

## Chapter 2

# Intrinsic Doping Dependence of Raman 2D Mode in Graphene: Signatures of Electron–Electron Interaction

### 2.1 Introduction

Raman spectroscopy has been one of the most useful experimental probes for both fundamental study and characterization of graphene thin layers [1, 2]. Raman 2D mode in graphene is originated from a coherent process that involves the scattering of the quasiparticles twice by near K-point phonons [3, 4]. Resonant with the Dirac cones, the 2D mode is sensitive to perturbations in the electronic states, and this property has made it a versatile diagnostic tool for characterizing layer number and stacking order of few-layer graphene [2, 5–7]. Apart from the above applications, the doping dependence of the Raman 2D mode is of particular interest as it provides a monitor for the charge density in graphene [8]. Here we reinvestigate this problem, but using ultraclean graphene exfoliated on hexagonal boron nitride (h-BN), which provides excellent charge homogeneity [9–11]. Contrary to the weak doping dependence of Raman 2D mode below a net charge density of  $2 \times 10^{12} \text{ cm}^{-2}$  in [8], we observed a significant blue shift of more than  $4 \text{ cm}^{-1}$  when the sample is gated over the same density range. Because of the strong doping dependence of the intrinsic shift, improved charge homogeneity is essential for proper measurement of the properties of this feature at low doping levels. The observed symmetric blue shift of 2D mode is shown to be a direct consequence of the density-dependent renormalization of electronic band structure by electron–electron ( $e$ – $e$ ) interactions [12–20]. Interestingly, direct renormalization of the phonon frequency with doping is found to be relatively weak for this range of doping and to imply a shift in frequency opposite to what has been observed experimentally [21].

In addition to the peak position shift, the 2D mode broadens by  $24 \text{ cm}^{-1}$  per eV doping, and its intensity decreases by 20 % at our highest doping level of  $2 \times 10^{12} \text{ cm}^{-2}$ . The observed broadening and intensity reduction of 2D mode are also signatures of  $e$ – $e$  interactions in graphene: enhanced  $e$ – $e$  scattering with doping [19] reduces the lifetime of photo-excited electron–hole ( $e$ – $h$ ) pairs, which makes the resonant condition less stringent and thereby increases the width of the feature and

decreases its strength. By identifying  $e-e$  interactions as the predominant cause of the doping dependence of graphene 2D mode, we demonstrate the double-resonant Raman mode as a sensitive probe of change in electronic self-energy from  $e-e$  interactions. Interestingly, renormalization of the phonon frequency with doping is found to be relatively weak for this range of doping and to imply a shift in frequency opposite to what has been observed experimentally [22]. In contrast to previous complementary experimental approaches for the study of electronic structure renormalization by  $e-e$  interactions near the Fermi level [12, 14, 15], we are able to probe here the properties of quasiparticles more than 1 eV above the Fermi level.

## 2.2 Experimental Details for Raman Measurement of Ultraclean Graphene on h-BN

Our Raman measurements were performed on graphene field-effect transistors (FETs) fabricated using h-BN as the gate dielectric [23]. The device structure is illustrated in Fig. 2.1a. A piece of exfoliated graphene of size  $2\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$  was transferred onto an h-BN layer of 16 nm thickness. Three metal electrodes were used in our FET device, with one of them placed under the h-BN layer to electrostatically gate graphene and the other two placed on top of graphene as source and drain electrodes. Figure 2.1b shows an optical image of our device. Its electrical characteristics were examined through measurement of the device resistance at low bias ( $V_{sd} = 0.1\text{V}$ ) as a function of gate voltage  $V_{gs}$  (Fig. 2.1c). Electron/hole mobilities

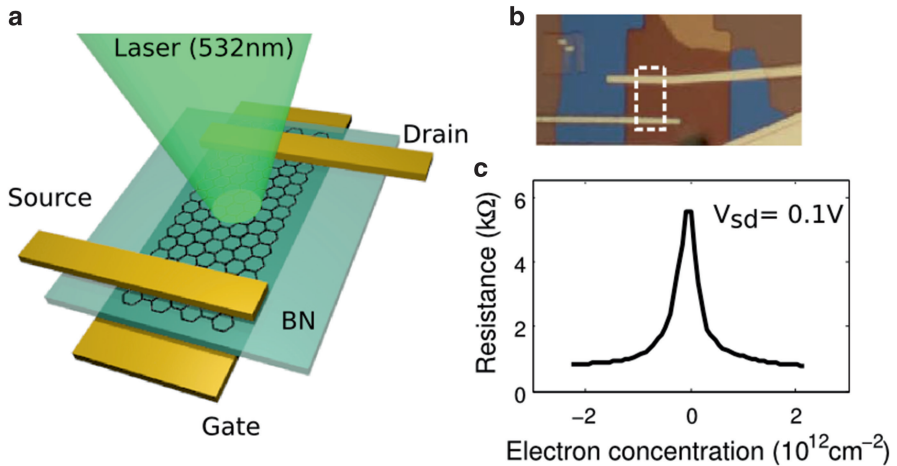


**Fig. 2.1** (a) Schematic representation of the graphene FET device using an h-BN gate dielectric under laser illumination. (b) Optical image of the graphene FET device. The area occupied by the graphene layer is indicated by the *dashed lines*. (c) Measured I–V characteristics of our graphene FET device. The carrier mobility near the charge neutrality point exceeds  $1.7 \times 10^4\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$

exceeding  $1.7 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were extracted from the slope of doping dependence of the device resistance near charge neutrality at room temperature. From the width of the same curve, we obtain an upper bound for the charge inhomogeneity in our sample of  $1.5 \times 10^{11} \text{ cm}^{-2}$ . The Raman spectra of the gated graphene were obtained using a commercial Raman microscope (Renishaw). The excitation source was a 532 nm laser, focused to a spot size of  $\sim 0.5 \mu\text{m}$  on the sample and having power of 0.2 mW. The spectral resolution for the Raman measurements was  $< 1 \text{ cm}^{-1}$ .

### 2.3 Intrinsic Doping Dependence of the Raman G Mode: Signatures of $e$ - $p$ Interactions

The dominant Raman features in high-quality graphene are the G and 2D modes [1, 2]. Although our primary focus will be the 2D mode, we briefly discuss the behavior observed for the G mode as a function of doping level. The G peak is a first-order Raman process (Fig. 2.2a) associated with the emission of a zone-center optical phonon. In several recent experimental studies, a narrowing and blue shift of the G mode (Fig. 2.2c) were observed when the Fermi level of graphene is tuned away from the Dirac point [8, 24–30]. These phenomena are understood to arise from the Pauli blocking of electron–phonon ( $e$ - $p$ ) coupling when doping prevents decay of an optical

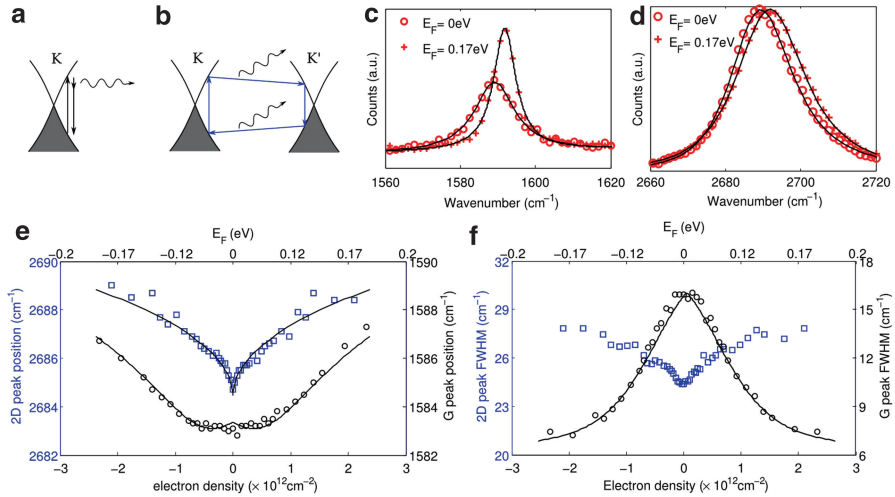


**Fig. 2.2** (a, b) Illustration of Raman scattering processes corresponding to Raman G and 2D modes. (c, d) Measured G and 2D spectra (symbols) at charge neutrality point ( $E_F = 0$ ) and at our highest doping level ( $E_F = 0.17 \text{ eV}$ ). The black lines are theoretical fits as described in the text. The 2D peak heights are normalized for clearer comparison. (e) Measured frequencies of the Raman 2D (blue squares) and G (black circles) modes versus charge density in the graphene layer. The theoretical results are shown as black solid lines. (f) Measured widths of the Raman 2D (blue squares) and G peak (black circles) modes as functions of charge density

phonon into an electron–hole pair [31–33]. However, appreciable differences are generally observable between experiments and theoretical calculations, likely due to experimental uncertainties. With the ultraclean graphene sample on BN, our measured G mode position and FWHM doping dependencies at room temperature conform to the perturbative calculations almost perfectly (Fig. 2.2e, f), reconfirming superior device quality and very good experimental control of doping level in graphene.

## 2.4 Intrinsic Doping Dependence of the Raman 2D Mode: Signatures of $e$ – $e$ Interactions

The Raman 2D mode, unlike G mode, is originated from a coherent double resonant process [3, 4], as illustrated in Fig. 2.2b. It involves the excitation of an  $e$ – $h$  pair near K point by absorbing a photon, the inter-cone scattering of the charged particle twice by near K point phonon and the emission of a Stokes photon by  $e$ – $h$  recombination near K' point. One important consequence of the double resonant process is that phonons involved in the Raman process are selected by the resonant condition, and as a result, a change in the resonance condition will lead to a change in the selected phonons in momentum space. Comparing to the G mode case, the doping dependence of the 2D mode is much less understood. A recent study of graphene on SiO<sub>2</sub> [22] shows a red shift of  $\sim 16$  cm<sup>−1</sup>/eV and a broadening of  $\sim 12$  cm<sup>−1</sup>/eV in 2D mode with doping. The shift of the 2D mode observed in [22] is in the opposite direction of the 2D mode shift we observed for graphene on h-BN and the peak broadening observed in [22] is smaller. These differences may reflect the role of different substrates used in the experiments. In graphene with low charge inhomogeneity, slight doping by a few hundred meV cannot block the resonant  $e$ – $p$  scattering processes far away from the Dirac point. Perturbative calculation shows that the position shift of the Raman 2D mode with doping due to modified  $e$ – $p$  coupling is smaller than 0.2 cm<sup>−1</sup> at the doping level of  $2 \times 10^{-12}$  cm<sup>−2</sup> [21].

As the line-shape of the Raman 2D mode for intrinsic graphene is slightly asymmetric [34–37], we extract the doping-dependent position and full-width at half maximum (FWHM) by fitting the spectra to a phenomenological asymmetric function (Fig. 2.2d). We found the 2D mode blue shifts for either electron or hole doping (Fig. 2.2e). Moreover, the shifts on the electron and hole sides are essentially symmetrical, with an absolute peak shift per eV doping of 25 cm<sup>−1</sup>/eV.

Since the renormalization of phonon energy is expected to be too small to account for the observed blue shift of the 2D peak, we turn our attentions to an important effect for the resonant Raman process, the renormalization of electronic bands. Prevailing experimental evidences have shown that Coulomb interactions among the charged carriers renormalize the graphene's electronic structure and enhance the Fermi velocity [12–20]. Doping reduces the absolute value of electron energies and the resonance condition pushes the vertical electronic transition away from the K and K' points, thus setting the resonant phonons further away from the K point (Fig. 2.3). Because of the anomalous phonon energy dispersion near the K point

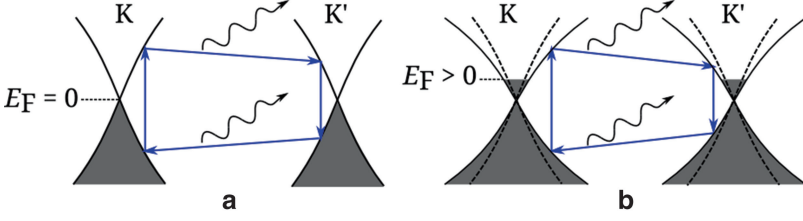


**Fig. 2.3**  $e$ - $e$  interactions responsible for the symmetric blue shift of Raman 2D mode in the doping range below  $2 \times 10^{12} \text{ cm}^{-2}$ . (a) Schematic in momentum space of the resonant Raman 2D scattering process in undoped graphene showing the electronic structure of graphene near the K and K' points. Two near K point phonons are emitted in this process. The blue arrows describe possible scattering pathways of charge carriers. (b) At finite doping, the electronic bands of graphene (solid lines) become flatter compared to the undoped case (dashed lines). The resonant electronic processes for the Raman 2D mode are then pushed further away from the K and K' points and involve phonons of decreased momentum

[31, 38, 39], the 2D Raman scattering process involves phonons of higher energies, increasing the 2D mode Raman shift. Far above the Fermi surface, the self-energy correction due to  $e$ - $e$  interaction has been calculated theoretically [14, 20, 40–44]

$$\Re \Sigma_{e-e}(k) = \frac{\alpha}{4} \hbar v_F^0 |k - k_F| \ln \left( \left| \frac{k_c}{k - k_F} \right| \right), \quad (2.1)$$

where  $\alpha$  is the coupling constant in graphene and  $v_F^0$  is the Fermi velocity of the bare electrons.  $k$  is the momentum of the quasiparticles,  $k_F$  is the Fermi vector, and  $k_c$  is the ultraviolet cutoff momentum taken to be  $1.703 \text{ \AA}^{-1}$ . Note that we have approximated the electron gas to be degenerate and neglected finite temperature effect since the scale of the ambient temperature is comparable to our doping step size. To understand from (2.1) how does the 2D mode shift depend on other parameters, we approximate the logarithmic term to be 1, which is appropriate in our case where  $k$  is comparable to  $k_c$ . We then apply the double resonance condition and obtain  $\frac{d\hbar\omega_0}{dE_F} < \alpha \frac{\beta_K}{v_F}$  where  $\beta_K$  is the slope of graphene's phonon band structure

near the K point and  $v_F$  is the renormalized Fermi velocity. Quantitatively, we fit our experimental data to (2.1) using  $v_F^0 = 10^6 \text{ m/s}$  and  $\beta_K = 940 \text{ cm}^{-1}$  (determined from the 2D mode dispersion with excitation energy).  $\alpha$  is treated as an adjustable fitting parameter. A very good fitting to our experimental data is achieved with  $\alpha = 0.60$  (Fig. 2.2e). This value of  $\alpha$  agrees with the values of  $\alpha$  for graphene on h-BN obtained from other experiments [18, 45]. At much higher doping level, however, the modification of phonon energy by the change in atomic bond lengths becomes increasingly significant and the 2D mode shifts to the red side [8].

We can check the consistency of the band renormalization picture with the well-known dispersion of 2D mode with excitation photon energy [46, 47] by comparing the peak shift in 2D mode with doping at different excitation energies (Fig. 2.4a).

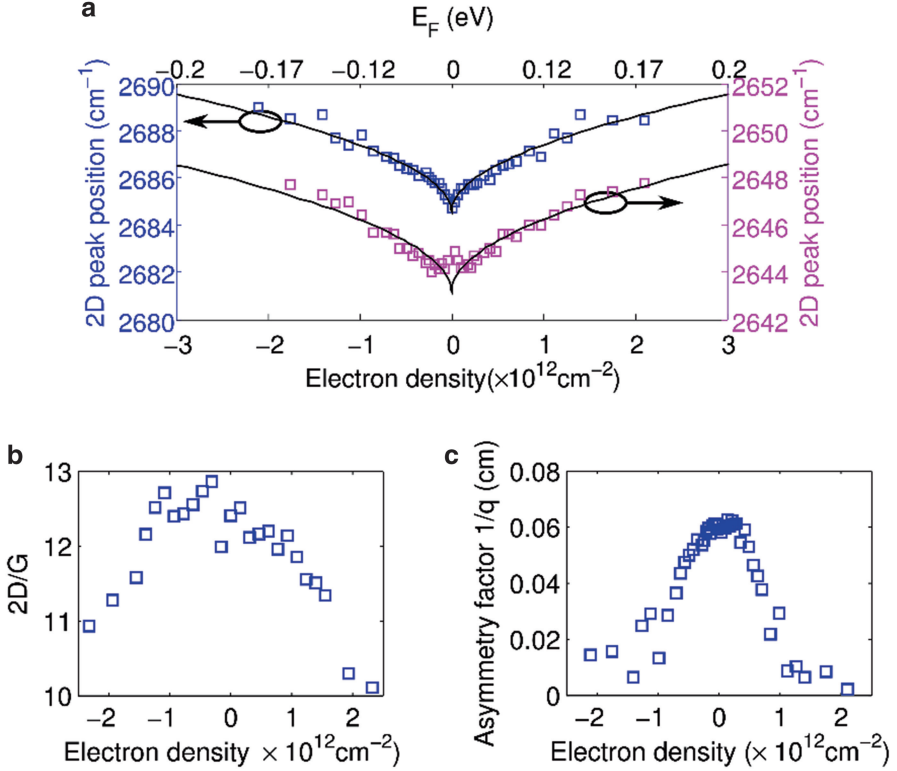


**Fig. 2.4** (a) 2D mode position versus doping excited by photons at 2.33 eV (blue squares) and 1.96 eV (magenta squares). The solid lines are theoretical models taking into account the effects of electron energy renormalization due to  $e-e$  interactions as discussed in the text. (b, c) Measured 2D/G intensity ratio and the asymmetry factor  $1/q$  as a function of electron density

We fit our experimental results with 2.33 eV excitation and 1.96 eV excitation simultaneously using the double resonance picture. We used two fitting parameters, the phonon energy exactly at K point  $E_K$  and  $\alpha$ . The 2D peak shift by doping and the 2D peak dispersion with excitation energies can be understood simultaneously using  $E_K = 1229\text{cm}^{-1}$  and  $\alpha = 0.60$ .

Our measured shift in the 2D mode position is in apparent contradiction with the experimental studies using electrochemical gating [8], where the 2D mode position has variation smaller than  $1\text{ cm}^{-1}$  when the absolute charge density is below  $2 \times 10^{12}\text{ cm}^{-2}$ . We can reconcile these two pictures by noting that with electrochemical gating, the higher charge inhomogeneity is likely to smear out the sharp non-analytical feature near the charge neutrality point. In addition, the extra layer of electrolyte can enhance the screening of  $e-e$  interactions, thus reducing the interaction effect in the Raman spectra. At higher doping levels, however, even in the presence of a relatively large amount of charge inhomogeneity, the experimental observed variation in Raman 2D peak position shift with doping should represent

closely the intrinsic doping dependence [8] due to the absence of any abrupt non-monotonic change in the 2D position. On a practical aspect, our results show that it is not appropriate to use 2D mode position to predict the sign of doping in graphene in the doping region below  $3 \times 10^{12} \text{ cm}^{-2}$ . A comparison of the G and 2D peak positions doping dependencies clearly indicates that the non-analytic shift of 2D mode is more susceptible to inhomogeneity in doping concentration than the relatively flat G mode doping dependence within  $10^{12} \text{ cm}^{-2}$  from the Dirac point (Fig. 2.2e).

In addition to the Raman 2D mode peak shift, the peak FWHM is broadened by  $\sim 4 \text{ cm}^{-1}$  when the Fermi level is shifted from the Dirac point by 0.2 eV (Fig. 2.2f). The width of the Raman 2D peak is induced mainly by the interference of all the possible Raman scattering pathways satisfying the double resonance condition instead of the intrinsic phonon lifetime. It is natural then that the finite electronic line width contributes to the total line width of the Raman 2D mode. This is because at any fixed momentum, there is a distribution of electronic states with different energies, loosing the constraint of double resonance condition. Charge doping increases the phase space for the  $e$ - $e$  scattering processes, and reduces  $e$ - $h$  pair lifetime. Thus it is expected that doping will broaden the Raman 2D peak. In a similar way as we estimate the 2D peak shift, we can estimate a lower bound for the broadening of electronic states from the peak broadening:  $\Delta_{\gamma_e} \gtrsim \frac{1}{4} \Delta_{\gamma} v_F / \beta = 10 \text{ meV}$ , where the factor  $\frac{1}{4}$  accounts for the initial and final states of the two phonon emission events.

The lower bound of electronic broadening is about 10 % of the experimental measured quasiparticle lifetime of  $\sim 0.1 \text{ eV}$ , near 1 eV above or below the Fermi level [20, 48]. This agrees with the 20 % decrease of 2D/G intensity ratio with doping (Fig. 2.4b), as it is predicted theoretically that the 2D/G intensity ratio is proportional to inverse square of the quasiparticle lifetime [19].

Slight asymmetry of the Raman 2D mode was observed near the charge neutrality point [49] for our graphene sample on BN substrate, similar to that observed in suspended graphene with ultralow net charge density [34, 35, 37]. Theoretical calculations show that the interference among all the Raman scattering pathways could result in qualitatively similar asymmetry [4, 36]. Interestingly, as the Fermi level is moved away from the charge neutrality point, we observed that the 2D line-shape becomes increasingly symmetrical (Fig. 2.4c). We note that excitonic effect may give further corrections to the simple band picture. It can potentially give corrections to the position, width, and even the line shape of the 2D mode. This is, however, beyond the scope of discussion in this work.

## 2.5 Conclusion

In summary, we measured the doping dependence of the Raman G and 2D modes in ultraclean graphene on h-BN substrate. The G mode doping dependence shows similar features as in previous studies, but the better agreement with theory confirms the outstanding sample quality. The 2D mode shifts symmetrically by  $25 \text{ cm}^{-1}$  per

eV doping to higher energy below a doping level of  $2 \times 10^{12} \text{ cm}^{-2}$ . We attribute this symmetric blue shift to the change in double resonance condition through the renormalization of electronic band structure by  $e-e$  interactions. The width of the graphene 2D mode increases with doping by  $24 \text{ cm}^{-1}$  per eV doping while the 2D/G intensity ratio decreases with doping by 20 % at our highest doping level. These two trends of the Raman 2D mode with doping are shown to be natural consequences of the reduction of photo-excited carrier lifetime.

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