Pressure-Mediated Doping in Graphene

Jimmy Nicolle, Denis Machon, Philippe Poncharal, Olivier Pierre-Louis, and Alfonso San-Miguel*

Université de Lyon, F-69000, France; Université Lyon 1, Laboratoire PMCN; CNRS, UMR 5586; F-69622 Villeurbanne Cedex

ABSTRACT: Exfoliated graphene and few layer graphene samples supported on SiO₂ have been studied by Raman spectroscopy at high pressure. For samples immersed on a alcohol mixture, an electron transfer of \( \partial n/\partial P \sim 8 \times 10^{12} \text{ cm}^{-2} \text{ GPa}^{-1} \) is observed for monolayer and bilayer graphene, leading to giant doping values of \( n \sim 6 \times 10^{13} \text{ cm}^{-2} \) at the maximum pressure of 7 GPa. Three independent and consistent proofs of the doping process are obtained from (i) the evolution of the Raman G-band to 2D-band intensity ratio, (ii) the pressure coefficient of the G-band frequency, and (iii) the 2D band components splitting in the case of the bilayer sample. The charge transfer phenomena is absent for trilayer samples and for samples immersed in argon or nitrogen. We also show that a phase transition from a 2D biaxial strain response, resulting from the substrate drag upon volume reduction, to a 3D hydrostatic compression takes place when going from the bilayer to the trilayer sample. By model calculations we relate this transition to the unbinding of the graphene–SiO₂ system when increasing the number of graphene layers and as function of the surface roughness parameters. We propose that the formation of silanol groups on the SiO₂ substrate allows for a capacitance-induced substrate-mediated charge transfer.

KEYWORDS: Carbon, graphene, Raman spectroscopy, strain sensors, high pressure, piezoelectric actuator

Graphene\(^{1-4}\) raises an increasing interest due to its unusual electronic properties,\(^{2-6}\) for its extraordinary membrane-type mechanical response,\(^{4,7-12}\) or its electromechanical response.\(^{13}\) Pressure application continuously modifies the interaction of low-dimensional systems with its environment,\(^{14}\) which in the case of supported graphene under hydrostatic pressure\(^{15}\) are the pressure transmitting medium (PTM) and the substrate on which graphene lays. Because of the weakness of the interlayer van der Waals interactions, the in-plane elastic properties of graphene have been proposed to be directly transposed from the graphite ones as confirmed by a number of experiments and calculations.\(^{16-18}\) Moreover, the interaction of graphene with a rough probe surface also the out-of-plane elastic behavior. It has been shown that graphene can conform to high rough surfaces down to subnanometric features with nearly 99% fidelity.\(^{19}\) This situation allows for very strong substrate–graphene interactions that can be additionally increased by pressure through a double mechanism: substrate–graphene distance reduction and substrate shrinkage haul of the carbon system.\(^{15}\) With an increasing number of layers, the carbon-based membrane is expected to rigidify and a modification of this scenario seems plausible. Exploring the high-pressure behavior of different number of graphene layers supported by SiO₂-covered substrates appears then as an appealing method to probe both the graphene–substrate interactions and the elastic properties of the graphene system.

Using Raman spectroscopy, a powerful tool for graphene and carbon nanotube studies,\(^{20}\) we have studied the pressure-induced evolution of exfoliated samples with a number of graphene layers, \( n = 1, 2, \) and 3 supported on silica-coated silicon substrates. Samples were loaded in a diamond anvil cell (Figure 1a) up to a maximum pressure of 7.0 GPa using three different pressure transmitting media (PTM): a standard mixture of (4:1) methanol/ethanol, nitrogen, and argon. In Figure 2 is shown the pressure evolution of the graphene and bilayer graphene Raman spectra under pressure in the alcohol mixture PTM.

Spectra obtained on trilayer samples or for the other PTM were of similar quality. We appreciate at ambient pressure the G and 2D bands of these two samples. The 2D band allows the identification of the number of layers\(^{21,22}\) (Figure 1b). These Raman bands can be distinctly followed under pressure, but the additional signal from the diamond anvils or from the PTM need to be taken into account in the fitting protocol as shown in Figure 2. The distinct pressure evolution of these two bands as function of the number of graphene layers or the PTM will constitute the key experimental information.

With increasing pressure, we observe in all cases an expected blue shift of the G band which is linear with the applied pressure (Figure 3a). The pressure-induced evolution is reversible except for a partial peak broadening. Values of the linear coefficients, \( \partial \omega_{G}/\partial P \), are plotted (Figure 3b) as a function of the number of layers. The most striking result is that the monolayer and bilayer samples show similar values of \( \partial \omega_{G}/\partial P \) and that a sudden drop takes place at \( n = 3 \), which adopts a value close to graphite.

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To understand the origin of such differences, let us consider the mechanical response of graphene. The pressure induced biaxial hydrostatic strain ($\epsilon$) in the plane, which will modify the G-band frequencies, can be related to the applied stress ($\sigma$) by the compliance tensor $S_{ij}$, as $\epsilon_{ij} = 2S_{ij} \sigma$ if we consider a pure biaxial compression or $\epsilon_{ij} = 2(S_{11} + S_{12} + S_{13})\sigma$ if we consider the effect in the biaxial compression of the c-axis interaction. Furthermore, it is possible to calculate the G band shift as a function of applied biaxial stress using the relation$^{23}$ $\omega_{G} - \omega_{0} = A \epsilon \omega_{0}$ with $\omega_{0}$ and $\omega_{G}$ the position of the G band, respectively, at ambient pressure and at a given pressure and the $A$ parameter derived from the data obtained by Blakslee et al.$^{24}$

We can then calculate the G band pressure derivative in case of pure biaxial compression ($\epsilon = \epsilon_{2D}$). We obtain, $\partial \omega_{G}/\partial P = 7.4$ cm$^{-1}$ GPa$^{-1}$ in close agreement with our obtained values for $n = 1, 2$ in argon and nitrogen PTM. We then apply this model for graphite by placing $\epsilon = \epsilon_{2D}$. The calculated pressure slope is then $\partial \omega_{G}/\partial P = 4.4$ cm$^{-1}$ GPa$^{-1}$, which is close to graphite values in literature and to our values measured for graphite and trilayer graphene samples (see Figure 3b). The observed transition at $n = 2$–3 is then well explained as a transition in the mechanical response of graphene from biaxial compression to hydrostatic compression. We note here that for graphene ($n = 1$) in argon PTM we find $(\partial \omega_{2D}/\partial P)/(\partial \omega_{G}/\partial P) = 2.8$, that is, exactly the same value that can be obtained from the data of Ding et al.$^{10}$ for biaxially strained graphene using piezoelectric actuators.

In order to investigate more precisely the observed change in graphene mechanical response with the number of layers, we can consider the adhesion potential of a membrane (the graphene plane) on a rough surface that can be quantified by comparing surface roughness, adhesion energy, and bending rigidity modulus of the membrane. The morphology of supported graphene on a rough substrate results from a competition between adhesion forces, which are minimized when the graphene shape perfectly follows that of the substrate, and the elastic cost of graphene shape changes, which are minimized when graphene is perfectly flat. This competition, which has been addressed in detail in ref 25, results in a complex sequence of partial unbinding transitions. Following ref 25, the unbinding transition depends on a single dimensionless parameter ($\alpha$), which compares the typical curvature of our substrate with the adhesion equilibrium curvatures of the graphene layers. We consider that the main contribution to the elastic energy of graphene is bending, and we neglect the contributions related to in-plane strain. The unbinding transition then depends on a single dimensionless parameter $\alpha = (k_{ad}/k_{eq})^{1/2}$, where $k_{ad}$ is the typical substrate curvature, and $k_{eq} = (2y_{n}/C_{n})^{1/2}$ is the adhesion equilibrium curvature, with $y_{n}$ and $C_{n}$ respectively, the multilayer graphene adhesion energy on SiO$_2$ and the bending rigidity. Considering typical values given for the accurate determination of the roughness of an SiO$_2$ surface,$^{19}$ perfect adhesion is expected for $\alpha > 0.8$–0.86, and partial unbinding starts for $\alpha < 0.8$–0.86 (0.8 for sharp needlelike patterns, and 0.86 for smooth sinusoidal patterns). We plot the evolution of ($\alpha$) parameter versus the number of graphene layers (see Figure 4), and we obtain that the transition between perfect adhesion everywhere along the surface and partial or total unbinding appears to take place precisely between the bilayer and the trilayer sample. As a consequence, the carbon-layered system goes from the biaxial compression through the substrate for $n \leq 2$ (surface adhesion) to the hydrostatic compression by the PTM for $n \geq 3$ (insufficient adhesion). This transition represented graphically in Figure 2b and Figure 4 could then be dependent on the type of surface and of its roughness characteristics (for more information about calculation see Supporting Informations).

Let us turn now to the particular values of $\partial \omega_{G}/\partial P$ in the alcohol experiment (Figure 3b). Strong n-doping effects of systems...
having alcohol radicals interacting with sp² carbon materials have been already reported. The relation between doping and both the G-band position and the ratio of intensities of the 2D- and G-bands have been well characterized for \( n = 1 \) and \( n = 2 \) samples. We plot the relative pressure evolution of the \( \frac{I(2D)}{I(G)} \) ratio for \( n = 1, 2 \) in Figure 5a both for argon and alcohol PTM. For \( n = 2 \) for which 4 peaks are needed to describe the 2D band, we take the full integrated intensity. Argon is not expected to induce any doping and in fact \( \frac{I(2D)}{I(G)} \) does not evolve significantly. We have used the measured values of \( \frac{I(2D)}{I(G)} \) and their pressure evolution to quantify both the initial doping values at the pressure cell loading (some kbars) and to calculate the doping rate with pressure. The origin of the initial doping could be associated to the samples alcohol cleaning protocol. At these doping levels, following Das et al., \( \frac{I(2D)}{I(G)} \) evolves linearly with pressure both with increasing p- or n-type doping. We obtain much more consistent results considering n-type doping, which is in good correspondence with other observations. We find an electron initial doping at loading conditions of \( \sim 7 \times 10^{12} \text{ cm}^{-2} \) both for \( n = 1 \), \( n = 2 \) independently of the used PTM. We obtain a doping rate with pressure of \( \frac{\partial n}{\partial P} \sim 8 \times 10^{12} \text{ electrons cm}^{-2} \text{ GPa}^{-1} \), both for the mono- and bilayer samples in alcohol. The value of \( \frac{\partial n}{\partial P} \) can be neglected within error bars for samples immersed in argon or nitrogen. In the doping domain here observed, the G-band frequency linearly increases with charge injection, and we can then evaluate the associated contribution of doping to \( \frac{\partial \omega_G}{\partial P} \). As it is shown in Table 1, this contribution is of \( \sim 3.5 \text{ cm}^{-1} \text{ GPa}^{-1} \) and corresponds perfectly to the observed difference between \( \frac{\partial \omega_G}{\partial P} \) in alcohol and argon PTM (Figure 3b), providing a cross-check of the pressure doping effect.

**Figure 2.** Evolution with pressure of the Raman signal of (a) monolayer and (b) bilayer samples immersed in a mixture of (4:1) methanol/ethanol using a red laser (\( \lambda = 647.1 \text{ nm} \)) as excitation light. The blue areas show the G band (\( \omega_G = 1580 \text{ cm}^{-1} \) at ambient pressure) and the 2D band (\( \omega_{2D} = 2680 \text{ cm}^{-1} \) at ambient pressure), and the red areas show the additional signal due either to the PTM (i) or to the second order Raman active band of diamond (ii) diamond (not visible) due to the sample environment. These bands have also been taken into account on fitting as presented under each spectra with the blue lines corresponding to the sample Raman signal. The fitting process is shown for both G and the 2D graphene bands, using for the 2D-band one component for the single layer sample and four components for the bilayer sample. All sample peaks shift to higher energies with pressure application.
For the \( n = 2 \) case, the doping effect can even be confirmed when considering the relative pressure evolution of the four 2D-band Raman components (Figures 2 and 5b). There is no additional pressure-induced splitting of these modes for argon PTM, while there is a progressive splitting in alcohol PTM, which has been predicted as having its origin on doping.30

For the \( n = 3 \) sample, a detailed analysis of the small differences between the measured values of \( \partial \omega_G / \partial P \) in the different PTM and their proximity to the graphite ones, allow us to bound the doping effect to values at least two times smaller than for \( n = 1, 2 \). The mechanical transition between \( n = 2 \) and \( n = 3 \) from a biaxial to a hydrostatic response associated to graphene–substrate unbinding is then concomitant with a reduction of charge injection.

All these observations allow us to propose that the electron charge injection observed in alcohol-immersed samples takes place through the SiO\(_2\) substrate as it has been observed for O\(_2\) or H\(_2\)O.21 This is reinforced by the fact that both the initial doping

\[ \frac{\partial \omega_G}{\partial P} = \frac{\gamma_1 \alpha}{\kappa_g} \]

values of the \( n = 1, 2 \) samples and their pressure derivatives are the same. This is consistent with a one-layer charge transfer process.

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**Figure 3.** Evolution of the Raman G-band position with pressure for different number of graphene layers (\( n \)) and different pressure transmitting media. (a) G-band frequency for \( n = 1, 2, \) and 3 immersed in alcohol. The solid line is the measured evolution under pressure for graphite, and the dotted lines are the linear fit of graphene data. The inset shows the evolution of the monolayer G band loaded in alcohol mixture during a pressure cycle. (b) Summary of the G band pressure linear coefficients obtained in alcohol (red squares), argon (blue circles), and nitrogen (green triangle) depending on the number of layers (\( n \)). Two effects are illustrated in the figure and discussed in the article: (i) a change of behavior between \( n = 2 \) and \( n = 3 \) due to a modification of the sample—substrate binding as illustrated by the inserts and (ii) an electron doping process observed in the \( n = 1, 2 \) samples immersed in alcohol, which is highlighted by the red arrows.

**Figure 4.** Dimensionless parameter \( \alpha \) as a function of \( n \). The red (empty) and the blue (filled symbols) symbols respectively represent the results with \( \kappa_g = 0.3 \) nm\(^{-1}\), and \( \kappa_g = 0.4 \) nm\(^{-1}\). Triangles and circles correspond to \( \gamma_1 = 0.6 \) eV·nm\(^{-1}\), and \( \gamma_2 = 0.5 \) eV·nm\(^{-2}\). Unbinding is expected to occur in the vicinity of the shaded area between \( \alpha = 0.8 \) and \( \alpha = 0.86 \).

**Figure 5.** Doping effect on the Raman signal. (a) Relative evolution with pressure of the ratio of the intensities of the 2D and G Raman peaks. The closed symbols are used for the monolayer samples and the opened symbols for the bilayer samples, loaded in mixture of alcohol (black squares) and in argon (red triangles). These ratios have been quantified as doping dependent.28 (b) Pressure evolution of the bilayer 2D-band components in alcohol (b1) and in argon (b2). The different colors correspond to the four different components of the bilayer 2D band.21 The observed splitting in alcohol has been predicted as originated by doping.30
The formation of silanol groups (Si–O–H) on the surface of oxidized silicon substrates, which has been proposed as a potential source of charge injected through the surface in carbon nanotubes, could then be here at the origin of the observed doping in graphene. The pressure linear evolution of such charge injection could be associated to a capacitive mechanism, which is in correspondence with the expected approximate linear evolution of the van der Waals driven evolution of the graphene–SiO₂ distance. At our maximum pressure of 7 GPa, the observed doping corresponds to a Fermi level shift close to 1 eV (1.4 eV in the Dirac cone approximation). On the basis of the observed mechanism, it is possible to conjecture about the development of strain sensors based on contacted graphene immersed in selected fluids.

### Associated Content

#### Supporting Information

Description of experimental methods, samples preparation, high pressure apparatus, Raman spectra under high pressure of the different samples, and the development of the theoretical model. This material is available free of charge via the Internet at http://pubs.acs.org.

#### Author Information

**Corresponding Author**

*E-mail: alfonso.san.miguel@univ-lyon1.fr*

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#### References