# These authors contributed equally

Substrate Sensitive Mid-Infrared Photoresponse in Graphene - Supplementary Information -

Marcus Freitag[1#*], Tony Low[1#], Luis Martin-Moreno[2#], Wenjuan Zhu[1], Francisco Guinea[3] and Phaedon Avouris[1]
[1] *IBM T.J. Watson Research Center, Yorktown Heights, NY 10598, US*
[2] *Instituto de Ciencia de Materiales de Aragon and Departamento de Fisica de la Materia Condensada, CSIC-Universidad de Zaragoza, E-50009, Zaragoza, Spain*
[3] *Instituto de Ciencia de Materiales de Madrid. CSIC. Sor Juana Ines de la Cruz 3. 28049 Madrid, Spain*

* mfreitag@us.ibm.com

Supplementary Note 1: Calculating the RPA loss function

Here we describe the modeling of the loss function in graphene on SiO_2 as shown in the intensity plot of Fig. 3 in the main manuscript. We consider the interaction of the electronic degrees of freedom with graphene's internal optical phonon[1, 2] and that due to the surface polar phonon on SiO_2[3, 4]. The plasmon response of graphene begins with finding the dielectric function where a satisfactory approximation can be obtained by adding the separate contributions *independently*. An effective interaction between electrons is given by the sum of the direct Coulomb interaction $v_c(q) = e^2/2q\epsilon_0$ where q is the wave-vector. The two electrons interaction mediated by surface phonon and optical phonon are denoted by $v_{sp,\lambda}(q,\omega)$ and $v_{op}(q,\omega)$ respectively, where their explicit expressions are given elsewhere[5].

The RPA expansion of the dielectric function, $\epsilon_T^{rpa}(q,\omega)$, can be expressed with this effective interaction[6, 7]

$$v_{eff}(q,\omega) = \frac{v_c(q)}{\epsilon_T^{rpa}(q,\omega)} = \frac{v_c(q) + \sum_\lambda v_{sp,\lambda}}{1 - [v_c(q) + \sum_\lambda v_{sp,\lambda}]\Pi^0_{\rho,\rho}(q,\omega)} \tag{1}$$

where $\Pi^0_{\rho,\rho}(q,\omega)$ is the non-interacting part (i.e. the pair bubble diagram) of the charge-charge correlation function given by a modified Lindhard function[8, 9],

$$\Pi^0_{\rho,\rho}(q,\omega) = -\frac{g_s}{(2\pi)^2}\sum_{nn'}\int_{\mathrm{BZ}} d\mathbf{k}\frac{n_F(\xi_\mathbf{k}) - n_F(\xi_{\mathbf{k}+\mathbf{q}})}{\xi_\mathbf{k} - \xi_{\mathbf{k}+\mathbf{q}} + \hbar\omega}F_{nn'}(\mathbf{k},\mathbf{q}) \tag{2}$$

where $n_F(\xi_\mathbf{k})$ is the Fermi-Dirac distribution function, $F_{nn'}(\mathbf{k},\mathbf{q})$ is the band overlap function of Dirac spectrum, g_s is the spin degeneracy. While the polar surface phonons couple to the charge density operator, the intrinsic optical phonon couple instead to the current operator. Its contribution to the dielectric function is given by $v_{op}(q,\omega)\Pi^0_{j,j}(q,\omega)$, where $\Pi^0_{j,j}(q,\omega)$ is the current-current correlation function. We note that from the usual charge continuity equation, $i\partial_t\hat{\rho}_\mathbf{q} = \mathbf{q}\cdot\hat{\mathbf{j}}_\mathbf{q}$, it follows that,

$$q^2\Pi_{j,j}(q,\omega) = \omega^2\Pi_{\rho,\rho}(q,\omega) - v_F\left\langle\left[\mathbf{q}\cdot\hat{\mathbf{j}}_\mathbf{q}, \hat{\rho}_{-\mathbf{q}}\right]\right\rangle \tag{3}$$

where the second term in Eq. 3 is purely real and $\propto q^2$ as calculated in Ref. [10]. The imaginary part of $\Pi_{j,j}(q,\omega)$ can be obtained just from $\Im[\frac{\omega^2}{q^2}\times\Pi_{\rho,\rho}(q,\omega)]$. Collective modes with self consistent oscillations of the carrier charge can be obtained from the zeros of the full dielectric function

$$\epsilon_T^{rpa}(q,\omega) = \epsilon_{env} - v_c\Pi^0_{\rho,\rho}(q,\omega) - \epsilon_{env}\sum_\lambda v_{sp,\lambda}\Pi^0_{\rho,\rho}(q,\omega) - \epsilon_{env}v_{op}\Pi^0_{j,j}(q,\omega) \tag{4}$$

where ϵ_{env} is the dielectric constant of graphene's environment. Damping is included phenomenologically through the following modifications; $\Pi^0_{\rho,\rho}(q,\omega)\to\Pi^0_{\rho,\rho}(q,\omega+\tau_e^{-1})$, $v_{sp,\lambda}(q,\omega)\to v_{sp,\lambda}(q,\omega+\tau_{sp}^{-1})$ and $v_{op}(q,\omega)\to v_{op}(q,\omega+\tau_{op}^{-1})$, where τ_e^{-1}, τ_{sp}^{-1} and τ_{op}^{-1} describes the electron, surface optical phonon and internal optical phonon lifetimes respectively. In this work, τ_{sp} and τ_{op} are phenomenological constants to be fitted to the experiments, while τ_e is modeled rigorously, see below.

Here, we discuss model description of the electron lifetime τ_e. Including relevant scattering mechanisms in our experiments, τ_e is given by,

$$\tau_e(q,\omega) \approx \left[\tau_0^{-1} + \tau_{edge}(q)^{-1} + \tau_{ep}(\omega)^{-1}\right]^{-1} \tag{5}$$

where τ_0 describes a background damping due to scattering with impurities and $\tau_{edge}(q) \approx a/(W)^b$ is related to scattering off the ribbon edges. W is the ribbon's width, measured using AFM. $\tau_0 \approx 85\,\mathrm{fs}$ as measured from the Drude response of large area, unpatterned graphene. $a \approx 2\times10^6$, of the order of Fermi velocity and $b = 1$ as discussed in the main text. $\tau_{ep}(\omega)$ is electron lifetime due to scattering with optical phonons. It is related to the electron self-energy Σ_{ep} via $\tau_{ep} = \hbar/2\Im[\Sigma_{ep}]$. According to density functional calculations, the imaginary part of Σ_{ep} can be approximated by[11],

$$\Im[\Sigma_{ep}(\omega)] = \gamma_0\left|\hbar\omega + \hbar\omega_0 + E_f\right| \times \frac{1}{2}\left[\mathrm{erf}\left(\frac{\hbar\omega - \hbar\omega_{op}}{\Delta_{ph}}\right) + \mathrm{erf}\left(\frac{-\hbar\omega - \hbar\omega_{op}}{\Delta_{ph}}\right) + 2\right] \tag{6}$$

where γ_0 describes the effective e-ph coupling and Δ_{ph} accounts for various energy broadening effects such as the deviation from the Einstein phonon dispersion model. They are estimated to be $\gamma_0 \approx 0.018$ and $\Delta_{ph} \approx 50\,\mathrm{meV}$ from density function calculations[11].

Using the above theory, we plot the loss function in graphene on SiO_2 as shown in Fig. 3 of the main manuscript. The calculations include interactions with the intrinsic and SiO_2 substrate phonons. Graphene doping of $E_f = -0.43\,\mathrm{eV}$ and an effective $\epsilon_{env} = 1.5$ is chosen to fit the plasmon modes determined from the extinction spectra. We assume a typical $\tau_{sp} = 1\,\mathrm{ps}$ while a much smaller $\tau_{op} = 70\,\mathrm{fs}$ accounts for broadening effects due to finite phonon dispersion. Related to $v_{sp,\lambda}(q,\omega)$ and $v_{op}(q,\omega)$, we have the frequencies of the various phonon modes at $\omega_{op} = 1580\,\mathrm{cm}^{-1}$, $\omega_{sp0} = 460\,\mathrm{cm}^{-1}$, $\omega_{sp1} = 806\,\mathrm{cm}^{-1}$ and $\omega_{sp2} = 1168\,\mathrm{cm}^{-1}$. Their respective electron-phonon coupling parameters used are $g_0 = 7.7\,\mathrm{eV}\mathring{A}^{-1}$, $\mathcal{F}^2_{sp0} = 0.1\,\mathrm{meV}$, $\mathcal{F}^2_{sp1} = 0.2\,\mathrm{meV}$ and $\mathcal{F}^2_{sp2} = 2\,\mathrm{meV}$.

Dielectric	ϵ_0	ϵ_∞	ω_{TO1}	ω_{TO2}	ω_{TO3}	$\delta\epsilon_1$	$\delta\epsilon_2$	$\delta\epsilon_3$	γ_1	γ_2	γ_3	κ
SiO_2	3.9	2.3	451	752	1098	1.1	0.08	0.45	17.6	28	24	1.5
h-BN	7.03	4.95	767	1367	-	0.21	1.87	-	17.6	14.4	-	30
6h-SiC(0001)	9.54	6.4	760	-	-	3.14	-	-	16	-	-	360

TABLE I: Parameters for the dielectric function of common polar substrates used for graphene, i.e. SiO_2 [12], h-BN [13], 6h-SiC(0001) [14]. The dielectric function is parameterized as $\epsilon(\omega) = \epsilon_\infty + \sum_\alpha \delta\epsilon_\alpha \omega_{TO\alpha}^2 [\omega_{TO\alpha}^2 - (\omega + i\gamma_\alpha)^2]^{-1}$, where ϵ_∞ is the high frequency dielectric constant, and the low frequency dielectric constant $\epsilon_0 = \epsilon_\infty + \sum_\alpha \delta\epsilon_\alpha$. $\omega_{TO\alpha}$ are the bulk transverse optical phonons, $\delta\epsilon_\alpha$ are the oscillator strength and γ_α the damping constants of the phonon mode α. $\omega_{TO\alpha}$, $\delta\epsilon_\alpha$ and γ_α are expressed in units of cm^{-1}. Data for the γ_α in high-κ dielectrics are not tabulated. Order-of-magnitude estimate for γ is $\approx 10\,\mathrm{cm}^{-1}$. Heat conductivity κ in units of W/mK.

Supplementary Note 2: Substrates

Parameters used for the substrates in the calculations in Fig. 4 are summarized in Table. 1.

References

1. Ando, T. Anomaly of Optical Phonon in Monolayer Graphene. *J. Phys. Soc. Jpn.* **2006**, 75, 124701.
2. Ishikawa, K.; Ando, T. Optical Phonon Interacting with Electrons in Carbon Nanotubes. *J. Phys. Soc. Jpn.* **2006**, 75, 084713.
3. Fratini, S.; Guinea, F. Substrate-limited electron dynamics in graphene. *Phys. Rev. B* **2008**, 77, 195415.
4. Schiefele, J.; Sols, F.; Guinea, F. Temperature dependence of the conductivity of graphene on boron nitride. *Phys. Rev. B* **2012**, 85, 195420.
5. Yan, H.; Low, T.; Zhu, W.; Wu, Y.; Freitag, M.; Li, X.; Guinea, F.; Avouris, P.; Xia, F. Damping pathways of mid-infrared plasmons in graphene nanostructures. *Nature Photonics* **2012**, 7, 394-399.
6. Mahan, G. D. Many-particle physics, *Springer* **2000**
7. Hwang, E. H.; Sensarma, R.; Das Sarma, S. Plasmon-phonon coupling in graphene. *Phys. Rev. B* **2010**, 82, 195406.
8. Wunsch, B.; Stauber, T.; Sols, F.; Guinea, F. Dynamical polarization of graphene at finite doping. *New Journ. Phys.* **2006**, 8, 318.
9. Hwang, E. H.; Sarma, S. D. Dielectric function, screening, and plasmons in two-dimensional graphene. *Phys. Rev. B* **2007**, 75, 205418.
10. Sabio, J.; Nilsson, J.; Neto, A. H. C. *f*-sum rule and unconventional spectral weight transfer in graphene. *Phys. Rev. B* **2008**, 78, 075410.
11. Park, C. H.; Giustino, F.; Cohen, M. L.; Louie, S. G. Velocity Renormalization and Carrier Lifetime in Graphene from the Electron-Phonon Interaction. *Phys. Rev. Lett.* **2007**, 99, 086804.
12. Palik, E. D. Handbook of optical constants of solids II ; Boston: *Academic Press*, **1991**.
13. Geick, R.; Perry, C. H.; Rupprecht, G. Normal Modes in Hexagonal Boron Nitride. *Physical Review* **1966**, 146, 543-547.
14. Koch, R. J.; Seyller, T.; Schaefer, J. A. Strong phonon-plasmon coupled modes in the graphene/silicon carbide heterosystem. *Physical Review B* **2010**, 82, 201413.