Nitrogen ion implantation in Graphene

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The fine tuning of electronic properties by suitable functionalization methods leading to the grafting of heteroatoms to the graphene hexagonal lattice is a key challenge for the fabrication graphene-based devices [1-3]. In this context, the introduction of nitrogen atoms into the graphene lattice has attracted a great deal interest; nitrogen has an atomic radius similar to that one of carbon and one electron more, in principle available for conduction. Nitrogen atoms can have different bonding configurations in the graphene lattice: the pyridinic-like and graphitic-like nitrogen, are sp^2 coordinated, and the pyrrolic-like nitrogen, sp^3 coordinated (Figure 1).

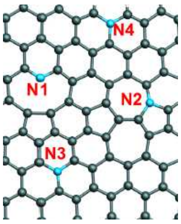

Figure 1: Nitrogen atoms (blue) : pyridinic N1, pyrrolic N2, graphitic N3, graphitic ‘‘valley’’ N4.

Heteroatom doping is commonly performed by introducing dopant species to the feedstock during chemical vapour deposition (CVD). Alternatively, post-synthesis doping methods have the advantage to avoid growth-induced segregation effects, to be spatially selective by the use of appropriate masks, and offer the possibility of doping after the integration of the carbon nanostructure in a device. Among the available post-synthesis doping methods, the most commonly used are plasma treatments and ion implantation [4,5]. The bonding nature of the nitrogen doping atom in the carbon lattice is reported to depend on doping conditions [6,7].

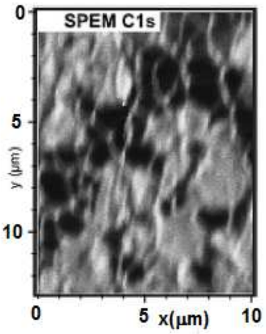

Figure 2 : C1s SPEM image of multiple flakes.

The aim of the current work is (i) to N-dope suspended graphene sheets produced by CVD using nitrogen ions implantation, (ii) to investigate the N-implantation degree as a function of time and temperature, (iii) to evaluate the nature of N atoms implanted within the carbon lattice of graphene using scanning photoemission microscopy (SPEM) analysis, and (iv) to assess the effect of heat treatments in the N-implanted graphene. Few-layer graphene flakes were synthesized at 1050 °C by atmospheric pressure CVD on copper foils using methane as carbon precursor. The copper foils were cleaned by sonication in acetone and isopropanol and washed in acetic acid. After the synthesis, the copper foils were etched by aqueous ammonium persulfate and the flakes rinsed in distilled water. Finally, typical TEM grids with lacey carbon were dipped into the distilled water to collect dispersed graphene flakes; this transfer method is polymer-free. The X-ray scanning photoelectron microscope available at Escamicroscopy (ELETTRA - Italy) was used to investigate the doping effect on suspended flakes. The photon energy used was 490 eV. The nitrogen implantation was performed in situ in the ultrahigh vacuum (UHV) preparation chamber. A total ion acceleration of 1 kV was used to accelerate the nitrogen ions towards the sample; fast ions induce defects essential for nitrogen implantation. We emphasize damage coming from backscattered atoms and recoils from the substrate are not present on suspended graphene.

Two N-implantation treatments were performed: N^+ ions irradiation of 5 and 15 min, resulting in 8.4% and 12.8% of nitrogen respectively. These values indicate that ion implantation reaches high nitrogen content with respect to CVD doping which generally does not exceed

2–3% [6], [8]. The N1s core level spectra recorded after N$^+$ ions implantation during 5 and 15 min is shown in Figure 3. These can be reproduce by four Voigt profiles associated to different nitrogen chemical environments in the graphene hexagonal lattice: N1 is associated to pyridine-like nitrogen (yellow, 398.45 eV) and N2 is associated to pyrrole-like (blue, 399.45 eV). The N3 (dark green, 400.92 eV) and N4 (light green, 402.82 eV) are both assigned to graphitic-like (or substitutional) nitrogen, distinguished as nitrogen in a center or valley position. In Fig. 3b, we can see the absolute concentration variation of the nitrogen components for different implatation time. The increase in the amount of pyridinic-like nitrogen is consistent with nitrogen neighboring defects created during the ion implatation. However, the sp^2 structure of the graphene lattice is still preserved; the relative intensity of the sp^3 carbon peak at 399.45 eV does not increase with implantation time. Fig. 3b shows a decrease of the sp^3 pyrrolic component and a corresponding increase in the graphitic signal, which is the most thermal stable species. The increase in graphitic-N content after the first annealing suggests transformation of the pyrrolic into substitutional. At 430 °C the nitrogen content has an absolute decrease of about 3%. We can observe the complete loss of pyrrolic nitrogen which is clearly unstable at these temperatures. Pyridinic and graphitic are the most thermal stable species.

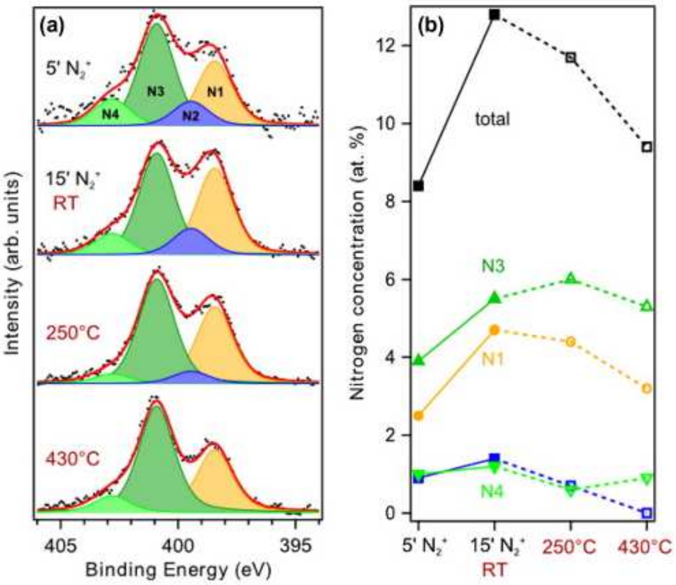

Figure 3: a) N1s core level after 5 and 15 min nitrogen implantation and heating at 250 °C and 430 °C. (b) Nitrogen content for each component and total amount (black squares) as a function of implantation time (full symbols connected by full line) and annealing temperature (open symbols connected by dotted line).

The binding energy of N4 has various possible assignments including graphitic-valley nitrogen. The decrease in the relative area of N4 after the first annealing step can be a small amount of N–O species who desorb at low temperature and whose binding energy is close to graphitic-valley nitrogen. Despite this potential ambiguity in peak assignment, its relatively low area (less than 10% of the N1s peak) does not affect the main conclusions.

In summary the high nitrogen content achieved, without disrupting the sp^2 structure of the graphene lattice network, and the possibility to tune the local bonding environment through a combination of controlled implantation and thermal post-treatment, testify that our strategy opens the door to custom nitrogen doped graphene with tunable properties for future applications such as metal free catalysts and sensor devices.

References

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