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# Raman spectroscopy study of Ar<sup>+</sup> bombardment in highly oriented pyrolytic graphite

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In this work, we discuss the effect of low energy Ar<sup>+</sup> ion bombardment on highly oriented pyrolytic graphite (HOPG). The evolution of the G and D peak intensities are analyzed as a function of ion dose, as well as the evolution of a broad density-of-states (DOS)-like background. For low ion doses, a small D band is observed. It increases and finally gives place to the broad

DOS-like feature. The  $I_D/I_G$  analysis clearly shows three distinct regimes. No frequency shifts are observed, indicating sp<sup>2</sup> bondings are mostly preserved. Comparison between preliminary work on single-layer graphene and HOPG shows the effect observed in HOPG is limited to the top surface.

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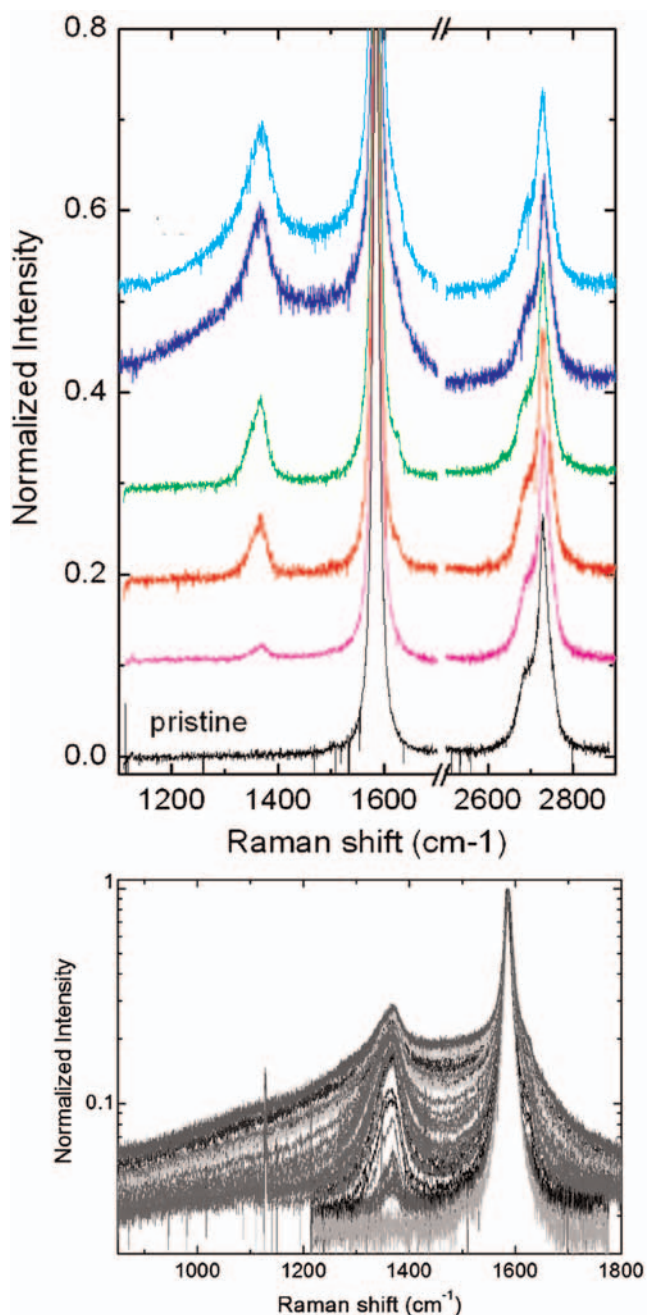
**1 Introduction** In a first phase of exploration, a lot has been learned about graphene by studying graphite [1]. Recently, the interest on graphene and graphite raised due to the possibility of studying isolated graphene sheets [2, 3]. Single and many layers graphene are now the prototype for studying layer interaction and the transition from single layer to highly oriented pyrolytic graphite (HOPG) [4]. Due to the anomalous linear dispersion of electrons near the Fermi level (like a photon, or a massless electron), graphene is also attracting attention as a solid-state physics prototype for studying different phenomena [2–7]. However, disorder has been evocated by theorists to either explain or forbid the observation of many of those interesting phenomena, like the minimum conductivity [3] and the Veselago lens [5]. Understanding how disorder takes place in the surface of HOPG by using Raman spectroscopy is the subject of this work.

To achieve disorder in the surface of HOPG, we use the ion bombardment technique [1, 8]. Ion bombardment is a method for modifying near-surface properties of materials. In the micro-electronics industry, ion bombardment (or ion implantation) is used for introducing dopant atoms in semiconductors [8]. In carbon materials, ion implantation improves mechanical properties and induces the synthesis of new phases by introducing controlled amount of lattice damage [1, 9–13]. However, despite three decades of

intensive study on this theme, the effect caused by low ion dose and low energy is not fully understood. We find that in such a limit, ion bombardment in HOPG is useful to understand the evolution of disorder-induced effects in their Raman spectra.

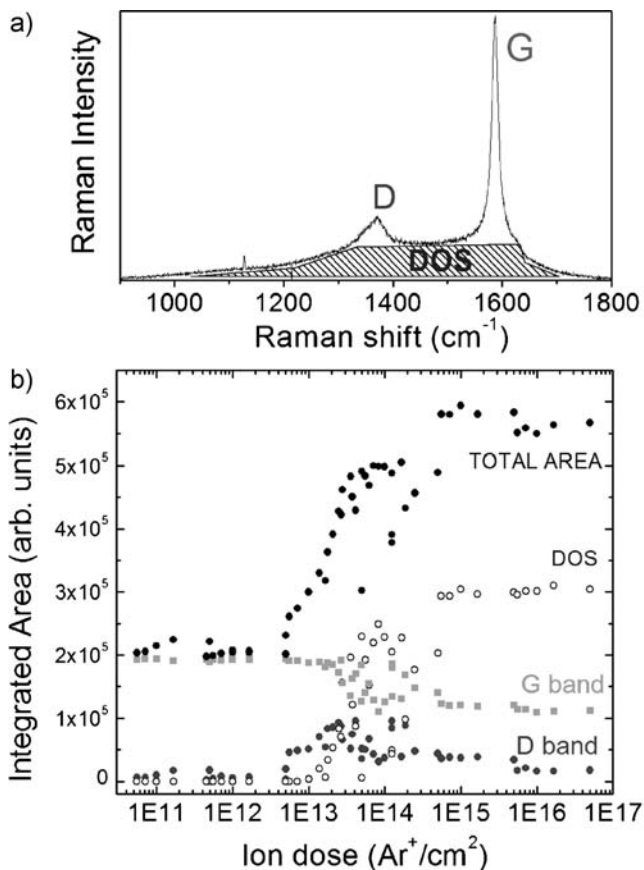
**2 Experimental details** Ar<sup>+</sup> ion bombardment and Raman spectroscopy were performed on HOPG ZYB grade (20 × 20 × 2 mm<sup>3</sup>, NT-MDT company). Ion bombardment experiments (with partial argon pressure lower than 2 × 10<sup>-5</sup> mbar) were carried out in an OMICRON VT-STM ultra-high vacuum system (base pressure 5.0 × 10<sup>-11</sup> mbar) equipped with an ISE 5 Ion Source. The ion beam incidence angle was 45° with respect to the sample's surface normal direction, and low (~80 eV) energy. Micro-Raman scattering measurements were performed with a Jobin-Ivon T6400 triple-monochromator equipped with N<sub>2</sub> cooled CCD detector, in the backscattering configuration using a 100× objective and excitation laser energy 2.41 eV (514.5 nm). The Raman measurements were performed right after each bombardment dose. The bombardments were accumulative.

**3 Results** Figure 1 shows the effect of Ar<sup>+</sup> bombardment on the Raman spectra of graphite. Raman spectroscopy, the inelastic scattering of light, is governed by energy and momentum conservation. The changes observed in the



**Figure 1** (online color at: [www.pss-b.com](http://www.pss-b.com)) The evolution of the D ( $1350\text{ cm}^{-1}$ ), G ( $1585\text{ cm}^{-1}$ ), and G' ( $2700\text{ cm}^{-1}$ ) bands under ion bombardment. In the upper spectra, the spectra are normalized to the largest peak and displaced according to ion dose. The doses, from bottom to top are zero (pristine),  $10^{11}$ ,  $10^{12}$ ,  $10^{13}$ ,  $10^{14}$  to  $10^{15}\text{ Ar}^+/\text{cm}^2$ . The lower spectra show the detailed evolution of the D and G spectral region, using logarithmic scale on the intensity axis to clearly show the changes in the background.

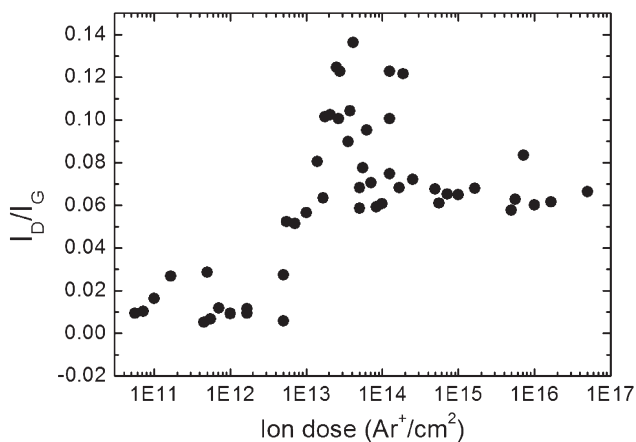
spectra in Fig. 1 are due to the introduction of disorder in the graphite crystalline structure. More specifically, the Raman spectra of the HOPG is composed of two bands, named G ( $1585\text{ cm}^{-1}$ ) and G' ( $2700\text{ cm}^{-1}$ ), as shown in the bottom spectrum of Fig. 1. When disorder is introduced, initially a



**Figure 2** (a) D and G band Raman spectrum from bombarded graphite. The DOS is defined by the hatched area. (b) Evolution of the D, G, DOS, and total integrated area with ion implantation level.

small peak appears at  $1350\text{ cm}^{-1}$ , named D band (D for disorder), and its intensity  $I_D$  increases with increasing disorder (see changes in the spectra in Fig. 1, from bottom to top). This phenomenon is well known in the field, largely studied in amorphous [14] and nanostructured carbons [15]. The D band is related to the breathing of the carbon hexagons, and its observation in the Raman spectra is forbidden by symmetry (the second-order process is allowed and gives rise to the G' band). Interestingly, the effect is explained in chemistry by the deformation of the hexagons in polycyclic aromatic hydrocarbons (PAH) [14], while in solid-state physics it is just related to a breakdown in momentum conservation requirement due to loss of translational symmetry in the graphene lattice [16]. Although the frequency of the D peak has been successfully explained by the double resonance process in graphene [16], the experimental studies on what governs the intensity of the disorder-induced Raman scattering are still on early stage. The dependence on the type of defects, structural arrangement, etc., are lacking in the science of disordered graphene/graphite Raman spectra.

Figure 2b shows the evolution of the G, D, the density-of-states (DOS)-like (as defined in Fig. 2a), and the total



**Figure 3** Evolution of the  $I_D/I_G$  intensity ratio with ion implantation dose.

integrated area. Up to a bombardment dose of  $10^{14}$   $\text{Ar}^+/\text{cm}^2$ , the intensity of the D band increases linearly (exponentially in the log scale of Fig. 2) with the dose, i.e., with the number of defects induced by the  $\text{Ar}^+$  ion. Above  $10^{15}$   $\text{Ar}^+/\text{cm}^2$  the D band intensity does not evolve significantly, and actually decreases toward  $10^{15}$   $\text{Ar}^+/\text{cm}^2$ , together with a decrease in the G band intensity. At this same bombardment range, a large development is observed in the inelastic scattering by what we call here DOS (see Fig. 2a). The DOS area in the Raman spectra is related to the scattering by all phonons in the same D/G phonon branch, in the whole Brillouin zone. Finally, the total inelastic scattering intensity of this phonon branch frequency region (total area in the  $900\text{--}1800\text{ cm}^{-1}$  range) increases substantially between  $10^{12}$  and  $10^{15}$   $\text{Ar}^+/\text{cm}^2$  range and saturates above  $10^{15}$   $\text{Ar}^+/\text{cm}^2$ . Therefore, the introduction of lattice disorder increases the probability for light scattering, and breakdown of momentum conservation happens in different stages, first generating the D band, second the DOS.

Figure 3 shows the evolution of the intensity ratio  $I_D/I_G$  as a function of the bombardment dose. The three regimes for the disorder implantation are clear. A large increase is observed above  $5 \times 10^{12}$   $\text{Ar}^+/\text{cm}^2$ , and it saturates above  $5 \times 10^{14}$   $\text{Ar}^+/\text{cm}^2$ . The saturation is probably related to sputtering of bombarded top layers, indicating that the low ion energy (80 eV) is not enough to penetrate in the graphite.

We have also measured the evolution of the Raman spectra from single-layer graphene deposited on top of a Si/SiO<sub>2</sub> substrate. The peak at  $900\text{--}1000\text{ cm}^{-1}$  from the substrate provides accurate intensity calibration. In general, the behavior of single-layer graphene under disorder is similar to that of graphite. However, the intensity of the D and DOS profiles is much larger, showing that, in graphite, the G band comes mostly from deeper layers that have not been affected by the bombardment procedure. These results will be published elsewhere.

**4 Discussions** In the field of nanocrystalline graphite [14, 15], the crystallite size ( $L_a$ ) has been obtained by

$L_a = 4.4/(I_D/I_G)$ . Clearly, the previous picture only holds for crystallite sizes, but not for defects induced on the surface of graphite or graphene. In our case, the evolution is given by the number of ion-induced defects, rather than the distance among them. Of course there is a relation, but it is not linear, as in the case of nanocrystallites. Therefore, the distance among defects cannot be directly correlated to the crystallite size. The difference comes from a fundamental aspect: for ion-implantation, defects are zero-dimensional, while for nanocrystallites, the defects are the edges, i.e., one-dimensional structures.

For the larger ion doses, it is complicated to compare our results with what is in the literature, since amorphous carbon has a high degree of  $\text{sp}^3$  bonding, and our samples apparently have not. There is a strong decrease in the total intensity observed in the Raman spectra of single-layer graphene after the  $10^{15}$   $\text{Ar}^+/\text{cm}^2$  ion dose, which could be understood by sputtering or a gap opening exceeding the excitation laser energy (2.41 eV) used in our experiments. However, the result strongly depends on the number of layers, on the laser power, and it is not possible to draw any conclusion at this stage.

Finally, there is also an interesting parallel between the Raman spectra of disordered graphene lattice and PAH, which consists of molecular clusters of  $\text{sp}^2$  hexagonal carbon rings [14]. In solid-state physics the breakdown in momentum conservation requirement due to loss of translational symmetry is evoked to explain the observation of the D band [16]. In molecular PAH chemistry, the observation of the D band is explained by the deformation of the hexagons [14]. We hope our result will shed light onto a converged picture between the solid-state physics and quantum chemical approach to describe delocalized  $\pi$ -states in  $\text{sp}^2$  hybridized carbon materials.

**5 Conclusions** We measured the evolution of the G and D peak intensities on HOPG as a function of low energy  $\text{Ar}^+$  bombardment ion dose. For low ion doses, a small D band is observed; it increases and finally gives place to the broad DOS-like feature in the D–G frequency background. The  $I_D/I_G$  analysis show distinct regimes between the increase and saturation. No frequency shifts are observed, indicating  $\text{sp}^2$  bondings are mostly preserved. We have also developed preliminary measurements on single-layer graphene, and comparison between the graphene and the HOPG results shows the effects observed in HOPG are limited to the top surface.

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