



Spatial dependence of Raman frequencies in ordered and disordered monolayer graphene

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ABSTRACT

A micro-Raman investigation was carried out on several flakes of monolayer (1 L) graphene obtained by the micro-mechanical exfoliation technique and, then, put on a c-Si wafer coated by a SiO₂ thin film. Some of the 1 L zones show a remarkable dispersion of the 2D-overtone wavenumber as a function of the position within the graphene sheet, and, in some case, a significant broadening of the E_{2g} phonon (G band) is associated to this wavenumber shift of 2D-band. Such effects were studied, in particular, for a 1 L zone characterized by a rather strong lattice disorder, as revealed by the strong D/G band intensity ratio, and for other zones quite ordered, showing a vanishing intensity of the D band. Moreover, by moving along different directions within 1 L graphene sheets, different trends for 2D wavenumber and E_{2g} phonon bandwidth vs. position were observed. All these reported behaviours are explained in terms of different distributions of intrinsic uniaxial strain occurring within the 1 L graphene sheets.

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1. Introduction

Micro-Raman spectroscopy is of paramount importance in the study of several carbon polymorphs, and recently provided essential information on the new discovered graphene materials [1]. It allows to determine the thickness of graphene samples [2–5], giving results in agreement with the interferometric method developed for such purpose, too [6]. Moreover, it permits to investigate the chemical, mechanical and electronic specific properties inside very small region of that material, and, therefore, to get insights about the structural disorder within the graphene sheets [5,7–14]. In fact, wavenumber, bandwidth and shape of the most relevant Raman bands of graphene, i.e. the one-phonon G band, from Brillouin zone center, the overtone 2D band and the one-phonon, disorder-induced D band, have been object of several micro-Raman investigations. These studies relate the above spectral parameters with the degree of order of the graphene lattice [11,13], with the chemical doping [12] and with the mechanical strain [14], due either to intrinsic origins or to the interaction with the substrate [7–11]. First at all, the D band, observed only in disordered samples, and its 2D overtone, observed in all the samples, exhibits a blue shift as a function of the increasing excitation energy. The blue-

shift has been explained within the scheme of the double resonance, adopted also for bulk graphite and carbon nanotubes [15–18].

On the other hand, the single-mode-like shape of 2D overtone and its Raman intensity, comparable or higher than the G band one, constitutes the characteristic spectral marker of monolayer graphene, allowing for a precise discrimination with respect to bi- and multi-layer graphene [2–5]. However, the comparison of the experimental findings from different samples of monolayer graphene does not allow to define sharp values for the position and widths of the Raman bands at fixed excitation wavelength, because several effects seem to induce the scattering of these values. The interaction with the substrate plays an important role in determining the phonon energy values: previous Raman measurements performed for graphene sheets grown on SiC [7–10] and on indium tin oxide (ITO) [11] show a remarkable variation of 2D-overtone wavenumber value. In fact, it turns out blue-shifted for epitaxial graphene on SiC with respect to graphene placed on Si by mechanical exfoliation, while it results red-shifted for graphene on ITO. The amount of doping due to charged impurities also affects the G band position of monolayer graphene [12]: in fact, increasing levels of both p-type and n-type doping induce a stiffening of the band, which is measured by decreasing width and increasing energy, while in the undoped, pure material a particular decay mechanism of phonons is favoured, leading to a maximum of bandwidth and a minimum for the peak wavenumber. This particular correlation is observed only for very ordered graphene sheets, while in the disordered ones the increasing wavenumber is associated to an increasing bandwidth, as it occurs in

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disordered bulk graphite. The relative Raman intensity of disorder-induced one-phonon D band provides a simple spectroscopic probe for the lattice order, so that the various trends of the relevant Raman modes can be analyzed taking into account the structural order of the investigated sample. In general, strong D band has been associated to the scattering from the edges of graphene sheets [5,13], but further investigation could be useful, also because of experimental evidences, presented here, of appreciable D band intensity far away from the mono layer sheets edges. Finally, the peak position of the Raman bands depends on the mechanical strains of the placed sheets, as demonstrated in an experiment with an externally applied uniaxial stress [14], where the G band undergoes a splitting for high enough stress values, causing the removal of the two-fold degeneration of this E_{2g} mode, and where, in the meanwhile, 2D overtone exhibits a strain dependent red-shift. It seems reasonable to apply the information on the observed trends from such experiment to the case of intrinsic strains developing during the deposition process of graphene flakes: we can suppose that different strains are associated to different spatial coordinates within the sample, where they induce appreciable changes of the wavenumber of 2D overtone band and the apparent increase of the G bandwidth, comparable to that observed for weak uniaxial applied stress. Very thrully speaking it is a small, unresolved splitting, related to small uniaxial strain values. However, more studies of real spatial dependence of the spectral parameters in monolayer graphene can be useful, aimed at comparing the results with the simple model suggested by specific experiments which take into account a single variable (doping, strain, substrate and so on); for this reason we try to explore by a Raman microspectroscopy approach several flakes obtained by mechanical exfoliation, and characterized by a different degree of structural order.

A detailed Raman microanalysis was carried out on carbon flakes of different thickness, in particular graphene single layer (1 L) over the entire vibrational spectrum, up to 4500 cm^{-1} . This study allows to identify the graphene 1 L, on the basis of the shape, wavenumber values and dispersion of G and 2D bands vs. excitation wavelength. Observed significant spatial dependences within 1 L zones of graphene concern the 2D overtone peak wavenumber and the FWHM of G band. The correlation between these two spectral parameters is found to be unlike within different 1 L regions. In particular the presence of strong crystal disorder, revealed by the anomalously high D band intensity, must be considered. The observed phenomena can be discussed in terms of mechanical strains, taking also into account the results of other investigations performed under external applied stress.

2. Experimental

Standard exfoliation method [1] has been used to obtain carbon layers of different thickness, including single layer graphene. The exfoliated layers were put on a c-Si substrate coated by a 300 nm thick SiO_2 layer, which ensures the maximum optical contrast with respect to the graphene flakes.

A micro-Raman apparatus (Horiba Jobin-Yvon mod. Labram), equipped with an Olympus microscope mounting objectives of 10 \times , 50 \times and 100 \times magnification and interfaced with a color TV camera, has been used to localize and analyze the flakes with minimum thickness. The Raman spectra have been collected through the 100 \times objective, by using a He-Ne laser source (632.8 nm emission), with about 5 mW power measured at the exit of the objective. The focused laser spot has an apparent diameter of about 2–3 μm , and the spectral resolution is about 2 cm^{-1} . The excitation energy dependence of Raman spectra on the same samples has been studied by using a different apparatus consisting of a triple-monochromator (Horiba-Jobin Yvon, mod. T64000), set in double-subtractive/single configuration and equipped with holographic gratings 1800 grooves/mm, a mixed Kr-Ar ion laser (Spectra Physics, model Satellite 2018 RM) with several emission lines ranging from 647.1 nm to 454.5 nm, and a

charge-coupled device (CCD) detector, with 1024×256 pixels, cooled by liquid nitrogen. An accurate wavenumber calibration, within $\pm 2\text{ cm}^{-1}$, was achieved based on standard values for the following markers: the vibrational stretching mode of atmospheric nitrogen [19] at 2331 cm^{-1} , the emission line of a Ne spectral lamp, which occurs at 2000 cm^{-1} in the Raman setup calibrated on He-Ne excitation line, and finally the first-order Raman mode of c-Si, assumed to fall at 520.2 cm^{-1} [20,21].

3. Results and discussion

3.1. Disordered graphene

A systematic search aimed at finding out the monolayer graphene zones among the exfoliated flakes of graphite placed on the oxidized c-Si substrate has been carried out. These 1 L zones give the minimum color contrast with respect to the substrate, while the thicker regions having two, three or more layers show more and more darker coloration.

Typical optical images of graphene monolayers are shown in Fig. 1a and b, which contain in their center, a disordered 1 L sheet and an ordered one, respectively, as demonstrated in the following by the Raman analysis. The sizes of the most interesting 1 L zones fall in the range 10–20 μm (see the the scale bar in Fig. 1a). The spectral shape of

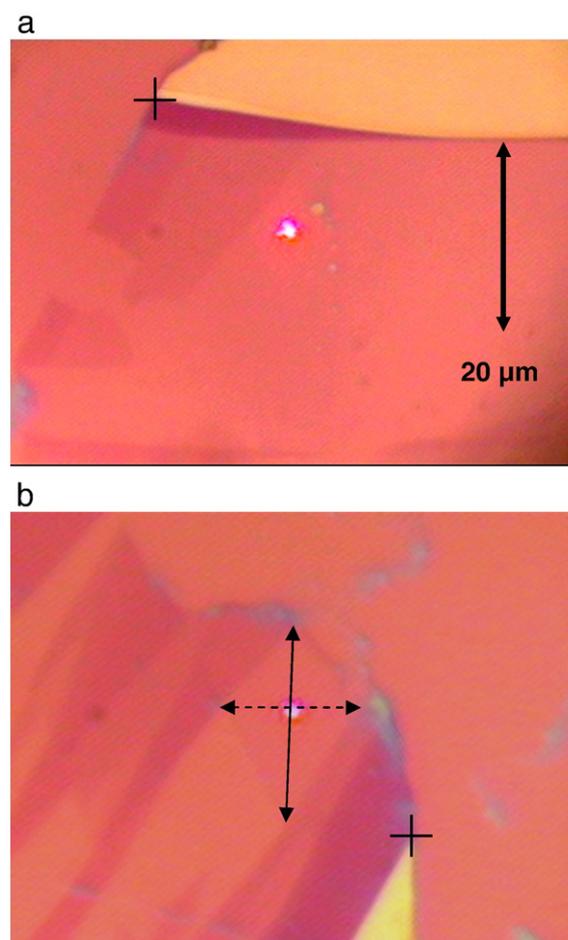


Fig. 1. (a): Monolayer graphene sheet revealed as “disordered” by analysis of D band intensity, sharing borders with a 2 L zone (left) and a thicker one (top), about 10 L. The black cross inside the image corresponds to the arbitrary origin chosen to define the spatial positions of illuminated spots and a bar of scale indicates the dimensions of the sheet. (b): Another 1 L zone, with rhombic shape, where Raman analysis reveals a well ordered lattice. Also in this case the cross indicates the arbitrary origin, and two diagonals of the rhombic zone are depicted, the vertical one (solid line, length about 15 μm) and the horizontal one (dashed line, length about 10 μm) indicating the directions of spatial scanning of the zone.

2D overtone and its intensity ratio with G band intensity allow to confirm the thickness estimates, or at least to discriminate 1 L from 2 L or thicker zones. Measurements carried out under excitation by green or blue laser lines allow to observe, besides the strong 2D overtone, others 2nd order and 3rd order Raman-active modes, typical also of highly oriented pyrolytic graphite (HOPG) [22] and nanotubes [22,23]. The most evident ones occur at about 2440 cm^{-1} (assigned either to the combination $D+D'$ [23] or, else, to the sum of a TO and of a LA phonon [24]), at 3235 cm^{-1} ($2D'$ overtone [23]) and at 4255 cm^{-1} ($2D+G$ combination [23]), respectively. Their intensity appears not appreciably dependent on the sample structural disorder. On the contrary, the weak second-order mode at about 2930 cm^{-1} (assigned either to the $D+G$ combination [22,23] or, else, to a $D+D'$ combination [25]), is observed only in disordered graphene regions, wherein the D band intensity is appreciable, as well as in other slightly disordered sp^2 carbon forms, like boron-doped HOPG [22], and nanotubes [23]. Even its peak wavenumber appears to depend appreciably on that of D band.

A full Raman spectrum of 1 L graphene, showing all the spectral features listed above, is reported in Fig. 2; to indicate the various Raman modes the assignments suggested by Ref. [23] are adopted. It was collected from a spot very close to the border between the 1 L region and the thicker zone characterized by the deepest violet color (see Fig. 1a). The typical markers of the lattice disorder can be observed, i.e. an appreciable D band intensity and the related combination mode $D+G$ (or $D+D'$) at 2930 cm^{-1} . In the spectra recorded from ordered zones the D band is absent or barely observable. Moreover, for all the 1 L zones the 2D overtone appears as a single-mode peak with intensity comparable or greater than that of G band.

The well known [15–18] wavenumber shift of 2D Raman bands of graphene vs. laser excitation energy has been also checked by using all the laser lines of the Kr/Ar ion laser, and it results almost linear vs. the laser line energy, both for spots near the border as for those at the center of the 1 L sheet. The plots of 2D peak wavenumber vs. excitation energy, reported in Fig. 3, show parallel linear dependences for two different spots. In a particular case, only for 488 nm excitation, a quite remarkable wavenumber shift of 2D band at the 1 L-zone border is measured.

The 1 L zone of the graphene flake shown in Fig. 1a, shares borders with a 2 L zone (left), slightly darker, and a thicker zone (about 10 layers) with the deepest violet coloration (upper side). It can be defined as “disordered 1 L zone” because very strong D band intensity has been observed near the zone border, while a still appreciable D band intensity can be observed even well inside the 1 L zone, as

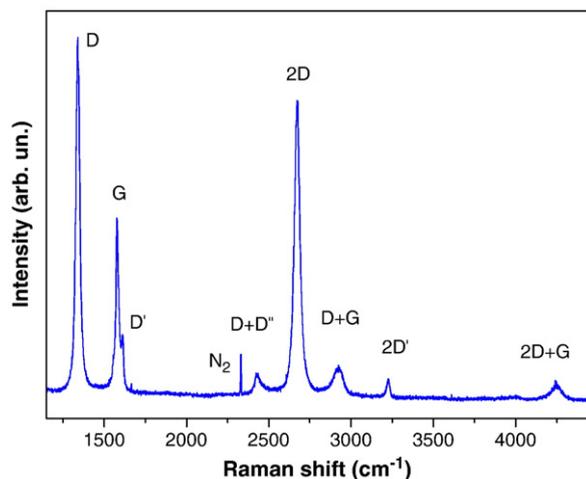


Fig. 2. Complete Raman spectrum from a spot near the border of the “disordered 1 L zone”, collected in parallel polarization by exciting with 488 nm laser line. The wavenumber scale is adjusted to have the N_2 stretching mode at 2331 cm^{-1} and the first-order Raman mode of c-Si at 520.2 cm^{-1} .

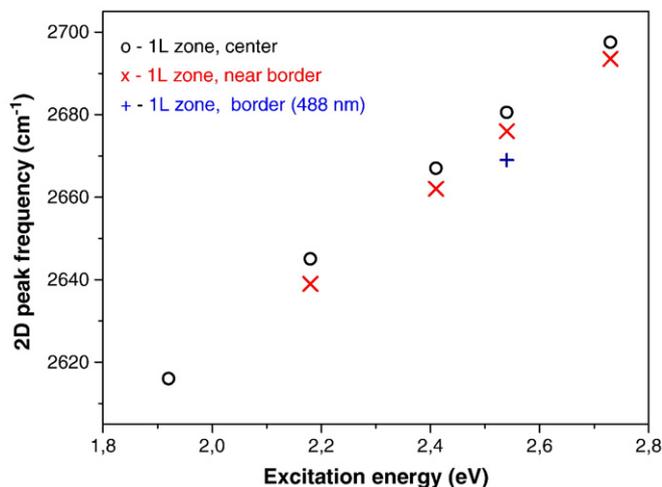


Fig. 3. Plot of peak wavenumber of 2D overtone vs. laser excitation energy, in eV, ranging from red (647.1 nm) up to violet (454.5 nm) line of a Kr/Ar laser. The linear plot results down shifted when the laser spot is displaced. \circ : center of the 1 L zone; \times : close to the upper border; $+$: very close to the upper border (only for 488 nm line excitation).

clearly depicted in Fig. 4, where, for sake of clarity, only three spectra are reported, collected near the border with the thicker graphene zone, at the center and near the opposite border, between the 1 L zone and the clean substrate, respectively (bottom side of Fig. 1a).

Additional spectra obtained from other positions inside the same 1 L flake (not reported in the figure, once again for sake of clarity) represent intermediate values of 2D-overtone wavenumber. When moving the laser spot close to the upper thick zone the D band is found even stronger than the G band, as clearly observed in the full spectrum of Fig. 2. However, for all the measured spots of the 1 L zone, the D band appears well down-shifted with respect to the spectra recorded from multi-layer zone and shows a single-mode shape; its peak wavenumber values have an observable dependence on the spatial position: the maximum dispersion for the spots where D band wavenumber is measurable is about 9 cm^{-1} , while the G band maximum dispersion is less than 5 cm^{-1} . In spectra having a strong D band the D' mode is also present, as previously observed for graphite [25]. It occurs at 1620 cm^{-1} as a peaked shoulder of the G band.

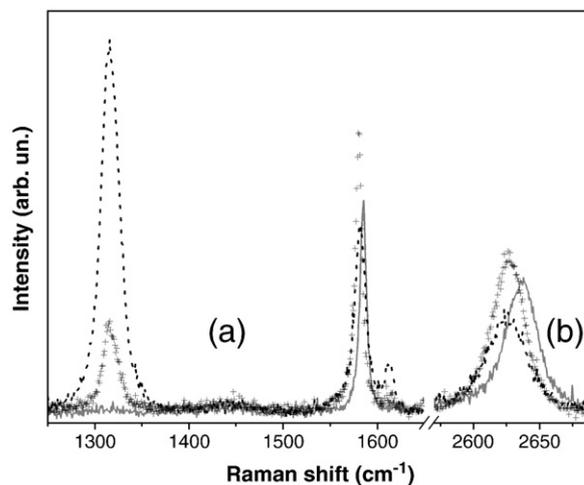


Fig. 4. Left side (a): Raman spectra, excited by 633 nm line of He-Ne laser, showing D and G band, collected from three spots of the “disordered” 1 L graphene zone (Fig. 1a), roughly located at the border with thicker zone (dashed spectrum, arbitrary coordinate $Y=6\text{ }\mu\text{m}$), at the centre (plus spectrum, $Y=12\text{ }\mu\text{m}$) and at the opposite side of the 1 L sheet (solid spectrum, $Y=20\text{ }\mu\text{m}$). Right side (b) high wavenumber range, expanded scale, of the same three Raman spectra of section a, centred on 2D mode.

A corresponding wavenumber dispersion of the 2D overtone is expected to be double than the D band one; in fact it is observed, by moving inside the “disordered” 1 L zone, from the lower border toward the thicker zone. Peak frequencies of 2D band vary from 2636 cm^{-1} down to 2616 cm^{-1} . By moving upward along this “vertical” direction, a softening of 2D overtone has been found, with a maximum amount of about 20 cm^{-1} (see Fig. 5(a)). A significant broadening of G band also occurs by moving in the same direction (Fig. 5(b)).

Wavenumber shifts and line broadenings of graphene Raman bands have been reported as effect of changing substrates [7–11] and of charged impurities [12]; in this last case, however, a significant shift of G band has been also observed, which is not found in our measurements. A proper explanation for the softening of D and 2D bands, observed in the present work, together with a correlated broadening of G band, could be found in terms of the presence of intrinsic strains in the various graphene flakes, generated during the deposition process.

To have an estimate of the strain associate to the deposition process of graphene flakes, a comparison can be made with the results of a Raman investigation on graphene under controlled external uniaxial stress [14], where experimental evidences are reported of a strong red-shift of 2D overtone and a splitting of G band, due to the removal of two-fold degeneracy for the G mode, belonging to a E_{2g} representation. The intrinsic stress affecting our graphene flakes is

surely smaller than maximum applied stress during the experiment cited above, as indicated by the smaller value of wavenumber dispersion of 2D band and the absence of visible splitting in the G peak. The observed broadening of this peak can be interpreted, however, as an unresolved small splitting, which is observed also when the applied external stress is below some threshold value. A quantitative comparison of our data due to intrinsic stress with those of externally controlled stress suggests that the upper limit of our strain variation is about 0.4, to be compared with the maximum value of 0.8 obtained by external stress [14]; in fact the measured 2D-overtone softening is about $20\text{--}25\text{ cm}^{-1}$, against about 50 cm^{-1} in the applied stress experiment. In our case, the value of the intrinsic strain is smaller than the threshold value necessary to induce an observable splitting of the G band.

3.2. Ordered graphene

To have a more complete view of the problem of intrinsic strain it can be useful to explore other monolayer graphene zones, obtained in the same experiment of mechanical exfoliation. In some of the zones, surely recognized as 1 L on the basis of their Raman spectral shape, no appreciable dispersion of the 2D wavenumber has been found, indicating that the occurrence of intrinsic strain is not general. In some other 1 L sheets, having a sufficient size, fruitful analysis of the wavenumber dispersion along relevant direction has been possible. In particular a 1 L sheet having rhombic shape has been analyzed, along two direction roughly corresponding to the “horizontal” and “vertical” diagonals of the rhomb (see Fig. 1b). As evidenced by the Raman spectra of Fig. 6, in most of the investigated spots of this 1 L zone the D band appears barely observable, even weaker than a band at about 1450 cm^{-1} , which can be surely assigned to a third order Raman mode of c-Si [26] since it is present in the Raman spectrum of naked substrate. The absence of any appreciable D band intensity suggests a high degree of crystal order, so that this region can be labelled as “ordered 1 L zone”.

Also in this “ordered 1L zone” the 2D-overtone band exhibits a spatial dispersion, as it can be seen from high wavenumber spectra of the figure (Fig. 6, right side). It is interesting to remark that different kinds of correlation are found between the spatial dependence of 2D-overtone wavenumber and the spatial dependence of the G bandwidth when moving along the two above-defined diagonals of the rhomb (see micrograph of Fig. 1b).

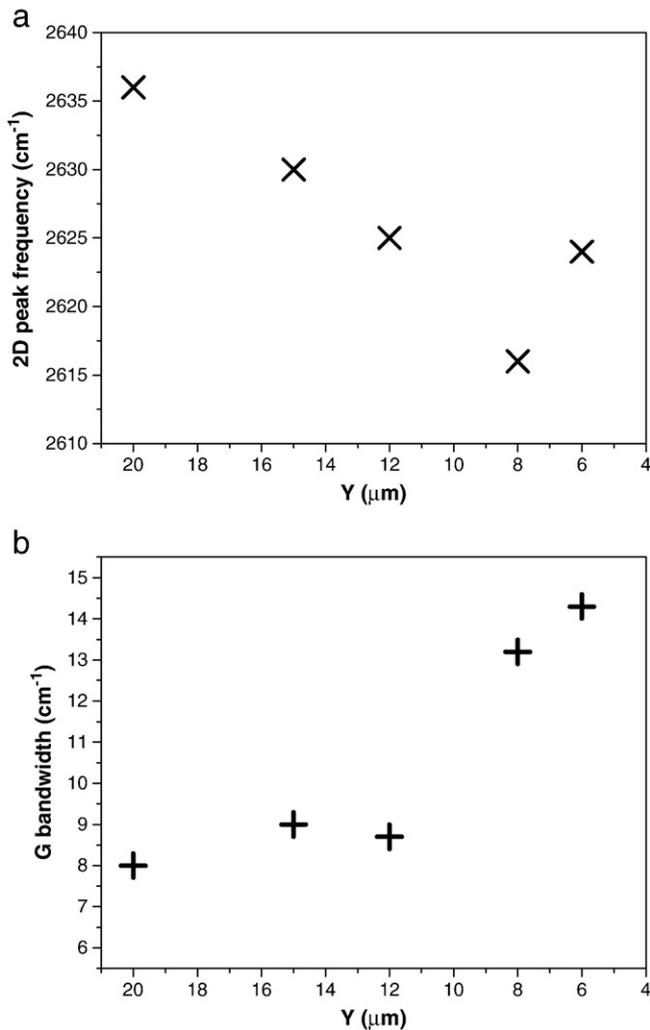


Fig. 5. (a): Plot of 2D peak wavenumber as a function of spatial position. The Y coordinate is the “vertical” projection of the distance between the irradiated spot and the arbitrary point chosen as origin in see Fig. 1a. (b): plot of the bandwidth of G mode as a function of the same spatial coordinate Y.

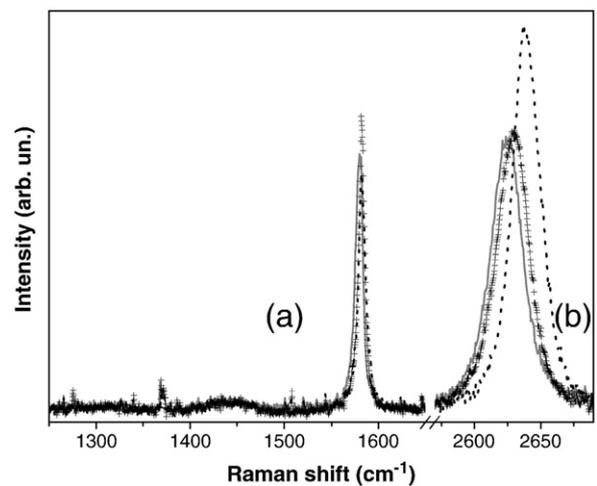


Fig. 6. Left side (a): Raman spectra from three spot of the rhombic 1 L region, shown in Fig. 1b. The absence of D band indicate the ordered character of such sheet. Right side (b): high wavenumber spectra, on enlarged scale, from the same three spots of the rhombic zone, showing the wavenumber dispersion of the 2D mode.

Fig. 7a and b report the variation of 2D peak frequency as a function of an arbitrary spatial coordinate, called X to indicate displacements along the “horizontal” diagonal, and the variation of the G peak bandwidth, vs. the same X coordinate, respectively. In this case the maximum dispersion of 2D position is about 15 cm^{-1} , while no significant trend can be extracted from the G bandwidth data, ranging between 7 and 10 cm^{-1} . By assuming the same interpretation adopted above, in terms of spontaneous strain, we can conclude that along the “horizontal direction” the gradient of strain is smaller, and its average value is not enough to induce neither an observable splitting of the G mode, nor an appreciable broadening which can suggest it.

As for the other direction, the “vertical” diagonal of this rhombic 1 L zone, a greater dispersion of the 2D position is found, amounting to about 20 cm^{-1} ; moreover the G mode bandwidth shows an appreciable, monotonic increase, from 7 up to 14 cm^{-1} , when the 2D-overtone wavenumber increases vs. the same arbitrary spatial coordinate, here labelled as Y (see Fig. 8(a) and (b)).

In this case, too, the observed correlation between the 2D wavenumber and G bandwidth behaviours can be still interpreted as due to a strain distribution. Here, the strain turns out higher in the spots of higher coordinate values, so that a unresolved splitting of the two-fold degenerate G mode occurs. However, the trend of the 2D-

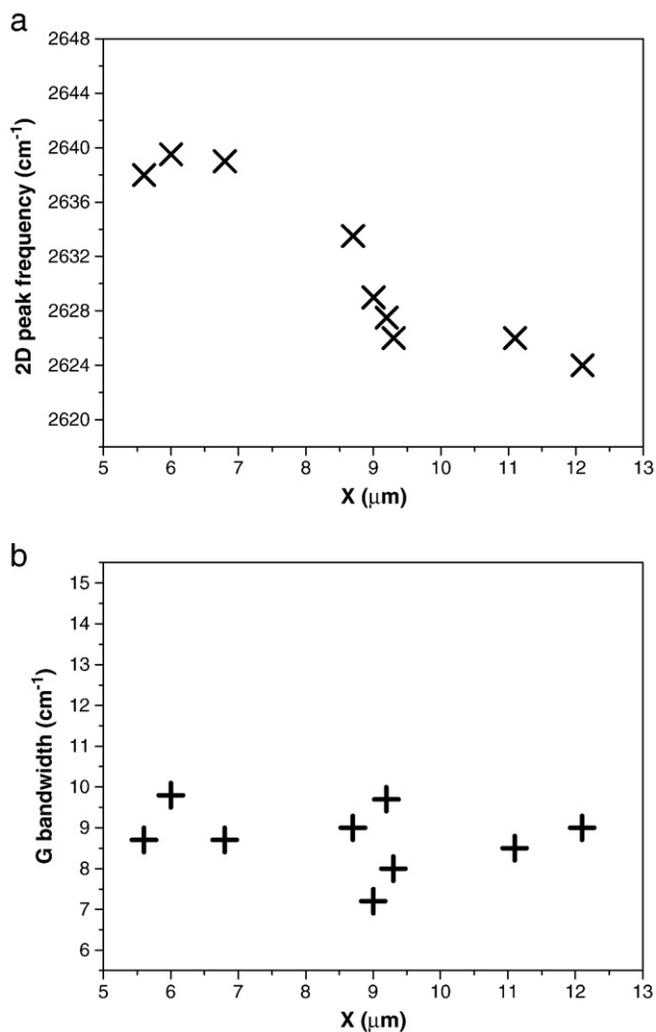


Fig. 7. (a): plot of the 2D wavenumber for spots moving along the “horizontal” diagonal of the rhomb; the spatial coordinate X is the horizontal component of the distance from the arbitrary point chosen as origin in Fig. 1b. (b): plot of the bandwidths of G mode, vs. the same spatial coordinate X.

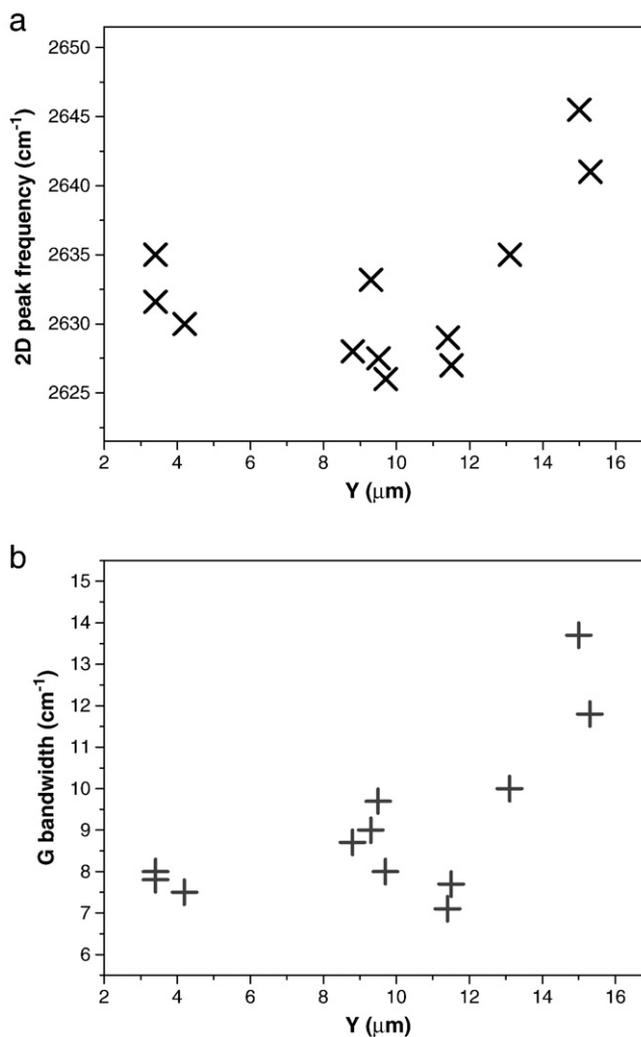


Fig. 8. (a): plot of the 2D-overtone wavenumber given by spots moving along the “vertical” diagonal of the rhomb; their spatial coordinate Y is defined as the “vertical” component of the distance from the arbitrary origin. (b): plot of the bandwidth of G mode, vs. Y, for the same spots.

overtone wavenumber suggests a different kind of stress, with respect to that discussed in Ref. [14], and that found in our investigation of the disordered 1 L sheet: in these two cases the applied stress was tensile and the spatial distribution showed greater tensile stresses, when the upper multilayered zone was approached. Correspondently a softening of the 2D mode was observed for displacements of the laser spot along that direction.

In contrast, in our last case the hardening of 2D overtone indicates an increasingly compressive intrinsic stress along the “vertical” direction, with different distribution of the stress along the two perpendicular directions over the graphene sheet. Obviously, the removal of degeneracy for E_{2g} phonon, inducing the splitting or the apparent broadening, does not depend whether the stress is tensile or compressive, but only on its value.

Finally, regions showing a stronger coloration, corresponding to multilayered graphene, have been also investigated along their spatial extension to check the amount of spatial dispersion for 2D-overtone wavenumber. No appreciable shift was found in these thicker zones; this experimental finding, not shown here, could suggest that only monolayer graphene sheets are appreciably affected by the variation of strain, while the thicker samples are less sensitive to the stress due to mechanical exfoliation process.

4. Conclusions

The paper reports on the results of a detailed micro-Raman investigation carried out on some monolayer graphene sheets, obtained by mechanical exfoliation and put on c-Si wafer coated by a SiO₂ thin film. In some cases a relevant dispersion of wavenumber values for 2D mode is observed, associated to apparent broadenings of G band, which can be interpreted in terms of intrinsic strain distribution. This phenomenon seems typical of 1 L graphene zone, but it is not general for all of them. In fact, not all the 1 L zones have a significant dispersion, and, among those showing an appreciable gradient of intrinsic strain, both tensile and compressive stress effects are observed. The strain value appear to have a smooth trend along the explored directions of the 1 L sheets and the maximum variation results smaller with respect to the values found for epitaxial graphene grown on SiC. The behavior of G band, non affected by appreciable wavenumber shift, suggests to rule out a different explanation for the observed phenomena, like the dependence on doping due to chemical impurities.

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