

Supporting Information

Harnessing high power factors with enhanced stability in heavy metal-free solution- processed thermoelectric copper sulfoselenide thin films

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Figure S1 and Table S1 shows the results of Scherrer analysis of XRD spectra of unsaturated $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ with increasing amounts of S. In accordance with the Scherrer equation, $D_S = \frac{K\lambda}{FWHM \cdot \cos\theta}$, it can be observed that the grains appear smaller with significantly increased

S content. In the Scherrer equation, D_S is the mean size of the crystalline domains, K is the shape factor (typically 0.9), λ is the wavelength of the incoming X-rays (1.54 Å for a Cu source), $FWHM$ is the full width at half maximum for the respective peak and θ is the Bragg angle.

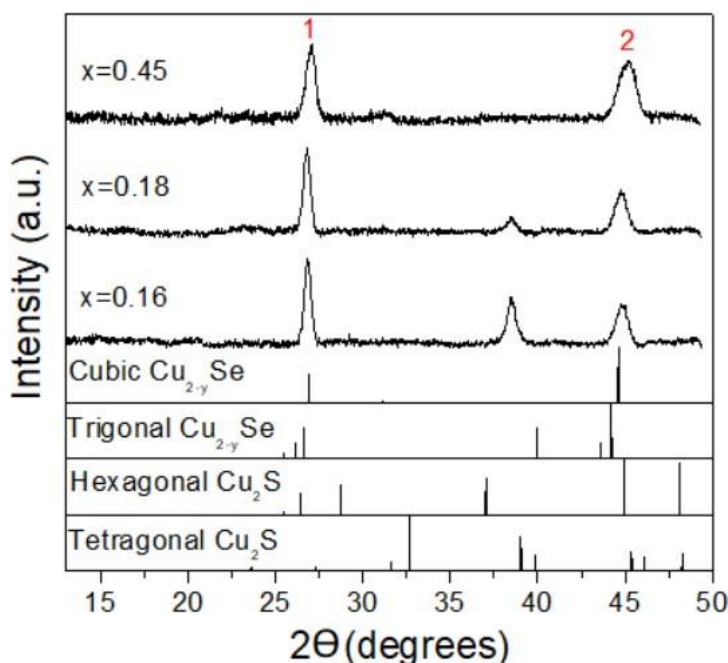


Figure S1. Baseline corrected XRD spectra for unsaturated $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ ($x = 0.16 \pm 0.02$, ± 0.06 , 0.45 ± 0.02) for Scherrer analysis. Comparison with reference spectra for cubic (ICSD 150758) and trigonal (ICSD 243952) Cu_{2-y}Se and hexagonal (ICSD 95397) and tetragonal (ICSD 16550) Cu_{2-y}S , respectively. The samples were exposed to temperature gradients (thermoelectric characterization) prior to XRD characterization. The origin of the peaks at $2\theta \sim 38$ is likely diffusion of metal ions from gold contacts, however this is still currently under investigation.

Table S1. Scherrer analysis of $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ direct thin films with varying S content

S content, x	D_S peak 1	D_S peak 2
0.45	121 Å	77 Å
0.18	171 Å	108 Å
0.16	173 Å	107 Å

The observed peak at $2\theta \sim 38-39$ was initially believed to be due to shifting of the trigonal Cu_{2-y}Se (ICSD 243952) peak at $2\theta \sim 40$. After a rigorous study taking into account substrate effects, the effect of annealing conditions, grain size effect and the effect of temperature cycling during Seebeck measurements, we finally arrived at the conclusion that the applied metal (Au) contacts for Seebeck and electrical conductivity measurements are the cause of these peaks, Figure S2. However, open questions remain, thus the origin is still under investigation.

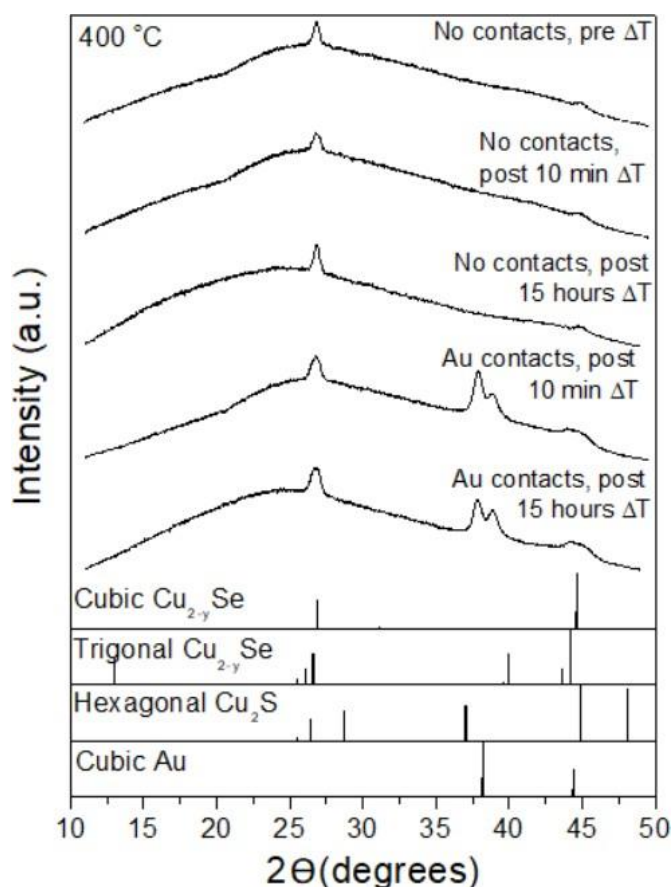


Figure S2. Room-temperature X-ray diffraction patterns for unsaturated $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ with no Cu_{2-y}S addition annealed at $400\text{ }^\circ\text{C}$ with/without Au contacts pre/post exposure to a temperature gradient compared to reference spectra for cubic (ICSD 150758) and trigonal (ICSD 243952) Cu_{2-y}Se , hexagonal (ICSD 200986) Cu_{2-y}S and cubic (ICSD 52249) Au. No new peak at $2\theta \sim 38$ is observed without metal contacts post 10 minutes or 15 hours ΔT . New peak at $2\theta \sim 38$ with Au post 15 hours ΔT matches cubic Au.

In order to investigate the effect of sample substrate, annealing conditions as well as exposure to a temperature gradient on the XRD spectra, the following experiments were performed:

1) Effect of annealing conditions

a) Annealing temperature:

Cu_{2-y}Se dissolved in thiol-amine solvent with no added Cu_{2-y}S was spin coated on [100]-oriented silicon (Si) substrates and annealed under N_2 atmosphere for 1 hour at 300 and 500 °C in an oven upon XRD characterization. Figure S3a) shows the resulting trigonal Cu_{2-y}Se structure with a peak (weak, but at the correct spot) at $2\theta \sim 40$. Hence, shifting of the peaks is not a temperature effect.

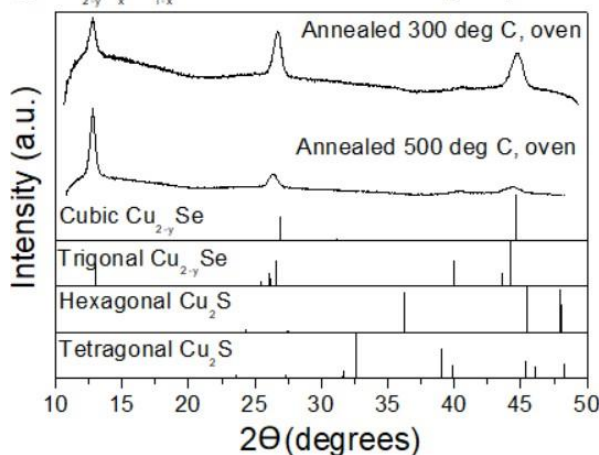
b) Type of annealing:

Cu_{2-y}Se dissolved in thiol-amine solvent with no added Cu_{2-y}S was spin coated on [100]-oriented Si and annealed under N_2 atmosphere for 1 hour at 300 °C in an oven or at 350 °C on a hot plate upon XRD characterization. Figure S3b) shows the resulting trigonal Cu_{2-y}Se structure (with a weak peak at $2\theta \sim 40$) in the oven and cubic Cu_{2-y}Se structure on the hot plate. Hence, heating the sample from one side on a hot plate as opposed to more uniform heating from all sides in an oven has an effect on the phase, but not peak shifting.

2) Effect of substrate

Cu_{2-y}Se dissolved in thiol-amine solvent with no added Cu_{2-y}S was spin coated on [100]-oriented silicon (Si) or glass (SiO_2) substrates and annealed under N_2 atmosphere for 1 hour at 300 °C or 500 °C in an oven upon XRD characterization. The sample on glass annealed at 300 °C, Figure S4, matches a cubic Cu_{2-y}Se crystal structure, while the sample on Si annealed at 300 °C matches a trigonal Cu_{2-y}Se crystal structure. After annealing at 500 °C, both samples on Si and glass have a trigonal phase. Hence, the substrate does have an effect on phase at lower annealing temperatures, but not peak shifting. Cu_{2-y}Se growth in certain lattice directions is preferred/suppressed on amorphous or monocrystalline substrates, likely due to the thin nature of these films (~60 nm) compared to the substrate thickness (0.56 mm glass/0.50 mm Si).

a $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ on Si at different annealing temperature



b $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ on Si at different annealing conditions

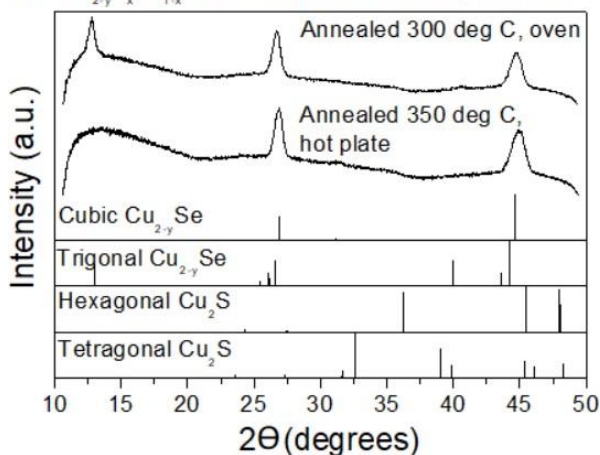


Figure S3. Room temperature X-ray diffraction patterns for unsaturated $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films with no added Cu_{2-y}S on Si showing effect of annealing conditions compared to reference spectra for cubic (ICSD 150758) and trigonal (ICSD 243952) Cu_{2-y}Se , and hexagonal (ICSD 95397) and tetragonal (ICSD 16550) Cu_{2-y}S . a) Annealing temperature. Shifting of peaks is not a temperature effect. b) Type of annealing. Monodirectional VS uniform heating has an effect on phase, but not peak shifting.

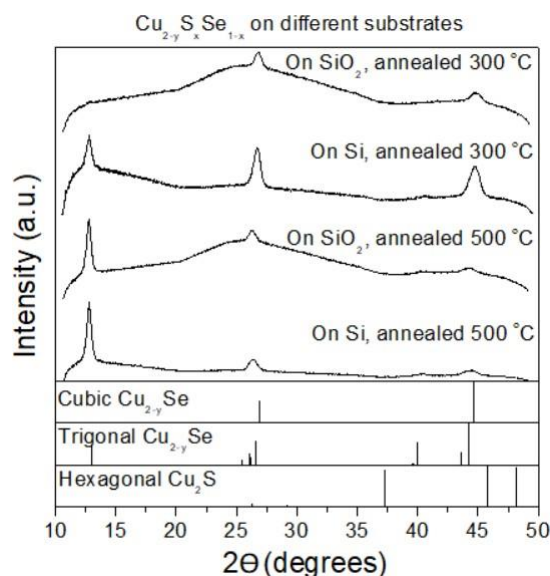


Figure S4. Room temperature X-ray diffraction patterns for unsaturated $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films with no added Cu_{2-y}S on different substrates showing effect of substrate annealing in an oven at 300 and 500 °C. Reference spectra for cubic (ICSD 150758) and trigonal (ICSD 243952) Cu_{2-y}Se , and hexagonal (ICSD 95397) Cu_{2-y}S . Substrate has an effect on phase at lower annealing temperature, but not peak shifting.

3) Effect of grain size

Scherrer analysis of XRD spectra in Figure S1, presented in Table S1, show that the calculated grain sizes are small (8 - 17 nm) and in comparable range to the total film thickness (60 nm). This could result in an effective strain on the lattice in one direction, causing peak shifting for only one of the peaks in the XRD spectra.

Figure S5 shows another set of thermoelectric performance data for Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ direct thin films with varying S content (Series II) compared to representative data for unsoaked films (Series I), both series annealed at 350 °C. Improved thermoelectric performance is observed after Cu soaking except at high S content.

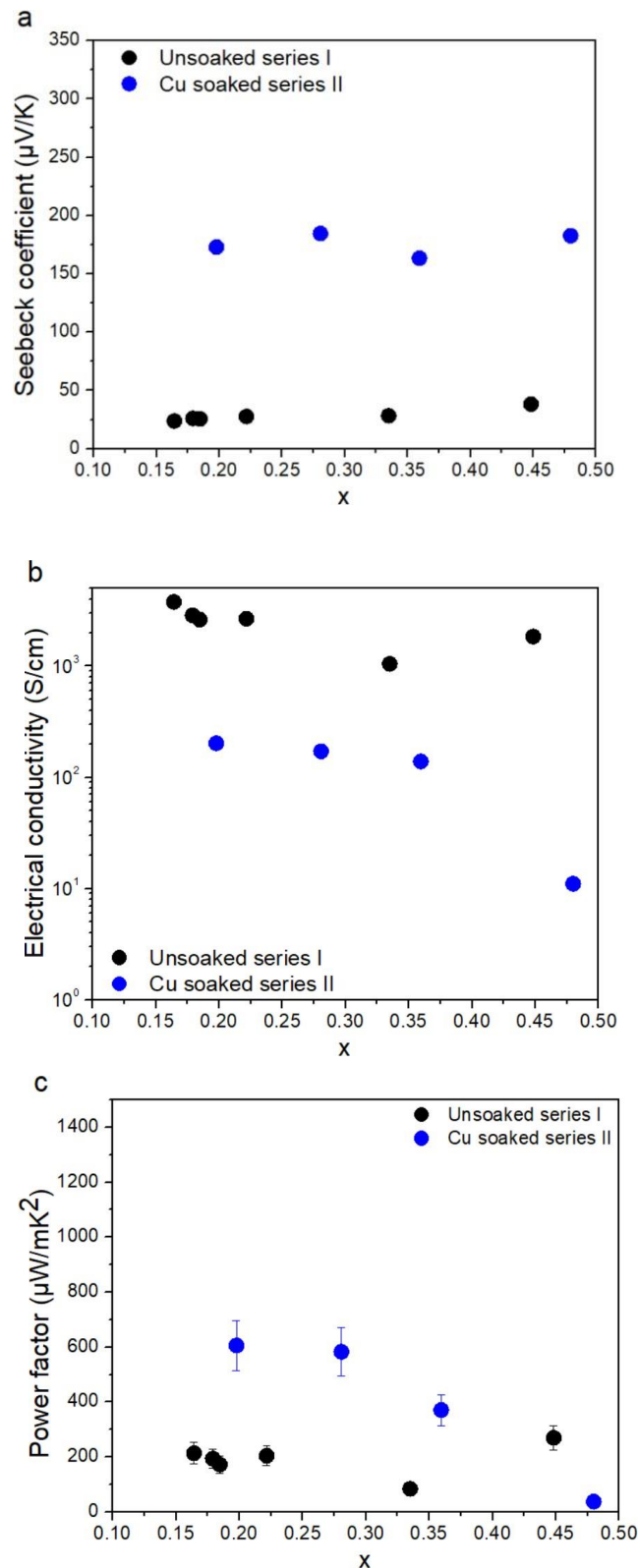


Figure S5. Thermoelectric properties of unsoaked (black) and Cu soaked (blue) $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed on hot plate at 350 °C as a function of S content, x . a) Seebeck coefficient as a function of S content before/after Cu soaking. A 5 – 7-fold increase in Seebeck coefficient is observed upon soaking as well as a slight increase upon increased S content. b) Electrical conductivity as a function of S content before/after Cu soaking. A significant decrease in electrical conductivity is observed with increasing S content, especially for Cu soaked samples. c) Power factor as a function of S content before/after 10 minutes soaking in 0.05 M Cu(I) in methanol. A 2 – 3-fold improvement of power factor is observed upon Cu soaking, except for $x > 0.37$. S substitution sustains power factor up to $x \sim 0.30$ for soaked samples.

Figure S6 shows backscattered electron (BSE) and EDS elemental maps for gold (Au) and Cu in the proximity of an Au metal contact for a Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ ($x = 0.15$) film after continuous Seebeck coefficient measurement for 117.5 hours. An increased Cu concentration close to the metal contact is observed, which is confirmed by elemental ratios for the same film shown in Table S2 at approximate locations indicated in Figure S7. Figure S8 shows XPS data at the Cu, Se and S edges at three different locations on the same sample.

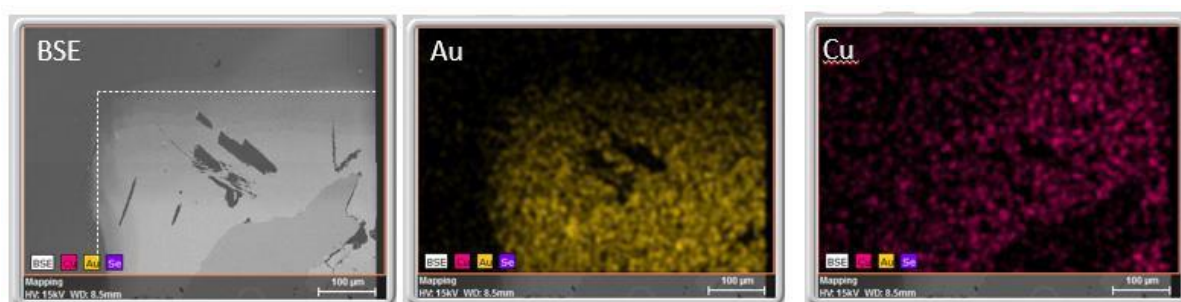
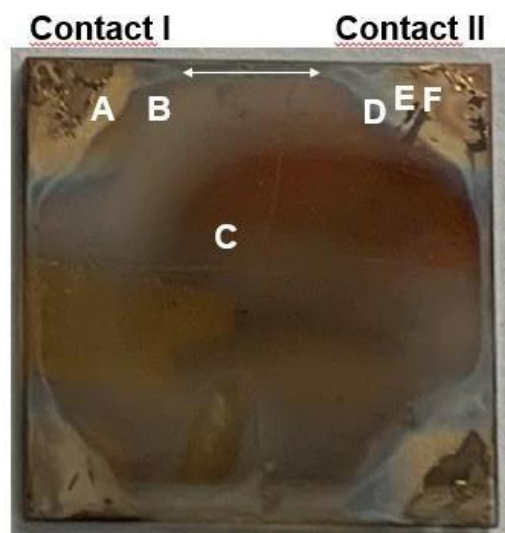


Figure S6. SEM backscattered electron (BSE) and EDS elemental maps for Au and Cu showing increased Cu concentration in the proximity of the metal contact for a Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ ($x = 0.15$) film after continuous Seebeck coefficient measurement for 117.5 hours. White dotted

lines in BSE image indicate Au contact area.

Figure S7. Optical image of Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ ($x = 0.15$) film after continuous Seebeck



coefficient measurements for 117.5 hours. Letters indicate approximate spots for elemental ratio quantification by SEM-EDS as presented in Table S2.

Table S2. Elemental ratios at approximate locations indicated in Figure S7 based on SEM-EDS in different parts of a Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ film ($x = 0.15$) after continuous Seebeck coefficient measurement for 117.5 hours

	Contact I(A)	Close to Au border I - Cu side (B)	Center of film (C)	Close to Au border II -Cu side (D)	Close to Au border II - Au side (E)	Contact II (F)
Cu:Se at%-ratio	2.6	2.5	2.2	2.5	2.7	3.1
Cu:S at% ratio	9.3	8.6	12.5	9.4	9.0	8.5
Cu:(S+Se) t%-ratio	2.0	2.0	1.8	1.9	2.1	2.3
Se:S at% ratio	3.6	3.4	5.6	3.8	3.3	2.7
x (S/(S+Se))	0.22	0.23	0.15	0.21	0.23	0.27

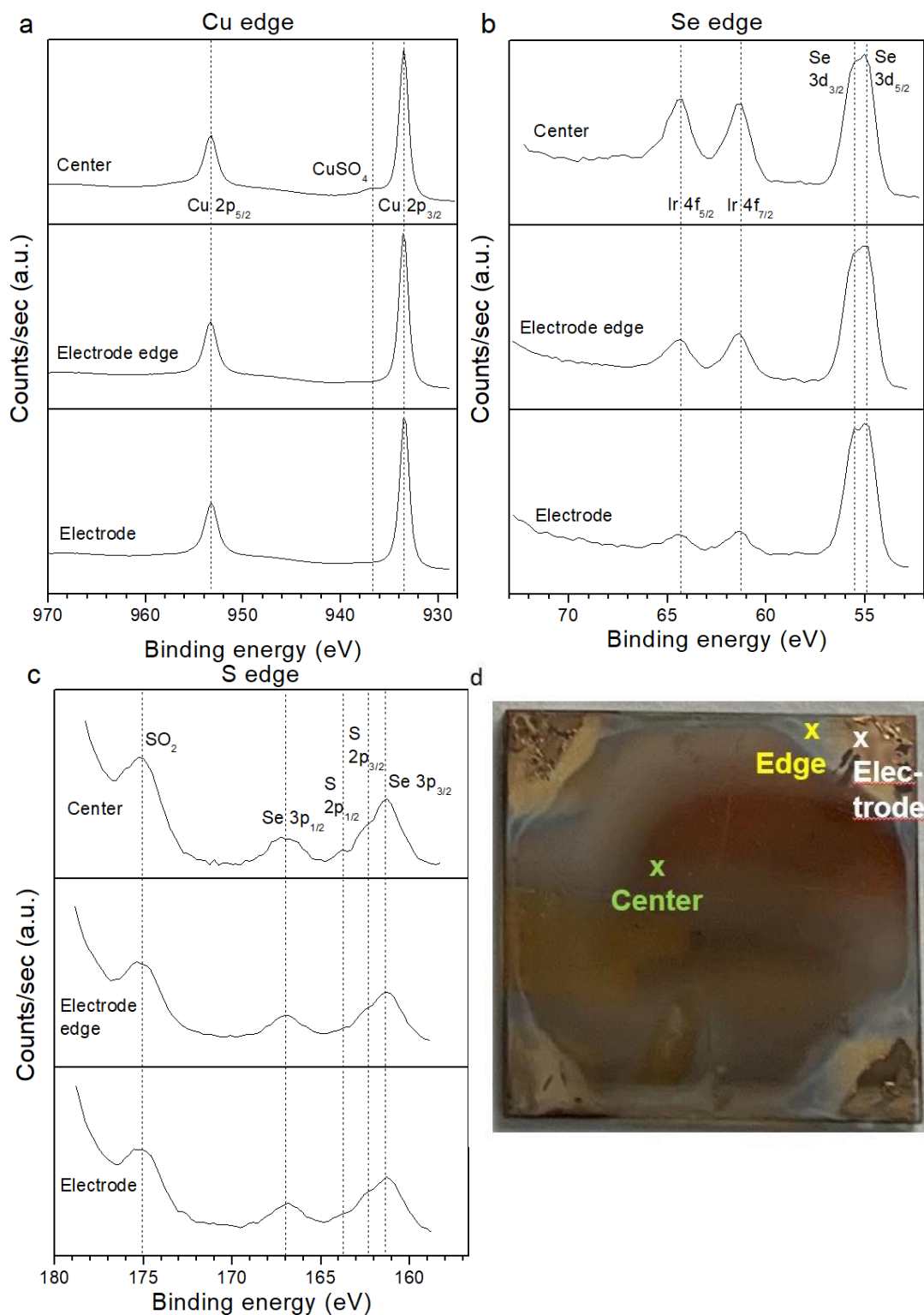


Figure S8. XPS data for Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films with $x = 0.15$ after 117.5 h continuous Seebeck measurement. a) Cu edge, showing match with $\text{Cu } 2p_{5/2}$ and $\text{Cu } 2p_{3/2}$ peaks both at the center of the film, electrode edge and at the electrode. Evidence of oxidation can be observed at ~ 937 eV at the center of the film. The data are inconclusive regarding the presence of weak satellite peaks ~ 945 eV enabling distinction between $\text{Cu}(0)$ and $\text{Cu}(I)$ species.^[1] b) Se edge,

showing match with Se 3d_{3/2} and Se 3d_{5/2} peaks. Residual iridium (Ir) after SEM study can be observed even after 90 seconds of argon sputtering. c) S edge, showing match with Se 3p_{1/2}, Se 3p_{3/2}, S 2p_{1/2} and S 2p_{3/2} peaks. Evidence of oxidation can be observed at ~175 eV, with the strongest intensity in the center of the film. d) Optical image of sample indicating scanning locations.

Figure S9 and Figure S10 show additional plots comparing the effect of S content on Seebeck coefficient stability for unsoaked and Cu soaked Cu_{2-y}S_xSe_{1-x} thin film samples, respectively.

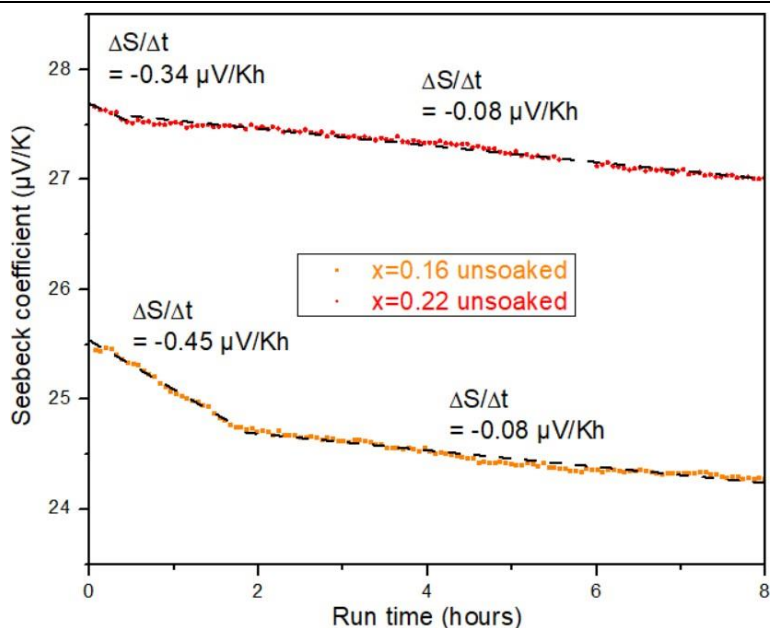


Figure S9. Seebeck coefficient stability for unsoaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ thin films with $x = 0.16$ and $x = 0.22$ annealed at 350°C . Increased absolute Seebeck coefficient is observed as well as improved Seebeck coefficient stability with increased S content, particularly due to shortening of the initial phase with sharp decrease.

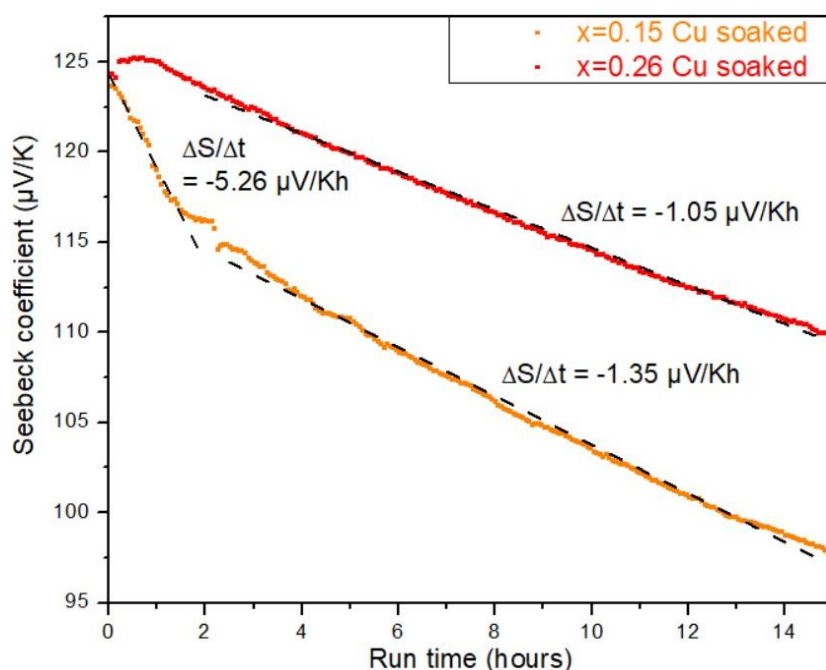


Figure S10. Seebeck coefficient stability for Cu soaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ thin films with $x = 0.15$ and $x = 0.26$ annealed at 350°C . Improved stability is observed with increased S content, particularly due to the minimization of the initial sharp decrease the first 2 hours.

Figure S11 shows the effect of sulfur after annealing at 400 °C, Cu soaking and 30 min air exposure. In this case the Seebeck coefficient stability is decreased with increasing S content, from -4 % to -14% the first 15 hours when increasing from $x = 0.13$ to $x = 0.51$. Theoretically, after annealing at 400 °C and Cu soaking, the number of Cu vacancies in these films should be very low. Exposure to air is believed to reintroduce vacancies in the material, but as previously discussed, an increased S content increases the barrier to Cu^+ migration in the material. We therefore hypothesize that, after exposure to air, the films with the highest S content have the lowest number of vacancies, thus the highest thermodynamic driving force for Cu^+ migration when exposed to a temperature gradient.

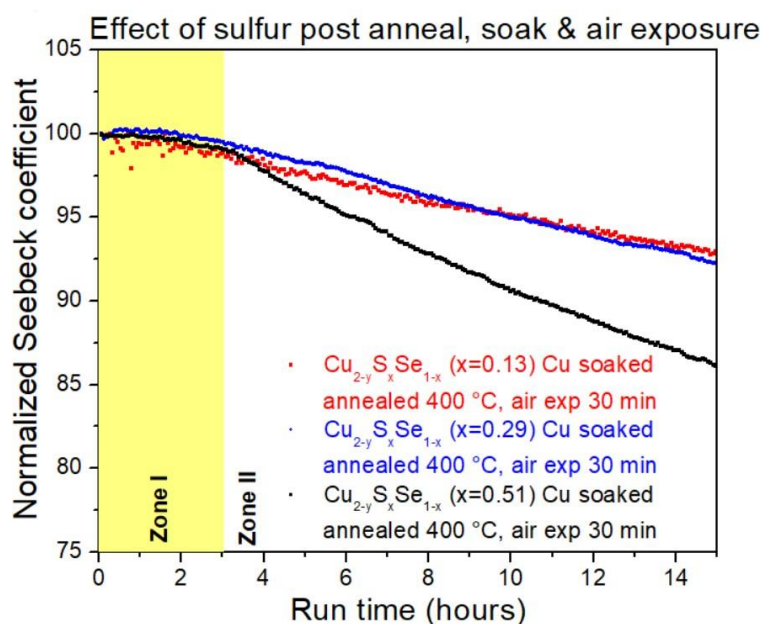


Figure S11. Stability of Seebeck coefficient over time - Effect of S after Cu soaking, annealing at 400 °C and 30 min air exposure: Decreased Seebeck stability with increasing S content. The yellow box indicates the period of initial degradation mechanism, Zone I.

Figure S12. shows the Seebeck coefficient and electrical conductivity as a function of S content for unsoaked and Cu-soaked ~60 nm $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed in an oven at 400 °C.

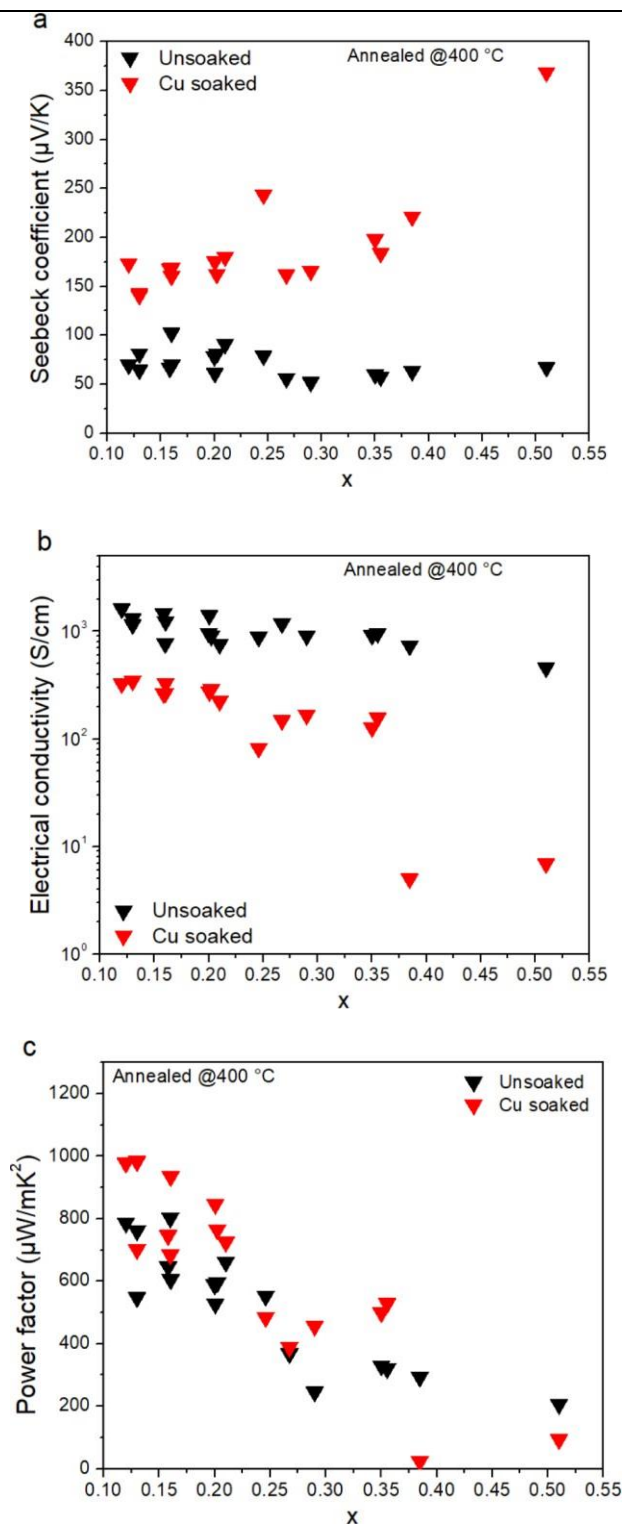


Figure S12. Full dataset showing thermoelectric properties of unsoaked (black) and Cu soaked (red) ~ 60 nm $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed in an oven at $400\text{ }^\circ\text{C}$ as a function of S content, x . The S content in unsoaked samples is estimated based on the S content in the corresponding Cu soaked sample. a) Seebeck coefficient. Seebeck coefficient increases 3-fold upon Cu soaking compared to the unsoaked sample. Additionally, the Seebeck coefficient of Cu soaked samples increases slightly with S content up to $x \sim 0.40$. b) Electrical conductivity. The electrical

conductivity was reduced significantly upon Cu soaking and decreases slightly with increasing S content. c) Power factor. The power factor increases 20 - 50% after 10 min soaking in 0.05 M Cu(I) in methanol compared to before soaking for x up to ~ 0.35 . A decreasing trend in power factor with increasing x is observed for both unsoaked and Cu soaked samples.

Figure S13 compares Seebeck coefficients, electrical conductivities and power factors for unsoaked (a, c, e) and Cu soaked (b, d, f) films annealed at 350 °C and 400 °C. Seebeck coefficients for unsoaked films annealed at 400 °C are 2 - 4 times higher than the values for unsoaked samples annealed at 350 °C. The electrical conductivities of unsoaked films annealed at 400 °C are $\sim 30\%$ of the electrical conductivities of unsoaked films annealed at 350 °C for $x < 0.25$. This results in up to 3 times higher power factors for unsoaked films annealed at 400 °C than the values for unsoaked films annealed at 350 °C at low S contents. At high S contents the power factors are in a similar range for both sample series. Additionally, the power factors have a decreasing trend with increasing x for unsoaked films annealed at 400 °C, and a flat trend for unsoaked films annealed at 350 °C.

For Cu soaked films, the difference in Seebeck coefficients and electrical conductivities for films annealed at 350 °C and 400 °C is less clear; Seebeck coefficients generally increasing and electrical conductivities generally decreasing with increasing x . However, the resulting power factors for the films annealed at 400 °C start to decrease at a lower S content than samples annealed at 350 °C. A decreasing trend with increasing S content is observed for $x > 0.25$ for all samples series of Cu soaked films.

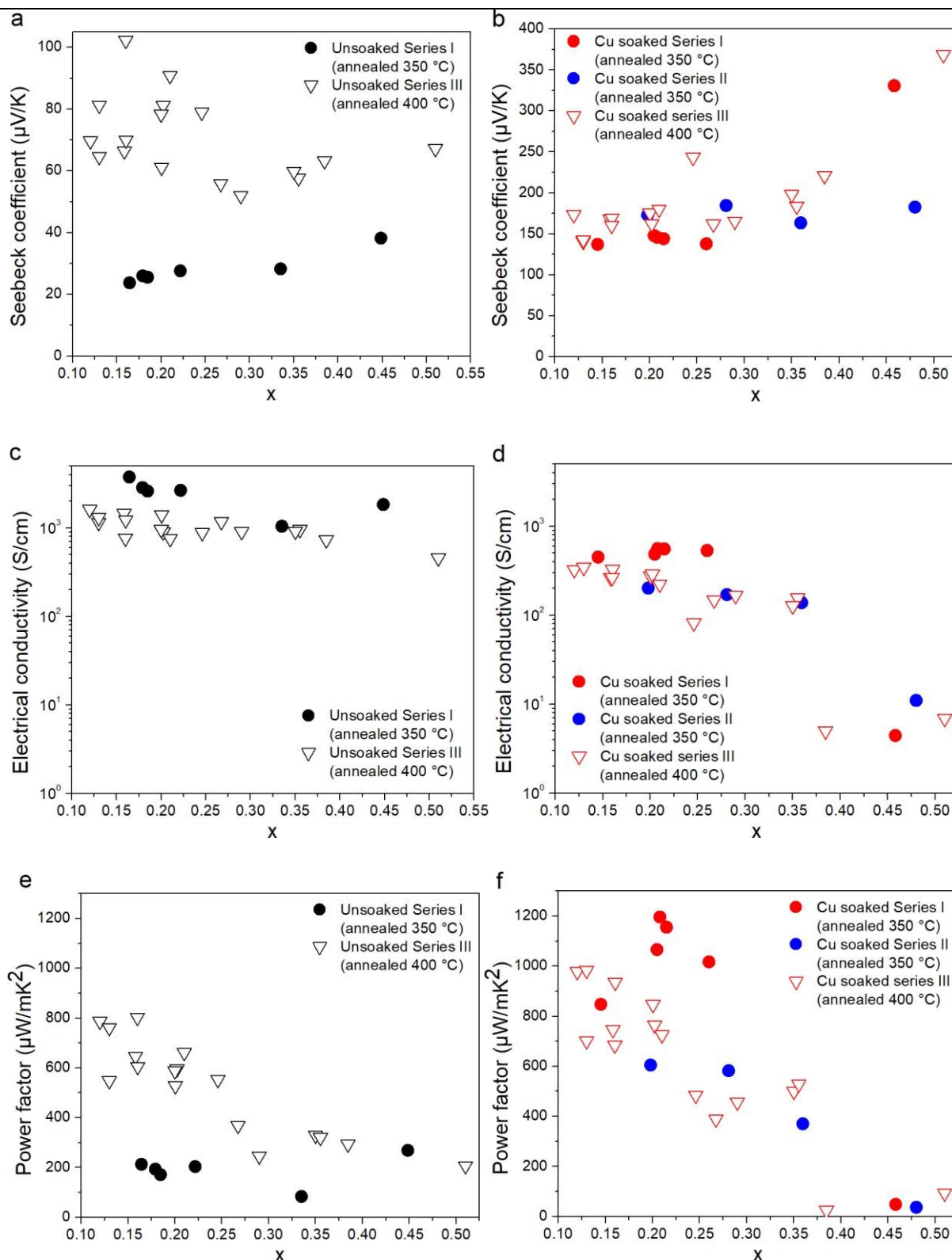


Figure S13. Seebeck coefficients (a, b), electrical conductivity (c, d) and power factor (e, f) of unsoaked (a, c, e) and Cu soaked (b, d, f) $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed on a hot plate at 350 °C (solid black, red or blue symbols) or in an oven at 400 °C (open black or red symbols) as a function of S content, x . Unsoaked films annealed at 400 °C have 2 - 4 times higher Seebeck coefficients and ~70% lower electrical conductivities than films annealed at 350 deg C,

resulting in ~3 times higher power factor for unsoaked films annealed at 400 °C for $x < 0.25$.

For Cu soaked films, the difference in Seebeck coefficients and electrical conductivity for samples annealed at 350 deg C and 400 deg C is less clear, resulting in similar power factors.

Average Seebeck coefficients at 23 °C and 50 °C were determined as a function of S content, as shown in Figure S14. For samples with slight addition of Cu₂S to the Cu₂Se ink, no change in average Seebeck coefficient was observed with slightly increased operating temperature. For samples with no extra addition of Cu₂S, the average Seebeck coefficient was reduced by 21% at slightly increased operating temperature. Continuous Seebeck measurements over 15 hours of operation at 50 °C were conducted using an adapted Labview program. The temperature was allowed to equilibrate for 60 seconds between each subsequent measurement. Figure S15 compares Seebeck stability at 50 °C for samples with and without extra addition of S. The sample with slight addition of S performs significantly better at 50 °C, strengthening our conclusion that slight addition of sulfur and annealing at 400 °C improves the stability of Cu_{2-y}Se.

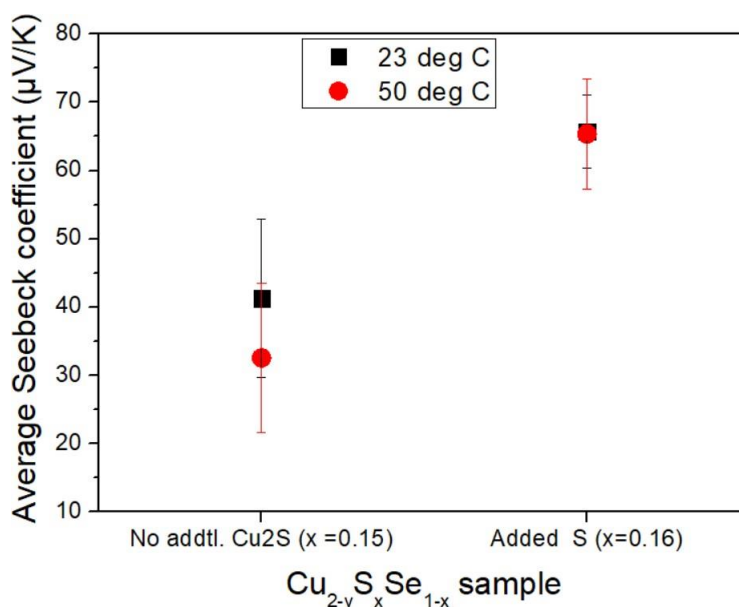


Figure S14. Average Seebeck coefficient at 23 °C and 50 °C for unsoaked Cu_{2-y}S_xSe_{1-x} samples annealed at 400 °C. No significant change in Seebeck coefficient is observed for sample with slight addition of Cu₂S ($x = 0.16 \pm 0.02$).

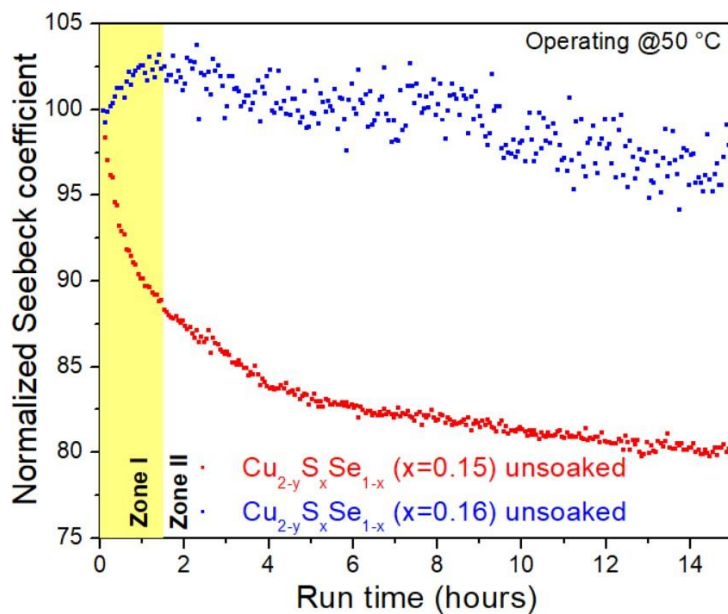
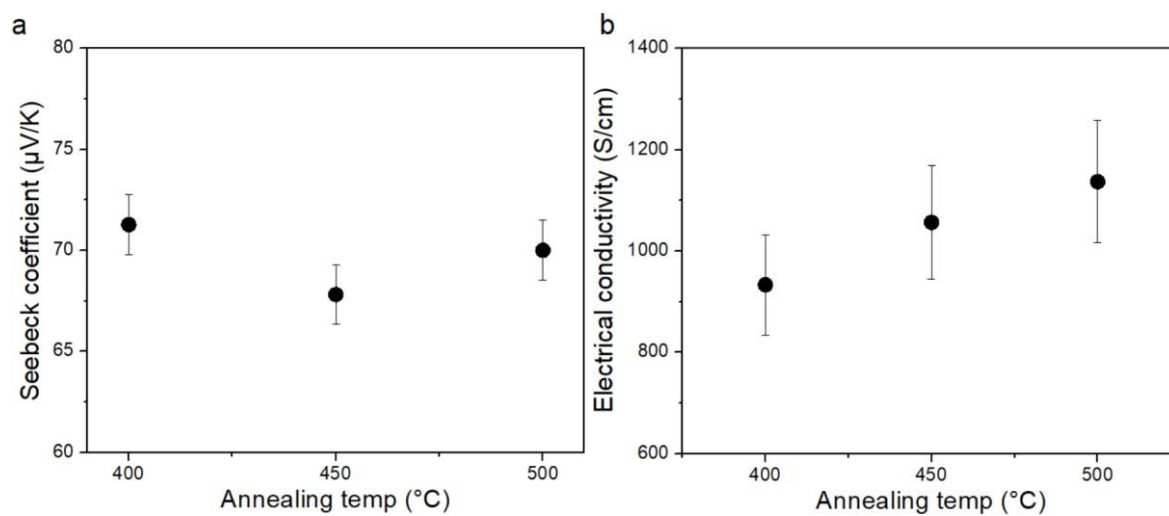


Figure S15. Continuous Seebeck measurements of unsoaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed at 400 °C, operated at 50 °C. The slight addition of S increases the Seebeck stability significantly.



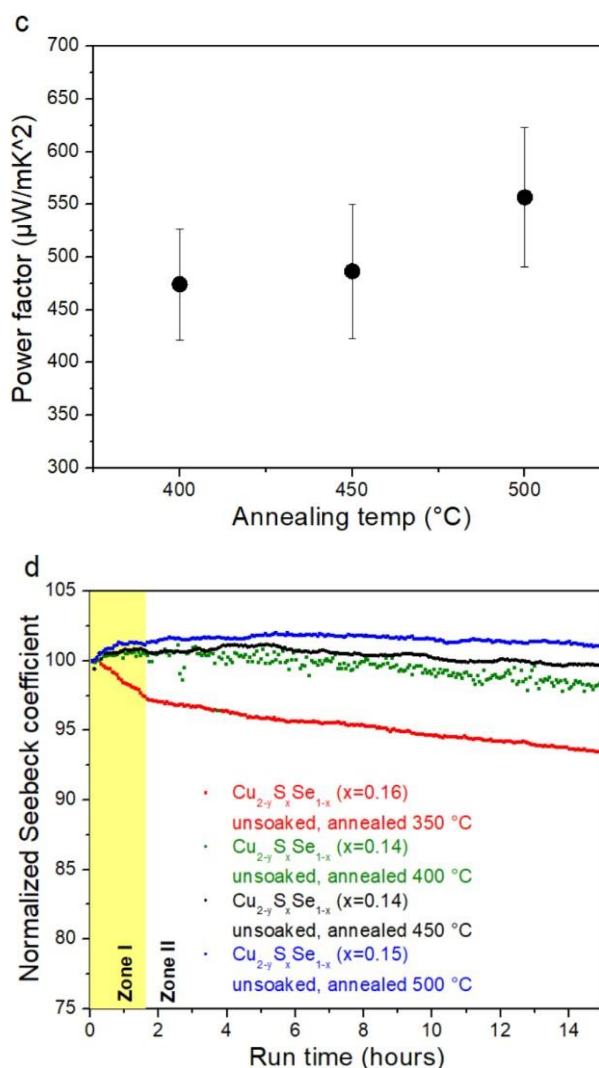


Figure S16. Average thermoelectric properties of unsoaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ film couples annealed in oven at 400 - 500 $^{\circ}\text{C}$. Seebeck stability of unsoaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed at different temperatures. a) Seebeck coefficient as a function of annealing temperature. No significant trend is observed. b) Electrical conductivity as a function of annealing temperature. An increasing trend with increasing temperature is observed, likely due to improved film quality and mobility. c) Power factor as a function of annealing temperature. A slight increase is observed above 450 $^{\circ}\text{C}$. d) Seebeck coefficient stability of unsoaked $\text{Cu}_{2-y}\text{S}_x\text{Se}_{1-x}$ films annealed at different temperatures during first 15 hours of operation. Film annealed at 500 $^{\circ}\text{C}$ (blue) shows best performance stability, and performance stability decreases with decreasing annealing temperature.

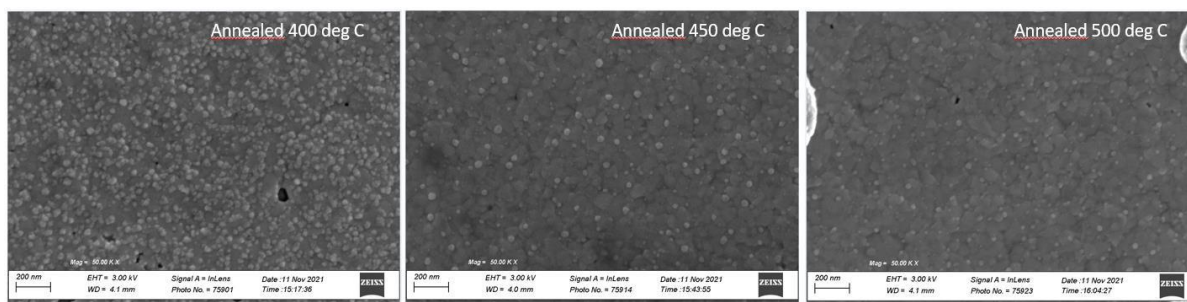


Figure S17. Backscatter SEM images of unsoaked Cu_{2-y}S_xSe_{1-x} films ($x \sim 0.15$) annealed in an oven at 400 – 500 °C. Smoother topography can be observed at higher annealing temperatures, indicating improved film quality and mobility, resulting in increasing electrical conductivity.

References

- [1] ThermoFischerScientific, Copper X-ray photoelectron spectra, copper electron configuration, and other elemental information, <https://www.thermofisher.com/us/en/home/materials-science/learning-center/periodic-table/transition-metal/copper.html>, accessed: September, 2022.