Nitrogen Doped Graphene Sheets Synthesized by Surface Wave Plasmas

J. Henriques[1], E. Tatarova[1], F. M. Dias[1], A. Dias[1], N. Todorov[2], N. Bundaleski[3], O. Teodoro[3]

[1]*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Portugal*
[2]*Faculty of Physics, Sofia University,1164 Sofia, Bulgaria*
[3]*Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Portugal*

Nitrogen doped graphene sheets, have attracted much attention due to their exceptional performance as parts of fuel cells, lithium-ion batteries, biosensors and ultracapacitors. In this work, surface wave discharges were applied for the production and N-doping of graphene sheets. High quality graphene sheets, produced by an atmospheric-pressure, Ar-ethanol surface wave axial discharge, were doped with nitrogen atoms using a large-volume, slot-antenna N_2-Ar microwave plasma driven by surface waves at low pressure. Pure and N-doped graphene sheets were characterized by Raman spectroscopy, scanning electron microscopy and x-ray photoelectron spectroscopy. A 3D theoretical model describing the large-volume N_2-Ar microwave discharge is used to interpret the results. This study shows that by incorporating nitrogen atoms into graphene, its physico-chemical properties are considerably altered.

1. Introduction

Nitrogen-doped graphene has demonstrated a high potential towards energy conversion and storage applications [1,2]. In this work a large-volume slot-antenna N_2-Ar microwave plasmas driven by surface waves [3,4] have been used to incorporate nitrogen atoms into the graphene lattice, thus producing nitrogen-doped, i.e. N-graphene. To this end self-standing graphene sheets has been processed in a remote zone of N_2-Ar plasma to avoid ion bombardment detrimental effect. Two important parameters like exposure time and distance to the slot-antennas have been changed. The obtained N-graphene sheets were characterized by Raman spectroscopy, scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS). When doping nitrogen into graphene three common bonding configurations are normally obtained: pyridinic N, pyrrolic N and graphitic N. The pyridinic and pyrrolic N usually lie at the edge or defect sites, for example in vacancies, while graphitic N is connected with three carbon atoms in the graphene lattice. The treatment of the graphene sheets by N_2-Ar plasmas can induce a non-negligible number of defects and bond disorders. A 3D theoretical model of N_2-Ar large-scale plasma has been developed and used to optimize plasma conditions for nitrogen doping of graphene sheets.

2. Experimental conditions

A slot-excited surface wave plasma source operating in N_2-Ar mixtures is used to N-Dope small graphene flakes. This large volume discharge takes place inside a Pyrex tube headed in its upper region by a water-cooled aluminium block that constitutes the discharge vessel, closed at the top by a 10 mm-thick quartz window with a 22 cm diameter (see Fig. 1.) . Gases are injected at the bottom of the vessel with flows ranging from 5 to 50 sccm. The gas pressure can vary from about 0.1 to 1.2 Torr. The microwave power is provided by a 2.45 GHz generator (Sairem), whose output power was varied from 400 to 600W. The generator is connected to a waveguide (WR-340) system, which includes an isolator, directional couplers, a 3-stub tuner and a slotted waveguide antenna as the field applicator. The slot-antenna launches surface waves, which form standing waves close to the plasma–dielectric plate interface. The energy carried by the surface waves propagating along the interface plasma-dielectric create the plasma. The waves form resonant eigen-modes satisfying boundary conditions, for the present conditions the proper mode is the TM_{410}. A robotized system equipped with a quartz sample holder is used to change the axial position of the graphene sample inside the plasma. The treatment of the graphene sheets has been performed in the remote plasma zone to avoid ion bombardment effect.

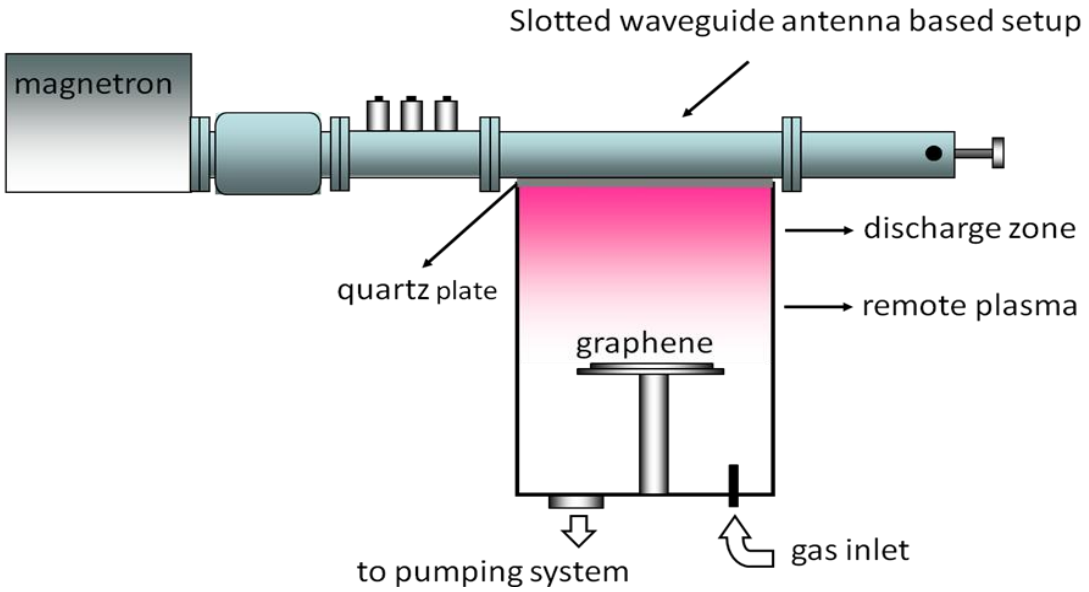

Fig. 1. Large-volume microwave plasma setup.

The SEM characterization was performed on a JEOL, JSM-7001F field emission gun scanning electron microscope operating in secondary electron imaging mode (SEI) with applied tensions in the range of 10 to 15 kV. The Raman spectroscopy analysis was performed using a LabRAM HR Visible (Horiba Jobin-Yvon) Raman spectrometer with 1 cm^{-1} spectral resolution and 633 nm Ne-Ne laser excitation with laser spot size of 2 μm. Measurements were carry out using a laser power of 0.054 mW to avoid overheating. Finally, the X-ray photoelectron spectroscopy elemental analysis was made using a KRATOS XSAM800 X-ray spectrometer with a double anode, operating in fixed analyzer transmission mode with an analyzer pass energy of 20 eV and non-monochromatic X-ray source (Mg Kα line) with a power of 120W (12 kV×10 mA). The spectra were collected in 0.1 eV steps, using a Sun SPARC Station 4 with Vision software (Kratos). X-ray source satellites were subtracted. Shirley backgrounds and Gaussian/Lorentzian line shapes were fitted using XPS Peak 4.1 (freeware). No flood gun was used for charge compensation.

3. Results

3.1. Scanning electron microscope analysis

SEM images of pristine graphene sheets and of N-doped graphene sheets are shown in Fig. 2a and 2b, respectively. N-doped graphene samples were

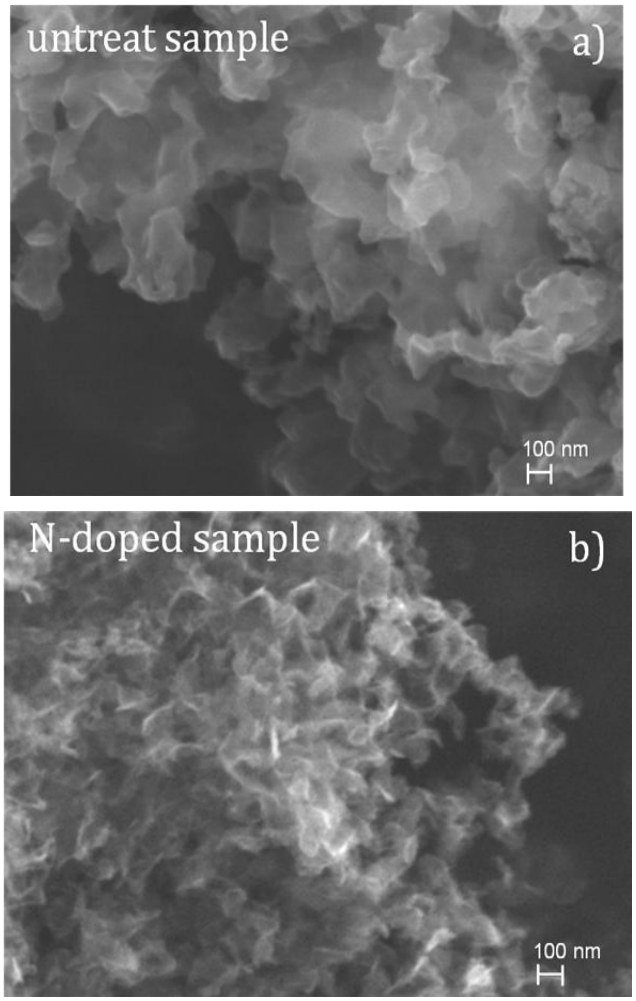

Fig. 2. SEM images of graphene sheets obtained before a) and after treatment b) with a N_2-Ar plasma.

produced by exposing pristine graphene sheets to an N_2-Ar plasma, rich in reactive nitrogen atoms, vibrationally and electronically excited nitrogen molecules, photons, ions, etc. In the SEM images, obtained with a 100 nm magnification bar, is possible to observe crystal clear untreated graphene flakes (Fig. 2a) and nitrogen doped graphene flakes (Fig. 2b) with a non-negligible amount of defects due to the incorporation of nitrogen atoms in the graphene lattice and to the interaction with other plasma species. Overall, nitrogen doped graphene flakes exhibit a much more rough surface that of the undoped ones. The graphene clusters are composed of individual graphene flakes approximately with the same dimensions of the scale bar.

3.2. Raman spectroscopy analysis

The evolution of the intensities of the D, G, D' and 2D peaks of graphene samples is presented in Fig. 3, the blue line corresponds to a pristine sample and the red one to a N-doped one, obtained after N_2(10%)-Ar(90%) plasma treatment for 5 minutes at 1 mbar and 600W. Due to the incorporation of nitrogen atoms into the graphene lattice the number of disorders in the graphene structure increases substantially and, as a consequence of that, the intensities of D and D' peaks increase and the intencity of the 2D peak decrease.

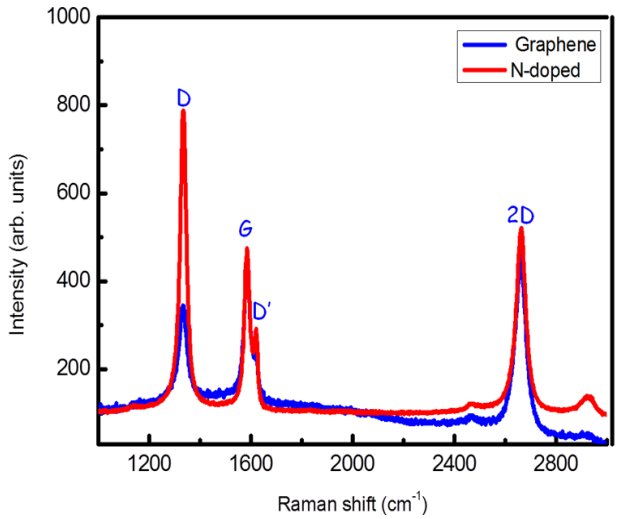

Fig. 3. The Raman spectra of two samples of graphene sheets, the blue one corresponds to a pristine sample and the red one to a N-doped one obtained after N_2(10%)-Ar(90%) plasma treatment for 5 minutes at 1 mbar and 600W.

3.3. X-ray photoelectron spectroscopy analysis

A detailed analysis [5] of the N 1s line (shown in Fig. 4.) reveals the presence of three types of N-C bonding: a strong pyrrolic N signal (N-5) located approximately at 399.7 eV, a pyridinic N signal (N-6) located around 401.4 eV and a weak graphitic N (N-Q) signal located about 398 eV. The samples analyzed in figures 4 and 5 were obtained after 5 minute exposure to a N_2(10%)-Ar(90%) plasma operating at 1 mbar with a total gas flow of 50 sccm and microwave power of 600W.

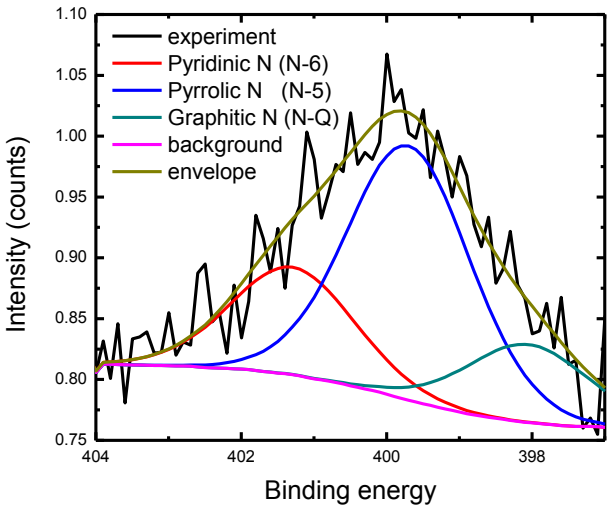

Fig. 4. Detailed XPS spectrum of the N 1s line of a nitrogen doped graphene sample treated for 5 minutes in an N_2(10%)-Ar(90%) plasma at 1 mbar and 600W.

A detailed analysis of the C 1s XPS line scan spectrum of nitrogen doped graphene sheets is presented in Fig. 5. The spectrum exhibits a strong peak located at 284.4 eV corresponding to the graphite-like sp^2 hybridized carbon. The C 1s line was fitted with six peaks corresponding to the contributions assigned to carbon sp^2 and sp^3 at 284.4 eV and 285.1 eV respectively, also to carbon in different carbon-oxygen bonds: C-O-C at 286.3 eV, C=O at 288.1 eV and COO at 289.5 eV, and finally to the π - π * excitation.

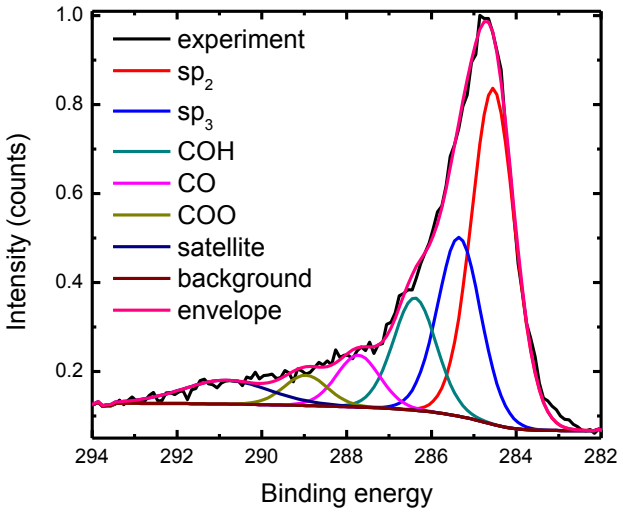

Fig. 5. Detailed XPS spectrum of the C 1s line, the samples were obtained under exactly the same condition as those in Fig. 4.

3.4. 3D Modelling

A 3D theoretical model for the large-volume microwave plasma source have been developed accounting in a self-consistent way the main plasma balances, including bulk and surface elementary processes, as well as wave electrodynamics. The used method describes in a self-consistently way the spatial structure of the plasma source, i.e. the spatial distribution of population densities of excited species, charged particles and ground-state molecules and atoms taking into consideration the main energy exchange pathways as well as plasma–wall interactions [3,4,6-8]. An isosurface of the ground state nitrogen atom density N(^{4}S) equal to $8.0x10^{-13}$ cm^{-3} is presented in Fig. 6, for better understanding of the figure, the dielectric quartz disk as well as a cut of the sample holder is also shown. The figure shows that the N(^{4}S) density is high and very homogeneous close to the sample holder, surrounding it.

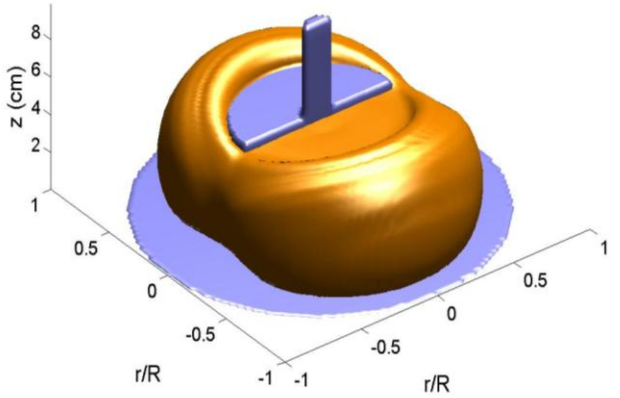

Fig. 6. Isosurface of the nitrogen atom density N(4S) with a density of $8.0x10^{-13}$ cm^{-3}, the dielectric quartz disk is shown in the base of the figure as well as the sample holder cut in half.

4. Conclusions

This work demonstrates the applicability of large-volume N_2-Ar surface wave plasmas to produce and incorporate nitrogen atoms into graphene, changing its physico-chemical properties.

Acknowledgements

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