

Supporting Information for

**Suspended Monolayer Graphene under True Uniaxial
Deformation**

**IOANNIS POLYZOS^{1*}, MASSIMILIANO BIANCHI^{2,+}, LAURA RIZZI^{2,+},
EMMANUEL KOUKARAS¹, JOHN PARTHENIOS¹, KONSTANTINOS
PAPAGELIS^{1,3}, ROMAN SORDAN² AND COSTAS GALIOTIS^{1,4*}**

**¹Institute of Chemical Engineering Sciences, Foundation of Research and
Technology-Hellas (FORTH/ICE-HT), Patras, Greece**

**²L-NESS, Department of Physics, Politecnico di Milano, Polo di Como, Via
Anzani 42, 22100 Como, Italy**

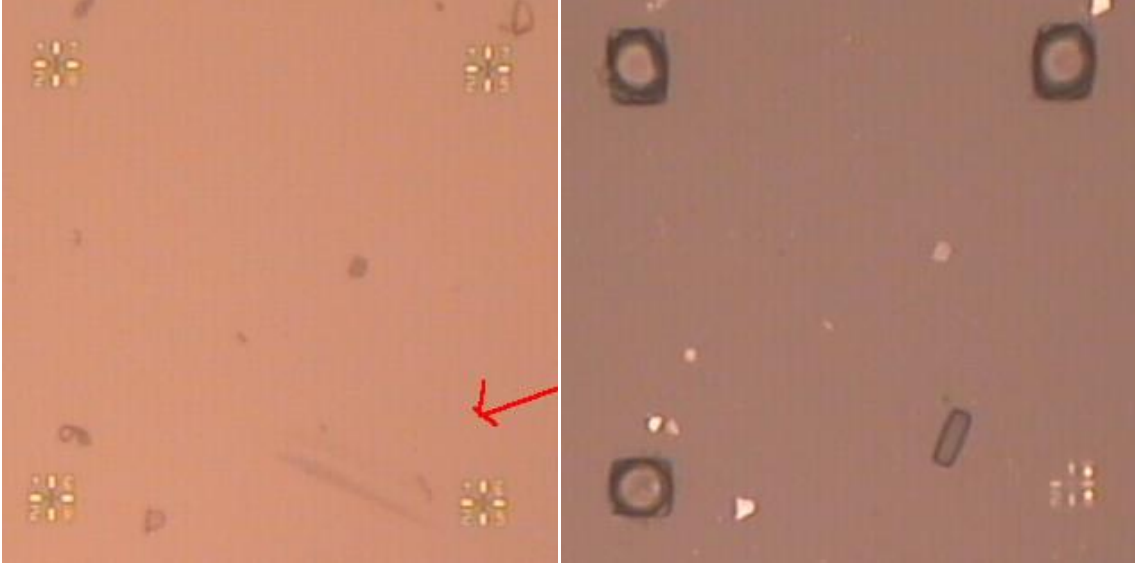
³Department of Materials Science, University of Patras, Greece

⁴Department of Chemical Engineering, University of Patras, Greece

***Corresponding authors: c.galiotis@iceht.forth.gr; ipolyzos@iceht.forth.gr**

⁺ Current address: DIRECTA PLUS S.p.A., c/o Parco Scientifico di ComoNExT, Via Cavour 2, 22074 Lomazzo (Co), Italy

S1. Sample preparation



(a) **(b)**
Figure 1 (a) Microscopy image of graphene flake between PMMA layers. The sample is deposited onto a Si/300nm SiO₂ substrate (3.8x3.8 mm²), pre-patterned with a 40x40 Au marking grid (each square is 80x80 µm²), (b) Microscopy image of suspended graphene inside the e-beam lithography window (3µm). The sample is transferred on a glass substrate.

S2. Strain calculation from Raman Spectra

The applied strain is calculated from the G-band peak shift according to the following well established secular equation¹

$$\Delta\omega_G^\pm = \Delta\omega_G^h \pm \frac{1}{2} \Delta\omega_G^s = -\omega_G^0 \gamma_G (\varepsilon_{ll} + \varepsilon_{tt}) \pm \frac{1}{2} \omega_G^0 \beta_G (\varepsilon_{ll} - \varepsilon_{tt})$$

in which ε_{ll} and ε_{tt} are the parallel and perpendicular strain components, γ_G is the Grüneisen parameter and β_G is the shear deformation potential¹. The phonon wavenumber at rest is ω_G^0 .

From the above equation we have:

$$\begin{cases} \Delta\omega_G^+ = -\omega_G^0 \gamma_G (\varepsilon_{ll} + \varepsilon_{tt}) + \frac{1}{2} \omega_G^0 \beta_G (\varepsilon_{ll} - \varepsilon_{tt}) \\ \Delta\omega_G^- = -\omega_G^0 \gamma_G (\varepsilon_{ll} + \varepsilon_{tt}) - \frac{1}{2} \omega_G^0 \beta_G (\varepsilon_{ll} - \varepsilon_{tt}) \end{cases} \Rightarrow$$

$$\Rightarrow \begin{cases} \varepsilon_{||} + \varepsilon_{\perp} = -\frac{\Delta\omega_G^+ + \Delta\omega_G^-}{2\omega_G^0\gamma_G} \\ \varepsilon_{||} - \varepsilon_{\perp} = \frac{\Delta\omega_G^+ - \Delta\omega_G^-}{\omega_G^0\beta_G} \end{cases} \Rightarrow$$

$$\Rightarrow \begin{cases} \varepsilon_{||} = \frac{-\frac{\Delta\omega_G^+ + \Delta\omega_G^-}{2\omega_G^0\gamma_G} + \frac{\Delta\omega_G^+ - \Delta\omega_G^-}{\omega_G^0\beta_G}}{2} \\ \varepsilon_{\perp} = \frac{-\frac{\Delta\omega_G^+ + \Delta\omega_G^-}{2\omega_G^0\gamma_G} - \frac{\Delta\omega_G^+ - \Delta\omega_G^-}{\omega_G^0\beta_G}}{2} \end{cases}$$

The numeric values of $\varepsilon_{||}$ and ε_{\perp} are calculated from the above general equations assuming

$\gamma_G = 1.99$, $\beta_G = 0.99$ and $\omega_G^0 = 1581\text{cm}^{-1}$.

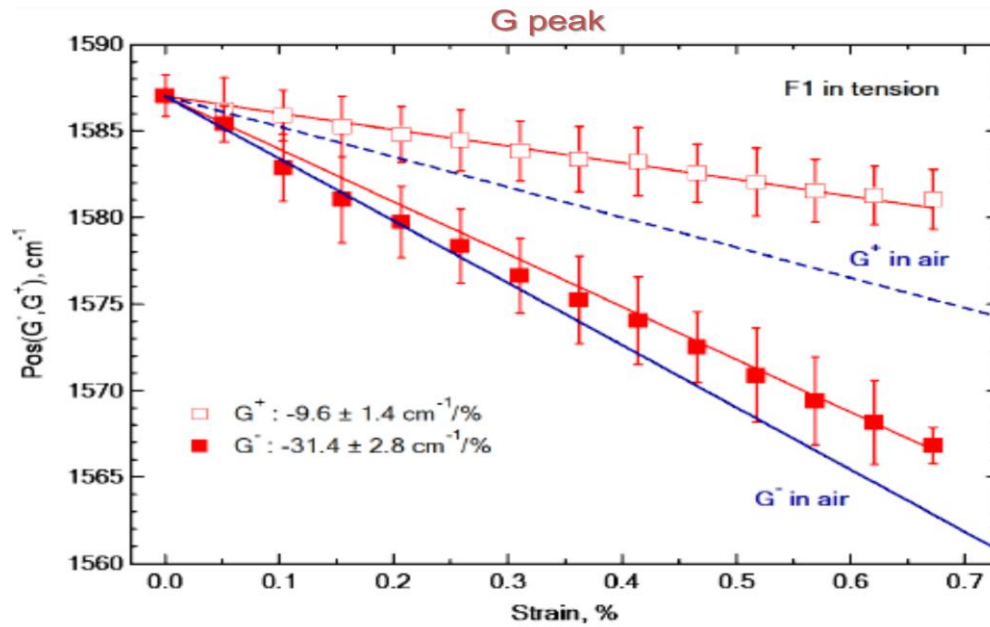


Figure 2 G^+ (empty rectangles) and G^- (full rectangles) peak positions for graphene embedded in polymer beam in tension. Labeled lines correspond to the predicted values for suspended graphene. This graph is taken from Frank et al. 2011, Nat Commun **2**: 255.²

S3. Converting spectroscopic data into stress- strain.

The procedure for converting the spectroscopic data into stress- strain is presented in the following^{2,3}. For carbon materials, the shift of the Raman frequency scales with the applied stress by a factor k :

$$|\Delta\omega| = k\sigma \quad (1)$$

Where $\Delta\omega$ is the shift of the 2D Raman band, k is a scale factor and σ is the mechanical stress. In tension the shift frequency of the 2D Raman band, can be captured by a first order polynomial curve (eq. 2), thus:

$$\Delta\omega = f_0 + f_1\varepsilon \quad (2)$$

By combining equations (1) and (2), the spectroscopically derived Raman shifts can be converted into mechanical stresses, with the factor $k=5.75 \text{ cm}^{-1}\text{GPa}^{-1}$ for the 514 nm wavelength. Finally the mechanical stress can be estimated from the next equation:

$$\sigma = \frac{f_0}{k} + \frac{f_1}{k}\varepsilon \quad (3)$$

where f_i are the polynomial constants estimated from the fitting of the graphs of $\Delta\omega(\varepsilon)$, σ and ε are the mechanical stress and strain respectively and k as defined previously.

S4. Critical buckling strain

With regards to compression, atomically thin membranes are not expected to have any compressive strength in air. The critical buckling strain for a flake in the classical Euler regime in air, can be determined through the following equation⁴

$$\varepsilon_c = \frac{\pi^2 kD}{Cab} \quad (4)$$

where a and b are the length and width of the flake for axial compression, k is a geometric term, and D and C are the bending and tension rigidities⁵, respectively. The above equation, is mainly valid for suspended thin films and yields extremely small ($\sim 10^{-9}$) ε_c values for graphene monolayers of thicknesses of the order of atomic radii. Such extremely small critical buckling strains are also predicted by molecular dynamics calculations⁶⁻⁸. This certainly explains the tendency of graphene to wrinkle easily⁹ because of its evidently low resistance to buckling instability as expressed by (4).

References

- 1 Mohiuddin, T. *et al.* Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gruneisen Parameters and Sample Orientation. *Physical Review B* **79**, 205433 (2009).
- 2 Frank, O. *et al.* Development of a universal stress sensor for graphene and carbon fibres. *Nat Commun* **2**, 255 (2011).
- 3 Androulidakis, C. *et al.* Experimentally derived axial stress–strain relations for two-dimensional materials such as monolayer graphene. *Carbon* **81**, 322-328, doi:<http://dx.doi.org/10.1016/j.carbon.2014.09.064> (2015).
- 4 Timoshenko, S. *Theory of elastic stability*. (McGraw-Hill, 1961).
- 5 Frank, O. *et al.* Compression Behavior of Single-Layer Graphenes. *ACS Nano* **4**, 3131-3138, doi:10.1021/nn100454w (2010).
- 6 Pereira, V. M., Castro Neto, A. H., Liang, H. Y. & Mahadevan, L. Geometry, Mechanics, and Electronics of Singular Structures and Wrinkles in Graphene. *Physical Review Letters* **105**, 156603 (2010).
- 7 Wang, C., Liu, Y., Lan, L. & Tan, H. Graphene wrinkling: formation, evolution and collapse. *Nanoscale* **5**, 4454-4461, doi:10.1039/C3NR00462G (2013).

- 8 Gao, Y. & Hao, P. Mechanical properties of monolayer graphene under tensile and compressive loading. *Physica E: Low-Dimensional Systems and Nanostructures* **41**, 1561-1566 (2009).
- 9 Meyer, J. C. *et al.* The structure of suspended graphene sheets. *Nature* **446**, 60-63, doi:http://www.nature.com/nature/journal/v446/n7131/supinfo/nature05545_S1.html (2007).