Electrical properties of in-plane-implanted graphite nanoribbons

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We studied the effect of low energy (30 keV) ionic implantation of Ga\(^+\) in the direction parallel to the graphene planes (perpendicular to c-axis) in oriented graphite ribbons with widths around 500 nm. Our experiments have reproducibly shown a reduction of electrical resistance upon implantation consistent with the occurrence of ionic channeling in our devices. Our results allow for new approaches in the modulation of the charge carrier concentration in mesoscopic graphite

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I. INTRODUCTION

Graphite is a material composed by loosely-stacked graphene planes, bound together by Van-der-Waals forces. Due to its similarities with graphene, graphite attracts broad technological interest. Most notably, few-layer graphite has been the focus of increasingly larger research efforts in the past few years, partially due to its high native charge carrier concentration (ranging from \(10^{18}\) to \(10^{21}\) cm\(^{-3}\) )\(^{4}\). Electrostatic doping is usually ineffective in samples with thickness above few nanometers because of charge screening. In addition, conventional ionic implantation is often problematic due to the disorder introduced in the graphite structure by the highly energetic ions \(^{5}\).

One of the greatest challenges posed by mesoscopic graphite structures is the difficulty to control its charge carrier density. Due to its high native charge carrier concentration (ranging from \(10^{18}\) to \(10^{21}\) cm\(^{-3}\) )\(^{4}\), electrostatic doping is usually ineffective in samples with thickness above few nanometers because of charge screening. In addition, conventional ionic implantation is often problematic due to the disorder introduced in the graphite structure by the highly energetic ions \(^{5}\).

In this letter, we address these issues by attempting ionic implantation parallel to the planes (perpendicular to c-axis) in narrow HOPG (highly oriented pyrolytic graphite) ribbons. Our results show a consistent resistivity reduction with the amount of implanted ions, suggesting implantation in this direction as a viable way to modulate the charge carrier density in the material.

II. RESULTS AND DISCUSSION

The samples studied here were HOPG ribbons extracted from two different bulk crystals: advanced ceramics ZYA HOPG (FWHM 0.5\(^\circ\)) and Great Wall Inc. GW (FWHM 0.39\(^\circ\)) \(^{5, 6}\). The bulk crystals had typical dimensions of 2 mm x 3 mm (in-plane) x 0.5 mm (c-axis) and room-temperature resistivities of 20 \(\mu\Omega\cdot\text{cm}\) (ZYA) and 5 \(\mu\Omega\cdot\text{cm}\) (GW). They presented a metallic-like behaviour (d\(\text{R}/d\text{T}>0\)) with saturation at high T, typical of well-graphitized bulk HOPG \(^{10}\). This is shown in the inset of Fig. 1.

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The ribbons were prepared as detailed in refs. \(^{11}\) and \(^{12}\). In short, they were etched from a freshly-cleaved HOPG surface with the 30 kV Ga\(^+\) ion beam from a FEI dual-beam electron microscope \(^{12}\). During the milling procedure, progressively smaller ion beam currents were used for etchings done near the ribbons edges. This was performed in order to polish the samples surfaces and limit the Ga diffusion in the material. SRIM simulations predict that, under these conditions, the lateral penetration of Ga\(^+\) in graphite should remain under 20 nm \(^{12, 14}\), resulting in ribbons surrounded by, at most, a 20 nm layer of amorphous carbon. To negate milling damage to the top of the ribbon, the sample was covered in-situ with an 800 nm-thick layer of insulating PdC, obtained by electron-beam induced deposition (EBID) \(^{12}\). The resulting samples had typical dimensions 20 \(\mu\text{m}\) x 500 nm (in-plane) x 5 \(\mu\text{m}\) (along the c-axis - see the cartoon in the inset of Fig. 1). With a micro-manipulator, the ribbons were transferred to a Si substrate coated with a 300 nm-thick layer of insulating Si\(_2\)N\(_3\). Due their narrow in-plane width, their c-axis was oriented parallel to the substrate surface. Subsequently, the samples were soldered to the substrate with four EBID PdC staircase
structures, in order to allow for an effective electrical contacting.

For the electrical addressing, the samples were submitted to a standard electronic lithography processes. In it, the devices were covered with a 1 µm thick layer of PMMA resist, which was allowed to cure for 30 min at 180°C in a furnace. The electron-lithography writing was carried out with a dose of 120 µC/cm² at an acceleration potential of 15 kV. After the developing process, the sample was exposed to a soft oxygen plasma (15 W) for 120 s to remove residues from the sample surface. This was followed by the sputtering deposition of a 10 nm-thick adhesion layer of Pd, followed by a 90 nm layer of Au. Pd was chosen as the adhesion layer due its low contact resistance and wide use in multigraphene samples (see, e.g., ref. [1]). All samples were exposed to a soft oxygen plasma (15 W) for 120 s, followed by developing and a soft plasma etching to remove PMMA residues and reduce the amorphous carbon layer surrounding the ribbon, which is partially removed during the plasma etching in the lithography process. These suggest that disorder on the ribbons' surface cannot be held accountable for the high resistivity of the samples. For example, in refs. [1,2,7], RT resistivities of HOPG ribbons vary between 10⁴ µΩ.cm and 10⁶ µΩ.cm. Such devices have shown the same insulating-like R(T) behavior found here when excited with electrical currents above few nano-Ampères.

After initial characterizations, our samples were covered with a 1 µm-thick layer of PMMA and a narrow window was patterned between the central sample electrodes with electronic lithography. The process was followed by developing and a soft plasma etching to remove PMMA residues and reduce the amorphous carbon layer coating our device. The samples were subsequently implanted with 30 kV Ga⁺ ions, which were available in the same FEI dual beam electron microscope employed during the etching process. Due the sample geometry, the implantation was performed with the ion beam parallel to graphene planes (perpendicular to c-axis).

Results for device L2 are shown in Fig. 2. In it, each implanted dose corresponds to a fluence of 2.6 × 10¹⁴ ions/cm². Measurements were done ex-situ with an AC resistance bridge operating at f = 13 Hz and excitation currents 1 nA ≤ I ≤ 10 nA (each curve was measured at constant excitation). All samples showed the same qualitative behavior and remained ohmic in the entire temperature range studied. Upon Ga implantation, all devices initially became less resistive (up to one order of magnitude). Higher implanted concentrations (above 10¹⁵ ions/cm²) caused a resistivity increase, which eventually led to the destruction of the devices. A diagram showing this effect for all our samples is presented in Fig. 3 and will be discussed further ahead.

Our results seem somewhat counter-intuitive, as Ga
implantation in HOPG is reported to dramatically increase the sample resistance, rather than causing the pronounced decrease observed. For example, experiments performed on thin HOPG films with the ion beam parallel to the sample c-axis have shown that implantations with doses as small as $5 \times 10^{11} \text{ ions/cm}^2$ result in the increase of sample resistance above an order of magnitude. However, this behavior is not universal and strongly depends on the type of ions implanted in the material. Implantation of HOPG with $\text{H}^+$ (parallel to sample c-axis), for example, has shown a weak (1 %) sample resistance reduction for an implanted dose of $10^{13} \text{ ions/cm}^2$, followed by a monotonic resistance increase at higher fluences.

The resistance increase observed in the literature is usually linked to the damage caused to in-plane chemical bondings in graphite. In our experiments, however, the ionic beam was oriented parallel to the sample planes (perpendicular to the c-axis). In this geometry, the implanted ions see atomic layers of C separated by planes (perpendicular to the c-axis). In this geometry, the doping can be understood as a consequence of channeled Ga ions acting as an interstitial linking between graphene planes in graphite, which donate electrons.

In order to verify the effect of ionic implantation on the sample structure, Raman measurements were performed. The experiments were carried out with the light incising perpendicular to the sample c-axis, with the electric field polarized along the graphene planes. Results for sample L2 at three implanted doses are shown in the lower pannel of Fig. 3. Such doses correspond to the points marked in the resistance-implantation diagram for all samples, which is shown in the upper pannel of the same figure. The G-peak and 2D peaks on the Raman spectra are fingerprints of graphite, whereas the one labeled D is a signature of structural disorder. The curve # 1 shows the presence of the D-peak due to the disordered carbon layer surrounding the sample (presumably formed during the milling process). For subsequent doses (curves # 2 and # 3) the D-peak intensity gets higher as it overlaps with the G-peak. At this stage ($I_G/I_D \approx 1$) the sample surface reaches the amorphization condition, no longer allowing measurements of the underlying graphite structure.

The Raman spectra can be compared with those previously obtained by B. S. Elman and M. Dresselhaus on HOPG implanted with different ions, albeit parallel to c-axis. For example, ref. 18 shows that the implantation of 100 keV He ions with a fluence of $1 \times 10^{14} \text{ ions/cm}^2$ is sufficient to produce amorphization of the sample surface. At the same time, lesser energetic ions are shown to produce more damage to HOPG surface than their higher energetic counterparts.

Considering these, it would be expected that the lower energy Ga$^+$ ions used here (30 keV) would not produce an early surface amorphization at fluences of $10^{14} \text{ cm}^{-2}$. This would happen due to the ions’ larger energy transfer for collision, smaller scatter angle, smaller range and larger defect density per volume when compared to lighter ions. These considerations suggest a channeling scenario for our graphite sample. As the implanted doses gets higher, however, the channels are progressively destroyed as dechanneling and random scattering events become important.

Hence, the ever increasing amount of damage can be conciliated with the sample resistance reduction by considering that our devices undergo a progressive amorphization which competes with the doping caused by Ga atoms. The doping can be understood as a consequence of channeled Ga ions acting as an interstitial linking between graphene planes in graphite, which donate electrons. Since the resistivity of graphite depends on the amount of charge carriers, this contribution reduces the sample resistance according to the inverse of the implanted dose.

As the progressive damage increases with the amount of implanted ions, however, ionic channeling becomes suppressed. This results in a positive contribution to the sample resistance due to the scattering of upcoming ions, creating cascade process which increases the sample amorphization rate. Its contribution to the resistivity is non-trivial, but positive. Assuming that only implanted ions...
In conclusion, in this work, we have shown ionic doping parallel to planes in HOPG as a viable way to modulate the sample resistivity. Our results can be interpreted as the occurrence of ionic channeling in our samples in competition to amorphization induced by higher fluence ionic implantation. Our results suggest that ionic implantation perpendicular to the c-axis in HOPG modulates the sample charge carrier density while introducing much less damage when compared to implantation parallel to the sample c-axis. Our results point new routes towards the modulation of charge carriers in multigraphene devices and the functionalization of graphite nano objects.

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[32] C. Wagner and F. Burkhardt, physica status solidi (a) 47, 131 (1978), ISSN 1521-396X, URL http://dx.doi.org/10.1002/pssa.2210470114