

Appendix A: Supplementary Data

Pump Probe Measurements:

The optical pump-probe measurements were performed using a regeneratively amplified Ti-sapphire laser (Coherent Libra) and optical parametric oscillator, which produces signal and idler pulses of approximately 100 fs duration at wavelengths of 1400 nm and 1880 nm, respectively. The signal at 1440 nm was used to optically stimulate the graphene samples under study. The signal and idler were further mixed in an external AgGaS₂ crystal to produce mid-infrared pulses at 5500 nm, which were used to probe the hot-carrier response of the graphene. The spectral content of the pump and the probe signal is shown in Figure S1, as obtained from FTIR measurements.

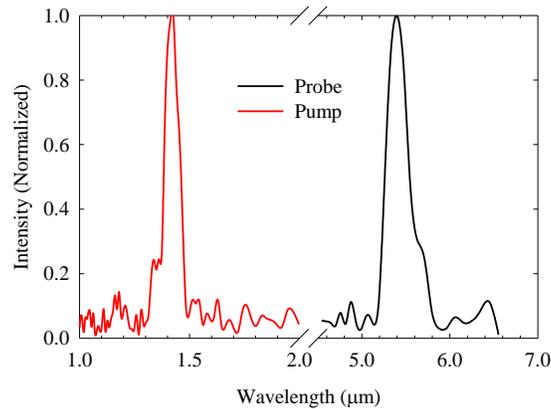


Figure S1: Measured spectrum of pump and probe beams, as measured with FTIR.

The pump and probe were co-polarized and co-focused onto the graphene samples under study, while the relative timing between them was adjusted using a delay stage. The table below outlines the experimental parameters of the 1 kHz co-polarized pump-probe measurements.

	Pump	Probe
Wavelength (μm)	1.4	5.5
Energy (meV)	885	225
Power (μW)	400	<10
Spot Size (μm)	100	40

Table S1: Parameters used for pump probe experiments.

Peak Electron Temperature

The evolution of electron temperature, T_e , in graphene can be described as:

$$\alpha T_e(t) \frac{dT(t)}{dt} + \beta_1 [T_e(t) - T_0] + \Sigma_2 [T_e(t)^3 - T_0^3] + \Sigma [T_e(t)^4 - T_0^4] = \eta I(t)$$

where $I(t)$ represents the intensity of the optical pump pulse, η is the fractional absorption in the graphene and the other parameters were introduced in the main manuscript.

Because the pump pulse is very short in duration compared to the relevant cooling timescales, the intensity $I(t)$ may be approximated as a delta function, $I(t) = F_0 \delta(t)$ with $F_0 = \frac{P_{pump}}{\pi w^2 R}$, where P_{pump} is the pump power and w is the width of optical beam at the focus.

Integrating the differential equation from $t = 0^-$ to $t = 0^+$, the initial electron temperature is found

to be:
$$T_{e,peak} = \left[T_0^2 + 2 \frac{\eta P_{pump}}{\alpha \pi w^2} \right]^{1/2} .$$

where the α is the heat capacity coefficient, $\alpha = \frac{C_e}{AT}$ and it is a function of the Fermi energy, as shown in the parameter summary table.

Heat Capacity coefficient	$\alpha = \frac{2\pi k_B^2 E_F}{3 \hbar^2 v_F^2}$	$\frac{J}{m^2 K^2}$
Ordinary-cooling coefficient	$\beta_1 = \frac{V_D^2 E_F^4 k_B}{2 \pi \rho \hbar^5 v_F^6}$	$\frac{W}{m^2 K}$
Super-cooling coefficient	$\Sigma_3 = \frac{\zeta(3) V_D^2 E_F k_B^3}{\pi^2 \rho \hbar^4 v_F^3 s^2 l}$	$\frac{W}{m^2 K^3}$
Fermi energy, carrier density	$n = \frac{E_F^2}{\pi \hbar^2 v_F^2}$	$J, \frac{1}{m^2}$
Fermi velocity	$v_F = 10^6$	m/s
Chemical Potential	$\mu_c = \sqrt{n_0 \pi \hbar^2 v_F^2}$	J
Areal Density	$\rho = 7.6 \times 10^{-7}$	$\frac{kg}{m^2}$
Acoustic velocity	$s = 2.1 \times 10^4$	$\frac{m}{s}$
Deformation potential	$V_D = 10$	eV
Carrier mobility	$\mu = e \frac{v_F}{\sqrt{\pi n} \Gamma \hbar}$	$\frac{m^2}{Vs}$

Table S2: Graphene parameters.

Optical properties:

A linearly polarized wave is normally incident on a two-dimensional conductive sheet, the transmission, reflection and absorption can be calculated using a simple transmission line model, where the incident and substrate regions are modeled with impedances $Z_1 = Z_0/\sqrt{\epsilon_1}$, and $Z_2 = Z_0/\sqrt{\epsilon_2}$. The frequency-dependent conductance of the graphene sheet is $\sigma(\omega)$. Using the notation $Z_{1(2)} = 1/Y_{1(2)}$, the reflection, transmission and absorption are found to be

$$r(\omega) = \left| \frac{Y_1 - Y_2 - \sigma(\omega)}{Y_1 + Y_2 + \sigma(\omega)} \right|^2 \quad (\text{Reflection})$$

$$\tau(\omega) = \frac{4Y_1Y_2}{|Y_1 + Y_2 + \sigma(\omega)|^2} \quad (\text{Transmission})$$

$$a(\omega) = 1 - r(\omega) - \tau(\omega) = \frac{4Y_1 \operatorname{Re}\{\sigma(\omega)\}}{|Y_1 + Y_2 + \sigma(\omega)|^2} \quad (\text{Absorption})$$

The conductivity can be separated in intra- and inter-band contributions,

$$\sigma(\omega) = \sigma_{intra}(\omega) + \sigma_{inter}(\omega)$$

$$\sigma_{intra}(\omega) = 2 i e^2 k_B T_e \frac{\ln \left[2 \operatorname{Cosh} \left(\frac{|\mu_c|}{2k_B T_e} \right) \right]}{\pi \hbar^2 (\omega + i \Gamma)},$$

$$\sigma_{inter}(\omega) = \frac{e^2}{4\hbar} \left[H(\hbar\omega - 2\mu_c) - \frac{i}{\pi} \ln \left(\frac{|\hbar\omega - 2\mu_c|}{|\hbar\omega + 2\mu_c|} \right) \right]$$

where, H is the step function that determines the cut-off edge of the interband absorption in graphene. The carrier scattering rate Γ also varies with the electron temperature [1] and it is described as:

$$\Gamma(T_e) = \Gamma_0 \left(1 + \frac{\pi^2 k_B^2 T_e^2}{6 E_F^2} \right) + \frac{E_F V_D^2 k_B T_e}{4 \hbar^3 v_F^2 \rho_S^2}.$$

Data Analysis:

The optical excitation pulse's temporal width is 150 fs and used to generate the non-equilibrium state in graphene. From the previous sections of this document, we have estimated the initial electron temperature of $\sim 10,000$ K. For the measurements taken at room temperature and the conditions of $T_{e-peak} \gg T_0$, the evolution of temperature in graphene, from peak to equilibrium, can be determined as follows:

$$\alpha T_e(t) \frac{dT_e(t)}{dt} + \beta_3 [T_e(t)^3 - T_0^3] = 0.$$

Here we assume that the cooling is dominated by the cubic term due to supercollisions.

The solution $T_e(t)$ is plotted in Figure S2 (the parameters used in the calculations are listed in the caption).

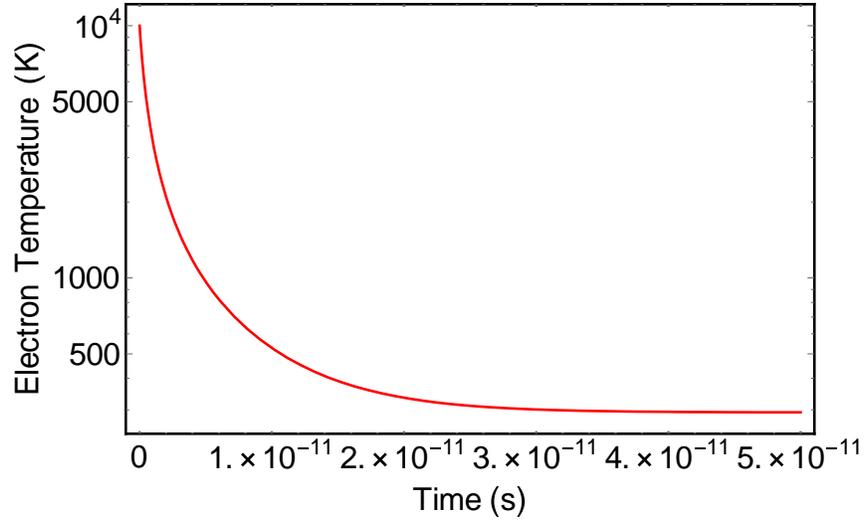


Figure S2: Time dependence of the electron temperature calculated from the model discussed in the text with parameters $\alpha = 2 \times 10^{-9} J/m^2 K^2$, $\beta_3 = 0.4 W/m^2 K^3$, $\mu = 100 cm^2/Vs$, $n_0 = 10 \times 10^{12} cm^{-2}$ and $T_{e,peak} = 10,000 K$.

The next task is to calculate the differential-transmission (i.e., fractional change in transmission) as a function of electron temperature, using the Kubo model of conductivity with the transmission line model of reflection and transmission. The fractional change in temperature caused by hot electrons is

$$\frac{\Delta\tau}{\tau} = \frac{\tau - \tau_0}{\tau_0}$$

where τ_0 represents the transmission in the absence of optical pumping and τ is the instantaneous transmission caused by hot carriers. For the same parameters listed above for the $T_e(t)$ calculations, the equivalent Fermi energy is estimated to be 368 meV. The fractional change $\Delta\tau/\tau$ as a function of electron temperature is shown below.

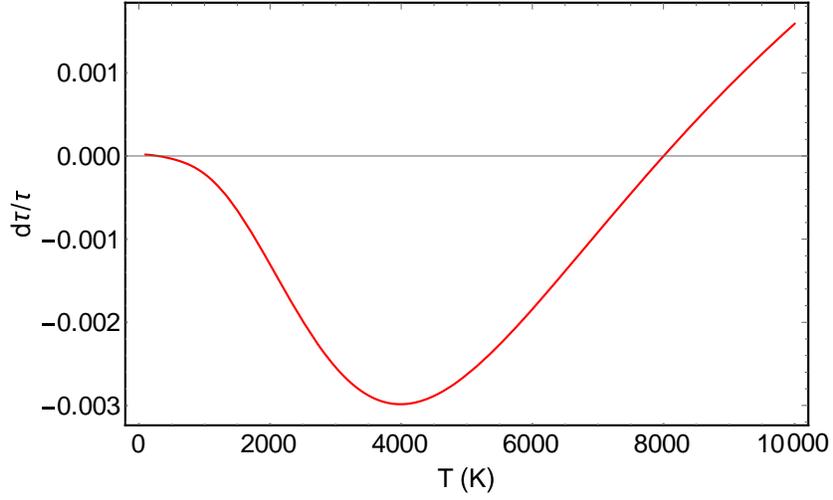


Figure S3: Temperature dependence of the differential transmission.

We note that at high carrier temperatures, the transmission increases. Then the electron temperature cools down to the 4000 K range, where the maximum change in negative differential transmission occurs. The minimum in the negative signal is determined by the carrier concentration and the mobility values.

Next, we insert the time-dependent electron temperature $T_e(t)$ into $\Delta\tau/\tau$ to obtain the time-resolved differential transmission values,

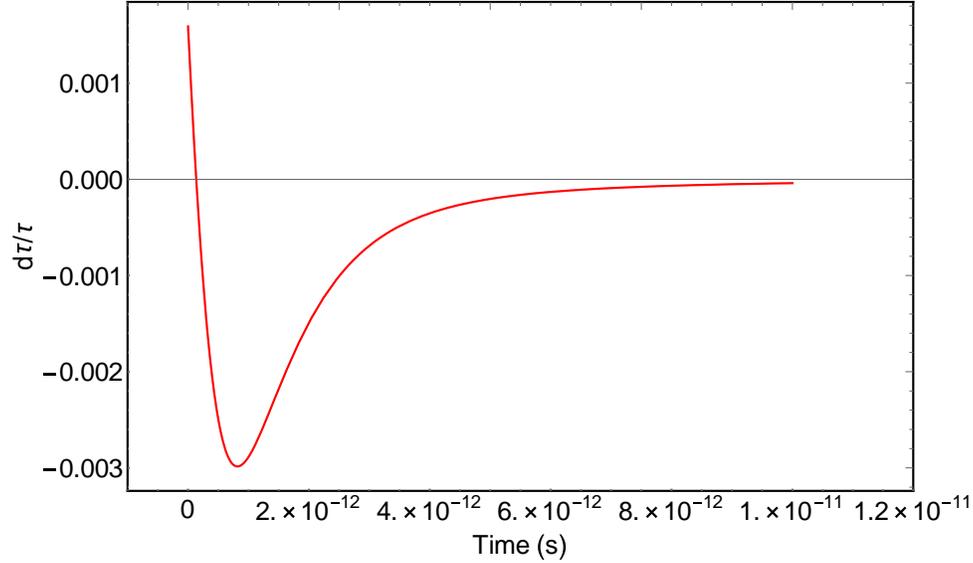


Figure S4. Time dependence of the differential transmission obtained by combining the data in Fig. S2 and S3.

At $t = 0$, the electrons begin at their peak temperature value, $T_{e,peak}$, where the differential transmission is positive. As the electrons cool, the differential transmission changes sign from positive to negative, reaching a minimum fractional change of -0.3% , before recovering to zero with a time-scale in the picosecond range.

Metal Deposition:

The samples S1, S2, S3, S4, S5, S5', and SA were all sputtered with palladium using argon-plasma magnetron sputtering at 60 W. To test the effects of different metal deposition methods, we fabricated additional samples with CVD-grown graphene transferred on Si substrates that were capped with 300 nm of SiO₂. Some graphene samples were coated with sputtered Pd, sputtered Au, or had Au deposited by thermal evaporation. In all cases, the metal was subsequently removed by aqua regia, using the same procedure that was used for the epitaxial graphene on SiC samples described in the manuscript. The Raman spectra for an uncoated (as-grown) graphene sample, a graphene sample with Au sputtered at 3 W then removed with aqua

regia, and a graphene sample with Au deposited by thermal evaporation then removed with aqua regia are shown below.

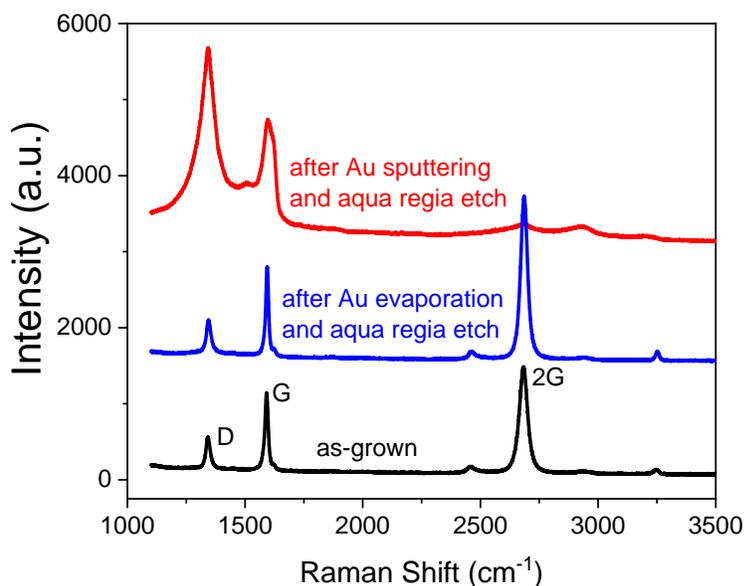


Figure S6: Raman spectra of CVD-grown graphene transferred on Si/SiO₂ substrate for an unprocessed sample (black), a sample coated with evaporated Au subsequently removed by aqua regia (blue) and a sample coated with sputtered Au subsequently removed with aqua regia (red). Both Au layers were 30-nm thick. The curves are shifted vertically for clarity.

From the Raman spectra, we see that sputtering has a much larger effect on the graphene than does thermal evaporation. Sputtering causes the D peak to increase greatly while the 2D peak is severely diminished. Evaporation and aqua regia cause much less change to the peaks.

- [1] Jadidi, M. M.; Konig-Otto, J. C.; Winnerl, S.; Sushkov, A. B.; Drew, H. D.; Murphy, T. E.; Mittendorff, M., Nonlinear Terahertz Absorption of Graphene Plasmons. *Nano Letters* 2016, 16 (4), 2734-2738.