

Effect of layer number and layer stacking registry on the formation and quantification of defects in graphene



Sara D. Costa, Johan Ek Weis, Otakar Frank, Martin Kalbac*

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, CZ-18223 Prague 8, Czech Republic

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ABSTRACT

Correct defect quantification in graphene samples is crucial both for fundamental and applied research. Raman spectroscopy represents the most widely used tool to identify defects in graphene. However, despite its extreme importance the relation between the Raman features and the amount of defects in multilayered graphene samples has not been experimentally verified. In this study we intentionally created defects in single layer graphene, turbostratic bilayer graphene and Bernal stacked bilayer graphene by oxygen plasma. By employing isotopic labelling, our study reveals substantial differences of the effects of plasma treatment on individual layers in bilayer graphene with different stacking orders. In addition Raman spectroscopy evidences scattering of phonons in the bottom layer by defects in the top layer for Bernal-stacked samples, which can in general lead to overestimation of the number of defects by as much as a factor of two.

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1. Introduction

The mechanical and electronic properties of perfect graphene layers are well described; however, defects are commonly found in real graphene samples. As defects are highly reactive sites, they can be useful for sensing applications [1,2], and for the functionalisation of graphene [3]. Consequently, an increase of the number of defects in graphene can be required. However, the creation of new defects should be done in a controlled way. Disorder in graphene can be categorised into two regimes: a low-defect-density regime, in which sp^2 -bonded sites are converted into sp^3 bonding, and a high-defect-density regime, in which vacancies in the carbon network are created, eventually leading to the amorphisation of the material [4]. Several techniques can be employed to induce defects in graphene layers, such as ion bombardment [5,6], laser irradiation [7], or oxygen plasmas [8–10]. In particular, the oxygen plasma seems to be a favourable approach because oxygen plasma instruments are commonly found in laboratories and they are used to clean substrates, cure polymers or etch carbon layers. In addition, oxygen plasma treatments represent an easy, and potentially controllable, way to induce defects in graphene layers, as a set of parameters such as power, pressure and time of exposure can be varied.

Oxidation of graphene via oxygen plasma treatment has also been shown to be a practical way to achieve enhancement of the Raman signal [9] and to decrease graphene's hydrophobicity [11].

However, an important question is if the oxygen plasma treatment affects graphene monolayers and bilayers (Bernal stacked or not) differently. Bilayer graphene has been widely investigated as it has great potential to be used in field-effect transistors (FETs) because of a better control of the band-gap. McEvoy et al. [10], reported on oxygen plasma treatments applied to single layers of graphene and mentioned the presence of secondary islands, probably bilayers, that were more resistant to the creation of defects than the monolayer background. Nourbakhsh et al. [12], exposed Bernal-stacked bilayer graphene to an oxygen plasma treatment and observed that oxidised 2-LG retains its semimetallic nature, in opposition to defected 1-LG, but after strong plasma treatment the Raman spectra of the defected bilayers became similar to 1-LG. Investigation of the randomly stacked bilayers is equally important, because most chemical vapour deposition (CVD)-grown graphene is a mixture of bilayer grains stacked with different rotational angles [13]. In general, two Bernal-stacked (2-LG AB) layers behave alike, whereas turbostratic (2-LG T) layers can show a more individual behaviour. Although both top and bottom layers in Bernal-stacked graphene show a similar behaviour in the Raman spectrum, it is not clear whether their properties are in fact similar, or if it is an effect of phonon scattering. The stacking order of two graphene layers is known to influence the effective

* Corresponding author.

E-mail address: martin.kalbac@jh-inst.cas.cz (M. Kalbac).

Young's modulus [14], the behaviour of the graphene at high temperatures [15] and the functionalization of graphene, e.g. fluorination [16]. If plasma treatments affect 2-LG AB and 2-LG T bilayers differently, a more detailed study is essential.

In this work, we report on the investigation of oxygen-plasma-induced defects on bilayers of graphene, both turbostratic and Bernal stacked, and of monolayers as well, for comparison. The creation of defects on the top and bottom layers was also investigated, using graphene bilayers containing carbon isotopes (^{13}C in the bottom layer and ^{12}C in the top layer). High-resolution Raman mapping was used to obtain large data sets and to improve the accuracy of the results. The defects creation was found to be indeed dependent on the number of graphene layer and their stacking order. In addition we found that the relation between the Raman signatures of defects and the actual amount of defects is also significantly influenced by the presence of another graphene layer and by the stacking order of the graphene layers. This finding is crucial for correct quantification of the number of defects in multi-layered graphene samples based on the Raman spectroscopy data.

2. Experimental

The graphene layers were grown by CVD on Cu foil. Briefly, the Cu foil (1600 mm², 127 μm thick, 99.9%, Alfa Aesar) used in the growth was placed in the centre of a furnace, heated to 1273 K and then annealed for 20 min under flowing H₂ (99.9999%, Messer), 50 standard cubic centimetres per minute (sccm). 5 sccm of CH₄ (99.9995%, Messer) was then introduced for another 30 min. Afterwards, the samples were annealed in H₂ for 5 min and then cooled from 1273 to 273 K, under a H₂ flow. The pressure was kept at 0.35 Torr during the whole process. The isotopically labelled graphene samples were obtained following a similar procedure, using ^{12}C CH₄ first and then ^{13}C CH₄ (99.5 atom %, Sigma-Aldrich), as described in Ref. [17]. In brief, Cu foil used in the growth was placed in the centre of a furnace, heated to 1273 K and then annealed for 20 min under flowing H₂ (50 sccm), then ^{12}C CH₄ was introduced first for 90 s, to grow a continuous single layer of graphene. Afterwards, the ^{12}C CH₄ flow was stopped and ^{13}C CH₄ was introduced for 30 min. Subsequently, the graphene was transferred onto SiO₂/Si substrates via poly(methyl methacrylate) transfer, as described elsewhere [18]. The graphene samples were then placed inside the chamber of the oxygen plasma etcher (PICO, Diener Plasma-Surface Technology, Germany). To find the optimal parameters, the plasma treatment was repeated several times using different pressures and plasma powers. After determining the most suitable parameters, the procedure was as follows. The chamber was first pumped out and then filled with O₂. When the set pressure was reached (0.80 mbar), the plasma was turned on (200 W), for 4 s. Afterwards, the plasma chamber was purged. The procedure was repeated several times on the same sample, until an 88 s total time of plasma exposure was reached. Between each plasma treatment, thus every 4 s of plasma treatment, Raman maps were acquired. The Raman maps were acquired using a WiTec Alpha300 spectrometer, equipped with a 532 nm laser and a 50 \times objective. Each Raman map contains 625 spectra. To ensure an accurate comparison between the different maps, the analysed areas were always identical. The fits of the Raman features were performed using Lorentzian lines.

3. Results and discussion

3.1. Effects of plasma exposure on the creation of defects

A plasma originates in a partially ionized gas in an electrically quasi-neutral state. When an electrical current is passed through a

gas, the gas breaks down to form a plasma, which is ionized, interacting with any surface exposed to it. Thereby, subjecting a graphene layer to an oxygen plasma treatment, even for times as short as one second, introduces oxygen-containing functional groups to the carbon lattice, affecting its electronic structure. Strong oxygen plasma treatments (high plasma powers, e.g. 1000 W, or long exposure times) are known to have adverse effects on graphene's mechanical and electronic properties [4,19]. Therefore, in the study reported here, a relatively low plasma power (200 W) has been used. To confirm that no visible damage is inflicted in the graphene layers, the samples were observed with an optical microscope, before and after plasma treatment, and no visible tearing or damaging was observed (see Fig. S2 in the supporting information). The effects of oxygen plasma treatments can, however, easily be followed via Raman spectroscopy, as the introduction of functional groups generates modifications in the sp² lattice of graphene, i.e. defects. As the disorder increases, the Raman spectrum of graphene evolves into a more intense D band, higher D/G area ratios, and broader peaks in general [20]. Fig. 1 presents Raman spectra of 1-LG, 2-LG AB and 2-LG T graphene before (0 s) and after 88 s of plasma treatment obtained from the same area of the sample. For as-grown graphene, before the plasma treatment, the G band is found in the Raman spectra at $\approx 1590\text{ cm}^{-1}$, while the 2D band is observed at $\approx 2690\text{ cm}^{-1}$ (measured at 2.33 eV). In addition, the D band, found at $\approx 1345\text{ cm}^{-1}$, is a defect-dependent Raman feature [20], which increases after the sample is exposed to the plasma. Moreover, for defected samples, a low-intensity band, the D' band, can be observed at about 1620 cm^{-1} . For highly defected graphene layers, the D' band may merge with the G band, resulting in a single broader band around 1600 cm^{-1} . For mild plasma treatments such as the ones reported here, the D' band is only detectable at longer exposure times.

Fig. 2a and b show the optical image and the 2D band full width at half maximum (FWHM) Raman map, respectively, of the analysed area in the graphene sample. Using a single sample containing 1-LG, 2-LG AB and 2-LG T is highly advantageous because it guarantees a more even treatment to all areas. However, it is also necessary to analyse the different areas separately. The 2D bandwidth varies according to the number of layers and the stacking order of graphene [20]. It is therefore a useful parameter to separate monolayer ($30\text{ cm}^{-1} \leq 2D_{\text{FWHM}} \leq 60\text{ cm}^{-1}$ for transferred CVD-

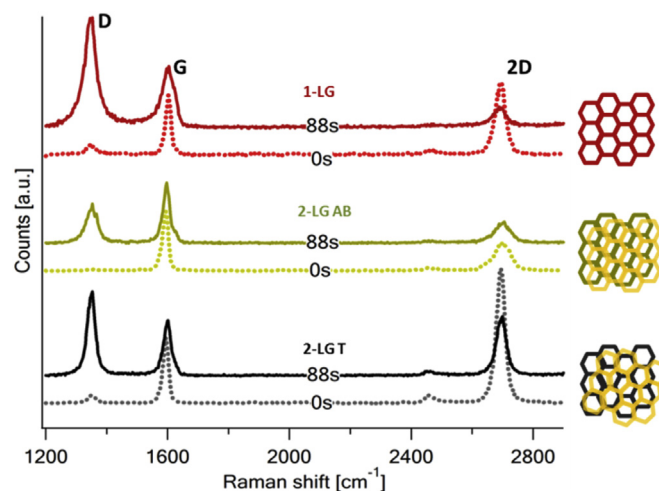


Fig. 1. Raman spectra depicting the main features (D, G and 2D bands) of 1-LG, 2-LG AB and 2-LG T, before and after oxygen plasma treatment. (A colour version of this figure can be viewed online.)

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