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Graphene under direct compression: stress effects and interlayer coupling

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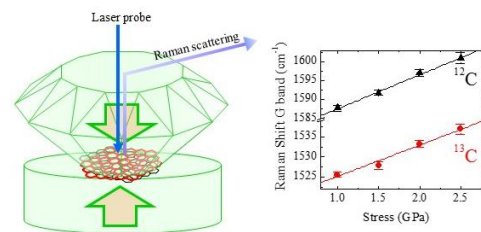
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In this work we explore mechanical properties of graphene samples of variable thickness. For this purpose, we coupled a high pressure sapphire anvil cell to a micro-Raman spectrometer. From the evolution of the G band frequency with stress we document the importance the substrate has on the mechanical response of graphene. On the other hand, the appearance of disorder as a consequence of the stress treatment has a negligible effect on the high stress behaviour of graphene.



Isotopic labelled twisted bilayer graphene under high compression characterized by Raman spectroscopy.

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1 Introduction Graphene has attracted great interest in the last decade due to its unique structure [1] which provides its fascinating mechanical and electrical properties [2]. Graphene is a zero gap semiconductor which also presents the greatest stiffness found in nature. Moreover, strain engineering of graphene has become a promising route for tailoring its electronic properties [3, 4]. Several approaches have been followed in order to induce strain in graphene [5-12], among which we can find high pressure experiments [9-12]. In most of these studies Raman spectroscopy is chosen as the main characterization technique since it represents a non-destructive tool for in-situ strain sensing, which also allows to address doping effects [13, 14]. Concerning the high pressure experiments, we find several studies of graphene in the literature, including samples prepared by exfoliation on Si/SiO₂ [9, 10] and by chemical vapour deposition (CVD) on copper [11]. All of these studies have been performed under hydrostatic conditions, using various pressure-transmitting media, to assure the same stress acting along all directions. Furthermore, some studies have been reported for suspended few-layers graphene flakes [12]. A comprehensive analysis of the mentioned previous studies reveals that the compressibility of the substrate plays a key role in the mechanical response of graphene. In contrast, doping phenomena have no influ-

ence on the mechanical response of graphene, and do not affect the strain coefficients showed by the G Raman peaks of graphene [11]. In this work we perform direct out-of-plane compression on exfoliated and CVD graphene samples, all supported on sapphire discs. We study graphene samples of different thickness, ranging from mono to tri-layer. Additionally, we isotopically label graphene, so that the behaviour of individual layers can be addressed [15], shedding some light on the graphene-substrate and graphene-graphene interaction under compression.

2 Methods A set of graphene samples with different number of layers (1 to 3) were prepared by mainly two methods: mechanical exfoliation and CVD. Specifically, the labelled twisted bilayer graphene (tBLG) were prepared by CVD as single layer graphene samples of ¹²C and ¹³C (as described elsewhere [16]) and then sequentially transferred to a sapphire disc by the common PMMA transfer method [17]. The exfoliated samples on Si/SiO₂ with different number of layers were transferred to a sapphire disc by a dry transfer method [18]. The experimental setup consists of a gem anvil cell coupled to a Raman spectrometer (LabRAM HR from Horiba Jobin-Yvon). In order to perform direct out-of-plane compression we use a modified sapphire cell where one of the anvils is substituted by

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a sapphire disc containing the sample. In such conditions, the use of conventional stress marker is inadequate and the stress is estimated from the evolution of the Raman features of sapphire [19]. At each stress step single spectra or Raman maps (depending on the sample) were registered using an Ar/Kr laser working at 488.0 nm, keeping the power below 1 mW in order to avoid sample heating. We used a 50x objective which provides a laser spot on the sample of about 2 μm in diameter.

3 Results Sapphire-supported exfoliated bilayer graphene (see Methods) was subjected to direct out-of-plane compression, up to 4.5 GPa, and characterized with Raman spectroscopy; Figure 1 shows the evolution of the Raman spectrum with increasing non-hydrostatic stress. We present the spectral region from 1200 to 3000 cm^{-1} which includes the most intense Raman features of graphene, the D, G and 2D bands. As expected, in comparison with graphite compressed under identical conditions [20], the Raman spectrum blue-shifts and broadens with stress.

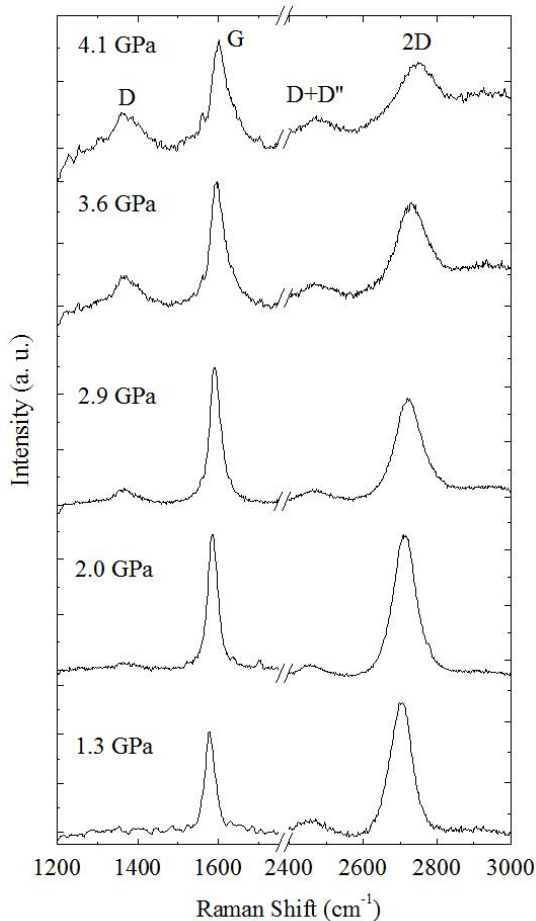


Figure 1 Selected Raman spectra of exfoliated BLG with increasing compression.

The same high stress experiments (up to 2.5 GPa) were performed on isotopically labelled tBLG samples. At each stress step of 0.5 GPa a Raman map in the same region of the sample was recorded. In Figure 2 we present selected Raman spectra measured in the same sample spot, corresponding to a random region with twist angle different from the critical angle of $\sim 13^\circ$ [21], thus with the 2D band as the most intense Raman contribution. In labelled tBLG we can distinguish two D, G, and 2D bands, originating from vibrations of the particular isotope [15]. The phonon frequency is inversely proportional to the atomic mass, therefore the Raman bands at lower frequency correspond to the ^{13}C isotope layer. Such a differentiation is highly advantageous since we can distinguish the effect of increasing stress on each layer and evaluate coupling effects in the graphene layers, between each other and with the substrate.

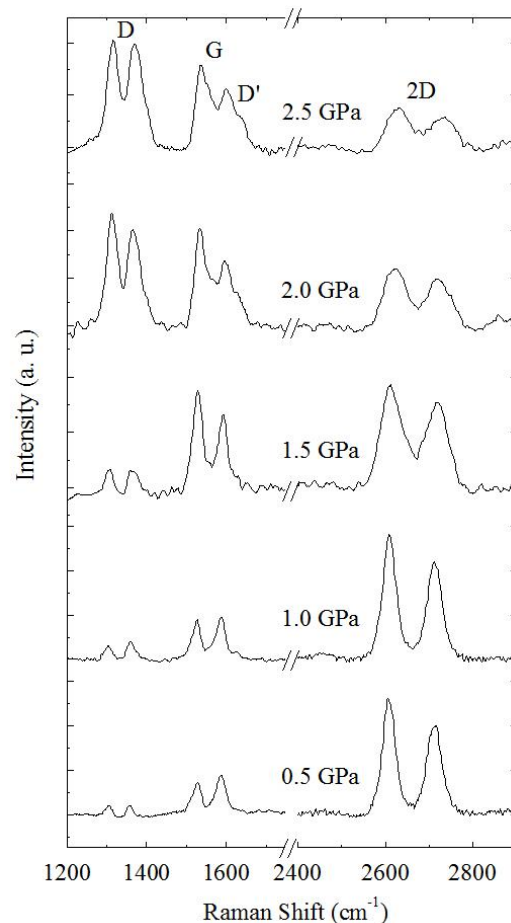


Figure 2. Selected Raman spectra of CVD labelled tBLG with increasing compression.

For both types of bilayer samples, i.e., exfoliated and CVD-grown, an increase of the intensity of defect related bands (D and D') is observed. Such increase of disorder

upon compression was observed in graphite and was related to the appearance of shear stresses [22]. A detailed analysis of the defects generation in the different samples, exfoliated and CVD, is shown later on, in Figure 4.

In analogy to exfoliated BLG, the spectrum of labelled CVD tBLG upshifts and broadens with stress. For the analysis of the stress response of the different graphene samples studied in this work we chose primarily the G band, since especially in bilayer samples, the 2D band could be prone to frequency changes depending on the twist angle [21]. Additionally, the Raman shift of the G band as a function of stress is usually employed as stress sensor and more data are available for the comparison [23].

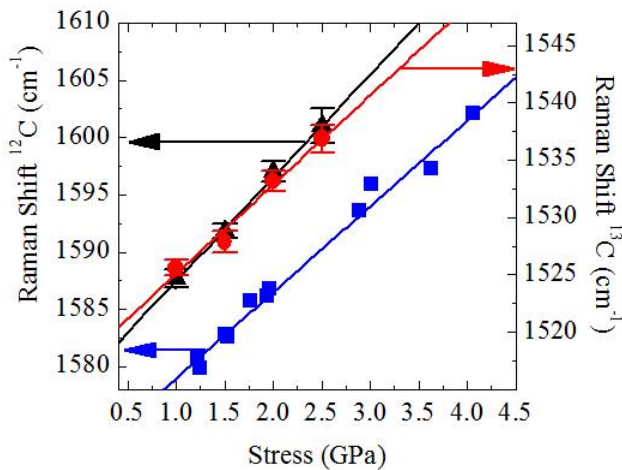


Figure 3 Raman shift of the G band as a function of stress for exfoliated BLG (blue squares) and for both graphene sheets in labelled tBLG (red circles and black triangles for the ^{13}C top and ^{12}C bottom layers, respectively).

We present the Raman shift of the G band with stress in Figure 3, for exfoliated BLG and for both graphene sheets in labelled tBLG. Additionally, the stress coefficients ($\delta\omega_G/\delta\sigma$) are reported in Table 1. We obtain a similar coefficient for the exfoliated BLG and the top layer of labelled tBLG; and a slightly higher coefficient is found for the bottom layer in the latter sample.

Table 1 Stress coefficients ($\delta\omega_G/\delta\sigma$) and frequency correlation between G and 2D bands ($\delta\omega_{2D}/\delta\omega_G$).

	$\delta\omega/\delta\sigma$ (cm $^{-1}$ /GPa)	$\delta\omega_{2D}/\delta\omega_G$
^{12}C (bottom)	9.0	2.0
^{13}C (top)	7.8	2.1
exfoliated	7.5	1.8

The expected $\delta\omega_G/\delta\sigma$ of a suspended graphene layer under hydrostatic conditions is about 5 cm $^{-1}$ /GPa [9]; however, we can find reported coefficients ranging from 5 to 10 cm $^{-1}$ /GPa, as summarized in Table 2 [9-12]. These different coefficients were obtained under hydrostatic conditions using differently supported samples (Si/SiO $_2$, Cu and suspended) and several pressure transmitting media, from argon to alcohols. The observed difference in the G band stress coefficient was at first wrongly attributed to the co-existence of doping and stress effects in the experiments. It is well known that the peak position of the G and 2D bands of graphene is affected by the type and amount of doping in the sample [13]; however, the pressure slope of the Raman bands frequencies is not affected by the initial or pressure-induced doping effects. Moreover, doping and strain effects can be distinguished using the 2D to G frequency correlation ($\delta\omega_{2D}/\delta\omega_G$), so that when only mechanical effects are present such correlation is expected to be 2.2 [13]. For both our experiments, the $\delta\omega_{2D}/\delta\omega_G$ slope is slightly lower than 2.2, thus indicating some doping effects, probably due to the presence of some remnant polymer or glue from the transfer or exfoliation process, respectively. However, as commented above, this fact does not affect the value of $\delta\omega_G/\delta\sigma$, and, by comparison with data in Table 2, we conclude that the stress response of graphene under direct out-of-plane compression is comparable to that under hydrostatic pressure (in supported samples).

Table 2 Reported pressure slopes of the G Raman band of graphene under hydrostatic compression, $\delta\omega_G/\delta P$.

Reference	$\delta\omega/\delta P$ (cm $^{-1}$ /GPa)
Proctor <i>et al.</i> [9]	5.0
Nicolle <i>et al.</i> [10].	7.6 – 10.5
Filintoglou <i>et al.</i> [11]	9.2 – 5.6
Soldatov <i>et al.</i> [12]	5.6 – 5.9

The differences found in the literature for the pressure slope of the G band can be understood taking into account two factors. First, the stress response of the substrate, since the compressibility of the substrate may affect the stress transfer to the graphene layer, as well as the adherence between sample and substrate [11]. And second, the interaction between graphene and the pressure medium could affect $\delta\omega_G/\delta P$, as it may increase under pressure and become as large as the graphene-substrate adherence, leading to a pressure response similar to that of suspended graphene (5 cm $^{-1}$ /GPa) [9]. In our experiments, we do not use pressure media and the samples (all of them supported by a sapphire disc) are subjected to out-of-plane compression along the perpendicular direction. For this reason, we should expect always a stress coefficient larger than for suspended graphene, since the sample is always sandwiched between sapphires and cannot experience any detachment during

the compression process. In agreement with that, our reported stress coefficients for the G band are in all cases larger than $5 \text{ cm}^{-1}/\text{GPa}$.

Let us now compare the stress response of each layer in labelled tBLG. We find a slightly different behaviour for the top and the bottom graphene layer; the top layer shows a lower stress coefficient, close to that of the exfoliated BLG. Note that the labelled tBLG is prepared by a sequential transfer process; in which the bottom layer is the first one transferred to the sapphire disc, while the top layer is transferred afterwards and therefore it is the one in contact with the sapphire anvil of the high pressure cell. Accordingly, we can expect a larger graphene-sapphire adhesion for the bottom layer than for the top layer. For a lower graphene-substrate interaction, we expect a smaller $\delta\omega_G/\delta\sigma$, closer to suspended graphene; thereby explaining the higher stress coefficient of the bottom layer in tBLG, 9.0 vs $7.8 \text{ cm}^{-1}/\text{GPa}$.

The stress coefficients reported in Table 1 were obtained in the stress range starting at 1 GPa. The reason for the higher onset of the fitting region is that the behaviour of $\delta\omega_G/\delta\sigma$ below 1 GPa, *i.e.* in the first stress step, differs from linear evolution. We found an anomalous shift of the G band at the first stage of compression, not reported before. In order to further analyse this phenomenon, we carried out a comparative study of graphene samples with 1 to 3 layers and compressed them in a low stress regime, up to 1 GPa. The Raman shifts of the G band for the different samples are presented in Table 3.

Table 3 Raman shift of the G band upon 1 GPa compression, for a set of 1 to 3 layers graphene samples.

sample	$\Delta\omega_G \text{ (cm}^{-1}\text{)}$
1L exfoliated	-0.1
1L CVD	-0.2
2L exfoliated	-1.1
2L CVD	-5.0
3L CVD	-7.0

Interestingly, in contrast to what one could expect, the G band of graphene down-shifts up to 1 GPa compression. Moreover, this down-shift is larger when increasing the number of layers in the sample; and when comparing a sample with the same number of layers, the mentioned downshift is larger for CVD samples than for the exfoliated ones. In the literature, the evolution of the G band frequency with the number of layers, from monolayer graphene to graphite, reveals an up-shift of the G band with the decreasing thickness [24]. The interaction between two graphene layers provokes a slight lattice expansion that leads to the G band frequency down-shift. According to

this and in view of the results presented in Table 3, we can diagnose that our pristine few layers samples consist of stacked individual layers with a weak interlayer interaction. Therefore, the initial stress application leads to an increase of the interlayer coupling and probably also to an increase of the substrate-sample coupling; so that the sample is not compressed until the applied stress exceed the 1 GPa threshold. Such effect is more pronounced in the case of CVD samples, since they may contain remnant polymer from the transfer method in between the layers, thereby manifesting a larger interlayer distance in the pristine state than exfoliated samples. Therefore, we observe that the first stages of compression increases the interlayer coupling, also expelling the polymer out of the sample.

Concerning the increase of disorder upon compression, the difference between the exfoliated BLG and the CVD tBLG samples is readily observed by comparison of Figures 1 and 2. In the case of the exfoliated sample, the generation of disorder as a consequence of the high stress treatment is less severe than for the labelled sample. For a more detailed analysis, in Figure 4 we present the intensity ratio between the D and the G bands, I_D/I_G , as a function of increasing stress. The Raman spectrum of exfoliated BLG before the compression cycle shows no D band (indicating that no defects are generated during the transfer process). The creation of defects with stress starts above ~ 2.2 GPa and gradually increases up to 3.5 GPa, but I_D/I_G remains below 0.5 until the end of the experiment.

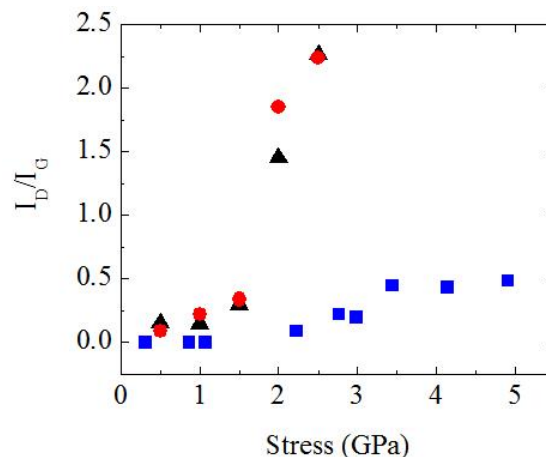


Figure 4 Intensity ratio between the D and the G bands as a function of stress for exfoliated BLG (blue squares) and for both graphene sheets in labelled tBLG (red circles and black triangles for the ^{13}C top and ^{12}C bottom layers, respectively).

For the CVD tBLG sample the observed behaviour is clearly different. The uncompressed sample shows some degree of disorder, probably originating during the transfer

process (note that in particular for this sample two sequential transfers are performed). During the first stages of compression, up to 1.5 GPa, the intensity of the D band slightly increases from 0.2 to 0.4; but when the applied stress surpasses the 1.5 GPa threshold, the intensity of the D band abruptly increases, becoming almost double the intensity of the G band. From 2.0 GPa the intensity of the D band continues increasing with stress but in a more moderate way, reaching the I_D/I_G intensity ratio of ~ 2.5 . However, it is interesting to note that despite the formation of defects is different for both the exfoliated BLG and the CVD tBLG samples, they present a similar stress behaviour with regards to the stress coefficient of the G band.

In summary, we have presented a high stress study of different graphene samples (exfoliated and CVD, isotopically labelled and of different thickness) in order to address some unknown aspects of the response of graphene to uniaxial out-of-plane stress. While the compressibility of the substrate plays a key role in the high pressure response, reflected in a modified stress coefficient of the G band, the interlayer and layer-substrate coupling effect is only visible at the first stages of compression, up to 1 GPa. Additionally, the doping state of the sample does not seem to have an effect on the mechanical response of graphene - in other words, the high stress shift rates of the Raman bands remain alike for the different specimens regardless the pronounced differences in the initial low stress behaviour. Finally, by comparison of the different studied samples in this work, we can conclude that the generation of defects upon compression does not affect the observed stress coefficient of the G band either.

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