GRAPHENE UNDER UNIAXIAL STRAIN: A RAMAN STUDY

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Introduction

With a few notable exceptions [1-4 and references therein], most works dealing with mechanical properties of graphene are of theoretical nature and generally limited to suspended graphene at the atomic scale. Hence, there is a growing demand for experimental data to validate the models and relate them to graphene attached to various substrates. In the present work, graphene flakes are subjected to a cyclic uniaxial deformation (tension - compression) using the polymer cantilever beam technique. In all cases the mechanical response was monitored by simultaneous Raman measurements. For the sake of a correct interpretation of the obtained data, we set up a complex approach utilizing both G and 2D phonons, both their frequency and width changes, measured in both compressive and tensile modes. Buckling behavior of embedded graphene flakes is described in detail.

Experimental

Graphene monolayers were prepared by mechanical cleavage and transferred onto the PMMA cantilever beam covered by a ~200 nm thick layer of SU8 photoresist. After placing the graphene samples, a thin layer of S1805 photoresist was spin-coated on the top. The cantilever beam technique was employed for subjecting tensile/compressive loads. MicroRaman spectra were recorded either with 785 nm or 514.5 nm excitation. In our typical experiments, the strain increment was 0.03 or 0.05%. The data presented in this study were measured on three different flakes (on different beams) on several points in each flake, sometimes in repeated tension and compression cycles. Altogether, more than 150 and 200 spectra were acquired under compression and tension, respectively.

Results and Discussion

Figure 1 shows representative Raman spectra of a graphene monolayer in the G peak region as a function of strain. As can be seen, the doubly degenerate E_{2g} optical mode (G peak) splits into two components both in tension and compression, which have been termed G^- and G^+ in analogy with nanotubes, referring to polarization along the strain and perpendicular to it, respectively [3,4]. The G^-:G^+ intensity ratios remain relatively constant during the course of loading and are the same for all investigated spots on a particular flake, being 1.5:1 for F2 flake and 1:1 for F1 flake. The difference between the two flakes is caused by their different crystallographic orientation with respect to the strain axis [3,4]. Table 1 shows the sensitivities of the individual G bands both under tension and compression. An important feature is the linearity of the slopes under tension evidencing only negligible prestrain levels on the measured flakes [2]. This was confirmed by pre-experiment mapping using 2D positions and linewidths as well.

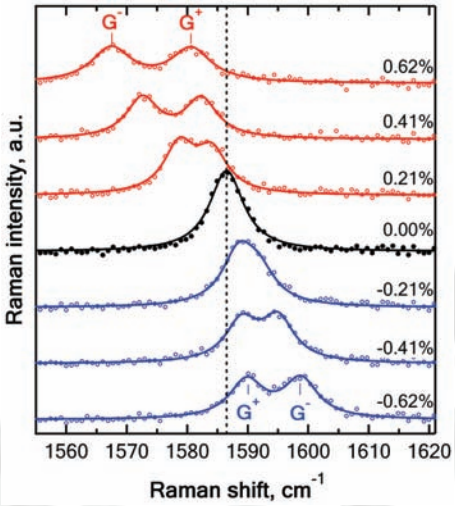

Fig. 1 G band Raman spectra of graphene flake excited at 785 nm under uniaxial strain (red for tensile and blue curves for compressive strain). The original measurements are plotted as points; solid curves are the Lorentzian fits.

Table 1. Summary of $\partial\omega_G/\partial\varepsilon$ values ($cm^{-1}/\%$).

	Compression		Tension	
	$\partial\omega_G^-/\partial\varepsilon$	$\partial\omega_G^+/\partial\varepsilon$	$\partial\omega_G^-/\partial\varepsilon$	$\partial\omega_G^+/\partial\varepsilon$
ref. [4]	---	---	-12.5 ± 2.6	-5.6 ± 1.2
ref. [3]	---	---	-31.7	-10.8
This work	22.3 ± 1.2 F1 33.1 ± 2.2 F2	5.5 ± 1.9 F1 10.1 ± 2.1 F2	-31.4 ± 2.8	-9.6 ± 1.4

In tension, the Raman shifts of all the considered bands follow almost perfectly linear trends up to the maximum applied strain. In contrast, as can be seen in Fig. 2 for the 2D peak positions (further denoted as Pos(2D)) under compression the linearity holds only for certain strain level, after which the Pos(2D) relaxes. The onset strain of the Pos(2D) relaxation is at different value for each flake and is accompanied by an abrupt G band broadening. Such spectral changes clearly evidence buckling. The moment of the final failure of the flakes can be expressed by the critical buckling strain (ε_c). For comparison purposes between flakes, we define ε_c as the local maxima in the 2nd order polynomials fitted to Pos(2D) vs. strain values (Table 2).

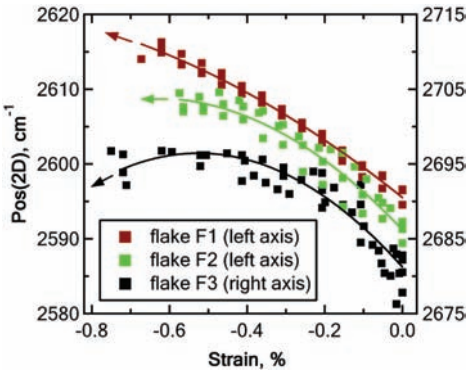

Fig. 2 Pos(2D) as a function of compressive strain for flakes with different orientations. Solid lines represent second order polynomial fits.

The critical buckling strain for a flake in the classical Euler regime in air can be determined through the following equations: $\varepsilon_c = \frac{\pi^2 kD}{Cw^2}$ and $k = \left(\frac{mw}{l} + \frac{l}{mw}\right)^2$, where l and w are the length and width of the flake, m is the number of half-waves into which the flake buckles and D (3.18 GPa nm^3) and C (340 GPa nm) are the flexural and tension rigidities, resp. The above equation is mainly valid for suspended thin films and yields extremely small (~10^{-9}) ε_c values for graphene monolayers of thicknesses of the order of atomic radii. However, for embedded flakes the above predictions are meaningless since current and previous experimental results[2] clearly point to much higher values of strain prior to flake collapse. Assuming that $\varepsilon_c \propto k/w^2$, the different response of the individual graphene flakes to compression can be determined by their geometries and orientation with respect to the strain axis.

Table 2. Critical buckling strain and approximate physical dimensions of the studied graphene flakes.

Sample	ε_c (%)	k/w^2 (μm^{-2})	k	l (μm)	w (μm)
F1	-1.25	0.028	89.12	6	56
F2	-0.64	0.011	22.71	11	50
F3	-0.53	0.006	4.02	56	25

If we now plot k/w^2 as a function of ε_c, a linear dependence for the three studied flakes is obtained (Fig. 3). The equation of the least-squares-fitted line is given by $(k/w^2) = a\varepsilon_c + b$, where the slope a=0.03 μm^{-2}. Since as shown in Fig. 3, an Euler type analysis can be applied to the embedded graphene, then the critical buckling strain should be given by:

$\varepsilon_c^{embedded} = \frac{k}{w^2}\frac{\pi^2 D^*}{C}$ where D* is now the flexural rigidity in the presence of the polymer. Using the slope a=-0.03 μm^{-2}, the D* can be estimated to 12 MPa μm^3, which is, indeed, 6 orders of magnitude higher than the value in air. This is truly a remarkable finding that indicates clearly that the support offered by polymer barriers to a rigid monolayer can provide a dramatic enhancement to its compression behavior.

Finally, a post-mortem mapping of the flake indicates the presence of permanent wrinkles at an angle dictated by the neighbouring bulk graphite, which acts as a "clamp" supporting one edge of the compressed graphene.

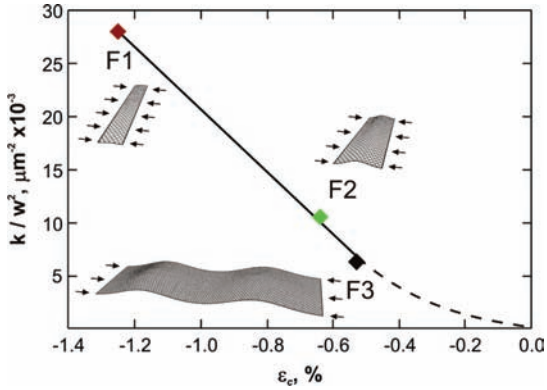

Fig.3 Geometrical term k/w^2 plotted against critical buckling strain ε_c for the three flakes under study.

Conclusions

In summary, we documented in detail the response of graphene monolayers to uniaxial strain by probing its optical phonons by Raman spectroscopy. The linearity of the G and 2D bandshift with tensile strain reflects a low pre-strain level of the flakes. In compression, the G and 2D band response is non-linear and varies from flake to flake. The gradual decrease of $\partial\omega_{G,2D}/\partial\varepsilon$ accompanied by an abrupt broadening of the bands is indicative of progressive buckling and an eventual final collapse of the flakes. The estimated critical buckling strain depends on size and geometry as would do any thin plate in an Euler buckling regime. The effect of the lateral support provided by the polymer matrix is dramatic and increases the effective flexural rigidity of graphene by 6 orders of magnitude.

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