Journal of Molecular Structure 993 (2011) 506–509

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Ion beam induced defects in graphene: Raman spectroscopy and DFT calculations

Giuseppe Compagnini [a,*], Giuseppe Forte [a], Filippo Giannazzo [b], Vito Raineri [b], Antonino La Magna [b], Iannis Deretzis [b]

[a] Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, Catania 95129, Italy
[b] CNR-IMM, Strada VIII 5, Catania 95121, Italy

ARTICLE INFO

Article history:
Available online 23 January 2011

Keywords:
Graphene
Ion irradiation
Raman spectroscopy
Defects
DFT calculations

ABSTRACT

Defects in graphene sheets have been introduced by 500 keV C^+ ion irradiation and have been studied by Raman spectroscopy. We have found marked differences in the vibrational behaviour for the irradiation of single layers, bilayers and multilayers which have been assigned to differences in the formation and evolution of damage. DFT calculations performed on circumcoronene monomer and its parallel dimers and trimers are in excellent agreement with the experimental results suggesting that graphitic islands of dimension comparable with circumcoronene can be obtained after the irradiation. The experimental and calculated Raman spectra have shown a blue shift of the D line by adding a second and a third layer to single layer graphene. This has been attributed to the energy interaction between the planes.

1. Introduction

Carbon nanomaterials are becoming day by day much more important for basic science and applied technology [1]. It is possible to obtain in a controlled way structures such as wires, tubes and sheets of arbitrary form and nearly arbitrary extension. In particular graphene, a two-dimensional (2D) sheet of carbon atoms arranged in a honeycomb lattice, attracted recently a huge scientific interest, due to its outstanding transport properties, chemical and mechanical stability and to the scalability of graphene devices to nano-dimensions [2,3].

Moreover the effect of disorder on the vibrational and electronic properties of graphene is a fundamental step on the way towards the application of graphene as thin membrane for ion beam analysis in volatile systems which cannot be put in high vacuum required for the operation of ion beams [4].

The intentional/unintentional presence of those defects strongly affects the electronic transport properties of graphene devices [3]. For these reasons, the controlled introduction of defects in graphene can be used to tailor physical, chemical and mechanical properties [5].

We have already shown that ion irradiation in the hundreds keV regime is a suitable tool to introduce gradually controlled amount of defects and isolate single graphitic domains with extension in the nanometer range [6]. This has been essentially monitored by Raman spectroscopy. Since the novelty about the irradiation of graphene consists in the damaging of a one-atom thick material, we compared the irradiation effects on a single layer with those observed for two or more layers, suggesting differences and analogies between the various cases.

In this paper we have considered these results as a starting point to compare experimental data with molecular simulations of Raman spectra of single and multilayer defected graphene. In general graphene can be thought as the limiting case of an infinitely large cluster of benzene rings. Planar polycyclic aromatic hydrocarbons (PAHs) with only benzenoid hexagonal rings can be viewed as fragments of graphene sheet with the external carbons saturated with hydrogen, and thus providing a suitable molecular model of graphene sheets. It is to note that the Raman spectra of PAHs show D and G bands strictly correlated to the ones observed in disordered graphite and defected graphene [7–9]. This feature is due to the similarity of the PAHs structure with graphitic/graphenic islands arising from defects; therefore we consider PAH molecules as models for confined portion of single and multilayer defected graphene, obtained by means of ion irradiation. In this sense, strong similarities are expected when Raman spectra of PAHs are compared to the ones shown by sp^2 carbon domains of comparable dimensions.

In this study, to mimic graphene single sheet, we have considered a PAH with D_{6h} symmetry, the circumcoronene, which is a coronene surrounded by another series of benzene rings, for a total of 19. Circumcoronene monomer was used to construct parallel dimers as models for graphene bi- and tri-layers, by using the geometrical disposition described in the Section 2.2.

---

[*] Corresponding author at: Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, Catania 95129, Italy. Tel.: +39 095 7385077, fax: +39 095 580138.

E-mail address: gcompagnini@unict.it (G. Compagnini).

0022-2860/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2010.12.065

2. Experimental section and calculation details

2.1. Ion irradiation and measurements

Few layers of graphene were obtained by micromechanical exfoliation of HOPG and deposited on a Si substrate coated with 100 nm thick thermal oxide. As-prepared samples were implanted with 500 keV C^+ ions at fluences up to 10^{14} ions/cm^2. Implants were carried out under high vacuum conditions (10^{-6} Torr) in order to minimize surface contaminations.

The incident ion beam releases energy to the graphene layer by direct collisions with lattice carbon atoms and by interaction with electrons in the sheets. For 500 keV C^+ ions incident on a single layer of graphene, the cross section of direct C^+–C collisions can be estimated as $\sigma \approx 1 \times 10^{-17}$ cm^2. Since the density of C atoms in graphene is $N \approx 4 \times 10^{15}$ cm^{-2}, the probability that a direct collision occurs, with the formation of a vacancy, is $N\sigma \sim 4 \times 10^{-2}$. Hence, the expected density of vacancies for ions fluences from 1×10^{13} to 1×10^{14} cm^{-2} is ranging from 4×10^{11} to 4×10^{12} cm^{-2}.

Both as-prepared and implanted samples were preliminarily inspected by optical microscopy, in order to identify the few layer graphene flakes, and, hence, by tapping mode atomic force microscopy using a DI3100 equipment by Veeco with Nanoscope V electronics. AFM analyses allowed the morphological characterization and the identification of the number of layers in the flakes without causing structural damage [6].

Raman spectra were measured both on as-prepared and irradiated samples preliminarily identified by AFM. The measurements were performed at room temperature with a Jobin Yvon spectrometer using a 633 nm exciting radiation (3 cm^{-1} resolution). A 100× objective is used. Extreme care is taken to avoid sample damage or laser induced heating. Measurements were performed at 1 mW incident power. No significant spectral change was observed in such a configuration. We also measured the reference bulk graphite used to produce the layers.

In Fig. 1, a typical optical image is reported representing a region in which single and multiple layers coexist. The identification and differentiation between the various regions has been done either by AFM or by micro-Raman investigation. In particular in Fig. 1 we also report a typical lateral resolution of the Raman microscopy indicated by gray spots.

2.2. Computational methods and models

The formation of graphene multilayers is mainly due to π–π interactions and the binding of the layers depends on the dispersion interactions which are pure electron correlation effects [10]. It is to note that wave – function – based methods which include the necessary electron correlation effects are either severe computationally demanding (e.g., single and double excitation coupled cluster) or are not accurate enough, overestimating the dispersion interaction (e.g., Møller–Plesset perturbation theory). In the last years Density Functional Theory (DFT) calculations, using generalized gradient approximation (GGA) functionals, together with empirical correction for dispersion (van der Waals) effects, have provided excellent results for unsaturated systems yielding very good geometries [11–13]. In particular the B97-D functional [14], which takes into account dispersion effects including atom – pairwise $C_6^{\alpha\beta}$. $R_{\alpha\beta}^{-6}$ corrections (where $C_6^{\alpha\beta}$ are dispersion coefficients while $R_{\alpha\beta}^{-6}$ are intermolecular distances), has been successfully employed for noncovalent interactions between multilayers of PAHs. For this reason in this work all geometry optimizations have been performed at the B97-D/DZP level, and these structures have been used for the Raman intensities calculation. All computations were performed with the Gaussian 09 software package.

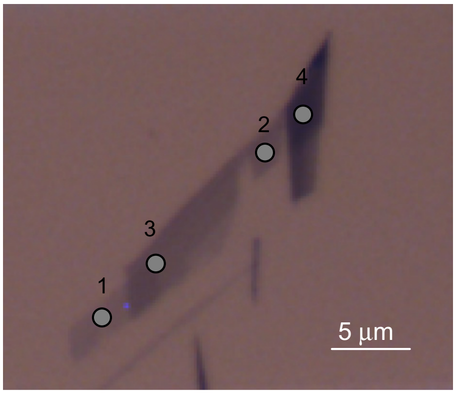

Fig. 1. Optical image of a region where different graphene layers with different thickness coexist. The gray spots individuate the locations where Raman spectra have been taken.

Two layers graphene sheet model was represented by a staggered disposition of two circumcoronene molecules (see Fig. 2a). In this arrangement, typically observed in graphite, one half of the carbon atoms in one layer lie above the carbon atoms in the neighboring layer, while the other half lie above the centers of hexagonal rings in the other layer.

Graphene sheets in stacks with three layers were modeled following the Bernal stacking order, e.g., ABA layer sequence, which exists in the highly oriented pyrolityc graphite (see Fig. 2b). In both cases, consistently with the experimental observations [15], an initial interlayer distance of 3.35 Å, together with a C–C distance of 1.42 Å were set.

3. Results and discussion

Raman spectroscopy is the technique of excellence for the study of carbon based materials; its response to any change in carbon hybridization state [16,17] as well as the possibility to detect and characterize different number of defects [18] or foreign species [19].

In general disorder in graphite introduces a Raman signal at 1360 cm^{-1} (D line) and a small feature located at 1620 cm^{-1} (D′ line). These features accompany two bands which are detected even in the case of defects free graphite (HOPG). They are the G line at 1580 cm^{-1}, due to the doubly degenerate zone center E_{2g} mode and the G′ (or 2D) line, appearing in the range 2600–2800 cm^{-1} and corresponding to the overtone of the D band. The nature and the dispersive behaviour of D, D′ and G′ bands have been nicely correlated invoking the so called double resonance Raman process [20], recently recognized and discussed also in single and few layers graphene [21].

Regarding the introduction of defects by ion irradiations, the effects on highly oriented single crystal graphite samples have been extensively studied more than 20 years ago by means of Raman spectroscopy [22]. It was observed that three regimes of damage can be achieved by evaluating the energy deposited into the collision cascade during the ions' slowing down inside the sample. At low fluences the disorder D line starts to appear and its intensity grows quite linearly with the ion fluence. In this regime the D peak is sharp and is related to the appearance of pockets of disorder within ordered domains. At intermediate fluences the first order Raman peaks start to broaden because of the percolation of single disordered regions (sometimes called microcrystalline regime). A final stage is obtained by further increasing the damage, thus leading to an amorphous carbon sample. A similar scenario has been observed to occur during ion irradiation of single and few layers