

## TENSILE MECHANICAL PROPERTIES OF EMBEDDED SINGLE, BI- AND TRI-LAYER GRAPHENE FLAKES

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### Abstract

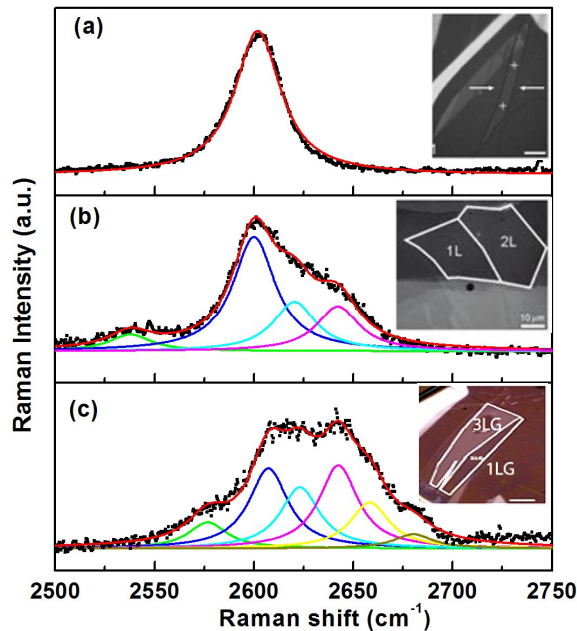
*Central to most applications involving graphenes flakes is its mechanical response under various stress/ strain states. In this work, we present an experimental study on single, bi- and tri-layer graphene flakes under uniaxial tensile strain, for low levels of strain. Graphene layers were subjected to tensile loading by employing a polymeric cantilever beam assembly, where the graphene flakes are embedded into the polymer beam. The mechanical response of graphenes is monitored by simultaneous Raman measurements through the shift of the G and 2D optical phonons, and their strain sensitivities are determined. The results can be used to quantify the amount of uniaxial strain, providing a fundamental tool for graphene based nanocomposites.*

### 1 Introduction

Graphene is the thinnest known one atom thick membrane [1], exhibiting exceptional electronic and mechanical properties [2]. Experiments have confirmed the extreme tensile strength and Young's modulus of graphene of about 130 GPa and 1TPa, respectively [2]. These properties make graphene an ideal candidate for use as mechanical resonators, strain sensors or as a reinforcement in graphene-based composites. It is well known that the electronic band structure of bi- (2LG) and tri-layer (3LG) graphene differs remarkably from that of a monolayer (1LG) resulting in materials with different electronic properties, suitable for next-generation optoelectronics and post-silicon nanoelectronics. However, their mechanical properties that can significantly alter their electronic properties are not well documented so far.

Raman spectroscopy is a rapid, sensitive and non-destructive tool for the characterization of graphene-based materials. The most intense modes that can be observed in graphene based samples are the G and the 2D. The G peak is due to the first-order Raman scattering process and corresponds to the in-plane, doubly degenerate E<sub>2g</sub> mode at Brillouin

zone (BZ) center. The 2D band arises from a double-resonance (DR) process that involves inter-valley (i.e. between the K and K' point) scattering in the BZ and resonant electronic transitions[3]. It involves two zone-boundary phonons (TO-derived) with opposite wavevectors and it does not require the presence of a defect for its activation. Importantly, it has been shown [3] that the shape of the 2D peak can be used for the determination of the number of graphene layers in Bernal AB stacking graphitic structures. However the frequency of the 2D mode for 1LG, 2LG and 3LG samples vary linearly as a function of the energy of the excitation laser line [3,4].



**Figure 1.** 2D-mode Raman spectra of (a) single layer, (b) bilayer,, and (c) trilayer graphene, excited by 785 nm. The black points are experimental data. The red lines denote fits by single (a), four (b) and six (c) Lorentzian components all with a FWHM of  $24\text{ cm}^{-1}$ . The scale bar in the microphotographs is  $10\text{ }\mu\text{m}$ .

In monolayer graphene the electronic band structure consists of a single valence and conduction band touching each other at K and K' points of the BZ. Hence, the 2D peak originated from a single DR process can be fitted by a single Lorentzian peak with a full width at half maximum (FWHM) of  $24\text{ cm}^{-1}$  (fig. 1a) [4].

Bilayer graphene has two valence ( $\pi_1, \pi_2$ ) and two conduction ( $\pi_1^*, \pi_2^*$ ) bands while the dispersion is parabolic near the K points. The  $\pi_1$  and  $\pi_1^*$  bands are degenerate at K, and the  $\pi_2$  and  $\pi_2^*$  ones exhibit a very small energy gap. Group theory for bilayer graphene predicts four distinct DR processes along the  $\Gamma$ -K-M-K'- $\Gamma$  direction of the BZ. Therefore, the 2D line shape of a Bernal-stacked 2LG can be fitted by four Lorentzian components, each having the same FWHM of  $24\text{ cm}^{-1}$  (Fig. 1b) [4].

Moreover, trilayer has three valence and three conduction bands, and thus many DR transitions can contribute to the 2D band. A recent group theoretical study shows that up to 15 different DR processes are possible in 3LG with Bernal (ABA) stacking order. However, we may consider fewer transitions, since many of them have close energy separations. It was found that a reliable fit can be achieved with 6 Lorentzian functions each having the same FWHM of  $24\text{ cm}^{-1}$  (Fig. 1c) [4].

In this work, we present an experimental study on 1LG, 2LG and 3LG under uniaxial tensile strain, for low levels of strain. The mechanical response of graphene is monitored by simultaneous Raman measurements through the shift of the G and 2D optical phonons, and their strain rates are determined and compared. The results of this work may have important implications for nanometrology applications of Raman spectroscopy on graphene based devices.

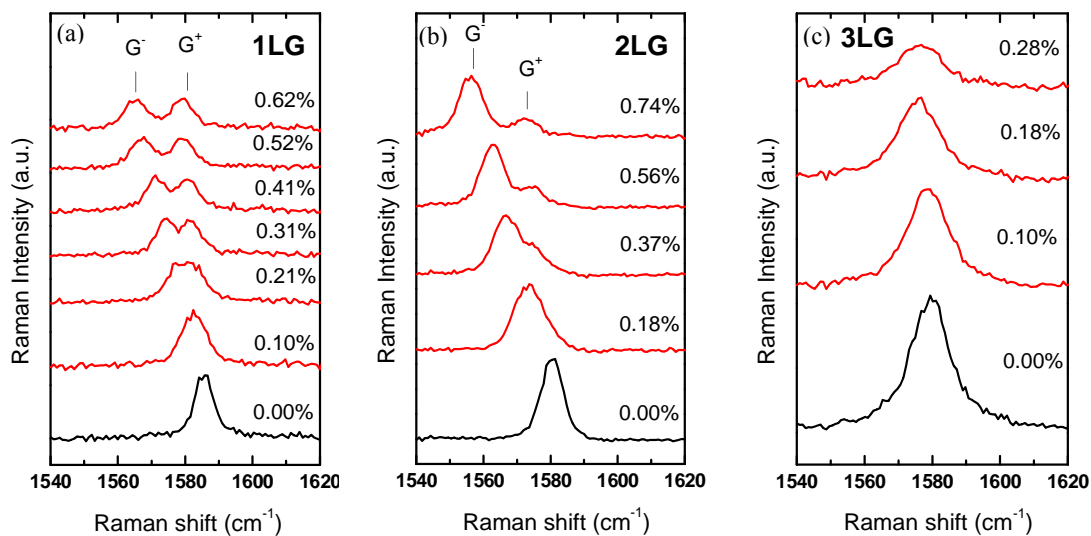
## 2 Experimental part

Single and multi-layer graphenes (Fig. 1a-c) were prepared by mechanical cleavage from natural graphite (Nacional de Grafite) and transferred onto a three different PMMA cantilever beams covered by a  $\sim 200$  nm thick layer of SU8 photoresist (SU8, MicroChem). Three different samples were covered using different types of polymeric layers by spin casting. Monolayer was covered by S1805 photoresist (Shipley). Bilayer was covered by PMMA dissolved in an anisole (PMMA, M.W. 495.000 A3, MicroChem) and trilayer by lower molecular weight PMMA dissolved in acetone (PMMA, M.W. 120.000, Aldrich).

Raman spectra were acquired using an InVia Reflex spectrometer (Renshaw, UK) using a 785 nm (1.58eV) excitation laser line, while the power was kept around 1 mW to avoid laser induced local heating on the sample. A 100x objective with numerical aperture of 0.9 was used, and the spot size area is estimated to be  $\sim 1 \times 2 \mu\text{m}^2$ . The polarization of the incident light was kept parallel to the applied strain axis. The cantilever beam technique was employed for applying uniaxial tensile strain to the samples. Details of the technique can be found in references [5-7].

## 3 Results - Discussion

Figure 2 shows the tensile strain evolution of the Raman spectra of the G mode for 1LG, 2LG and 3LG samples. The doubly degenerate  $E_{2g}$  optical mode for both 1LG (Fig.2a) and 2LG (Fig.2b) splits into two components  $G^-$  and  $G^+$  in analogy with carbon nanotubes, referring to polarization along the strain and perpendicular to it, respectively [5-9]. Both 1LG and 2LG show similar behaviour and the extracted tensile shift rates of the  $G^-$  and the  $G^+$  are  $-31.3$  and  $-34.0 \text{ cm}^{-1}/\%$  as well as  $-9.9$  and  $-10.9 \text{ cm}^{-1}/\%$ , respectively (Table 1). These shift rates are in accordance with previous measurements and theoretical calculations [5-10].



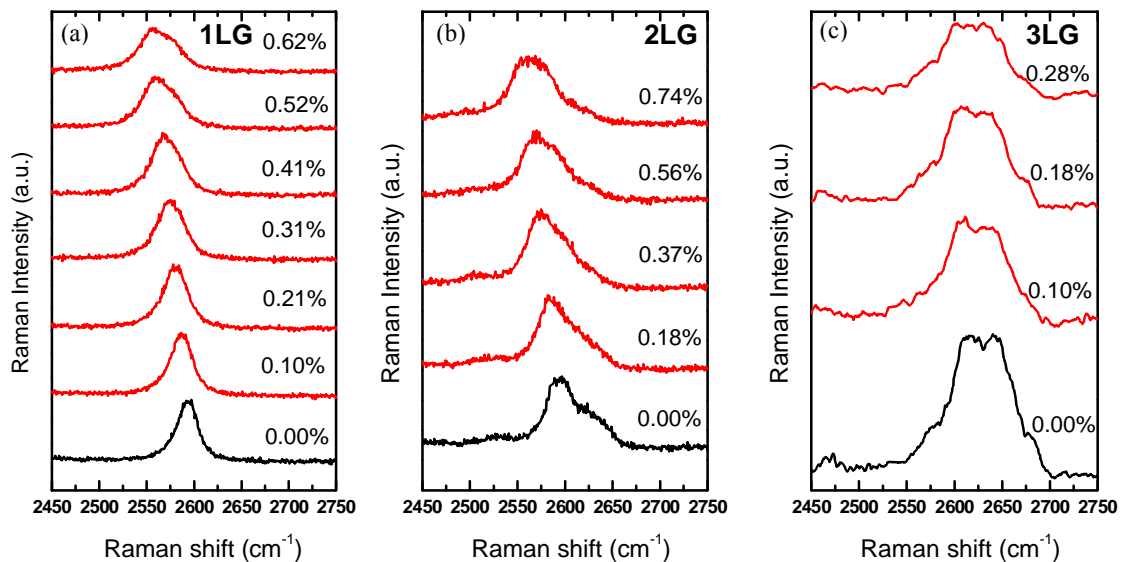
**Figure 2.** Evolution of the G-mode Raman spectra as a function of the tensile strain for (a) 1LG, (b) 2LG and (c) 3LG samples, excited by 785 nm.

As can be deduced from the inset image in fig. 1c, the examined 3LG sample was part of a flake in which one part is comprised of a single layer, whereas on the other part two more graphene layers are overlaid forming the 3LG. The level of tensile strain on the 3LG was is determined using the adjacent 1LG as a strain sensor. It was found that the maximum applied strain was around 0.3%, and thus the G band strain sensitivity of the 3LG is found to be -11 cm<sup>-1</sup>/‰ (Table 1). Splitting of the G band at high strains was not observed due to the low level of maximum applied strain; however, the band broadens by about 20% at 0.28‰ of the applied strain. It is worth noting here that the mean values of the strain sensitivities,  $\partial \text{Pos(G)}/\partial \epsilon$ , of 1LG and 2LG graphenes are quite similar of about -20.6 and -22.5 cm<sup>-1</sup>/‰, respectively. However, the mean G band strain sensitivity value of 3LG is almost half (-11 cm<sup>-1</sup>/‰, Table 1) of the corresponding values of 1LG and 2LG. Similar experimental results have been reported by Nicolle et al. [11] for graphene samples biaxially deformed at high pressures. 1LG and 2LG samples exhibit similar values for the G band pressure sensitivity, while in 3LG sample the corresponding values drop to a value close to that of graphite.

Sample	$\partial \text{Pos(G)}/\partial \epsilon$ [cm <sup>-1</sup> /‰]		$\partial \text{Pos(2D)}/\partial \epsilon$ [cm <sup>-1</sup> /‰]
	G <sup>+</sup>	G <sup>-</sup>	
1LG	-9.9	-31.3	-48
2LG	-10.9	-34.0	-49
3LG	-11		-31

**Table 1** Summary of strain sensitivities for G and 2D Raman bands in 1LG, 2LG and 3LG

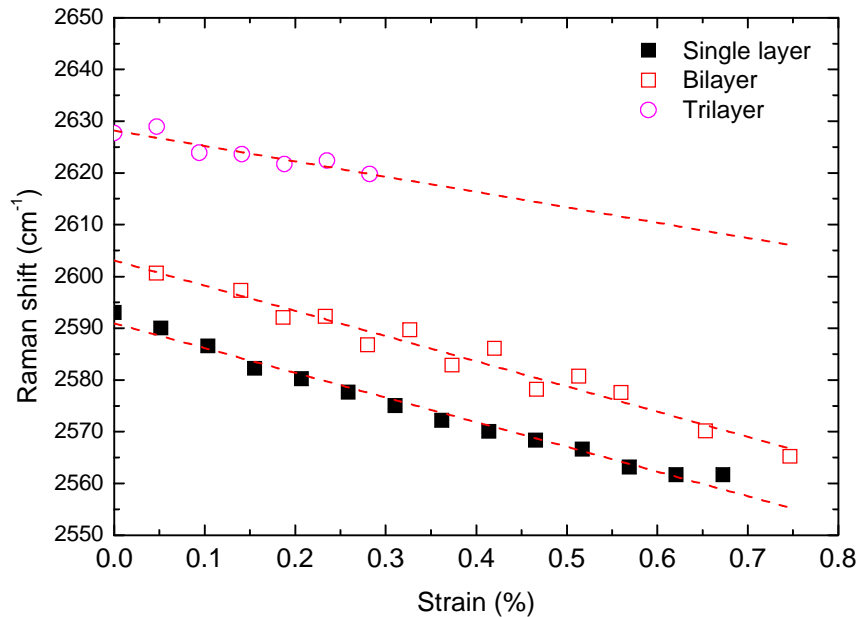
The strain evolution of the 2D Raman band for the 1LG, 2LG and 3LG are shown in Fig.3. In agreement with recent observations [6-7] there is a clear splitting in the monolayer 2D peak (Fig.3a). The origin of this splitting is explained elsewhere [6-7]. Commenting on the 2D band shapes of 2LG and 3LG samples (Figs. 3b-c), it seems that the higher the strain level, the more symmetric the band shape becomes. This behaviour is due to the strain-induced changes in the complex electronic band structure of both 2LG and 3LG samples.



**Figure 3.** 2D-mode Raman spectra strain evolution of (a) 1LG, (b) 2LG and (c) 3LG samples, excited by 785 nm.

For comparative reasons, the 2D bands of the examined samples are also fitted by a single Lorentzian peak and the corresponding mean strain sensitivities were calculated. The mean 2D peak positions as a function of strain are presented in Fig. 4 and the mean strain sensitivities,  $\partial\text{Pos}(2D)/\partial\varepsilon$  are summarized in Table 1. It is found that the 2D band strain sensitivities of 1LG and 2LG samples are quite similar of about  $-49 \text{ cm}^{-1}/\%$ . On the other hand, the 3LG appears with a significantly lower sensitivity of  $-31 \text{ cm}^{-1}/\%$ . Although, the range of tensile strains used in the deformation of the 3LG sample seems inadequate for this comparison, the results are in consistency with the work of Gong et al. [12]. Since 3LG is covered with a thin polymeric film, an inefficient adhesion between polymer and the 3LG might be a reasonable explanation of the measured low values of the mean strain sensitivities of both bands.

Besides, the additional graphene layer in 3LG may also reduce shear interlayer interactions resulting in inefficient strain transfer between the layers and thus lower strain rates. Gong et al [12] applied a shear transfer model in the case of polymer coated many-layer graphene flakes [13]. This model is completely analogous to the efficiency of stress transfer between the different walls in multi-walled carbon nanotubes (MWNTs) and has been used to successfully model stress transfer between the outer and inner walls of double-walled carbon nanotubes (DWNTs) in a nanocomposite [14]. The imperfect interface bonding between graphene layers is described by the stress transfer efficiency factor  $k$  that allows variable bonding strength between the layers. The limited cases corresponding to perfect ( $k = 1$ ) and no shear transfer ( $k = 0$ , full slip). The model shows that coated bilayer behave like monolayer graphene regardless of the  $k$  value; the  $\partial\text{Pos}(2D)/\partial\varepsilon$  is the same for both samples in close agreement with the results of this work. Surprisingly, the model shows  $[\partial\text{Pos}(2D)/\partial\varepsilon]_{3LG} = 2/3 [\partial\text{Pos}(2D)/\partial\varepsilon]_{1LG, 2LG} = 32 \text{ cm}^{-1}/\%$  for  $k$  almost zero (absence of stress transfer). As can be seen in Table 1, the aforementioned sensitivity value is in excellent agreement with the predicted one. It is worth mentioning here that past work on a thin graphite crystal produced by mechanical exfoliation [7] has confirmed efficient stress transfer in tension. and thus the above model does not seem to be applicable in that particular case. Intensive experimental work is currently in progress to gain a better insight in these results.



**Figure 4.** The 2D Raman band peak position as a function of tensile strain for 1LG, 2LG and 3LG graphenes. The 2D bands were fitted by a single Lorentzian component.

#### 4 Conclusions

In summary, we present a systematic uniaxial deformation Raman study of 1LG, 2LG and 3LG graphene samples embedded into a polymer matrix, using laser energies in the near-IR. Our experimental findings show that tensile strain sensitivities of 1LG and 2LG samples are similar for both G and 2D bands. On the contrary, the corresponding values for both bands in 3LG sample drops to significantly lower values. These results can be used to quantify the amount of uniaxial strain in single and multilayer graphene, providing a fundamental tool for graphene based nanocomposites.

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