

Bilayer graphene under uniaxial tension: A Raman study

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With a few notable exceptions, 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. However, up till now, no such experiments on bilayer graphene have been reported. Raman spectroscopy here is a key diagnostic tool to identify the number of layers in a sample and probe physical properties and phenomena [1]. The G band corresponds to the in-plane, zone center, doubly degenerate phonon mode (transverse (TO) and longitudinal (LO) optical) with E_{2g} symmetry. Under tension, the G mode shifts to lower frequencies (phonon softening), while under compression, it shifts to higher frequencies (phonon hardening). On top of that, due to a symmetry break-down induced by the strain, the G mode splits into two sub-bands, denoted G^- and G^+ for the component parallel and perpendicular to strain, resp. Their respective shifts rates were determined to be ca. 30 and 10 $\text{cm}^{-1}/\%$ [2-4]. Their intensities depend on the orientation of the graphene lattice with respect to the strain axis and polarization of the incident light. The D and 2D modes come from a second-order double resonant process between non-equivalent K points in the Brillouin zone (BZ) of graphene, involving two phonons (TO) for the 2D and one phonon and a defect for the D peak. The shift rates for the 2D band are in the range of 50-60 $\text{cm}^{-1}/\%$, and very recently its splitting has been reported [5,6]. The origin of the splitting lies in non-equivalent K-K' paths (three for an arbitrary strain orientation) and also depends on the excitation wavelength. For lower excitation energy (like 1.58 eV), inner resonance processes become stronger due to a lesser effect of trigonal warping, and hence all together the 2D band can be composed of six components with different shift rates, which leads to broadening and eventually splitting [5].

In the present work, bilayer graphene flakes have been subjected to a uniaxial tension using the polymer cantilever beam technique. In all cases the mechanical response was monitored by simultaneous Raman measurements using 785 nm (1.58 eV) excitation. The flakes were either laid bare on a polymer substrate or covered by another polymer layer to minimize a possible slippage during loading. For comparison, a monolayer graphene close to the studied bilayer was monitored during the same experiment. Figure 1a shows an example micrograph of embedded mono- and bilayer graphenes. Both of them show the same behavior under tension, with shift rates of 30.5 and 9.5 $\text{cm}^{-1}/\%$ for G^- and G^+ , resp. As can be deduced from Fig.1a as well as from the same G^-/G^+ relative intensities of the respective layers, they belong to the same flake, part of which is composed of a single layer, whereas the other part is overlaid by another layer with Bernal (AB) stacking. Therefore their lattice orientation of 23° , which can be calculated using the G^- and G^+ relative intensities, is the same.

Figure 1b shows the 2D band components evolution under tension for the embedded bilayer. The 4 components come from the splitting of the electronic bands due to interactions between the stacked layers [1,7] with the highest frequency component ($2D_{11}$) originating from resonance processes involving only the "original" π_1 and π_1^* bands belonging to the single layer. The FWHMs were set as

equal for all components and otherwise left unconstrained. The shift rates of the three lower frequency components involving the π_2 and π_2^* electronic bands are all similar - close to $50 \text{ cm}^{-1}/\%$. However, the $2D_{11}$ shifts at a rate of only $30 \text{ cm}^{-1}/\%$. The relative intensities of the components evolve differently. The $2D_{12}$ experiences a double intensity increase in the observed strain range, mainly at the cost of the $2D_{11}$. It has to be noted, a deconvolution of the 2D band with more than 4 components is very problematic and some of the parameters would need to be constrained – for which there are too few data available at the moment. The evolution of $2D_{11}$ and $2D_{12}$ resembles the behavior of the 2D band in a monolayer when excited with the same wavelength. There, the 2D band splits and can be fitted with two Lorentzians (even though there are more, see above) with shift rates of approx. 50 and $30 \text{ cm}^{-1}/\%$ for the lower and higher frequency component, resp. The evolution of the bilayer 2D band could lead to an assumption that the $2D_{11}$ splits as does in monolayer and only its higher frequency sub-component can be deconvoluted separately, while the lower frequency sub-component merges with the $2D_{12}$ and thus contributes to its huge intensity increase. However, more data complemented with first-principles calculations are necessary to fully explain the observed processes.

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References

- [1] Ferrari A.C., Meyer J. C., Scardaci V., Casiraghi C., Lazzeri M., Mauri F., Piscanec S., Jiang D., Novoselov K.S., Roth S., Geim A.K. *Phys.Rev.Lett.*, **97** (2006) 187401.
- [2] Mohiuddin T.M.G., Lombardo A., Nair R.R., Bonetti A., Savini G., Jalil R., Bonini N., Basko D.M., Galotis C., Marzari N., Novoselov K.S., Geim A.K., Ferrari A.C. *Phys.Rev.B*, **79** (2009) 2054338.
- [3] Tsoukleri G., Parthenios J., Papagelis K., Jalil R., Ferrari A.C., Geim A.K., Novoselov K.S., Galotis C. *Small*, **5** (2009) 2397.
- [4] Frank O., Tsoukleri G., Parthenios J., Papagelis K., Riaz I., Jalil R., Novoselov K.S., Galotis C. *ACS Nano*, **4** (2010) 3131.
- [5] Frank O., Mohr M., Maultzsch J., Thomsen C., Riaz I., Jalil R., Novoselov K.S., Tsoukleri G., Parthenios J., Papagelis K., Kavan L. and Galotis C. Raman 2D-band splitting in graphene: theory and experiment. *ACS Nano*, submitted.
- [6] Huang M., Yan H., Heinz T.F., Hone J. *Nano Lett.*, **10** (2010) 4074.
- [7] Cançado L.G., Reina A., Kong J., Dresselhaus M.S. *Phys.Rev.B*, **77** (2008) 245408.

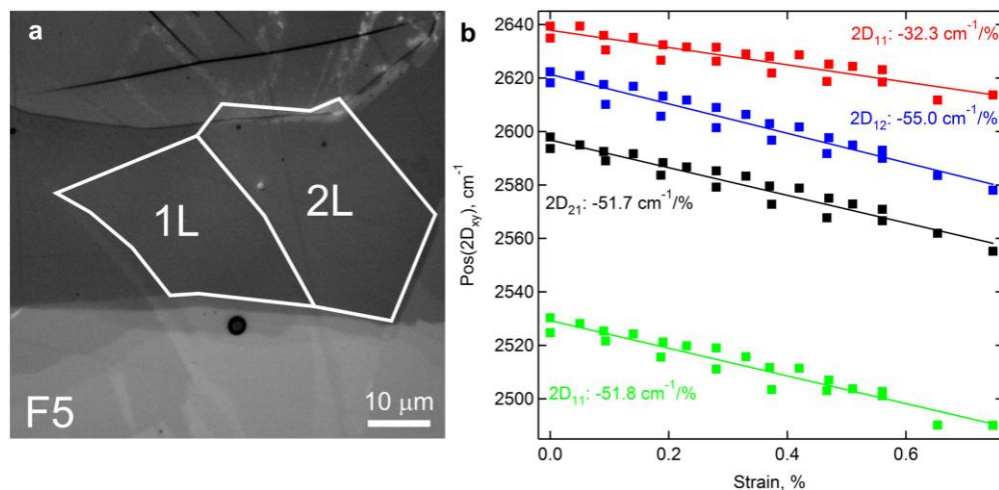


Figure 1. a) optical micrograph of the graphene under study. b) evolution of the Raman 2D band components of the bilayer graphene under tension (excitation wavelength 785 nm).