Probing the electron-phonon coupling in ozone-doped graphene by Raman spectroscopy

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We have investigated the effects of ozone treatment on graphene by Raman scattering. Sequential ozone short-exposure cycles resulted in increasing the p doping levels as inferred from the blue shift of the 2D and G peak frequencies, without introducing significant disorder. The two-phonon 2D and 2D' Raman peak intensities show a significant decrease, while, on the contrary, the one-phonon G Raman peak intensity remains constant for the whole exposure process. The former reflects the dynamics of the photoexcited electrons (holes) and, specifically, the increase of the electron-electron scattering rate with doping. From the ratio of 2D to 2D' intensities, which remains constant with doping, we could extract the ratio of electron-phonon coupling parameters. This ratio is found independent on the number of layers up to ten layers. Moreover, the rate of decrease of 2D and 2D' intensities with doping was found to slowdown inversely proportional to the number of graphene layers, revealing the increase of the electron-electron collision probability.

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I. INTRODUCTION

Graphene linear carrier dispersion in the vicinity of two inequivalent points (K, K') of the Brillouin zone creates the conditions for the occurrence of unusual effects on the dynamics of both electrons (holes) and phonons, which are related to the electron-phonon (e-ph) interaction.

In graphene, doping can be tuned by means of the field effect, i.e., electric charge induced by capacitive coupling. Moreover, being a system entirely exposed to its environment, modification of the carrier concentration in graphene can follow from molecules adsorbed on the surface by charge transfer. The control of the carrier concentration allows the study of electron-phonon coupling (EPC) effects since the e-ph interaction is directly modified by changing the Fermi energy level. Raman scattering measurements in field-effect devices showed the dependence of the G peak position and linewidth with doping, where G is the one-phonon mode at the Γ point, unveiling tunable optical phonon anomalies. The possibility to monitor doping-oriented studies in graphene by Raman spectroscopy has provided the basis for a large range of application.

Besides the effects of doping on the frequency and linewidth of the Raman G peak, the intensity of the 2D two-phonon signature, or the ratio of peak intensities $I(2D)/I(G)$, was found to decrease with increasing doping and used as a tool to qualitatively establish the presence of charged impurities. More recently, an understanding of how the two-phonon Raman peaks intensity depends on doping has been provided based on fully resonant processes and their dependence on the e-ph and electron-electron (e-e) collision rates established. In Refs. 19 and 20, the e-ph scattering rate was not entirely obtained from experiments as the analysis of the 2D peak intensity requires the calculation of the e-e scattering rate.

Ozone treatment is considered as a promising route to enhance the otherwise weak chemical reactivity of graphitic structures. The conductivity of carbon nanotubes (CNTs) was found to increase at low ozone dose or exposure time. The proposed mechanism for this increase was the ozone adsorption on the CNT surface, which induces charge transfer effects. At high ozone dose (or exposure time), the generation of structural modifications and defects seems to be the cause of a reduced conductivity. In this paper we investigate the effects of sequential ozone treatment cycles on graphene flakes by analyzing the Raman spectrum. Our studies show that graphene displays similar changes with ozone as those reported in CNTs, i.e., p-type doping without introducing significant disorder at low exposure, and different degrees of bond disruption and surface etching at high exposure. Here, we restrict our study to low exposure conditions and a full account on graphene oxidation by ozone will be published elsewhere. Raman spectroscopy tracks the process of gradual p doping of the samples, as concluded from both the position and the intensity of the Raman peaks. From the latter we could determine the EPC for the phonon modes near the K point, and to monitor the e-e scattering contribution with increasing charge concentration as well as with the number of graphene layers. We found a good correlation between the rate of the intensity decrease upon doping and the number of graphene layers.

II. SAMPLES AND EXPERIMENTAL METHOD

Graphene sheets, prepared by micromechanical cleavage of highly-ordered pyrolytic graphite (HOPG), were deposited on Si wafers with 300 nm thick thermal silicon
oxide. Ozone treatment of the samples was performed at room temperature with a Novascan UV-Ozone cleaning system. The morphology of the graphene sheets was studied using a Nanoscope AFM in tapping mode. Micro-Raman measurements were carried out at room temperature in backscattering geometry using a T64000 Jobin-Yvon spectrometer with a cooled charge-coupled-device detector. In micro-Raman measurements the light was focused to a spot with diameter of about 1 μm through a 100x objective. The 514.5 nm emission line of an Ar laser was used for excitation with a typical power of only 120 μW, in order to prevent structural damage of the graphene surface by the laser irradiation. Raman peak lineshape and visible light absorption were used to determine the number of layers. Graphene samples were placed on the ozone cleaner for cycles of fixed duration. After each exposure, samples were analyzed morphologically by AFM and by Raman spectroscopy. The exposure time of 2.5 min during each cycle ensures the graphene surface quality is preserved. In Fig. 1 AFM images taken from the same sample region before and after five exposure cycles [Fig. 1(loop 0) and (loop 5), respectively] reveal smooth surfaces. Here, loop 0 refers to no exposure to ozone while loop 5, respectively, involves two-phonon processes with opposite wavevectors, which do not require the presence of defects for their activation. The strongest and featureless 2D peak in monolayer graphene evolves to a structured lineshape as the number of layers increases, revealing the electronic band structure, which, in turn, depends on the number of stacked layers.

III. RESULTS AND DISCUSSION

The Raman spectrum of graphitic structures shows common features, i.e., the main one-phonon G peak [cf. Fig. 2(a)], and defect-assisted one-phonon D and D' peaks, the expected frequencies of which are indicated by arrows in Fig. 2(a). The G and D' peaks correspond to phonons at and near the Brillouin Γ point (Eg mode), respectively. The D peak comes from phonons near the K points (A1 mode). Both D and D' peaks, which are evidence of inter- and intra-valley double resonance processes, respectively, require defect scattering for their activation. Thus, these peaks are only detected when carbon planes present structural imperfections. Notice the undetectable presence of the latter modes in the spectrum of the pristine sample [cf. Fig. 2(a)(loop 0)] indicating high structural order.

The peaks denoted as 2D and 2D' in and D' peaks, respectively, involving two-phonon processes with opposite wavevectors, which do not require the presence of defects for their activation. The strongest and featureless 2D peak in monolayer graphene evolves to a structured lineshape as the number of layers increases, revealing the electronic band structure, which, in turn, depends on the number of stacked layers.

A. Second-order Raman peaks intensity

With increasing ozone exposure, the two-phonon 2D and 2D' Raman peak intensities show a significant decrease [see Fig. 2(b) and inset to Fig. 2(b)] while, in contrast, the one-phonon G Raman peak intensity remains unchanged with ozone doping.

The activation of 2D and 2D' peaks involves four-step processes where all the states are real, and require energy and momentum conservation at every elementary step, which means that both two-phonon Raman processes are fully resonant. As a consequence, two-phonon Raman spectroscopy is sensitive to the dynamics of the photoexcited electron-hole (e-h) pairs, i.e., other than e-ph inelastic-scattering processes they can undergo, for example, e-e collisions. Assuming that these two processes are the main scattering mechanisms, the integrated intensities over the full linewidth of the 2D and 2D' Raman peaks, which represent the probabilities of the respective Raman processes, can be expressed as:

\[
A(2D) = C(\gamma_K / \gamma)^2 \tag{1a}
\]

\[
A(2D') = C'(\gamma_{K'} / \gamma)^2, \tag{1b}
\]

where C and C' are constants and 2γ denotes the inelastic scattering rate of the photoexcited e-h pair written as:

\[
\gamma = \gamma_{e-ph} + \gamma_{e-e}, \tag{2}
\]

and the phonon emission rate γ_{e-ph} includes phonons near Γ and K,

\[
\gamma_{e-ph} = \gamma_{\Gamma} + \gamma_{K}. \tag{3}
\]

Since the e-e scattering is dependent on carrier density, both 2D and 2D' intensities are sensitive to doping level. The e-e scattering rate, 2γ_{e-e}, was found to be proportional to the Fermi energy, E_F, and up to first order in E_F it is expressed as:

\[
\gamma_{e-e} = |E_F| f, \tag{4}
\]

where the proportionality coefficient f depends on the Coulomb coupling constant. The intensity of the G peak
peak intensity, could be attributed to a change of the peak intensity variation shown in Fig. 2, i.e., decrease frequency with doping, and therefore effects arising from alone does not explain the behavior of the Raman peaks frequency. It has been shown that in graphene this effect (stiffening/softening), reflected in the variation of the phonon chemical-bond induces variations of bond lengths (stiffening/softening), therefore the changes in frequency of the Raman spectrum features, indicating that the charge concentration, i.e., the ozone adsorption, reached a constant value.

B. Frequency shift of Raman bands

The above interpretation is reinforced by monitoring the changes in frequency of the Raman spectrum feature after each ozone cycle, given the extensively reported dependence of the Raman modes frequency on doping in graphene. Charge-transfer modification of the chemical-bond induces variations of bond lengths (stiffening/softening), reflected in the variation of the phonon frequency. It has been shown that in graphene this effect alone does not explain the behavior of the Raman peaks frequency with doping, and therefore effects arising from the suppression of the Kohn anomaly at $\Gamma$ and K points must be invoked. Anomalous phonon softening, which is seen at low temperature but is smeared at 300 K, reflects a resonant $e$-$ph$ coupling effect when the $e$-$h$ energy gap is smaller than the phonon energy. Moreover, when the $e$-$h$ energy gap reaches a value higher than the phonon energy a sharp linewidth reduction occurs as the phonon decay process into $e$-$h$ pairs suddenly ceases.

The 2D peak shows a different dependence on doping, which helps discerning between n- and p-type doping. For electron doping, the 2D peak frequency does not change much until a high electron concentration is reached, showing a softening for further increase. For hole doping, the frequency of the 2D peak increases at a rate higher than solely expected from variations of lattice spacing. Although phonon modes contributing to 2D peak are away from K points, the effects of the Kohn anomaly are not negligible due to the strong $e$-$ph$ coupling. As the doping level increases, the Kohn anomaly close to K points is smeared out contributing to the stiffening of the 2D peak. In contrast, the influence of the Kohn anomaly at $\Gamma$ becomes weaker as the phonon wavevector departs from this point. Therefore, the 2D' peak frequency is expected to be almost insensitive to changes in doping level.

Finally, charge concentration changes are not the only possible source of phonon spectrum variation. Strain effects have already been measured in the Raman spectrum of graphene. The splitting of the G band into two components displays a shift with applied uniaxial strain at a rate of 11 and 32 cm$^{-1}$/%. The 2D and 2D' bands do not split and they show a shift amounting to 64 and 35 cm$^{-1}$/%, respectively.

Figure 3 displays the Raman G and 2D peak frequencies showing a blue shift with increasing exposure to ozone. The Raman 2D' peak position, on the contrary, displays no variation within the experimental resolution (see inset to Fig. 3). The larger frequency variation of the G peak compared to the 2D peak, together with a constant 2D' peak frequency, rules out the effect of strain. Therefore, we conclude that the graphene surface increases its p doping level with each ozone exposure cycle. The present method to change the amount of doping does not require additional processing to fabricate contacts, which can affect the crystal quality and the homogeneity of the properties of the graphene flakes. Comparing the measured phonons frequency shift in the present study with those found in the literature, we obtain the overall change of the carrier concentration to be $\Delta n_{tot} \approx 5 \cdot 10^{12}$ cm$^{-2}$. The Raman spectrum after four ozone exposure cycles (not displayed) shows no further changes, neither in the two-phonon peak intensities nor in the peak position of the G and 2D features, indicating that the charge concentration, i.e., the ozone adsorption, reached a constant value.
of the Raman 2D vs G peak obtained after each ozone exposure cycle. The inset shows the evolution of the Raman 2D' vs G peak frequency.

C. Electron-phonon coupling parameters ratio

Figure 4 (solid circles) shows the integrated intensity of the 2D peak, \( A(2D) \) as a function of the integrated intensity of the 2D' peak, \( A(2D') \), both normalized to the integrated intensity of the G peak, \( A(G) \), calculated from spectra of Fig. 2. This dependence, besides showing the common decrease of the intensity values, as expected from Fig. 2, unveils a constant \( A(2D)/A(2D') \) ratio, as they closely follow a straight line. The decrease in intensity is a direct consequence of the increase of \( \gamma_{\text{ph}} \) with doping [cf. Eqs. (1a) and (1b)]. On the contrary, the constant \( A(2D)/A(2D') \) ratio indicates a weaker dependence of \( \gamma_{\text{ph}} \) on doping. This point becomes clear taking the ratio of Eqs. (1a) and (1b), which is found to be proportional to the square of the emission rates ratio of \( E_g \) and \( A_1 \) phonons,

\[
A(2D)/A(2D') = 2(\gamma_K/\gamma_{\Gamma})^2. \tag{5}
\]

The linear fit to the single-layer data in Fig. 4 gives a value of the slope of 26±3% and, from Eq. (5), we then obtain the ratio of phonon emission rates, \( \gamma_K/\gamma_{\Gamma} = 3.6 \). This ratio is related to the adimensional EPC parameters \( \lambda_{\Gamma} \) and \( \lambda_K \), as defined in Ref. 18, according to

\[
\frac{\gamma_K}{\gamma_{\Gamma}} = \frac{\omega_{\text{out},K}}{\omega_{\text{out},\Gamma}} \frac{\lambda_K}{\lambda_{\Gamma}}, \tag{6}
\]

where \( \omega_{\text{out},\Gamma} \) and \( \omega_{\text{out},K} \) are the frequencies of the emitted photons in the respective Raman processes involving phonons at \( \Gamma \) and \( K \) point. In order to compare with available calculated and experimental values, we relate the EPCs parameters to the square of the \( c\text{-}ph \) interaction matrix elements averaged on the Fermi surface, \( \langle D_{2\Gamma}^2 \rangle_F \) and \( \langle D_{2K}^2 \rangle_F \), as follows\textsuperscript{18,34}

\[
\frac{\lambda_K}{\lambda_{\Gamma}} = \frac{\omega_{\Gamma}}{\omega_{K}} \frac{\langle D_{2K}^2 \rangle_F}{2\langle D_{2\Gamma}^2 \rangle_F}. \tag{7}
\]

Finally, concerning the doping dependence of EPC parameters in graphene, it has been calculated that \( \langle D_{2K}^2 \rangle_F \) reduces by \( \approx 16\% \) for a variation of \( \Delta p = 1.9 \cdot 10^{13} \text{ cm}^{-2} \), while \( \langle D_{2\Gamma}^2 \rangle_F \) remains unaffected\textsuperscript{39}. Taking into account that our estimated \( \Delta p_{\text{tot}} \) is about four times smaller, the expected decrease of \( \langle D_{2K}^2 \rangle_F \) stays within the experimental error.
D. Electron-electron coupling and number of graphene layers

In Fig. 4 we included data of Raman measurements from bilayer and ten-layer graphene deposited on the same SiO$_2$/Si wafer as the monolayer sample, solid squares and triangles, respectively. The experimental Raman intensities show a good correlation with the monolayer data, as they closely follow the linear relation with slope value of 26 (thick line in Fig. 4). A significant feature is the decrease of the intensity rate change, given by the difference between intensities in successive treatment loops, which is seen as a higher concentration of data points in Fig. 4, when comparing single-layer (SL), bilayer (BL) and ten-layer (TL) samples. The dot-dashed line arrows in Fig. 4 are plotted to illustrate the data contraction with increasing number of layers, which is found to be related by the ratio $\Delta A(2D)_{\text{SL}} \approx 2 \Delta A(2D)_{\text{BL}} \approx 10 \Delta A(2D)_{\text{TL}}$, within an error of approximately 10%. Since, as discussed previously, the decrease of $A(2D)$ and $A(2D')$, that follows ozone treatment, is related to the increase of hole concentration, the result of Fig. 4 suggests that the rate of decrease of the intensity, $\Delta A(2D) \cdot \Delta A(2D')$, with doping becomes smaller by a factor inversely proportional to the number of graphene layers.

In order to understand the relation $\Delta A(2D) \propto N^{-1}$ [$\Delta A(2D') \propto N^{-1}$], we first recall that a Bernal stack with $N$ layers, $N$ even [$N$ odd], has $N/2 [(N+1)/2]$ electron-like and $N/2 [(N+1)/2]$ hole-like subbands almost touching at the $K$ point, with a band overlap smaller than 41 meV. Additional $N/2 [(N+1)/2]$ electron-like and $N/2 [(N-1)/2]$ hole-like outer subbands appear with decreasing energy separation with layer number, reaching a maximum value of 0.4 eV in bilayer graphene. The outermost subband is found in the range from 0.4 eV in bilayer to $\approx 0.8$ eV for 20 graphene layers. As the number of layers increases, the number of $e$-$ph$ processes that contributes to the 2D ($2D'$) integrated intensity also grows and it is determined by the selection rules for optical excitations and for electron scattering by phonons. Since the integrated intensities contain the weighted probability of the different processes involving phonons with close wavenumber, the $A(2D')/A(2D)$ ratio only depends on the EPC parameters which, up to ten layers, remain constant as inferred from the linear relation of the data in Fig. 4. The $\gamma_{e-e}$ scattering rate, on the other hand, experiences an increase as the intersubband $e$-$e$ collisions are allowed, following the appearance of more subbands with increasing number of layers. Although for the $E_F$ range studied in the present work the parabolicity of the energy subbands should be taken into account, for illustrative purposes the high doping case is considered where the energy dispersion of the subbands can be taken as linear. Then, in the approximation of small momentum transfer, we can generalize Eq. 4 to $N$ layers as, $\gamma_{e-e} = N |E_F| f$. Considering linear dispersive subbands, the carrier concentration, $p$, is given by $p = N\mu E_F^2$. For highly doped samples, the contribution from $e$-$ph$ scattering to the total scattering rate can be neglected compared to the much bigger $e$-$e$ scattering component. Thus, the integrated intensity for multilayer graphene can be written as:

$$A(2D)_{\text{NL}} \approx C \frac{\gamma_e^2 N}{N^2 f^2 p^2}, \quad (8)$$

and its rate of decrease upon the change of the carrier concentration, $\Delta p$, is

$$\frac{\Delta A(2D)}{\Delta p} = -C \frac{\gamma_e^2 N}{N^2 f^2 p^2}, \quad (9)$$

which accounts for the contraction of the data in Fig. 4 with increasing number of layers.

Based on Eq. 9 the approximate dependence of the experimental two-phonon Raman intensity with the inverse of $N$ proves that the amount of initial, $p$, and transferred, $\Delta p$, charge concentration in the different samples, SLG, BLG and TLG, ought to be similar. Taking into account that all samples were placed on the same wafer and exposed to the same treatments, it is reasonable to assume that the extent of unintentional or background doping and adsorbate coverage was comparable among them. The dependence of the two-phonon integrated intensity on the number of layers is two-fold, as seen from Eq. 8. First, the charge concentration is distributed among the subbands, the number of which increase with the number of layers, leading to a decrease of the probability of $e$-$e$ collision. Second, with increasing number of subbands the number of allowed $e$-$e$ processes also increases and, with it, the probability of $e$-$e$ collision. Nevertheless, the overall effect is a decrease of the two-phonon Raman intensity because there is the contribution in the scattering rate from the simultaneously excited electron and hole, as the square in Eq. 1a reflects.

IV. CONCLUSIONS

In conclusion, we have shown that the carrier concentration in graphene gradually increases with sequential ozone short-exposure cycles while preserving its crystallinity. The blue-shift of the $G$ and $2D$ peak frequencies is evidence of $p$ doping of the samples. In contrast to the $G$ peak intensity, which is found to remain constant, the $2D$ and $2D'$ peak intensities decrease with increasing number of ozone exposure cycles, i.e., with increasing doping. This effect reflects the responsiveness of the two-phonon Raman intensity to the dynamics of photoexcited $e$-$h$ pairs and, in particular, to the contribution of the $e$-$e$ scattering. We used this dependence to extract the EPC of phonons near the $K$ point and found a close agreement with previous experimental and theoretical values. We also demonstrated an inverse dependence of the rate of decrease of the intensities upon doping on the graphene...
number of layers, reflecting the increased probability of e-e scattering with increasing number of layers.

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