

Supplementary Information

High-Performance Thermoelectric Silver Selenide Thin Films Cation Exchanged from a Copper Selenide Template

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Experimental Section

The experimental details are described in the main text.

Structural and Compositional Characterization Section

SEM, EDX, XRD and XPS were used to characterize the morphology, structure and composition of the pre-soaked Cu_{2-x}Se thin films and post-soaked Ag_2Se thin films.

Scanning Electron Microscopy

SEM Images were performed on a Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope using beam energy of 5 kV for imaging.

X-Ray Diffraction

A Bruker AXS D8 Discover GADDS XRD micro-diffractometer was utilized to collect wide-angle spectra using a $\text{Co-K}\alpha$ source at a wavelength of 0.179 nm.

X-ray Photoelectron Spectroscopy

XPS was used to identify Cu, Se and Ag valence states in pre-soaked Cu_{2-x}Se samples and post-soaked Ag_2Se samples. A Versa Probe II XPS system from Physical Electronics with an $\text{Al K}\alpha$ source operated at 50 W and 15 kV with 200 μm spot size was used for this purpose. Pass energy of 29.4 eV was used for narrow scan spectra, corresponding to an energy resolution of ~ 700 meV.

Thermoelectric Measurement Section

Electrical and Seebeck Coefficient Measurements

Sheet resistance of each film was measured using Keithley 2400 Sourcemeters in 4-point van-der Pauw configuration. Film thickness was measured by scratching the film and measuring the step height with a Veeco Dektak 150 profilometer. Electrical conductivity of the bulk film was calculated by multiplying the sheet resistance with the thickness of each film. Seebeck coefficient (thermopower) was measured using a homemade probe setup where the thin film sample was placed across two Peltier devices. A constant current was passed through the two Peltier devices that were placed ~4mm apart, which heated up one side and cooled down the other, establishing a heat gradient across the sample. The temperature gradient (ΔT) was measured using two T-type thermocouples mounted in micromanipulators. The magnitude of the temperature gradient is directly correlated to the amount of current driven through the two Peltier devices. The induced open circuit voltage due to the ΔT was measured using Keithley 2000 multimeters. Normally, within one measurement, eight different thermal gradients were established, and 10 voltage measurements were recorded and averaged at each ΔT . For all samples, the open circuit voltage exhibited a linear relationship with ΔT . The Seebeck coefficient was calculated by obtaining the slope of the voltage vs. ΔT plot for each sample. Electrical conductivity and Seebeck coefficient measurements were performed in a nitrogen-filled glovebox using homemade LabVIEW programs.

Thermal Conductivity Measurements

The thermal conductivities of Ag_2Se thin films were measured using the differential 3ω method.¹ Two different configurations were set - referred to as "sample" (with Ag_2Se thin film on

a silicon substrate) and "reference" (bare silicon substrate), respectively. Since the Ag₂Se is highly electrically conducting, another 150-nm Al₂O₃ layer was then deposited on top of the Ag₂Se thin film to achieve electrical insulation. A 100-nm thick gold heater line was then deposited on the insulating layer using thermal evaporation, as shown in **Figure S1**. The dimension of the heater line is 80 μm wide and 1.5 mm long. The heater lines were bonded to copper wires by silver paste.

In the thermal conductivity measurement, an AC current at frequency ω is applied to the heater line. The precision resistance is tuned to the same resistance as the sample, which is about 34 Ω . The 3ω voltage is obtained by subtracting the 1ω signal using a SR860 lock in amplifier. The heating frequencies were carefully selected in the range wherein the penetration depth is not higher than the substrate thickness but large enough to avoid the heater linewidth effect. After this testing, we select the frequency between 100 to 200 Hz as heating frequency. The substrate thermal conductivity has been evaluated by using the frequency-dependent in-phase 3ω in-phase voltage. It has also been verified using the 3ω out-phase voltage. The temperature across the substrate $\Delta T_{\text{substrate}}$ is extracted from the reference sample. And the total temperature difference ΔT_{total} across both the thin film and substrate is obtained from the Ag₂Se sample. Subtracting the reference temperature $\Delta T_{\text{substrate}}$, the temperature across the thin film ΔT_{film} will be obtained. The ΔT_{film} is related to the thin film thermal conductivity κ by¹

$$\Delta T_{\text{film}} = \frac{P}{l\kappa} \frac{t}{2b} \quad (1)$$

where P is the power supplied to the heater line, l is the line length, t is the film thickness, b is the half linewidth. The frequency-dependent temperature differences are shown in **Figure S2**. A constant temperature difference of 0.01K is extracted. Thus, the thin film thermal conductivity κ is evaluated from the Eq. (1), which is about 0.53 $\text{Wm}^{-1}\text{K}^{-1}$ with an uncertainty of about 35%. By

comparing the 3ω voltage of reference sample with the thin film sample, the major uncertainty source is from the film thickness.

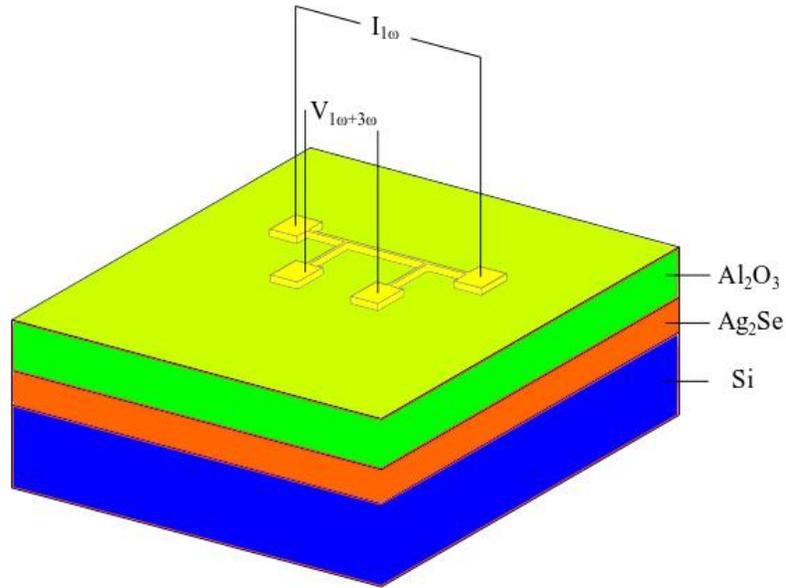


Figure S1. Schematic of the heater line pattern on Ag₂Se film (red). An electrical insulating layer Al₂O₃ (green) is deposited on top of the film sample.

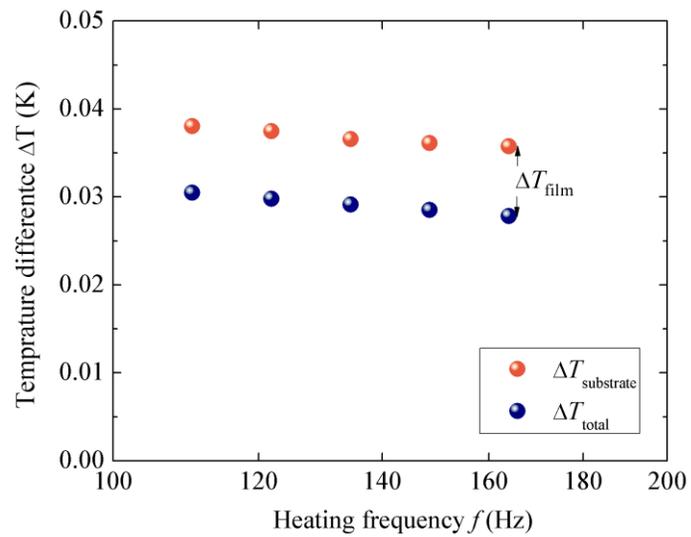


Figure S2. Heating frequency-dependent temperature across the total sample (orange) and across the silicon substrate (blue). The temperature across the film sample ΔT_{film} is the difference.

Error Analysis

1). Sample calculation for Seebeck coefficient instrumental error

	Hot Temp.(°C)	Cold Temp.(°C)	ΔV_i (mV)
1	17.7	27.9	-0.1596
2	8.3	46.9	-0.5350

$$\Delta T_1 = 46.9 - 8.3 = 38.6^\circ\text{C}$$

$$\Delta T_2 = 27.9 - 17.7 = 10.2^\circ\text{C}$$

$$\Delta T = \Delta T_1 - \Delta T_2 = 28.4^\circ\text{C}$$

$$\Delta(\Delta T_1) = \Delta(\Delta T_2) = 1^\circ\text{C}$$

$$\Delta(\Delta T) = \sqrt{\Delta(\Delta T_1)^2 + \Delta(\Delta T_2)^2} = \sqrt{2}^\circ\text{C}$$

The instrumental uncertainty for Seebeck Coefficient is estimated to be 0.025% of the measured $\Delta V_i + 0.04$ mV.

$$\Delta W = \Delta V_1 - \Delta V_2 = 0.3754 \text{ mV}$$

$$\Delta(\Delta W)_{V_1} = \Delta(\Delta V_1) = 0.025\% \times -0.1596 + 0.04 = -0.03996 \text{ mV}$$

$$\Delta(\Delta W)_{V_2} = -\Delta(\Delta V_2) = -(0.025\% \times -0.5350) + 0.04 = 0.04013 \text{ mV}$$

$$\Delta(\Delta W) = \sqrt{(-0.03996)^2 + (0.04013)^2} = 0.05663 \text{ mV}$$

$$S = \frac{\Delta V_1 - \Delta V_2}{\Delta T_1 - \Delta T_2} = \frac{\Delta W}{\Delta T}$$

$$\Delta S_w = \frac{1}{\Delta T} \Delta(\Delta W) = \frac{1}{28.4} \times (0.05663) \times 10^3 = 1.9929 \mu\text{VK}^{-1}$$

$$\Delta S_T = -\frac{\Delta W \Delta(\Delta T)}{(\Delta T)^2} = (-0.3754) \times \frac{\sqrt{2}}{(28.4)^2} \times 10^3 = -0.6582 \mu\text{VK}^{-1}$$

$$\Delta S = \sqrt{1.9929^2 + (-0.6582)^2} = 2.0988 \mu\text{VK}^{-1}$$

Since the Seebeck coefficient error is very small, we used the same Seebeck coefficient error for each sample.

2). Sample calculation for electrical conductivity measurement errors – sample at 5 min soaking time

Soaking time (min)	R (Ω)	σ (Sm ⁻¹)	S (μVK ⁻¹)	PF (μWm ⁻¹ K ⁻²)
5	155	80906	-101	825

Note: Sample thickness (d) is 0.8×10^{-7} m, thickness uncertainty is $\Delta d = \pm 10$ nm

The instrumental uncertainty of resistivity is estimated to be 0.5% of the measured value for each sample.

$$\sigma = \frac{1}{Rd}$$

$$\Delta\sigma_d = -\frac{1}{Rd^2} \Delta d = -\frac{1}{155 \times (0.8 \times 10^{-7})^2} \times 1 \times 10^{-8} = -10080.645 \text{ Sm}^{-1}$$

$$\Delta\sigma_R = -\frac{1}{dR^2} \Delta R = -\frac{1}{0.8 \times 10^{-7} \times 155^2} (0.005) \times 155 = -403.225 \text{ Sm}^{-1}$$

$$\Delta\sigma = \sqrt{\Delta\sigma_d^2 + \Delta\sigma_R^2} = \sqrt{(-10080.645)^2 + (-403.225)^2} = 10080.706 \text{ Sm}^{-1}$$

3). Sample calculation for power factor (PF)

$$PF = S^2\sigma$$

$$\Delta PF_\sigma = S^2 \Delta\sigma = (-101)^2 \times 10080.706 \times 10^{-6} = 102.833 \mu\text{Wm}^{-1}\text{K}^{-2}$$

$$\Delta PF_S = 2 \sigma S \Delta S = 2 \times 80906 \times (-101) \times 2.086 \times 10^{-6} = -34.092 \mu\text{Wm}^{-1}\text{K}^{-2}$$

$$\Delta PF = \sqrt{\Delta PF_{\sigma}^2 + \Delta PF_S^2} = \sqrt{102.833^2 + (-34.092)^2} = 108.336 \mu W m^{-1} K^{-2}$$

Nomenclature

<i>Symbol</i>	<i>Definition</i>	<i>Unit</i>
R	Sheet resistance	Ω
σ	Electrical conductivity	$S m^{-1}$
S	<i>Seebeck coefficient</i>	$\mu V K^{-1}$
d	Thickness of the sample	m
PF	Power Factor	$\mu W m^{-1} K^{-2}$
V	Voltage	mV
ΔV_i	Voltage change at one reading	mV
ΔT_i	Temp. difference at one voltage change reading	$^{\circ}C$
W	Difference between two voltage change readings	mV

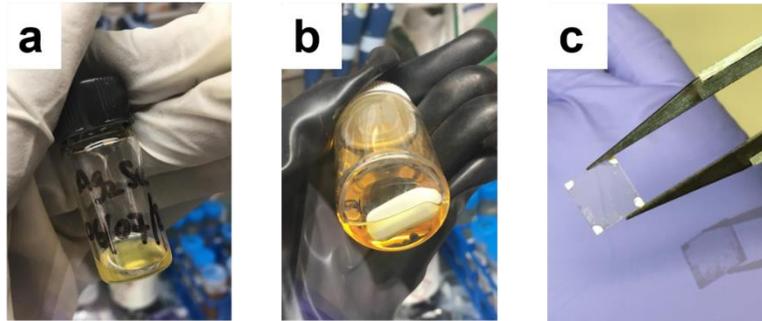


Figure S3. (a, b) Two vials showing that the Ag₂Se bulk powder only partially dissolved in thiol-amine solution as some dark pellets remained at the bottom after stirring and sonicating, (c) a low-quality spin-coated Ag₂Se thin film on a glass substrate using the solution made by dissolving

Ag₂Se bulk powder into thiol-amine solution. The photograph of the film shows that a very small amount of Ag₂Se adhered to the glass substrate and the film was not uniform or evenly coated which made it impossible to perform any characterization or analysis on the sample. The above photos prove that this pathway of fabricating Ag₂Se thin films from Ag₂Se bulk powder dissolved in thiol-amine solution is not feasible; therefore, we adopted a totally different approach: cation exchange via soaking to generate Ag₂Se thin films.

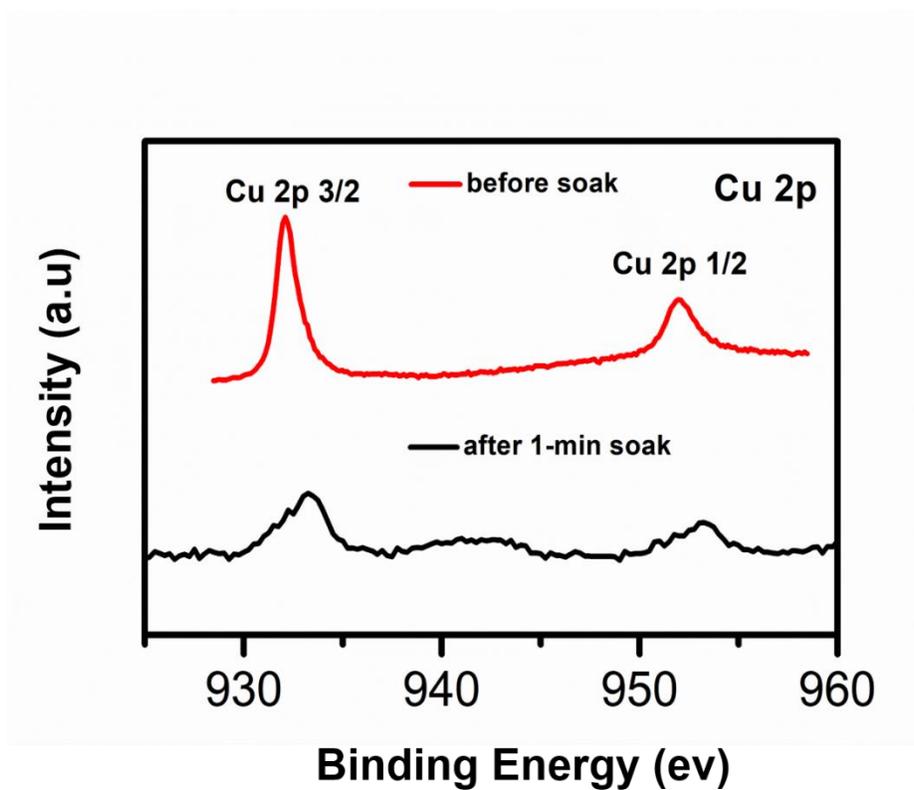


Figure S4. X-ray photoelectron spectroscopy (XPS) images of Cu peaks at 2p orbital in Cu_{2-x}Se sample before (red) and after soaking for one minute (black) in Ag-ion solution. The presence of residual Cu peaks in the black spectrum shows that one minute is not long enough to convert the Cu_{2-x}Se into Ag₂Se. Based on our results, the full exchange occurs when the Cu_{2-x}Se film is soaked for around 30-40 minutes.

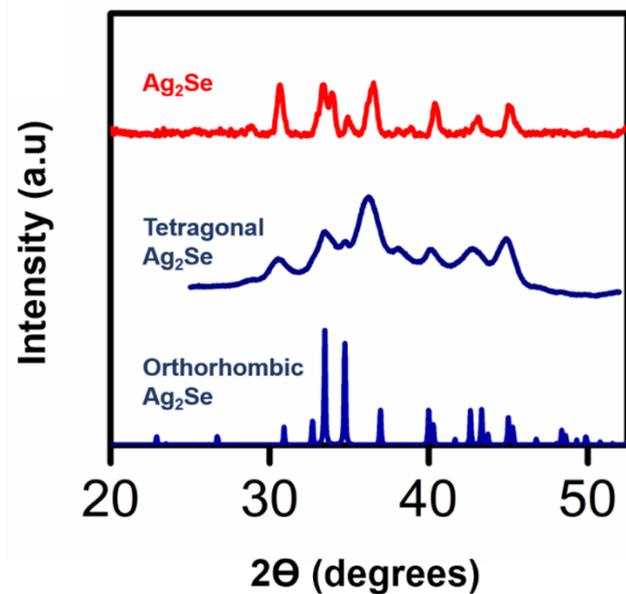


Figure S5. XRD data for a Ag_2Se film (red) after soaking in Ag^+ ion solution for 40 minutes before annealing, reference data for a tetragonal Ag_2Se film (blue)² and reference data for an orthorhombic Ag_2Se film (blue, ICSD-261822)³. The XRD patterns show that the before-annealing Ag_2Se film also shows a mixed phase of tetragonal and orthorhombic structures which are similar to the XRD patterns of the post-annealing Ag_2Se film from the main text.

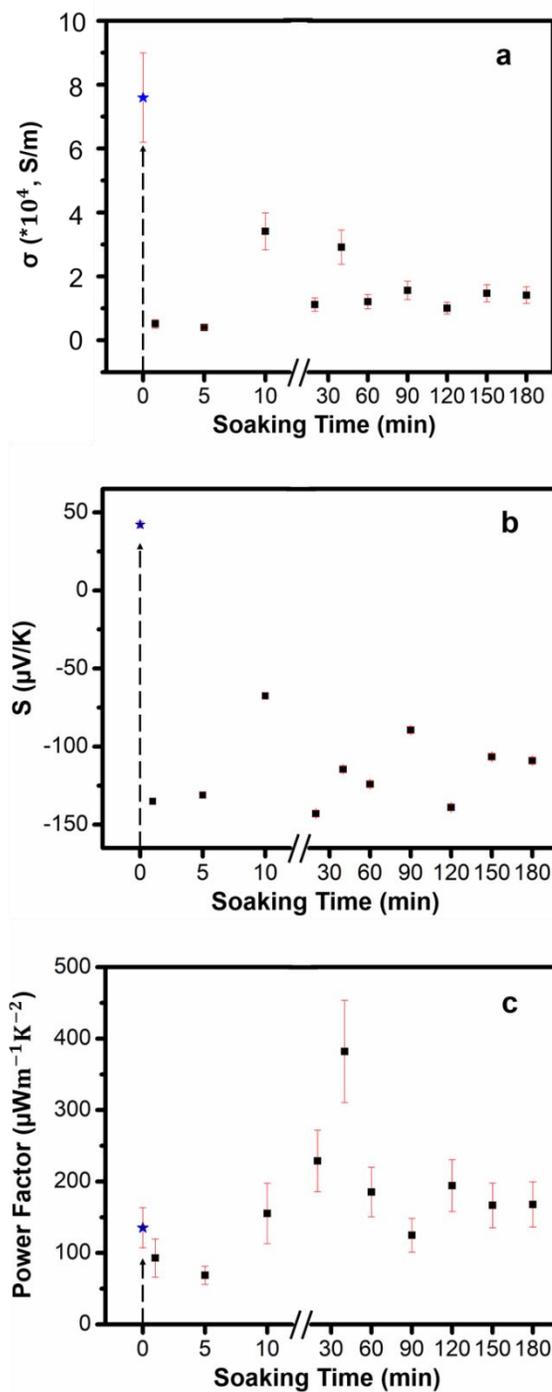


Figure S6. (a) Electrical conductivity of as-fabricated Cu_{2-x}Se sample (blue star) and Ag_2Se samples (black squares) as a function of soaking time in Ag^+ ion solution before annealing. The dotted line at 0 minutes indicates the electrical conductivity of the p -type Cu_2Se thin film. (b)

Seebeck coefficient of Cu_{2-x}Se sample and Ag_2Se samples as a function of soaking time before annealing. The sign of Seebeck coefficient changes from positive to negative indicating a transformation from p -type Cu_{2-x}Se to n -type Ag_2Se . (c) Power factor (PF) data as a function of soaking time before annealing. The optimal soaking time is approximately 30-40 minutes of which the PF peaks at a maximum value of $382 \mu\text{Wm}^{-1}\text{K}^{-2}$.

This batch of Ag_2Se samples were prepared in a similar fashion as described in the experimental section except that the inks used for spin coating was $50 \mu\text{L}$ instead of $35 \mu\text{L}$ from the main text and the post-soaked samples were not annealed at 350°C for 30 minutes. We tested several different soaking times: 1 min, 5 min, 10 min, 20 min, 40 min, 60 min, 90 min, 120 min, 150 min and 180 min at room temperature. Results show that the TE properties vary with different soaking times before annealing. This batch of Cu_{2-x}Se templates with a higher average thickness of $163 \pm 30 \text{ nm}$ exhibit an average electrical conductivity of nearly $7.6 \pm 0.1 \times 10^4 \text{ S/m}$ at room temperature. After the soaking process, the electrical conductivity of each post-soaked sample decreases as shown in Figure S6a. Among all soaking times, the samples corresponding to 1 min and 5 min soak times exhibit a significant drop in electrical conductivities due to the rapid diffusion of Ag^+ guest ions into both the vacant sites and interstitial sites leading to early phases of transformation from p -type Cu_2Se to n -type Ag_2Se . Also, at these short soaking time regimes, as discussed in the main text the thin films could have residual Cu atoms or mixed phase $\text{Ag}_2\text{Se}/\text{Cu}_2\text{Se}$. As the Ag ions infiltrate the lattice, electron concentrations rise, causing the electrical conductivity at 10 min to be higher than at 1 min or 5 min. The electrical conductivities vary little over time after around 40 min.

With increasing soaking time, Seebeck coefficients fluctuate greatly in the first few soaking points due to the increase in the electron concentration, which then reach a saturated value,

following the similar trend observed in electrical conductivities. The PF data of the samples plotted against the soaking time starts with a small drop, followed by a steady increase to the optimal value, and eventually drops again to maintain a roughly constant value. The maximum PF we have obtained is $382 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 40 min of soaking time. Because these Ag_2Se samples were not annealed after soaking, there might be residual Cu atoms sticking on grain boundaries causing carrier scattering which might result in the peak in PF and the large variation in electrical conductivities and Seebeck coefficient values for different soaking times. Post heating, these variations are annealed out leading to much more uniform numbers.

Reference

1. D. G. Cahill, M. Katiyar and J. R. Abelson, *Physical Review B*, 1994, **50**, 6077-6081.
2. A. Sahu, D. Braga, O. Waser, M. S. Kang, D. Deng and D. J. Norris, *Nano Letters*, 2014, **14**, 115-121.
3. J. Yu and H. Yun, *Acta Crystallographica Section E*, 2011, **67**, i45.