	[Cu]:[Zn]:[Sn]:[S]+[Se]
R1	1.45	0.7	1.45:1.05:1:4
R2	1.53	0.75	1.53:1.05:1:4
R3	1.64	0.8	1.64:1.05:1:4
R4	1.74	0.85	1.74:1.05:1:4

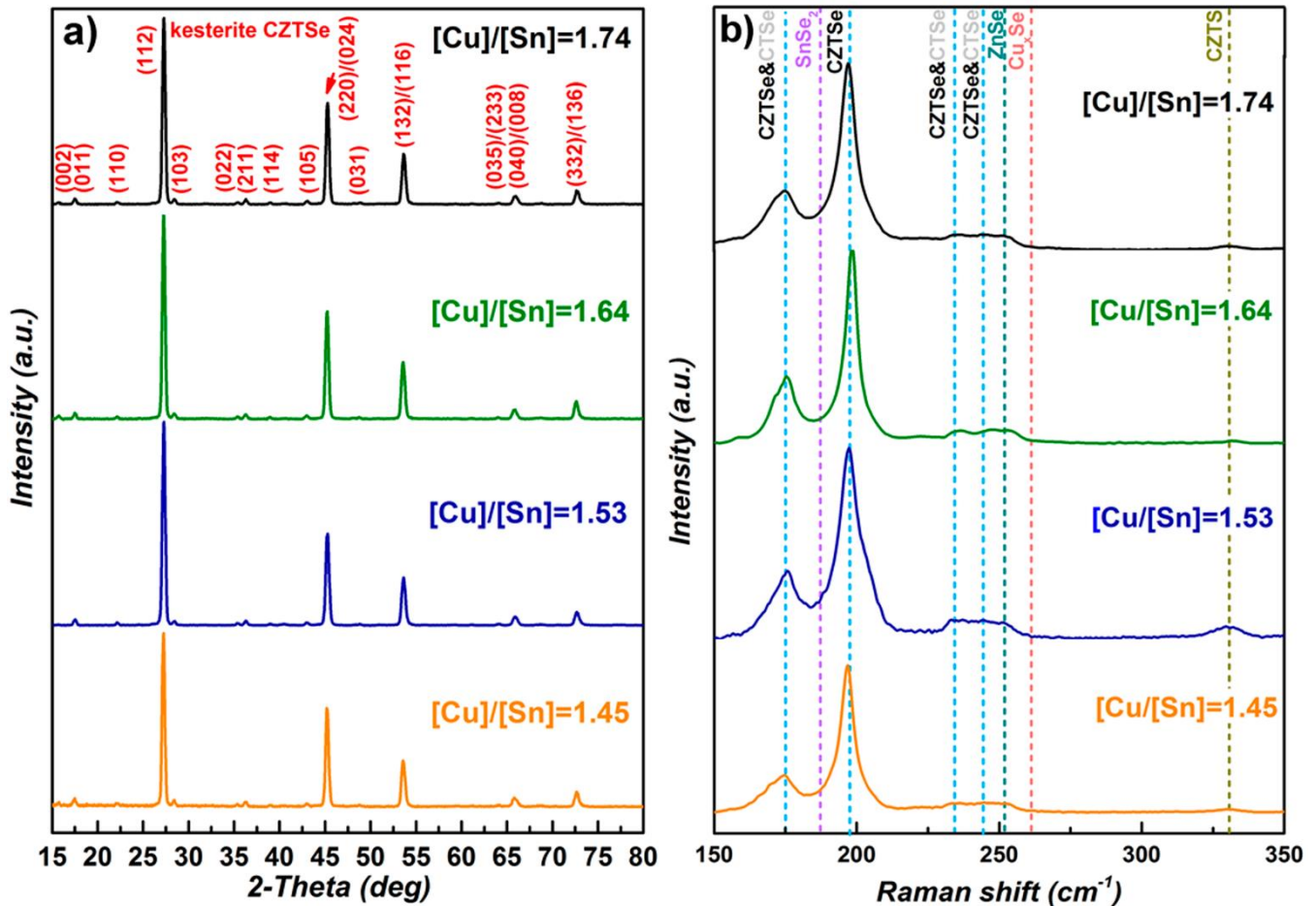


Figure S5. a) XRD and b) Raman spectra of CZTSSe films prepared from molecular precursors with different [Cu]/[Sn] ratios as shown in Table S1.

VI. Statistics of solar cells prepared using different precursors

Solar cells were fabricated using the aforementioned four precursor recipes (Table S1) and the total area power conversion efficiencies (PCEs) for a total cell area of 0.47 cm² were measured under standard AM 1.5 illumination. For each precursor recipe, the average total area PCE and the standard deviation were plotted in Figure S6. At least six device measurements contributed to the data point for each precursor recipe. It should be noted that devices prepared from recipe 1 and recipe 2 precursor solutions were coated with antireflective coatings, while devices

prepared from recipe 3 and recipe 4 precursor solutions were not coated. The use of antireflective coatings did not influence the trend.

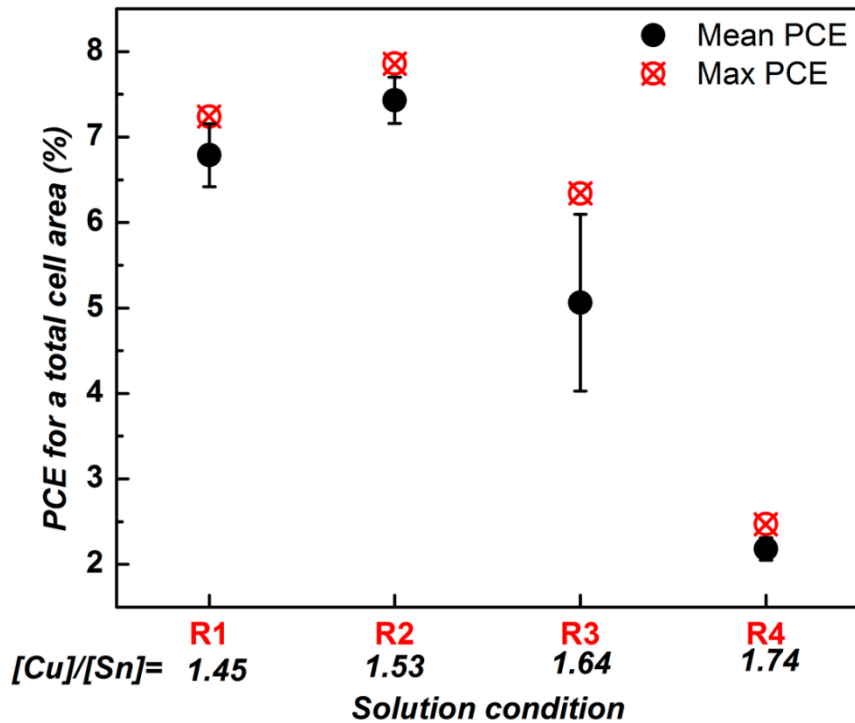


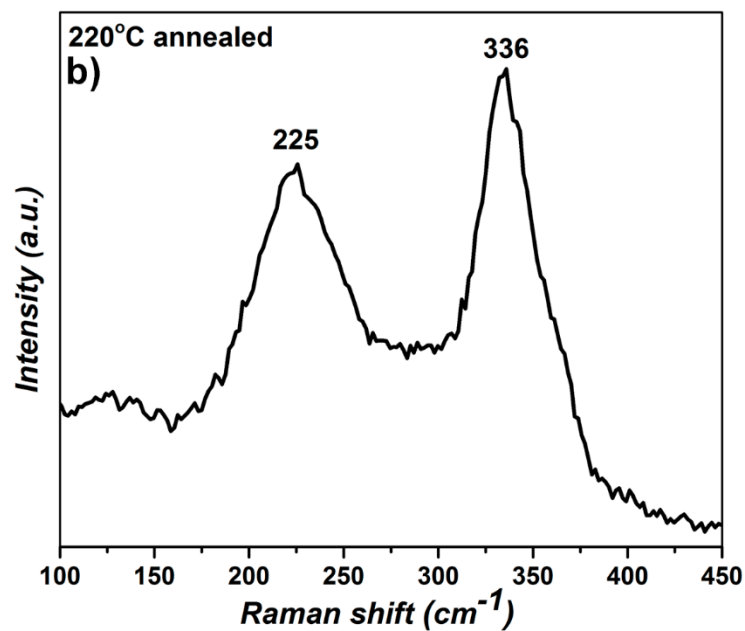
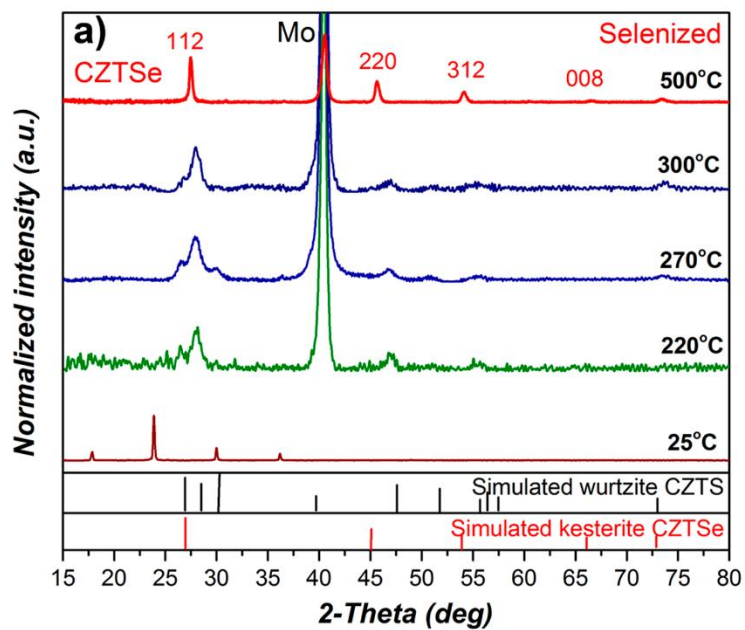
Figure S6. Statistics of the total area PCEs of CZTSSe solar cells prepared using four precursor solution recipes.

VII. CZTSSe thin films prepared from molecular precursors with butylamine-propanethiol solvent mixture

The CZTSSe molecular precursors were prepared by dissolving Cu(I)Cl, ZnCl₂, Sn(II)Cl₂, S, and Se using butylamine and propanethiol in a volume ratio of 1:1. Three precursor recipes used in this study were shown in Table S2. Figure S7 (a) shows XRD patterns of the as-deposited and annealed precursor films. The precursor films shown here were prepared using recipe 1 molecular precursor in Table S2. At room temperature, only four peaks at low angles were observed in the XRD pattern, which did not correspond to any phases in the JCPDS inorganic materials database. At 220°C, 270°C, and 300°C annealing temperatures under nitrogen atmosphere, the three main peaks observed at 26.5°, 28.0° and 30.0° correspond to the (010), (002) and (011) planes of wurtzite CZTS. In the Raman spectrum (with 632.8 nm excitation wavelengths), the peak at 336 cm⁻¹ corresponds to wurtzite CZTS, while another peak at 225 cm⁻¹ belongs to CZTSe. The shift of A1 mode for CZTS and CZTSe was observed due to the coexistence of S and Se in the crystal lattice. The size of CZTSSe nanoparticles formed at 220°C is ~10-20 nm based on the Scherrer equation. After selenization at 500°C for 20 min, the precursor films prepared using all different recipes were converted into kesterite CZTSe large grains (Figure S7 (a), (c) and (d)). No secondary phases have been detected. So far, the highest PCE achieved using the butylamine-propanethiol based CZTSSe molecular precursor is 3.66%, and this CZTSSe molecular precursor solution is prepared following recipe 1 in which [Cu]:[Zn]:[Sn]:[S]+[Se]=1.45:1.05:1:4. The J-V curve of the device is shown in Figure S7 (d). The phase transformation from wurtzite to kesterite of the CZTSSe films during the selenization process may result in the lower efficiencies observed with butylamine-propanethiol solutions. In particular, pinholes generated during the wurtzite-kesterite phase transformation lead to a significant decrease in the shunt resistance, J_{sc}, and FF as reported in the study of Yang et al.¹

Table S2. Recipes of CZTSSe precursor solutions based on butylamine-propaenthiol solvent mixture.

Precursor recipe	[Cu]/[Sn]	[Cu]:[Zn]:[Sn]:[S]+[Se]
R1	1.45	1.45:1.05:1:4
R2	1.76	1.76:1.05:1:4
R3	2	2:1:1:4



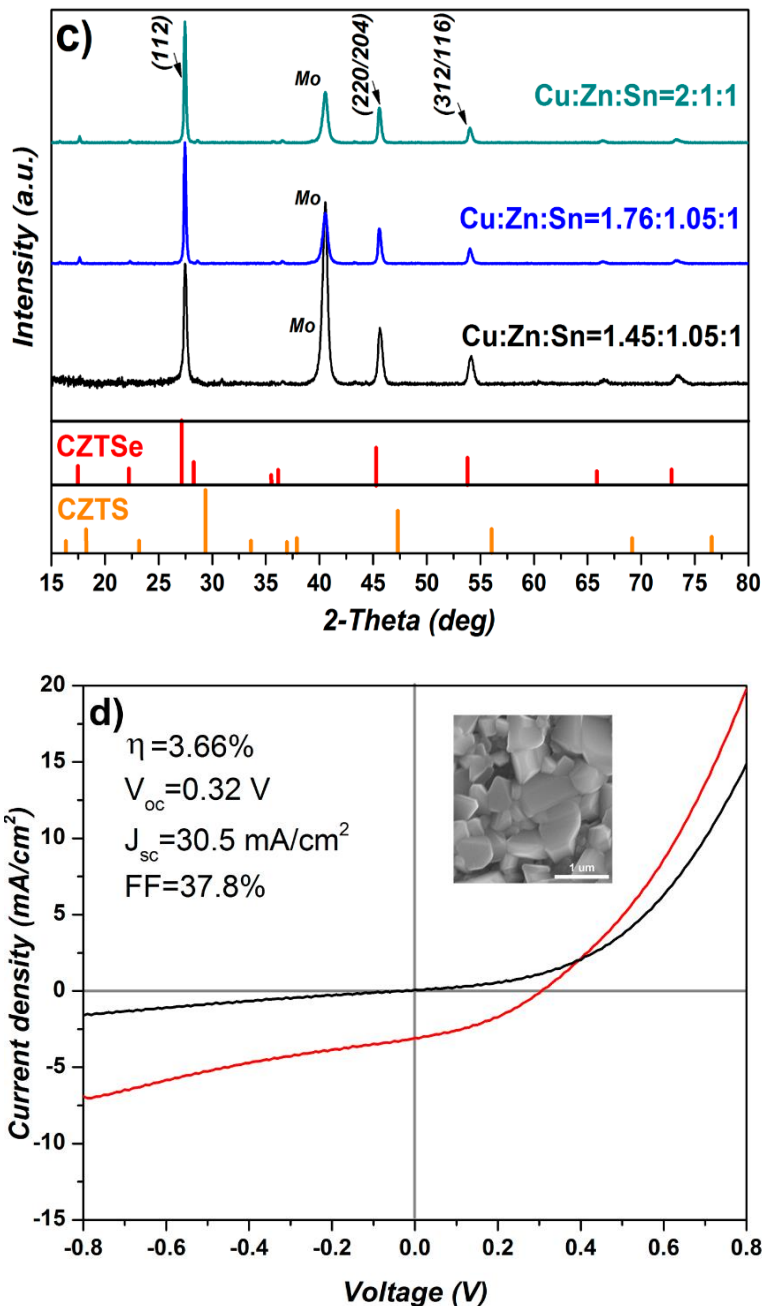


Figure S7 (a) XRD patterns for CZTSSe precursor films annealed at different temperatures. The precursor films were prepared using precursor solution recipe 1 in Table S2. Note that the final annealing was performed under selenium atmosphere at 500°C. (b) Raman spectrum of the CZTSSe precursor film annealed at 220°C for 5 min. The precursor films were prepared using precursor solution recipe 1 in Table S2. (c) XRD patterns for the selenized films prepared using three precursor solution recipes in Table S2. (d) J-V curves of a CZTSSe device fabricated using precursor recipe 1. The inset is a top-view SEM image of the selenized film.

VIII. Selenization condition

A temperature controlled tube furnace was used for the selenization purpose. The samples and selenium pellets were put into a sealed graphite box. The sample box was parked at the cold zone of the quartz tube while the temperature inside the tube furnace was ramping. After the temperature at the center of tube became stable at 500°C, the graphite box was pushed into the center of the tube furnace by a push-pull rod. The selenium pellets melted and

created a saturated selenium atmosphere around the samples. The amount of selenium pellets was well-controlled to create a saturated atmosphere. Before pre-heating, the tube furnace also was purged three times using Ar to ensure the purity of the gas atmosphere. After the desired time passed, the furnace was quickly cooled to the room temperature. This selenization condition has been reported by previous studies in our group.^{2,3}

IX. Dynamic light scattering

A dynamic light scattering measurement was performed on a CZTSSe precursor solution (Recipe 2 in Table S1) using Zetasizer Nano ZS90 (Malvern, size measurement from 0.3 nm to 5 μm using 90 degree scattering optics). This solution was prepared and stored in a sealed quartz cuvette for the measurement. No particles has been detected.

Reference:

1. Yang, W. C.; Miskin, C. K.; Hages, C. J.; Hanley, E. C.; Handwerker, C.; Stach, E. A.; Agrawal, R. *Chem Mater* **2014**, 26, 3530.
2. Miskin, C. K.; Yang, W.-C.; Hages, C. J.; Carter, N. J.; Joglekar, C. S.; Stach, E. A.; Agrawal, R. *Progress in Photovoltaics: Research and Applications* **2014**, DOI: 10.1002/pip.2472.
3. Guo, Q.; Kim, S. J.; Kar, M.; Shafarman, W. N.; Birkmire, R. W.; Stach, E. A.; Agrawal, R.; Hillhouse, H. W. *Nano Lett* **2008**, 8, 2982.