

Measuring disorder in graphene with the G and D bands

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Here we analyse the evolution of the disorder induced D-band ($\sim 1350\text{ cm}^{-1}$) and of the first-order allowed G-band ($\sim 1584\text{ cm}^{-1}$) in the Raman spectra of ion bombarded graphene. By increasing the bombardment time, we increase the disorder and, consequently, decrease the average distance (L_D) between defects. We describe how the intensity, full width at half maximum (FWHM) and integrated area vary for the D

and G bands as a function of L_D . Finally, we compare the evolution of the intensity ratio I_D/I_G and of the integrated area ratio A_D/A_G between the D and G bands as a method for quantifying disorder in graphene. For practical use and inter-laboratorial comparison, the authors advise using the intensity ratio for a more suitable measure for analysing defect density.

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1 Introduction Last year we published a Raman spectroscopy study of Ar^+ bombardment in highly oriented pyrolytic graphite (HOPG) [1]. The evolution of the disorder induced D-band ($\sim 1350\text{ cm}^{-1}$) and the first-order allowed G-band ($\sim 1584\text{ cm}^{-1}$) in the Raman spectra of HOPG subjected to $\sim 80\text{ eV}$ ions were analysed, generating the amorphization trajectory for the upper graphene layers in HOPG. The intensity ratio I_D/I_G , between the D and G bands, increases between $10^{12}\text{ Ar}^+/\text{cm}^2$ and $10^{14}\text{ Ar}^+/\text{cm}^2$, remaining constant for higher ion bombardment doses [1]. In sequence, we started to work on a similar experiment, but studying mechanically exfoliated graphene samples. We showed the full amorphization trajectory for single layer graphene, exhibiting an increase in I_D/I_G for increasing disorder up to a point where the average distance between defects (L_D) reaches about 4 nm. For $L_D < 4\text{ nm}$, I_D/I_G ratio was observed to decrease. The results were explained based on a phenomenological model based on (i) the defect creating a disordered region plus (ii) an area near the defect where the D-band process is activated [2]. By fitting the experimental data, we found that the coherence length for the Raman process was $l = 2\text{ nm}$ (for $E_{\text{laser}} = 2.41\text{ eV}$). Finally, we have recently extended our analysis to N -layer graphene

samples, to learn how the I_D/I_G ratio depends on the number of layers [3]. The maximum value of I_D/I_G was found to scale with N , being maxima for one-layer graphene and the maximum divided by N in N -layer graphene. The results can be further scaled showing that $N(I_D/I_G)$ follows a universal dependence showing that the ion-induced disorder can be normalized, irrespective of the number of carbon atoms in the sample.

All this analysis is based on the intensity ratio I_D/I_G , because absolute Raman intensities are hard to measure. However, it is likely that the G-band intensity itself is not insensitive to disorder, as well as the linewidths of the peaks. Historically some authors have considered the intensity ratio instead of the ratio between the D to G band integrated areas (A_D/A_G), and *vice versa* [4–7]. Here we present the evolution of the D and G peak intensity, linewidth and integrated areas for one-layer graphene subjected to the low energy Ar^+ bombardment. We then compare the results obtained for I_D/I_G and for A_D/A_G in our sample.

2 Experimental details Single-layer graphene was prepared on top of a 300-nm- SiO_2 Si substrate by the mechanical exfoliation of HOPG. Ar^+ ion bombardment

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were carried out in an OMICRON VT-STM ultra-high vacuum system equipped with an ISE five-ion source. Micro-Raman spectra were acquired with $E_{\text{laser}} = 2.41$ eV and recorded with a Horiba Jobin Yvon T64000 triple-monochromator equipped with a N₂-cooled charge-coupled device. We employed backscattering configuration, using a 100× objective. For intensity calibration, accumulation time has been kept constant and large care was taken with focus location. The consistency of the Si peak intensities when comparing the measurements indicates a good procedure. More details can be found in Refs. [1–3].

3 Results and discussions Figure 1 shows the evolution of the D and G band intensity (a), full width at half maximum (FWHM) (b) and integrated area (c) parameters, as a function of the average distance between defects (L_D). For the calibration procedure between ion dose and L_D , see Ref. [2]. The G-band frequency ($\omega_G \sim 1584$ cm⁻¹) lies within a ± 2 cm⁻¹ uncertainty in the full range, with a larger fitting uncertainty below $L_D \sim 3$ nm, where the G and D' ($\omega_{D'} \sim 1620$ cm⁻¹) peaks coalesce. The D-band ($\omega_D \sim 1350$ cm⁻¹) shows a similar behaviour, with an apparent decrease in frequency by no more than 7 cm⁻¹ below $L_D \sim 3$ nm. These numbers come from Lorentzian fitting of the data using three peaks (D, G and D' peaks). However, at higher doses the background between the D and G band increases and the spectral profile departs from the lineshape of the three summed Lorentzians peaks (one peak between the D and G peak would be required for a perfect fitting – see Ref. [1]). This departure indicates inhomogeneous broadening.

Figure 1(a) shows the evolution of the peak intensities. The D-band intensity (I_D , black bullets) increases when increasing disorder (decreasing L_D) down to a maximum at about $L_D = 4$ nm, similar to what has been reported for the I_D/I_G ratio. However, the G-band intensity (I_G , open bullets) also shows an evolution with disorder: it is basically constant for L_D decreasing down to 10 nm, but below this value the I_G shows a large decrease. This large decrease is related to the broadening of the G-band scattering, as shown in Fig. 1(b), indicating the effect is not primarily related to the breaking of sp² bonds, but rather mostly because of relaxation of selection rules and disordering in the bond strengths.

Figure 1(b) shows the evolution of the FWHM for the two peaks. They both exhibit a very small increase when decreasing L_D down to 4–5 nm. However, below $L_D \sim 4$ –5 nm there is a large increase in the FWHM for both D and G bands.

Figure 1(c) shows the evolution of the integrated areas for the D and G peaks. In general, their integrated areas increase with increase in disorder. For the D-band the increase in integrated area (A_D) is larger below $L_D \sim 10$ nm, following the large increase in I_D . For the G-band, the increase in integrated area (A_G) is larger below $L_D \sim 5$ nm, following the large increase in the G-band FWHM. Therefore, the decreases in intensity for both peaks (below $L_D \sim 10$ nm for G and below $L_D \sim 4$ nm for D, see Fig. 1(a))

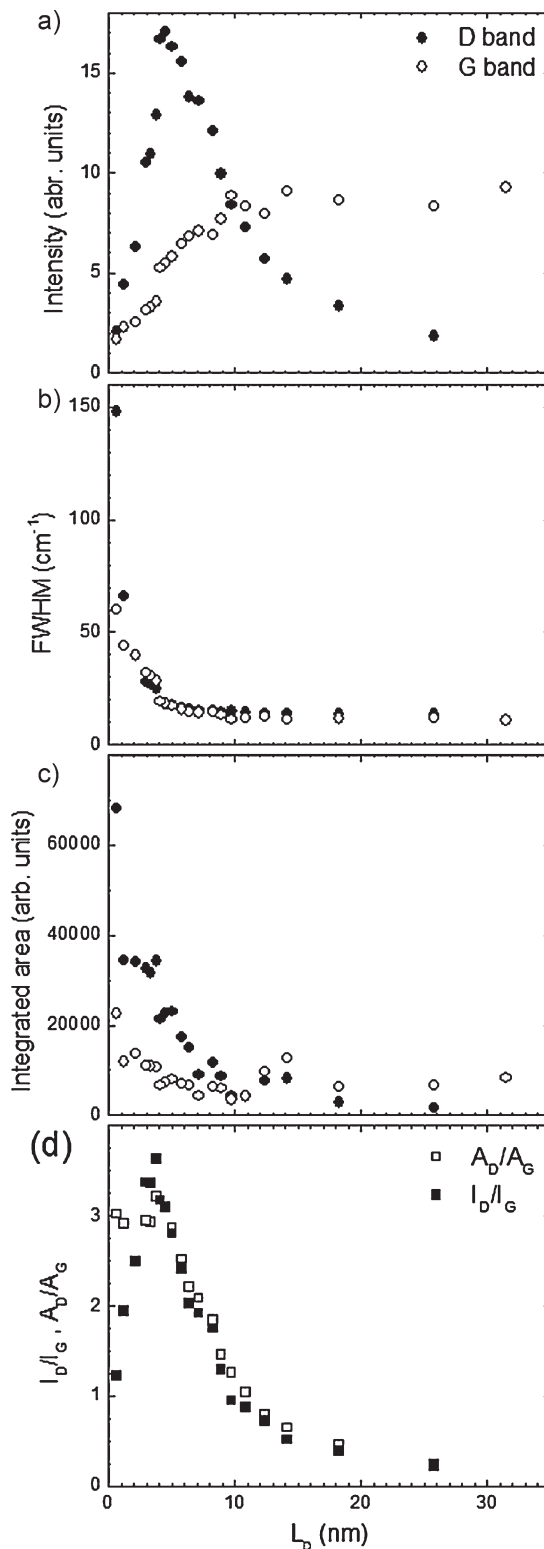


Figure 1 Evolution of (a) intensity, (b) FWHM and (c) integrated area for the D and G Raman peaks of single-layer graphene. Panel (d) shows a comparison between the D to G ratio for their intensities and integrated areas.

are compensated by the large increase in linewidth [Fig. 1(b)].

Finally, Fig. 1(d) shows a comparison between the D to G intensity ratio (I_D/I_G , black squares) and the D to G integrate area ratio (A_D/A_G , open squares). The behaviour for the weak disorder regime ($L_D > 5$ nm) seems not to be much different, and this is related to the fact that the FWHM for both peaks do not change substantially in this regime. However, for $L_D < 5$ nm, the I_D/I_G and A_D/A_G behave very differently. While the intensity ratio drops dramatically, the integrated area ratio shows a saturation behaviour with no big change below $L_D < 5$ nm. Here the decrease in intensity is compensated by the increase in FWHM.

4 Concluding remarks We have analysed the evolution of the intensity, FWHM and integrated area for the D and G band peaks in graphene, as a function of the average distance between ion bombardment induced defects. All the parameters are observed to vary strongly below $L_D = 4\text{--}5$ nm. This variation results in a very different behaviour of I_D/I_G as compared to A_D/A_G below this L_D limit, whereas for larger values of L_D , the intensity ratio and integrated area ratio exhibit similar behaviour.

An important question can be raised: is the peak ratio or the area ratio the more suitable measure for analysing defect density? Of course both can be used and both are important for further advancing the physics of the defect induced processes in graphene. But for practical means and inter-laboratorial comparisons, the advice of the authors here is for using the peak intensity ratio. The peak intensities are information that can be extracted more directly from the

data, while the areas depend more sensitively on the peak FWHM, which depends on the fitting procedure. However, researchers should be careful because the peak ratio increases and decreases, and there will be always two values of L_D for a given value of I_D/I_G . The correct L_D value to choose is evident from the spectral lineshape, since below the turn-over point ($L_D \sim 4$ nm here) the spectral profile starts to look like amorphous carbon [2].

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