A versatile plasma-based method for the nitrogen doping of graphene

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Abstract

The chemical doping of graphene, which influences its electronic and chemical properties (opening band-gap, altering carriers densities, etc…), is currently a critical aspect in graphene research and development. [1] In particular, the nitrogen doping of graphene has attracted intensive attention due to a relative facility for nitrogen to substitute carbon atoms in the honeycomb lattice of graphene.[2] The doping nitrogen may be bound in various configurations, such as in graphitic-like, pyridinic-like or pyrrolic-like configuration (see figure 1a), depending on the presence of any neighbor vacancies.[2] Moreover, the N-doped graphene has also been reported to exhibit superior performance over the pristine material in several applications (field-effect transistors, batteries, fuel cells, super-capacitors, and biosensors).[3-8] Though, methods to realize a reliable and controlled doping have still to be mastered, if graphene is to enter the realms of practical devices.

The substrate on which the pristine graphene is grown also plays an important role in the fabrication of graphene-based devices. Epitaxial monolayers grown on the Si-termination of SiC are a promising route to produce high-quality graphene on wafer-size area on top of a semi-insulating substrate, especially when the graphene monolayer can be effectively decoupled from the substrate (and the so-called buffer layer) by foreign atom intercalation.[9] However, there is only a very limited number of published works devoted to the nitrogen-doping of epitaxial graphene layers grown on SiC. Most of these studies consist of simulations, and the reported experimental realizations are still in their infancy: additional efforts are thus necessary in order to obtain control and reproducibility of graphene chemical doping by N atoms.

In this work, we present an effective, versatile plasma-based method for the nitrogen-doping of graphene grown on 6H-SiC(0001). By using a tunable hybrid plasma source, the graphene monolayers are exposed to a stream of low-energy nitrogen ions and/or to a neutral flow of thermalized nitrogen species. A thermal annealing is applied during (or after) nitrogen doping to reduce the defects created by the plasma exposure. The electronic properties of the nitrogen-doped graphene are investigated using angle-resolved inverse photoemission spectroscopy (ARIPES). This technique reveals the energy and dispersion of the unoccupied electronic states of graphene, in particular the π^* states which form the upper Dirac cone at the K points of its Brillouin zone. We used the shift of these π^* states upon nitrogen exposure to estimate the magnitude of the n-type doping. The results show that low-energy nitrogen ions (5~35 eV) cause an n-type doping (up to 0.4 eV), as shown in figure 1b, associated to a majority of graphitic-N (up to 8.7%), as revealed by XPS (figure 1c). On the other hand, thermalized neutral nitrogen species, at even lower energy, rather form pyridinic-N (figure 1c) in the presence of defects, and induce nearly neutral doping with respect to the pristine one (figure 1b).

In brief, we show how a simple plasma-based technique can be used in a versatile way to control the bonding environment of nitrogen atoms in graphene. It will certainly be of great interest for the processing of future graphene-based nano-devices using widespread technologies like plasma-processing.

References

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Figures

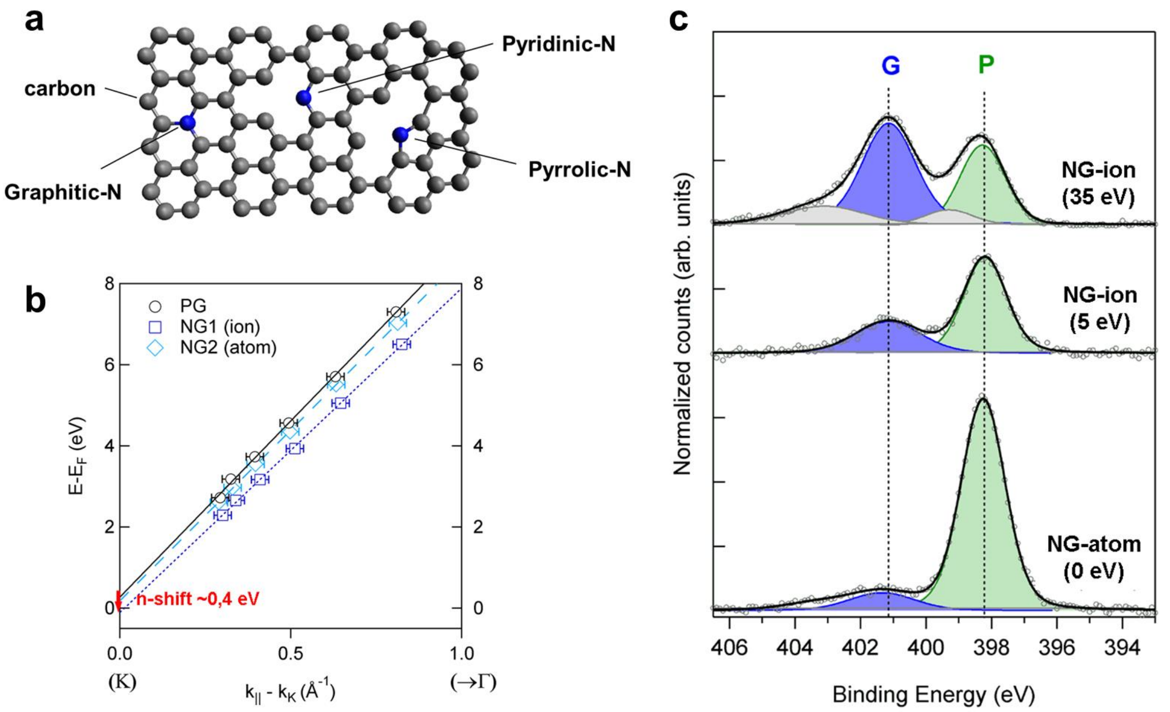

Figure 1. (a) Schematic representation of the three principal configurations of doping nitrogen in graphene: Pyridinic-N, Pyrrolic-N and Graphitic-N. (b) Linear extrapolation of the π* states obtained by ARIPES for pristine graphene (circle), NG-ion (square) and NG-atom (rhombus) with respect to $k_{//}$ along the Γ-K direction of the graphene Brillouin Zone. (c) N 1*s* XPS spectra of the studied NG samples. The top two spectra are characteristic of the monolayer graphene exposed to nitrogen ion species of 35 and 5 eV for 10 min. NG-atom is the same pristine graphene exposed to neutral species for 10 min.