## Evaluation of the elastic constant C<sub>33</sub> of multilayer graphene through the Layer Breathing Modes measured by Raman spectroscopy

S. Milana<sup>1</sup>, D. Yoon<sup>1</sup>, M. Ijäs<sup>1</sup>, P. H. Tan<sup>2</sup>, N. Pugno<sup>3</sup>, A. C. Ferrari<sup>1</sup>

<sup>1</sup> Cambridge Graphene Centre, University of Cambridge, Cambridge CB3 0FA, United Kingdom <sup>2</sup> State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

<sup>3</sup> Department of Structural Engineering and Geotechnics, Politecnico di Torino, 10129 Torino, Italy

Contact: sm874@cam.ac.uk

## Abstract

The set of elastic constants of a material is typically used to describe its mechanical properties. In crystals with uniaxial hexagonal layered structure such as graphite, the elasticity matrix describing mechanical properties contains five non vanishing, independent elastic moduli, namely C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>, C33, and C44 [1]. In multilayer graphene, the elastic constants C11 and C12 are related to the strong bonding between carbon atoms within a layer, therefore describing in-plane deformations [2]. C<sub>44</sub> represents the shear modulus of the layer-layer interface, accounting for displacement of the graphene planes with respect to each other [5]. C<sub>33</sub> determines the Young's modulus in the normal direction, thus describing the out-of-plane compression or expansion of the graphene layers [2]. Raman spectroscopy is the prime nondestructive characterization tool for graphene and related layered materials [3, 4]. In layered crystals, the shear (C) [5] and layer breathing modes (LBMs) [3, 6, 7, 8], are due to relative motions of the planes, either perpendicular or parallel to their normal. According to these definitions, it is therefore possible to associate these Raman modes to their respective elastic constants accounting for such displacements. Here we measure by multi-wavelength Raman scattering the anti-Stokes and Stokes combinations of the G and LBM phonons in multilayer graphene, as a function of the number of layers (M), as shown in Fig. 1. By using a linear-chain model based on a normal interlayer force constant per unit area,  $\alpha_{\perp}$ , we evaluate C<sub>33</sub> of multilayer graphene to be 37 GPa. A similar Raman analysis can be applied to any layered materials: the C<sub>33</sub> of multilayer MoS<sub>2</sub> is found to be 59.6 GPa.

## References

[1] G. Grimvall, North-Holland (1986).

[2] G. Savini, Y. J. Dappe, S. Oberg, J. C. M. I. Katsnelson, and A. Fasolino, Carbon, 49 (2011) 62.

[3] A. C. Ferrari and D. M. Basko, Nat. Nanotechnol., 8 (2013) 235.

[4] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, Phys Rev Lett., **97** (2006) 187401.

[5] P. H. Tan, W. P. Han, W. J. Zhao, Z. H. Wu, K. Chang, H. Wang, T. F. Wang, N. Bonini, N. Marzari, N. Pugno, G. Savini, A. Lombardo, and A. C. Ferrari, Nat. Mater., **11** (2012) 294.

[6] X. Zhang, W. P. Han, J. B. Wu, S. Milana, Y. Lu, Q. Q. Li, A. C. Ferrari, P. H. Tan; Phys. Rev. B, 87 (2013) 115413.

[7] F. Bonaccorso, P.H. Tan, A.C. Ferrari ; ACS Nano, 7(3) (2013) 1838.

[8] F. Herziger, P. May, and J. Maultzsch, Phys. Rev. B, 85 (2012) 235447.

## Figures



**Figure 1**: (a) Raman spectra of few layer graphene as a function of number of layers, measured at 632.8 nm (1.96 eV) excitation in the shear mode (left panel) and G peak (right panel) regions. Schematic diagrams of the normal mode displacement for (b) the shear mode (C peak), (c) the layer breathing mode (ZO')