Supporting Information

Doping-induced Superconductivity in the van der Waals Superatomic Crystal $Re_6Se_8Cl_2$

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Single crystal Re₆Se₈Cl₂ synthesis

Re (330 mg, 1.80 mmol), Se (190 mg, 2.41 mmol), and ReCl₅ (200 mg, 0.55 mmol) are ground with a mortar and pestle and pressed into a pellet under N₂ atmosphere. The pellet is sealed in a quartz tube of approximately 30 cm in length under vacuum. Large single crystals are grown by chemical vapor transport method, with ReCl₃ acting as the transport agent. The tube is heated in a tube furnace to 1100 °C at 1 °C/min and held at 1100 °C for 3 days. With the pellet in the hot end, the tube is cooled to a 970 - 925 °C gradient over 7 hours and held for 200 hours. The tube is further cooled to a 340 - 295 °C gradient over 100 hours, and the furnace is shut off. Large 0.5 mm single crystals are recovered from the middle zone of the tube. Excess ReCl₃ is removed from the single crystals by using a gradient of 300 °C - RT to condense the liquid ReCl₃ to the cooler end.

Transport measurements

Before current annealing, transport measurements are performed in a voltage bias scheme, where a lock-in amplifier sources an AC voltage (at a frequency of 17.777 Hz) and auxiliary lockin amplifiers measure the AC current, 4-probe longitudinal voltage, and Hall voltage. After current annealing, measurements are performed in a current bias scheme where a large resistor (1-10 MΩ) is placed in series before the sample to limit the AC current to ~100 nA. In both schemes, the longitudinal resistance R_{xx} is defined as $\frac{V_{xx-AC}}{I_{AC}}$ and the hall resistance R_{xy} is defined as $\frac{V_{xy-AC}}{I_{AC}}$. For all equilibrium transport measurements, the DC voltage and DC current are zero. For non-equilibrium measurements, a DC+AC current bias scheme is used where a lock-in amplifier is connected in parallel with a DC voltage source. A 10 MΩ resistor is placed after the lock-in output and a 100 kΩ resistor is placed after the DC voltage source output. The AC current is measured with the source lock-in and the DC current is measured with the DC voltage source. The resistance is defined as $R(I_{DC}) = \frac{dV}{dI} / \frac{1}{I_{DC}} = \frac{V_{xx-AC}}{I_{AC}}$. An AC current of ~100 nA is used.

Bulk transport measurements are performed in a two-terminal configuration where a lockin amplifier sources AC voltage and measures AC current (at a frequency of 17.777 Hz). The bulk resistance is defined as $R = \frac{V_{source-AC}}{I_{AC}}$, which includes the line and contact resistance (which is small compared to the sample resistance).

Device fabrication

Prepatterned metal electrodes are fabricated on a p^+Si/SiO_2 (285 nm) substrate using electron beam lithography and deposition to define the device geometry. The electrodes are fabricated in two steps. The first defines the Re₆Se₈Cl₂ flake contact area, consisting of Cr + Pd with a thickness of 2 nm + 10 nm respectively. The second defines the wire bonding pads, which consist of Cr + Pd + Au with a thickness of 2 nm + 40 nm + 50 nm respectively. Electrodes are cleaned before use with a low power O₂ plasma etch for 5 minutes and screened for cleanliness and homogeneity with an atomic force microscope. Thin Re₆Se₈Cl₂ flakes (100 – 600 nm) are prepared by mechanical exfoliation with scotch tape,^[38] then transferred onto a polydimethylsiloxane (PDMS) substrate. Once on the PDMS, flakes are optically identified and deterministically transferred onto the prepatterned electrodes using the dry polymer transfer technique (Figure S1).^[39] The substrate is then glued to a DIP socket with conducting epoxy (SPI Silver Paste Plus) and wire bonded for transport measurements. To perform chemical and structural analyses on the current annealed flakes, we first expose the Re₆Se₈Cl₂/electrode interface using the flip-chip transfer technique (Figure S1). Distinctive metallic features are then deposited in the vicinity of the flake using electron beam lithography and deposition to help identify the sample region for micro X-ray photoemission spectroscopy (µ-XPS), energy dispersive X-ray spectroscopy (EDX) and micro Raman spectroscopy.

Bulk synthesized Re₆Se₈Cl₂ crystals are bonded to a DIP socket using a low temperature non-conducting epoxy (Loctite EA 1C). Connections to the sample are made directly with silver paint (Dupont 4929N).

Current Annealing

We source DC voltage and measure DC current in a 2-terminal configuration. To protect the samples from current spikes, we set a current compliance to limit the maximum current through the sample and add a 100 k Ω resistor in series. We then ramp the source voltage incrementally until the compliance current is met. The voltage is then ramped down to zero after which we measure the sample resistance with low biases. This process is repeated, incrementally increasing the compliance current (thus the maximum power passed through the sample), until the sample resistance decreases significantly (<10 k Ω) and saturates (Figure S2). We anneal the shortest sample channels sequentially to produce a longer sample path that exhibits metallic behavior. For example, in Figure S2A, we would anneal channels 1-4 in order, which produces a longer metallic sample that can be measured in a 4-terminal voltage configuration. Figure S2B presents the measured sample resistance vs. annealing current for a Re₆Se₈Cl₂ flake. Empirically, we take ~10⁻⁴ A as an upper limit, after which samples often degrade. This corresponds to an input electrical power of ~2-30 mW (range represents all samples). The entire procedure is done at 1.6 K.

The current annealing procedure is identical for bulk single crystal $Re_6Se_8Cl_2$ samples except the annealing was done at 200 K and the upper limit on current was taken as ~10⁻¹ A. This corresponds an input electrical power of ~2-3 W (Figure S2C).

Modelling temperature rise during current annealing

Simulation details

To estimate the temperature rise due to current annealing, a steady-state thermal simulation was performed in ANSYS Workbench 18.1. The three-dimensional model with lateral dimensions based on the device in Figure 1B was built using SpaceClaim. The cross-plane thicknesses were 300 nm of Re₆Se₈Cl₂, 12 nm of Pd, 285 nm of SiO₂, and 1 μ m of Si. Temperature dependent thermal conductivities of Si, SiO₂ and Pd were used in the simulation.^[40-44] The thermal conductivity of Re₆Se₈Cl₂ was independently measured using Frequency Domain Thermoreflectance.^[45] An in-plane thermal conductivity of 7.5 ± 1.2 W m⁻¹ K⁻¹ and a cross-plane thermal conductivity of 1.2 ± 0.2 W m⁻¹ K⁻¹ were obtained at 300 K and assumed to be independent of temperature in the simulation. Predictions suggest that current annealing brings the Re₆Se₈Cl₂ temperature above 300 K where similar superatomic crystals have exhibited temperature independent thermal conductivity.^[46] Interface thermal conductance values were set to be 50 MW m⁻² K⁻².

The spatial extent of heat deposition by joule heating is unknown and hence two heated spot sizes, shown in Figure S3, were simulated. Figure S3A considers a larger lateral region between the biased electrodes, while Figure S3B considers the smallest possible lateral region. Heat was deposited on the bottom surface of the Re₆Se₈Cl₂ where current densities are expected to be

highest. The simulations were run at steady state because the timescale for transient heat transfer is far shorter than the annealing process: less that 1 s due to the small size of the heat source.

Boundary conditions

- 1. Our truncated domain meets the macroscopic Si substrate at the Si bottom and side boundaries. Here, the conduction shape factor for a disk (representing our simulation domain) in a semi-infinite medium (representing the macroscopic substrate) was used to establish the convection style heat transfer boundary condition (i.e. $q'' = Sk(T-T_{\infty})/A$ where S is the shape factor, k is the thermal conductivity of the Si, A is the area of the boundary, and $T-T_{\infty}$ is the temperature difference between the boundary nodes and the cryostat base temperature).⁴⁷
- 2. In the region without Pd electrodes underneath, a 12 nm gap exists between the bottom of Re₆Se₈Cl₂ and the top of the SiO₂. Heat transport across this gap is based on kinetic theory of He, the monatomic gas. Thermal conductivity $k = \frac{1}{3}c_v v \Lambda$, with a mean free path $\Lambda = 12$ nm (because intrinsic mean free paths of gaseous He exceed the gap size), volumetric heat capacity $c_v = \frac{1}{3}k_B\eta$ where the number density η is calculated from the ideal gas law, and average speed $v = \sqrt{3k_BT m^{-1}}$ from the Maxwell Speed Distribution for molecules of mass *m*.
- 3. All other exposed surfaces of SiO₂, Pd and Re₆Se₈Cl₂ were set to have a convection heat transfer with flowing gaseous He. The convection heat transfer coefficient was calculated using the average Nusselt number $\overline{Nu}_L = 0.664 \overline{Re}_L^{1/2} P r^{1/3}$ for laminar flow over a flat plate. A flow velocity of 6.8 mm s⁻¹ (based on He flow measurements) and length of 100 µm were used for \overline{Re}_L . Viscosity, thermal conductivity, and Prandtl number were set based on the film temperature using values from reference.^[47]

Results

The temperature map with heat source A is given in Figure S4, and that with heat source B is given in Figure S5. The results of the maximum temperature rise are summarized in Table S1. The temperature maps indicate that the maximum temperature occurs at the bottom surface of the Re₆Se₈Cl₂ coincident with the heat source. The 12 nm gaseous He gap is a large thermal resistance that prohibits heat transfer directly into the underlying substrate and leads to a large temperature jump shown in Figure S4 and S5. Instead, the heat spreads laterally within the Re₆Se₈Cl₂ and then transfers into the substrate across the Pd contacts. The temperature rise is not linear with the magnitude of the heat input due to temperature dependent material properties. Reducing the heat source size has a significant influence on the temperature rise, and the maximum possible temperature rise exceeds 4500 K assuming the minimum possible heat source size and the maximum heat input.

Details of annealed Re₆Se₈Cl₂ superconducting properties

Variability in superconducting transitions

In Figure S6, we present resistance measurements vs. temperature and magnetic field for 3 devices, whose properties are representative of the entire sample set. Each device shows two clear kinks in the resistance corresponding to T_C^{High} and T_C^{Low} (Figure S6A,B,C) and corresponding peaks in non-equilibrium measurements, I_C^{High} and I_C^{Low} (Figure S6D,E,F). Most devices exhibit multiple

peaks for both I_C^{High} and I_C^{Low} , which we attribute to sample inhomogeneity. The multiple I_C^{High} and I_C^{Low} peaks were assigned based on their corresponding temperature dependence. The percentage change in sample resistance across T_C^{High} and T_C^{Low} are independent of sample thickness (Figure S11).

Angle dependence of the upper critical field

In Figure S8, we examine the effect of magnetic field direction on the superconducting properties of Re₆Se₈Cl₂ flakes. Figure S8A,D presents two devices which exhibit clear, sharp transitions for both T_C^{Low} and T_C^{High} . We examine the magnetic field-temperature phase diagram for magnetic fields both perpendicular (Figure S8B,E) and parallel (Figure S8C,F) to the ab plane. We observed no significant difference between field directions, indicating the superconductivity in this system is not dominated by two-dimensional confinement effects.^[32]

Vortex activation energy

Examining in detail the dependence of resistance vs. temperature and magnetic field for both devices presented in Figure S8, we can fit both transitions to the Arrhenius equation, $R = R_0 e^{-\frac{U(B)}{k_B T}}$ (Figure S9A,C for T_C^{Low} and Figure S9B,D for T_C^{High}). Note that in order to properly fit the Arrhenius equation, we need to subtract any offset resistance, so the saturated regimes are set to zero resistance. The field dependent vortex activation, U(B) is well fit by a logarithmic field dependence, $U(B)=U_0\log(H_0/H)$, which is characteristic of layered type-II superconducting systems.^[33] U_0 is the strength of vortex pinning and interaction and H_0 is the upper critical field, H_{C2-0} . Extracted H_0 values agree with our measured upper critical fields (Figure S7).

Superconductivity in bulk current and thermally annealed Re₆Se₈Cl₂

We were able to achieve superconductivity through both current and thermal annealing in several bulk devices. Through thermal annealing (Figure S12C,D) we observed only a single transition in the resistance at low temperature. We believe this transition is due to metallic Re, which is created when annealing temperatures approach the synthesis temperature (>900 °C). Through current annealing we were able to achieve two transitions in certain devices, T_C^{High} and T_C^{Low} (Figure S12A), and only a single lower transition, T_C^{Low} , in others (Figure S12B).

Chemical and structural analysis

Details of thermal annealing

For all measurements which present single crystal and microcrystalline $Re_6Se_8Cl_2$ characterization vs. annealing temperature, we outline the details of the thermal annealing process. Individual (2-3) $Re_6Se_8Cl_2$ crystals or ~15 mg of microcrystalline powder is sealed in a fused silica tube under vacuum (~40 mTorr). The tube is placed in a box oven pre-heated to the selected temperature 200 - 1000 °C. The tube is removed after 1 hour and quenched in water.

FIB cut and TEM measurements

For transmission electron microscope (TEM) studies, focused ion-beam (FIB), FEI Helios NanoLab 660, was used to prepare a cross sectional foil. To protect the contacts against ion-beam damage during sample preparation, amorphous platinum (2 µm thick) was sputtered on the surface of the wafer by electron then ion beam. During initial steps of FIB sample preparation, an

accelerating voltage of 30 kV was used to make a lamella of ~100 nm thickness. Further thinning was done at 5 kV for longer time with a gradually decreasing ion current to remove the damaged layers on each side and achieve an electron transparent foil. TEM and high-resolution scanning TEM (HR-STEM) analyses were performed on a FEI Talos F200X at an accelerating voltage of 200 kV. In order to achieve the highest resolution without damaging the sample, the spot size was set to 9 to reduce the electron beam current and the condenser 2 aperture was set to 50 μ m to obtain a small beam-convergence angle.

Scanning electron microscopy and energy dispersive X-ray spectroscopy

Scanning electron micrographs of the devices were collected on a Zeiss Sigma VP SEM. EDX of the single crystal and microcrystalline powder samples was performed with a Bruker XFlash 6130 attachment. Spectra were collected with a beam energy of 15 keV. Elemental compositions and atomic percentages were estimated by integrating under the characteristic spectrum peaks for each element using Bruker ESPRIT 2 software. Atomic percentages were calculated assuming only Re, Se and Cl were present. To estimate the relative loss of Cl, the atomic percentage of Cl at each temperature was divided by the atomic percentage of Cl of the non-annealed sample. The same process was used for Se.

In Figure S13, we examine Cl and Se concentration vs. annealing temperature for both single crystal and microcrystalline $Re_6Se_8Cl_2$ samples. We find a significant difference between single crystal and microcrystalline powder. Microcrystalline powder shows a decrease in Cl concentration at temperatures lower than that of the single crystal. We believe this is due to the dramatic difference in particle surface area and volume. In the main text (Figure 4D), we showed that surface Cl desorbs at lower temperatures than bulk Cl. In this context, the high surface area microcrystalline powder will show a larger decrease in Cl concentration at the surface desorption temperature (~400 °C), whereas single crystals only show significant Cl decrease at the bulk desorption temperature (~800 °C).

Single crystal X-ray diffraction

We measured the Re₆Se₈Cl₂ single crystal lattice parameters after treatment at various thermal annealing temperatures. Single crystal X-ray diffraction data was collected on an Agilent SuperNova diffractometer using mirror-monochromated Mo K α radiation. Each crystal was mounted under oil at room temperature using a MiTeGen MicroMount. Data collection and unit cell determination was performed in CrysAlisPro. We find no change in lattice parameters up to 1000 °C (Figure S14).

X-ray photoemission spectroscopy

Microcrystalline powder

A small amount (~10 mg) of pristine or thermally annealed microcrystalline powder was pressed into In foil and mounted onto a chuck. The sample was measured using a Phi 5500 XPS with Mg source. Regions collected were Re 4f, Se 3d, and Cl 2p. Background subtraction, peak fitting and integration were performed using the XPST (X-ray Photoelectron Spectroscopy Tools) package (v.1.3) in Igor Pro. For each sample, the total area of each element's characteristic set of peaks was summed. To estimate the relative loss of Cl, the total Cl peak area was divided by the total Re peak area at each temperature, and this ratio was normalized to the untreated sample. The same process was used for Se. We present a summary of the XPS measurement results for select thermal annealing temperatures in Figure S15.

Exfoliated flakes

In an attempt to better quantify the Cl loss after current annealing Re₆Se₈Cl₂ flakes, we performed μ -XPS on exfoliated Re₆Se₈Cl₂ flakes contacted on the top surface by metal electrodes embedded in hexagonal boron nitride (h-BN), called "window via contacts" (Figure S16A).^[48] This allows for the collection of μ -XPS spectra within a localized spatial region before (Figure S16C,E) and after current annealing the top surface (Figure S16D,F). μ -XPS measurements were performed using a Physical Electronics VersaProbe II XPS with Al source. The device was located using scatter X-ray imaging (SXI). An X-ray spot size of 15 μ m was focused over the sample. Regions collected were Re 4f, Se 3d, and Cl 2p. Background subtraction, peak fitting and integration were performed using the XPST package (v.1.3) in Igor Pro. To estimate the relative loss of Cl after current annealing, the total Cl peak area was divided by the total Re peak area and normalized to the untreated sample (Figure S16H). Overall, we were able to measure a significant decrease in Cl concentration and sample resistance (Figure S16G) after current annealing. The same μ -XPS procedure was used to collect μ -XPS spectra on flipped current annealed Re₆Se₈Cl₂ flakes.

Raman spectroscopy

Raman spectra were taken in a Renishaw inVia using a 532 nm wavelength laser. A laser power of $\sim 1 \text{ mW}$ was used. Spectra were accumulated for 3 minutes with a grating of 2400 gr mm⁻¹. A 100x objective was used, with a spot size of $\sim 1 - 2 \mu m$.

Thermal annealing mass spectrometry

To perform a real time analysis of desorbing elements, we developed a technique dubbed thermal annealing mass spectrometry (TA-MS). A ceramic boat was filled with 100 mg of Re₆Se₈Cl₂ microcrystalline powder and placed in a long fused silica tube (50 cm x 2 cm ID). The tube was placed into a tube furnace with the sample located in the center with N₂ gas flowing through the tube at a pressure of 5 psi. The outlet of the tube was connected to an APCI source on an Advion CMS mass spectrometer (Figure S17). Volatiles were ionized using APCI (negative mode), and data were collected in selected ion monitoring (SIM) mode. For Cl monitoring, the m/z's for the ions Cl⁻ and Cl₂ were recorded. For Se monitoring, the m/z's for the ions Se⁻, Se⁻₂, and Se⁻₃ were recorded. The furnace was heated to 800 °C at a rate of 20 °C min⁻¹ and then held at 800 °C for 30 minutes. For Se monitoring, the furnace was then further heated to 920 °C at a rate of 7 °C min⁻¹.

In Figure S18, we show an extended plot of Se⁻, Se⁻₂, and Se⁻₃ counts measured vs. temperature up to 920 °C. We see the onset of Se desorption at ~850 °C, which is consistent with our EDX results.

References

- (38) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, A. A. Firsov, *Science*. 2004, *306*, 666.
- (39) L. Wang, I. Meric, P. Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L. M. Campos, D. A. Muller, J. Guo, P. Kim, J. Hone, K. L. Shepard, C. R. Dean, *Science*. 2013, *342*, 614.
- (40) M. Asheghi, M. N. Touzelbaev, K. E. Goodson, Y. K. Leung, S. S. Wong, J. Heat Transfer. 1998, 120, 30.
- (41) A. V. Inyushkin, A. N. Taldenkov, A. M. Gibin, A. V. Gusev, H.-J. Pohl, *Phys. status solidi*. 2004, 1, 2995.
- (42) D. G. Cahill, S. K. Watson, R. O. Pohl, Phys. Rev. B. 1992, 46, 6131.
- (43) R. W. Powell, R. P. Tye, M. J. Woodman, Platin. Met. Rev. 1962, 6, 138.
- (44) H. M. Rosenberg, Philos. Trans. R. Soc. London. Ser. A, Math. Phys. Sci. 1955, 247, 441.
- (45) J. A. Malen, K. Baheti, T. Tong, Y. Zhao, J. A. Hudgings, A. Majumdar, *J. Heat Transfer*.
 2011, 133, 081601.
- W.-L. Ong, E. S. O'Brien, P. S. M. Dougherty, D. W. Paley, C. Fred Higgs III, A. J. H. McGaughey, J. A. Malen, X. Roy, *Nat. Mater.* 2017, 16, 83.
- (47) T. L. Bergman, A. S. Lavine, F. P. Incropera, D. P. DeWitt, *Fundamentals of heat and mass transfer*, Wiley, Hoboken, NJ, **2011**.
- (48) E. J. Telford, A. Benyamini, D. Rhodes, D. Wang, Y. Jung, A. Zangiabadi, K. Watanabe, T. Taniguchi, S. Jia, K. Barmak, A. N. Pasupathy, C. R. Dean, J. C. Hone, *Nano Lett.* 2018, 18, 1416.



Figure S1. Re₆Se₈Cl₂ device fabrication and analysis. Process flow for fabrication of prepatterned Re₆Se₈Cl₂ transport devices and analysis of the current annealed region.



Figure S2. Re₆Se₈Cl₂ current annealing procedure. A, Schematic of the current annealing procedure. Inset presents the current annealing geometries. Each number refers to a 2-terminal voltage bias configuration. B, Sample resistance vs. annealing current for a prepatterned Re₆Se₈Cl₂ device. Inset presents the annealing geometries. C, Sample resistance vs. annealing current for three bulk single crystal Re₆Se₈Cl₂ devices. Inset shows the annealing geometry. For (A) and (B), resistances were measured in the low bias regime.



Figure S3. Top down schematic of the simulation domain. Pd electrodes are beige and Re₆Se₈Cl₂ is transparent green to clarify the electrode positions. The distance between adjacent contacts is ~500nm, the width of the 6 middle voltage contacts is ~1 μ m, and the width of the 2 current contacts is ~4 μ m. The two sizes of heat spot are outlined in red. A, Setup A, representing the upper limit of heat spot size in the annealing process. B, Setup B, representing the lower limit of heat spot size in the current annealing process.



Figure S4. Temperature map of heat spot with setup A. 2 mW heat is input in (**A**) and (**B**), and 30 mW heat is input for (**C**) and (**D**). (**A**) and (**C**) are the top view for the temperature map where the heat source is outlined in thin black. (**B**) and (**D**) show the cross-sectional view of the temperature distribution at the heat source.



Figure S5. Temperature map of heat spot with setup B. 2 mW heat is input in (**A**) and (**B**), and 30 mW heat is input for (**C**) and (**D**). (**A**) and (**C**) are the top view for the temperature map where the heat source is outlined in thin black. (**B**) and (**D**) show the cross-sectional view of the temperature distribution at the heat source.



Figure S6. Superconductivity in various current annealed Re₆Se₈Cl₂ flakes. A-C, Resistance vs. temperature at various magnetic fields for 3 prepatterned Re₆Se₈Cl₂ devices. D-F, Differential resistance vs. DC bias in the superconducting state (black) and the normal state (red) for the same or similar devices as in (A), (B), and (C) respectively.



Figure S7. Statistics for all superconducting Re₆Se₈Cl₂ flakes. T_C^{Low} , H_{C20}^{Low} , and ζ_0^{Low} (filled black circles) and T_C^{High} , H_{C2-0}^{High} , and ζ_0^{High} (filled black diamonds) are shown. Corresponding mean values and standard deviations are given by a solid line and grey region respectively.



Figure S8. Angle dependence of the critical magnetic field in current annealed Re₆Se₈Cl₂. A, Resistance vs. temperature at zero magnetic field for a current annealed Re₆Se₈Cl₂ flake. B, 2D color plot of resistance vs. temperature and magnetic field perpendicular to the ab plane for the flake in (A). C, 2D color plot of resistance vs. temperature and magnetic field parallel to the ab plane for the flake in (A). D, E, and F, Corresponding measurements in (A), (B), and (C) for a second Re₆Se₈Cl₂ flake. In all plots, T_C^{Low} and T_C^{High} are denoted. For all panels, a temperature independent background resistance was subtracted.



Figure S9. Thermal activation of vortices in current annealed Re₆Se₈Cl₂. A,B, Resistance vs. inverse temperature on a log scale at various magnetic fields (left) and the extracted vortex activation energy vs. magnetic field on a log scale (right) for T_C^{Low} (A) and T_C^{High} (B) for the same device in Figure S8A. C,D, Resistance vs. inverse temperature on a log scale at various magnetic fields (left) and the extracted vortex activation energy vs. magnetic field on a log scale in Figure S8A. C,D, Resistance vs. inverse temperature on a log scale at various magnetic fields (left) and the extracted vortex activation energy vs. magnetic field on a log scale (right) for T_C^{Low} (C) and T_C^{High} (D) for the same device in Figure S8D.



Figure S10. Fitting critical current vs. temperature and magnetic field. A, Extracted I_C^{High} (black diamonds) and I_C^{Low} (black circles) vs. temperature for the device in Figure 2D. B, Extracted I_C^{High} (black diamonds) and I_C^{Low} (black circles) vs. magnetic field perpendicular to the cluster planes for the device in Figure 2D. The best fitting equations are shown with corresponding fit parameters.^[21]



Figure S11. Dependence of Re₆Se₈Cl₂ thickness on the superconducting transition. A,B Percentage change in resistance across the upper (A) and lower (B) superconducting transitions vs. Re₆Se₈Cl₂ flake thickness.



Figure S12. Superconducting properties of bulk single crystal annealed Re₆Se₈Cl₂. A,B, Resistance vs. temperature at various magnetic fields for two current annealed bulk Re₆Se₈Cl₂ devices. Resistance is normalized to the 9 K (A) and 3 K (B) values. C,D, Resistance vs. temperature for bulk Re₆Se₈Cl₂ thermally annealed at 900 °C (C) and 1000 °C (D). Resistance is normalized to the 4 K (C) and 10 K (D) values.



Figure S13. EDX vs. thermal annealing on microcrystalline and single crystal Re₆Se₈Cl₂. A,B, Se and Cl composition measured in EDX vs. annealing temperature for Re₆Se₈Cl₂ single crystals (A) and microcrystalline Re₆Se₈Cl₂ powders (B).



Figure S14. Single crystal X-ray diffraction vs. annealing temperature. *a*, *b*, and *c* lattice parameters are shown vs. annealing temperature. Estimated uncertainties are within the area of the points.



Figure S15. Re₆Se₈Cl₂ XPS spectra vs. thermal annealing temperature. Optical image with corresponding XPS spectrum for Re, Se, and Cl for non-annealed (A), annealed at 600 °C (B), annealed at 900 °C (C), and annealed at 1000 °C (D). In all XPS spectra, dashed black lines represent single Gaussian fits and solid black lines represent the total spectra fits. Optical images are taken parallel to the c axis. The scale bar in (A) is 200 μ m and applies to the optical images in (B), (C), and (D). In (D), the dashed red lines represent the Gaussian fits to Re metal signal.



Figure S16. XPS on window via devices. A, fabrication process of window via devices. B, Optical image of a typical window via device. Scale bar is 10 μ m. C,D, μ -XPS spectra of the Re binding energies before (C) and after (D) current annealing. E,F, μ -XPS spectra of the Cl binding energies before (E) and after (F) current annealing. G, Resistance vs. current annealing power. H, Cl μ -XPS peak area normalized by Re μ -XPS peak area before (black) and after (red) annealing for 5 window via devices (1-5) and two reference top contacted flakes (6,7).



Figure S17. Thermal annealing mass spectrometry setup. N₂ gas (gray) is flowed continuously through a quartz tube containing bulk Re₆Se₈Cl₂ crystals, gradually heated to a set temperature (blue, red). The output is flowed into a mass spectrometer (yellow).



Figure S18. Thermal annealing mass spectrometry on Re₆Se₈Cl₂: Se⁻, Se⁻₂, and Se⁻₃ counts vs. sample temperature, measured in the TA-MS setup.

Max Temperature Rise (K)	Heat Source A	Heat Source B
2 mW Heat Input	116.9	362.1
30 mW Heat Input	1089.3	4579.4

 Table S1. Maximum temperature rise due to current annealing.