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Doping dependence of the Raman peaks intensity of graphene close to the Dirac point

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Here we use pristine graphene samples in order to analyze how the Raman peaks intensity, measured at 2.41 and 1.96 eV excitation energy, changes with the amount of doping. The use of pristine graphene allows investigating the intensity dependence close to the Dirac point. We show that the *G* peak intensity is independent on the doping, while the *2D* peak intensity strongly decreases for increasing doping. Analyzing this dependence in the framework of a fully resonant process, we found that the total electron-phonon scattering rate is ~40 meV (60 ps^{-1}) at 2.41 eV.

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Graphene continues to attract interest because of its unique electronic properties,[1–3] which make it a potential material for future nanoelectronics.[4,5] Graphene layers can be readily identified by elastic and inelastic light scattering, such as Raman[6] and Rayleigh[7] spectroscopies. Raman spectroscopy is able to identify graphene and also to provide several information such as the amount of disorder,[8] doping,[9–11] and the atomic arrangements at the edges.[12,13] Beside these practical applications, Raman spectroscopy in graphitic systems is extremely interesting because it involves resonant conditions,[14,15] defect-induced processes[14] and Kohn Anomalies (KA), which strongly affects the Γ-E_{2g} and K-A_1' modes.[16]

All carbons show common features in their Raman spectra in the 800–2000 cm^{-1} region, the so-called *G* and *D* peaks, which lie at around 1580 and 1360 cm^{-1}, respectively.[17] The *D* peak is due to the breathing modes of sp^2 rings and requires a defect for its activation.[18] It comes from TO phonons around the *K* point of the Brillouin zone.[17] The *G* peak corresponds to the E_{2g} phonon at the Brillouin zone center.[17] The Raman spectra of graphite and graphene also show second-order scattering.[6] The *D* peak and its second-order peak *2D* (also called *G*′) are activated by resonance processes.[14,15]

Raman spectroscopy can easily monitor doping in graphene, as reported in Refs. 10, 11, and 19. Here, the electron or hole concentration was directly controlled by applying a gate voltage, in top or back-gate configuration, which produces a shift of the Fermi energy (E_F) from the Dirac point. The Raman spectrum shows the following variations with doping:

(i) The *G* peak position increases for increasing $|E_F|$ and saturates for high doping.[10,11,19] This is due to the nonadiabatic removal of the Kohn anomaly at Γ.[20]

(ii) The *G* peak full width at half maximum decreases for increasing $|E_F|$ and saturates when the electron-hole gap becomes higher than the phonon energy.[11,20] This is due to the blockage of the phonon decay into electron-hole pairs due to the Pauli exclusion principle.[20]

(iii) The *2D* peak position increases for *p* doping, while it decreases for *n* doping, for increasing $|E_F|$.[10] The *2D* and *G* peaks show a different doping dependence because the nonadiabatic effects are expected to be negligible on the *2D* phonons, when measuring with visible energy.[10]

(iv) The ratio between the peaks intensity, I(2D)/I(G), decreases for increasing $|E_F|$.[10] In the framework of the fully Raman resonant process for the second-order *2D* peak, the intensity dependence on the doping is due to the electron-electron scattering contribution, which increases for increasing charge concentration.[22]

The same variations have been observed in the Raman spectrum of several pristine graphene samples, deposited on Si/SiO$_x$ substrate and they have been attributed to doping by charged impurities.[9] Pristine graphene samples can have charge concentration up to 10^{-13} cm^{-2}, and they are usually *p* doped.[8,9] Unintentional doping in graphene deposited on Si/SiO$_x$ was first observed in gating experiments: the *G* peak position obtained at $E_F=0$ did not correspond to the *G* peak position of an undoped graphene (~1580 cm^{-1}, see Fig. 4 in Ref. 19). Thus, it is not possible to reach the Dirac point by gating due to local charge density variations.[19] Transport measurements are strongly affected by the charge inhomogeneity, in particular close to the Dirac point.[23] Recent works[24–26] have finally confirmed the presence of charged impurities in graphene. In particular, Raman and transport measurements performed on suspended graphene have shown that by eliminating the substrate it is possible to produce graphene samples, which are essentially undoped, have little disorder and the highest mobility.[24,27]

Here we analyze the absolute intensity of the *G* and *2D* peak, I(G) and I(2D), respectively, of several pristine graphene samples with different amount of doping. The use of pristine graphene samples presents the following advantages: (i) low doping level can be investigated, in contrast to gated graphene; (ii) graphene is not in a device configuration, so contacts and lithography processes do not affect the properties of graphene;[9,23] (iii) the sample is stable and it cannot be damaged by electrostatic charge or high voltage. This is particular important when measuring the absolute Raman intensity, since these measurements can be drastically altered as a result of surface conditions and strongly depend on the experimental setup.[28] We will show that I(G) is insensitive to the doping, in contrast to I(2D), which strongly depends on the Fermi energy, as expected in the framework of the fully resonant activation process for the *2D* peak.[15]

We study several graphene samples, produced by micromechanical cleavage of bulk graphite and deposited on Si/SiO$_x$. Only single layers flakes that completely fills the laser focus (~1 μm^2) were selected in order to avoid the

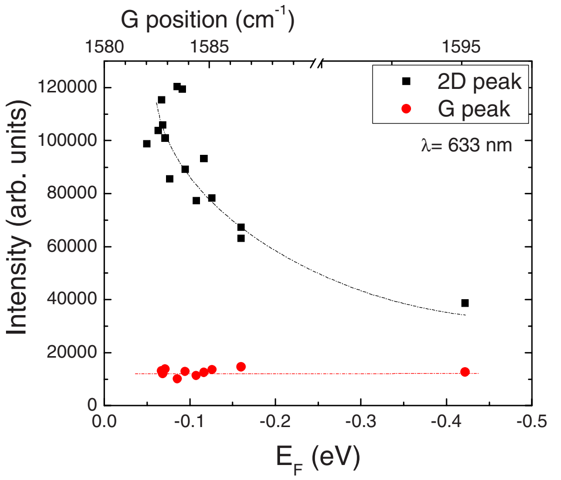

FIG. 1. (Color online) *G* and *2D* peak intensity as a function of the Fermi energy and *G* peak position, measured at 633 nm. The dotted lines are a guide for the eyes.

graphene edges, since they can strongly affect the peaks intensity.[12] Unpolarized Raman spectra are measured at 633 and 514.5 nm by using a Renishaw micro-Raman 1000 spectrometer. The Raman spectra are collected with a 100X objective and the spectral resolution is ~3 cm^{-1}. The power on the samples is always kept well below 2 mW in order to avoid damage.[6] The spectra have been fitted by using a Lorentzian spectral shape for both *G* and *2D* peaks and the intensity is calculated as integrated area. The Raman spectra of the samples do not show any *D* peak, indicating a high crystallinity. In the case of pristine graphene samples, the amount of doping is not directly accessible through a gate voltage. Thus, we used the dependence of the *G* peak position on the doping in order to derive the Fermi energy for every sample. We used the relations between *G* peak positions and E_F calculated for an ideal graphene at 300 K in Ref. 20.

Figure 1 correlates I(G) and I(2D) with E_F. This figure clearly shows that I(G) is insensitive to changes in E_F, in agreement with the predictions in Ref. 21. In contrast, I(2D) strongly decreases for increasing doping. This is in agreement with the Raman theory, under the assumption of a fully resonant process and for $E_F \ll 1$ eV.[22] Assuming two main scattering mechanisms, i.e., the emission of phonons (γ_{ep}) and the electron-electron collision (γ_{ee}), I(2D) can be written as[22]

$$I(2D) = C(\gamma_K/\gamma)^2, \tag{1}$$

where C is a constant and 2γ is the total scattering rate, so $\gamma = \gamma_{ep} + \gamma_{ee}$ and $\gamma_{ep} = \gamma_K + \gamma_\Gamma$. Note that the scattering rate γ_K and γ_Γ depends on the incident energy.[22]

It has been shown that only γ_{ee} depends on E_F, so Eq. (1) can be written as

$$\sqrt{1/I(2D)} = \frac{1}{\gamma_K\sqrt{C}}(\gamma_{ep} + f(\varepsilon)|E_F|), \tag{2}$$

where f is a function which depends on the dielectric environment.[22] In our case, the dielectric constant ε for SiO$_x$ is 4.5, so $f \simeq 0.07$.[22] Thus, Eq. (2) shows that I(2D) decreases for increasing E_F, as observed in Fig. 1.

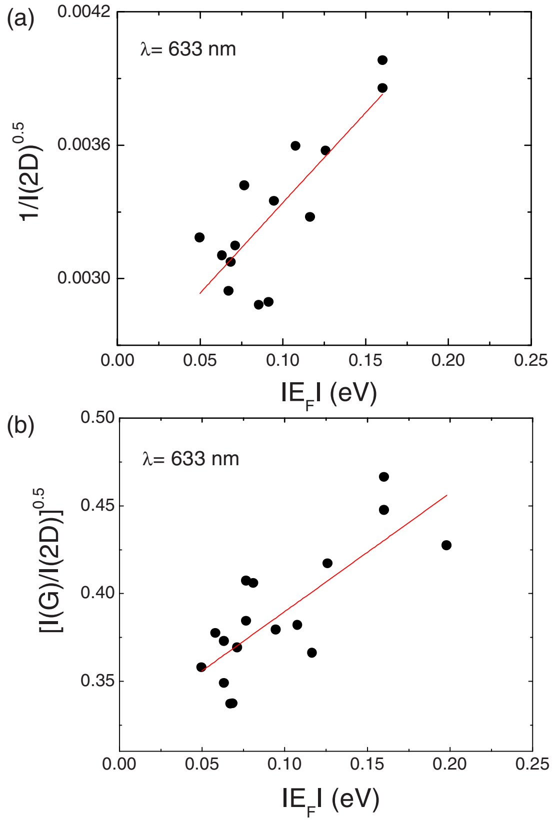

FIG. 2. (Color online) Fit of the experimental dependence: (a) $1/\sqrt{I(2D)}$ and (b) $1/\sqrt{I(G)/I(2D)}$ as a function of the Fermi energy, measured at 633 nm.

Equation (2) can be used to derive the electron-phonon scattering rate by measuring the variation of the absolute intensity of the *2D* peak with doping. However, this requires to compare the absolute Raman intensity, i.e., to measure all the spectra under exactly the same experimental conditions. This is not always possible, in particular, during gating experiments. Since I(G) is insensitive to the doping (Fig. 1), I(G)/I(2D) can be used in order to derive γ_{ep}:

$$\sqrt{I(G)/I(2D)} = C'(\gamma_{ep} + 0.07|E_F|), \tag{3}$$

where C' is another constant. Equation (3) has been used to find γ_{ep} of gated graphene.[22] There, values ranging from 18 to 65 meV, with an average of ~33 meV, have been reported, depending on the data set.[22] In particular, for a hole-doped graphene a good consistency between different data has been found, resulting in $\gamma_{ep} \sim 20$ meV at 514.5 nm.[22] Here we use Eqs. (2) and (3) in order to find γ_{ep} using pristine graphene samples. The present data, even though collected from many samples, are much less scattered than the data obtained by gating experiments, in particular close to the Dirac point, where Eqs. (2) and (3) are well valid. Thus, our data enable determining γ_{ep} with a significantly smaller uncertainty.

Figure 2(a) shows the linear fit of the experimental dependence $\sqrt{1/I(2D)}$ on the doping [Eq. (2)], measured at 633 nm. We found: $\gamma_{ep} = 22$ meV. The linear fit of the experi-

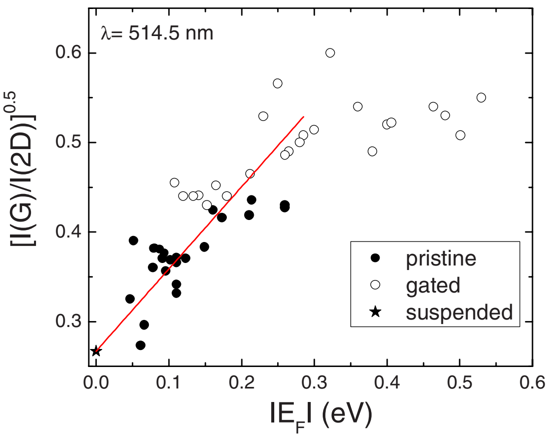

FIG. 3. (Color online) Fit of the experimental dependence $1/\sqrt{I(G)/I(2D)}$ as a function of the Fermi energy for pristine graphene, measured at 514.5 nm. The data for suspended graphene (Ref. 24) and the back-gated graphene (Ref. 22) have been included in the figure.

mental dependence $\sqrt{I(G)/I(2D)}$ on the doping [Eq. (3)], measured at 633 nm, is shown in Fig. 2(b) and gives γ_{ep} $=33$ meV and $C' \sim 10$ eV^{-1}. Thus, for an intrinsic graphene, i.e., for $E_F=0$, the fit in Fig. 2(b) gives I(2D)/I(G) ~10. Note that in general the intensity ratio between the Raman peaks depends also on the spectrometer sensitivity, as shown in Ref. 28. However, γ_{ep} only depends on the relative variation of the intensity ratio with the Fermi energy and not on its absolute value. Every dependence on the experimental setup is included in C'.

Figure 3 shows the linear fit of the experimental dependence $\sqrt{I(G)/I(2D)}$ on the doping [Eq. (3)], measured at 514.5 nm. Here, we included the data obtained for suspended graphene, by constraining the fit and we obtained γ_{ep} $=21$ meV. Furthermore, we included in Fig. 3 the data obtained for graphene in back-gate configuration for $|E_F|$ >0.1 eV, as taken from ref. 22. Figure 3 clearly shows that Eq. (3) is valid up to $E_F=0.3-0.4$ eV, as expected, since Eqs. (2) and (3) are valid only for $E_F \ll 1$ eV.

In conclusion, we have shown that the G peak intensity is independent on the doping, while the *2D* peak intensity is strongly sensitive to the dynamics of the photoexcited electron-hole pairs. By measuring the dependence of I(2D) on the Fermi energy close to the Dirac point, we have found that the total electron-phonon scattering rate ($2\gamma_{ep}$) of graphene is ~40 meV at 2.41 eV, in good agreement with the hole-doping side of the top and back-gated graphene experiments.[22]

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