Synthesis of nitrogen-doped epitaxial graphene via plasma-assisted method: Role of the graphene–substrate interaction

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ABSTRACT

Functionalization of graphene by substitution of carbon with nitrogen atoms is a promising way to tailor its electronic properties, but a good control over the heteroatomic configuration in the graphene network is most often a difficult task. In this paper, the synthesis of N-doped graphene by nitrogen plasma treatment of graphene/Ir(111) is presented. The formation of substitutional, pyrrolic and pyridinic nitrogen is analyzed by means of X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD). The graphene–Ir interaction is suggested to control the variation in the relative concentration of the nitrogen species. Annealing of the sample also leads to modifications of the nitrogen species incorporated in the graphene layer. Furthermore, the connection of the substitutional nitrogen arrangement with its corresponding spectroscopic fingerprint is unequivocally confirmed by XPD measurements, which give also a direct insight on the local geometry of the nitrogen atoms incorporated in the carbon network.

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1. Introduction

The combination of many outstanding properties in a single material makes graphene (GR) really attractive for a number of technological applications. In this regard, the use of graphene single layers into high-performance integrated circuits is one of the most intriguing prospects. However, the absence of a gap in its band structure, sets severe limits on the use of graphene in, e.g., transistors because of the low on–off ratio achievable [1]. This is the reason why the opening and fine tuning of an energy gap in the band structure of graphene has been an issue of fundamental importance since its discovery. Different routes have been followed to tailor the electronic properties of graphene. The first to be explored were methods based on the morphology control over the graphene structure. For instance, by making graphene nanoribbons it is possible to laterally confine the charge carriers. In nanoribbons, different types of edges show either metallic (zigzag edge) or semiconducting (armchair edge) character [2]. Furthermore, the possibility of opening a band gap in bilayer graphene by applying a strong electric field [3] or by selectively controlling the carrier density in each layer

[4] was also explored. However, these approaches resulted in a small band gap or in a strong degradation of the carrier mobility [1].

A promising alternative approach to modify the electronic properties of graphene is by chemical doping, which can be achieved by patterning the graphene surface with atoms [5] or molecules [6], or by introducing heteroatoms in the carbon network [7]. In the latter case, the substitution of carbon with nitrogen or boron atoms is of considerable interest not only because the shift of the energy of the Dirac point leading to n- or p-doped graphene can be achieved, but also because the characteristic features of the graphene electronic band structure can be modified [8]. For sp^2 carbon structures, like graphene or carbon nanotubes, the incorporation of nitrogen in the lattice has been already demonstrated to be a robust and efficient method to tune the electronic properties with only minor structural perturbations, due to the possibility to form covalent bonds [9,10].

Several methods have been developed to synthesize N-doped graphene. For instance, direct synthesis of N-doped graphene can be achieved by chemical vapor deposition (CVD) [11] or arc discharge [12] approaches. On the other hand, post-synthesis methods are also widely used, such as thermal annealing [13] in ammonia (NH_3) atmosphere or plasma treatment [14,15]. Although different atomic arrangements of the nitrogen atoms in the carbon network are possible (some of them are displayed in the top panel of Fig. 1), three main configurations have been characterized namely, graphitic, also known as substitutional, pyridinic and pyrrolic nitrogen. Several characterization tools
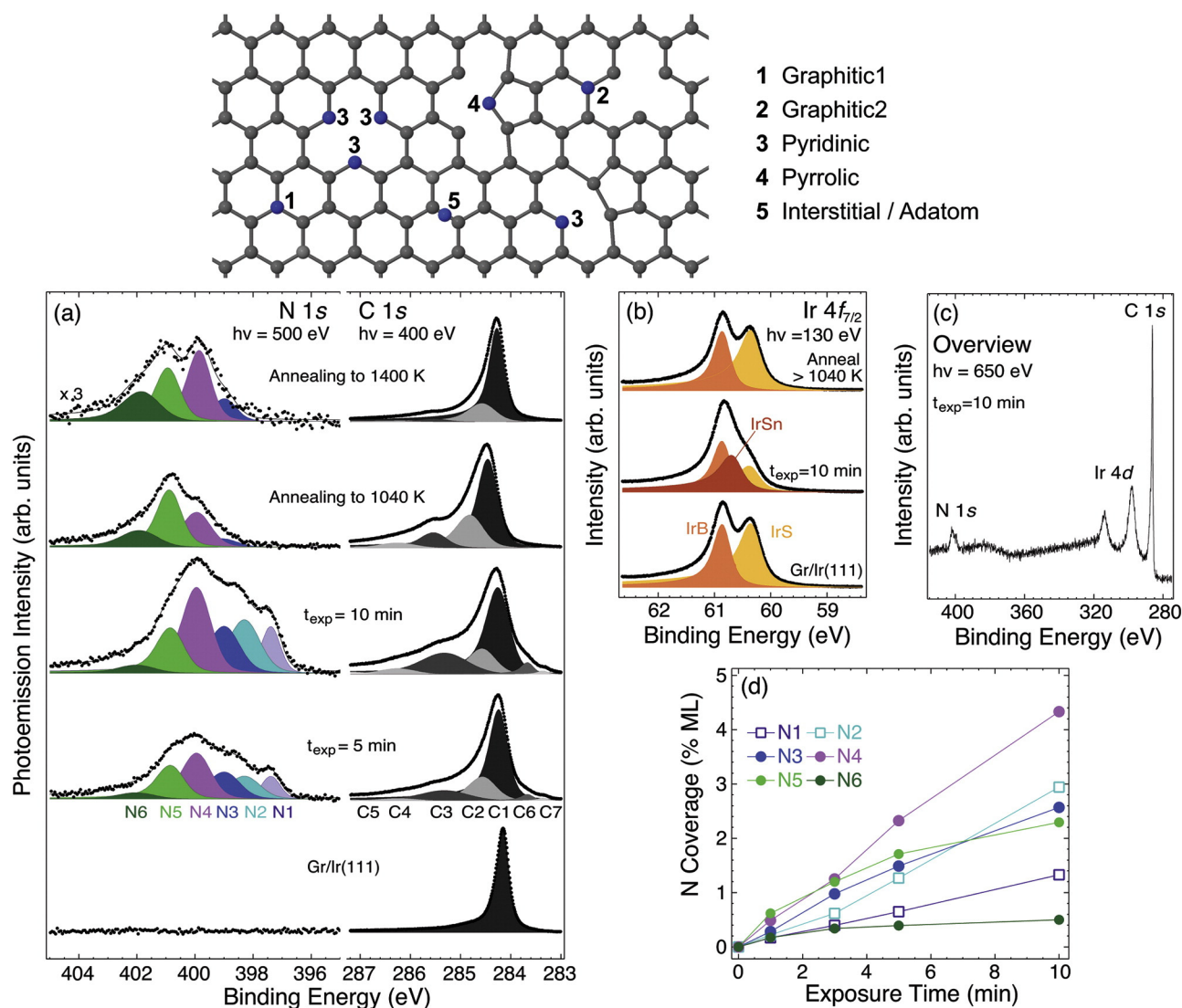
Fig. 1. (color online) (a) Evolution of N 1s and C 1s core levels after subsequent exposures of GR/Ir(111) to N plasma and after annealing to 1040 K and 1400 K. The filled peaks represent the spectral components as resulting from the deconvolution procedure (see main text for more details). (b) Comparison between the Ir 4f$_{7/2}$ core level measured for the pristine GR/Ir(111) (bottom), after 10 min of exposure to N plasma (middle) and after annealing to 1040 K (top). (c) Overview spectrum measured after 10 min of exposure to N plasma. (d) Coverage of the distinct N species during exposure of GR/Ir(111) to N plasma, as determined from the fitting of the spectra in (a). The top picture shows a schematic representation of the nitrogen configurations discussed in the paper: 1 and 2 are graphitic-N atoms within an intact graphene region and neighboring a defect site, respectively; 3 and 4 are N atoms in pyridinic and pyrrolic configuration while 5 is N atoms adsorbed on the graphene basal plane or in interstitial position.

based on microscopy and spectroscopy have been used to investigate the N-doped graphene layers (e.g., scanning tunneling microscopy (STM) [16,17], transmission electron microscopy (TEM) [18], X-ray photoelectron spectroscopy (XPS) [9,10] and Raman spectroscopy [11,19]), but the connection between the nitrogen bonding configuration and the synthesis method is not always straightforward.

Motivated by this lack of information, we exploited the potential offered by XPS and X-ray photoelectron diffraction (XPD) techniques to study the functionalization and to determine the surface structure of a N-doped graphene layer produced upon nitrogen plasma exposure of the GR/Ir(111) interface. In this paper we illustrate how a combined XPS and XPD investigation can provide insight into the correlation between the electronic and structural properties of N-doped graphene.

2. Material and methods

The experiments were performed at the SuperESCA beamline of Elettra, the synchrotron radiation facility in Trieste, Italy. The Ir(111) single crystal was cleaned by repeated cycles of Ar$^+$ sputtering and annealing in O$_2$ atmosphere between 600 and 1100 K, followed by

hydrogen exposure at 800 K to remove the residual oxygen. The graphene monolayer was grown on Ir(111) by doing 10 cycles of temperature-programmed growth, consisting in dosing ethylene at 520 K and annealing to 1470 K, followed by a prolonged annealing at high temperature with a base ethylene pressure of 1×10^{-7} mbar. This procedure ensures the growth of a complete layer of graphene that does not leave bare Ir regions. The as-grown graphene layer was then exposed to nitrogen plasma at room temperature using a Gen2 plasma source from Tectra GmbH, configured as atom source without ion-trap. Within this mode of operation the beam is mainly composed by neutral atoms with a fraction of residual ions with energy of about 25 eV, defined by the intrinsic plasma potential. Different conditions such as N$_2$ pressure, position of the sample surface with respect to the source and exposure time were tested. An efficient nitruration of graphene was achieved for exposures with N$_2$ base pressure of 2.5×10^{-5} mbar performed with the Ir surface placed in front of the plasma source.

The high-energy resolution XPS spectra of the Ir 4f$_{7/2}$, C 1s and N 1s core levels were measured in normal emission (in the present setup this corresponds to 70° of incidence of the photon beam) using photon