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Production of N-graphene by microwave N$_2$-Ar plasma

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Abstract

Self-standing N-graphene sheets were produced in low-pressure microwave N$_2$-Ar plasma. The graphene sheets were exposed to the plasma for various durations and doped with nitrogen atoms, which were incorporated into the hexagonal carbon lattice in pyridinic, pyrrolic and quaternary functional groups, mainly. Atomic nitrogen emissions at the substrate position in the plasma were detected using optical emission spectroscopy. Raman spectroscopy, x-ray photoelectron spectroscopy and transmission electron microscopy techniques were also applied for material characterization. Doping levels as high as 5.6% were achieved and an increase in the sp$^2$/sp$^3$ ratio was observed for a relatively short exposure time.

Keywords: microwave plasma, N-graphene, nitrogen atoms

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene, a one-atom-thick layer of sp$^2$ hybridized carbon tightly packed into a 2D hexagonal lattice structure, has attracted strong interest from academia and industry due to its unique physical properties and high application potential in many fields, such as energy storage and conversion devices, sensors, electronics, composite materials etc [1–9]. Additionally, graphene can be considered as an atomic-scale scaffold, based on which new 2D crystals can be created. Successful doping of graphene with nitrogen, denominated as N-graphene, was already demonstrated [3–6, 10–14]. It is noteworthy that nitrogen functional groups covalently attached to the graphene scaffold and the specific properties of graphene lead to an extraordinary electrochemical performance [3–5]. By simple replacement of some of the carbon atoms with nitrogen atoms in the lattice structure, N-graphene capacitors are capable of holding 99.8% of the nominal capacitance even after 100000 cycles [4].

N-graphene is also a very promising material for the development of metal-free, carbon-based catalysts with a better performance than even commercially available Pt-based electrodes for oxygen reduction reaction in fuel cells [3, 5]. Recently, lithium–sulfur batteries with a very high theoretical energy density (2600 Wh kg$^{-1}$) appeared as one of the most promising candidates for next-generation energy storage devices [15, 16]. However, several difficulties impeding the practical use of lithium–sulfur batteries, including the ‘shuttle effect’ and the irreversible loss of active materials, need to be addressed. To this end, incorporating graphene into the flexible sulfur containing electrodes as a scaffold material would greatly improve electrode performance. Nitrogen-doped graphene exhibits strong-couple interactions for anchoring sulfur-containing species, thus achieving higher stability and reversibility when compared with pristine graphene, as demonstrated in [16].

Numerous methods have been developed to synthesize graphene, including mechanical and chemical exfoliation,
chemical vapor deposition, and reduction of graphene oxide among many others [3]. However, only a few methods have been developed to produce N-graphene. The nitrogen doping of graphene applying high-power electrical annealing, thermal annealing [11, 12], and CVD of methane in the presence of ammonia [13] has been reported. The plasma-assisted doping of graphene has also been demonstrated. It should be noted that plasma-based methods for engineering graphene properties can be considered superior to chemical ones, since the former ensure a high level of controllability, good quality and reduced environmental risks [3, 17, 18]. On top of this, plasma methods have many idiosyncratic features which place them uniquely and very competitively in the nanoscale science and technologies domain [4, 18]. These methods are superior to other approaches due to the possibility of modifying only a nano-thick region without affecting bulk properties of the material. Under reactive plasma surface interaction, a wide variety of functional groups and foreign atoms can be attached covalently to form different atomic planes, depending on the chemical nature of the gas and plasma parameters. Hence, dramatic changes in the correlation of electronic and atomic constituents in nanostructures and the unique properties of matter can occur due to plasma-assisted doping and functionalization. By tuning the plasma environment, i.e. the amount of nitrogen radicals, the thermal velocity of heavy species, electron density and temperature, the doping can be controlled and optimized. Plasma treatment is also compatible with standard microfabrication procedures and can, therefore, be easily incorporated into device fabrication protocols. The successful doping of graphene with nitrogen by means of NH3 plasma exposure, for instance, was already reported [10]. N-graphene has also been produced using a DC arc discharge between pure graphite electrodes using NH3 or pyridine vapor as the nitrogen precursor [6]. Although achieving a high yield, the method lacks doping controllability (reaching only 1% in pure NH3 plasma), relies on the use of graphite electrodes and produces N-graphene containing metal impurities. N-graphene was also obtained by exposing graphene to RF nitrogen plasma [11]. The obtained material exhibited a much higher electrocatalytic activity of N-graphene toward oxygen reduction than that of pure graphene and had much higher durability and selectivity than standard Pt for oxygen reduction. However, the mechanisms responsible for the unique properties exhibited by plasma-created N-graphene nanostructures are still to be understood. Most of the works reported rely on ‘trial-and-error’ empirical approaches where plasma is treated as a ‘black box’. Therefore, essential information about the main plasma characteristics is missing, along with processing evidence.

We report a microwave N2-Ar plasma-based method for the production of N-graphene. Free-standing graphene sheets synthesized by microwave plasma in a single step and at atmospheric pressure conditions, as described in [19, 20], were subjected to the remote region of low-pressure N2-Ar plasma for different exposure times. Optical emission spectroscopy has been applied to monitor nitrogen atoms, the temperature and the electron density at the position of the substrate where the graphene sheets were processed. Raman and x-ray photoelectron spectroscopy (XPS) techniques, along with transmission electron microscopy (TEM), were used in the characterization of the fabricated N-graphene sheets.

2. Experimental

2.1. Graphene sheet synthesis

The synthesis of the graphene sheets used in this study has been reported previously [19, 20]. In brief, the free-standing graphene sheets were synthesized using microwave plasma at a 2.45 GHz stimulating frequency and at atmospheric pressure conditions. The method is based on injecting ethanol molecules through a microwave argon plasma environment, where decomposition of the ethanol molecules takes place and carbon species, i.e. atoms and molecules, are created. Gas-phase carbon atoms/molecules diffuse into colder zones, in both the radial and axial directions, and as a result gas-phase carbon is transformed into solid carbon nuclei. The main part of the solid carbon is gradually withdrawn from the hot region of the plasma in the outlet plasma stream where graphene nanostructures assemble and grow. Externally forced heating in the assembly zone of the plasma reactor has been applied to improve the structural quality of the synthesized graphene sheets. As demonstrated in [19], the fabricated graphene sheets are stable and highly ordered and consist of a few atomic layers of graphene (1–5).

2.2. Plasma source and nitrogen doping

A slot-antenna-excited, surface-wave-sustained N2-Ar plasma source, as described in [21, 22], has been used. The schematic diagram of the apparatus is shown in figure 1. A glass tube \((ID = 24\, \text{cm} \text{ and length } L = 70\, \text{cm})\) constitutes the discharge vessel, which is closed at the top by a 10 mm-thick quartz window. The plasma vessel was evacuated by an Edwards diffusion pump (model 100 Diffstak 100) backed by an Edwards two-stage rotary pump (model BS2212), which provide a base pressure of about 10^{-6} mbar when no gases are injected into the chamber. Argon and nitrogen gases with high purity (99.999%) were employed.

The slot antennas are cut in the broad wall of the feeding rectangular waveguide shown in the figure. Microwave power of 600 W at \(\omega/2\pi = 2.45\, \text{GHz}\) is fed to the chamber. The generator is isolated from the chamber by a high-power circulator with a high-power matched load connected to its third port. An impedance transformer matches the chamber impedance to the feeding waveguide. The other end of the waveguide is short-circuited.

Plasma is created by the energy carried by the surface waves propagating radially and azimuthally along the interface between the plasma and a quartz dielectric plate. The microwave power enters the vessel through a quartz window. The waves form a resonant eigenmode satisfying the pertinent boundary conditions and the plasma takes discrete density values, which ensure that the resonant eigenmodes appear exactly at the excitation frequency (2.45 GHz). For the stable operation of the system, selective excitation of a proper mode
is necessary. Pure TM̂_{40}, i.e. an evanescent wave along \( z \), surface mode excitation is considered. The power of the surface wave close to the interface sustains an overdense plasma. As the distance from the interface increases, the wave electric field decreases exponentially and vanishes at some critical distance (\( z_{cr} \sim 1 \) cm) [21, 22]. According to the main mechanisms governing the plasma production and sustaining, the plasma source can be separated into two different parts. The first one is close to the interface (at about 1 cm from the quartz plate for the present conditions), where the surface waves are propagating and their energy sustains the discharge; this is the active discharge zone of the plasma source. Due to diffusion, the plasma expands into a second region, where a ‘microwave electric field free’ diffusion plasma is formed, for \( z > z_{cr} \). Particle diffusion and heavy particle collisional processes dominate the remote plasma zone. The radially averaged electron density decreases exponentially along \( z \), from \( 3 \times 10^{12} \) cm\(^{-3} \) close to the quartz plate to approximately \( 2 \times 10^{11} \) cm\(^{-3} \) at a 5 cm distance from the plate in the substrate vicinity. The 2D spatial distribution of the electron density considering the TM\( _{140} \) surface mode sustaining the discharge is shown in [22]. As a rule, the axial length of the remote plasma zone is much larger than that of the active discharge zone. The samples were processed in the remote plasma zone at a distance \( z = 4.5 \) cm from the quartz plate.

The plasma emission spectra in the 230 – 750 nm range detected at two different axial distances are shown in figures 2(a) and (b). The light emitted by the plasma was collected by an optical system located inside the plasma and directed by an optical fiber to the entrance of a Jobin-Yvon Spex 1250 spectrometer (2400 g mm\(^{-1} \) grating) equipped with a CCD camera [21, 22]. The cryogenic, back-illuminated UV-sensitive CCD camera has a 2048 \( \times \) 512 matrix, featuring a 13.5 \( \mu \)m pixel-size, which provides high spectral resolution. As seen from the figure the spectrum is dominated by Ar atomic lines. The nitrogen molecular bands and nitrogen atomic lines are shown in the insets made. Intense nitrogen atomic lines at 821.6 nm and 822.3 nm belonging to the transition \( \text{N}(3p \rightarrow 3s) \) have been detected. As seen in figure 2(b) the nitrogen atomic lines’ intensity decreases nearly twice as the distance toward the antennas increases from 4 cm to 8 cm.

The rotational temperatures corresponding to the first positive system \( \text{N}_2^+(B^2\Sigma_u^+, \nu = 0 \rightarrow X^2\Sigma_g^-, \nu = 0) \) of nitrogen provide a good measure of the gas temperature. To this end, the rovibronic bands in the 389–391 nm range have been used. As seen from figure 3, the emission spectrum of the first negative system of nitrogen is well established and the rotational lines are well resolved. These transitions can be used to measure the rotational temperature, provided that an accurate spectroscopic model is available. The LIFBASE code [23] has been used for this purpose. Both the measured and calculated spectra are shown in figure 3. The gas temperature varies in the limits 1200 K–1000 K when the axial distance increases from 4 cm to 8 cm. Although the location in the remote plasma zone has been chosen to avoid to some extent the adverse ion bombardment effect, the measured gas temperatures indicated the presence of energetic neutrals, i.e. Ar atoms and \( \text{N}_2 \) molecules, at locations where the plasma processing of the graphene sheets was performed, i.e. at \( z = 4.5 \) cm. Additionally, the interaction of ions with graphene should also be considered. A simple estimation shows that the dc potential \( \Phi \) of the substrate with respect to the plasma potential, i.e.

\[
\Phi \approx \frac{kT_e}{2e} \ln \left( \frac{M_i}{2\pi m_e} \right)
\]

may reach nearly 2.2 V assuming an electron temperature \( kT_e \sim 0.5 \text{ eV} \) [21, 22] and taking into consideration that ions enter the sheet with ion acoustic velocity [24]. An average ion with
mass \( M \) was considered keeping in mind that under the conditions considered \([N_2\text{-Ar} (10\%–90\%), P = 600\text{W}, p = 1\text{ mbar}]\) the ions that reach the substrate are \( \text{N}^+ \), \( \text{Ar}^+ \) and \( \text{N}_2^+ \). The estimations, based on the model presented in [22], demonstrate that the ion densities in the remote plasma zone, at \( z = 4.5\text{ cm} \), are about \( \sim 10^{11} \text{ cm}^{-3} \), \( 5 \times 10^{10} \text{ cm}^{-3} \) and \( 2 \times 10^{10} \text{ cm}^{-3} \) for the \( \text{N}^+ \), \( \text{Ar}^+ \) and \( \text{N}_2^+ \) ions, correspondingly. Therefore, accelerated ions with energy above 2.2 eV could impinge the samples and create defects.

Before the plasma treatment the synthesized self-standing graphene sheets were dispersed in methanol using an ultrasonic bath and then applied onto cleaned glass substrates. After drying, the graphene sheets were firmly attached onto the glass. The samples were then placed on a holder localized in the remote plasma zone at a distance of 4.5 cm from the quartz plate, as mentioned. At this distance there is a significant flux of nitrogen atoms as proved by emission spectroscopy measurements. Moreover, the calculations made demonstrate that the density of ground-state \( \text{N}(4S) \) atoms at this distance is about \( 10^{14} \text{ cm}^{-3} \) while the density of excited \( \text{N}(2P) \text{N}(2D) \) atoms is one order of magnitude lower [22].

2.3. Material characterization

X-ray photoelectron spectroscopy (XPS) characterization was carried out on a VSW XPS system with a Class 100 energy analyzer being a part of the experimental setup (Multitecnica) assembled for surface investigation [25]. The survey spectra were taken in a fixed analyzer transmission mode with a pass energy of 44 eV, i.e. FAT 44, while the detailed spectra of characteristic lines were taken in FAT 22 mode. The analysis has been performed using the non-monochromatic Mg K\(_\alpha\) line (photon energy of 1253.6 eV). For the energy axis calibration, Ag (1 1 0) and polycrystalline Au samples (previously cleaned by ion sputtering) were used. The energy was calibrated to the peak position of the Ag 3d\(_{5/2}\) (binding energy of 368.22 eV) and Au 4f\(_{7/2}\) (binding energy of 83.96 eV) lines. The samples were analyzed \textit{ex situ} without cleaning, in order to avoid bond breaking.

Raman spectra of the samples were taken on a LabRAM HR Visible (Horiba Jobin-Yvon) Raman spectrometer at 633 nm, with 5 cm\(^{-1}\) spectral resolution and a laser spot size of 2 \( \mu \text{m} \). Measurements were performed with a laser power \( P_L = 0.054 \text{ mW} \) to avoid overheating on the spot.

The doped graphene flakes were placed directly as a solid powder onto a copper grid for transmission electron microscopy (TEM). The N-graphene sheets were then characterized by a high-resolution TEM JEOL JEM-2010F, operating at 200 kV accelerating voltage.

3. Results and discussion

Raman spectroscopy is the most efficient way to provide a quick and easy structural and quality characterization of the samples. Figure 4 shows the Raman spectra of ‘pure’ graphene...
in-plane bond-stretching motion of pairs of sp\(^2\)-C atoms. The G band at ~1585 cm\(^{-1}\) 
there are three dominant peaks. The three peaks are attributed to the G-peak appears. As seen from the figure, the D-peak intensity is sensitive to the charge density.

Figure 5(a) shows the TEM image of a large area of high-purity multilayer N-graphene sheets, with a size of 100–200 nm. An HRTEM image of the N-graphene sheets is presented in figure 5(b). In principle, the layers of flat graphene cannot be seen by HRTEM. However, the edges of the graphene sheets are folded and appear at the HRTEM image as black fringes. From these folded edges the number of mono-layers can be determined. As seen, the number of mono-layers in the multi-layered N-graphene sheets is eight. The result indicates that the N-graphene sheets bear an excellent crystalline structure. We suppose that the number of mono-layers is mainly influenced by the dispersion of the graphene sheets in methanol rather than by plasma doping. It should be stressed that dissolving graphene in methanol causes the agglomeration of mono-layers and consequently an increase of the number of mono-layers in graphene sheets.

Furthermore, \textit{ex situ} XPS analysis has been performed to determine the elemental composition of the samples and to identify the chemical bonds. The survey XPS spectrum shown in figure 6 confirms the existence of N atoms attached to the graphene scaffold. Peaks appearing at about 284.5 eV, 400 eV, and 533 eV can be assigned to the C1s, N1s and O1s lines, respectively. A detailed analysis of additionally appearing small peaks enables us to assign them to the glass substrate, i.e. Si 2p, Si 2s, and the Auger sodium line (NaKLL). The estimation of the relative intensity of the O1s line, attributed to the glass substrate, is in accordance with the intensity of the Si lines using the relative sensitivity factors from [28]. After removing the signal that is coming from the glass substrate, the elemental composition of the N-doped graphene sheets was determined.

The initial sample contains about 88\% carbon and 12\% oxygen. When the sample is treated by pure Ar plasma for 5 min, the relative amount of oxygen increases to about 20\%. Adding nitrogen to the carrier gas results in the N-doping of graphene. The evolution of the elemental composition of the N-doped graphene with plasma exposure time is shown in figure 7. As can be observed, the relative amounts of carbon and nitrogen drop with the exposure time; meanwhile oxygen rapidly increases. The largest amount of nitrogen (5.6\%) is incorporated in the graphene scaffold at an exposure time of 5 min. It should be emphasized that the maximum nitrogen incorporated in graphene by applying the simultaneous synthesis and doping of graphene in arc discharge is about 1\% only [6].

The relative amount of oxygen in the samples rapidly increases with plasma treatment time, implying the discharge is mainly responsible for this contamination. Lack of oxygen in the working gas used in nitrogen doping indicates that oxygen was not incorporated into the graphene scaffold during the processing. It is much more likely that structural
defects were created during the plasma treatment, with an increased amount of unsaturated bonds at the graphene edge sites. Later on, when exposed to air, these sites become saturated by oxygen atoms. As for the originally synthesized graphene samples, their oxygen contamination can be caused by the incorporation of oxygen from the ethanol used as a carbon precursor [20]. Alternatively, it could be a consequence of the saturation of the dangling bonds by oxygen from air after the synthesis, just as in the case of nitrogen doping. Finally, some contamination of all samples by methanol might be observed as increased oxygen content. Depending on the envisioned application, thermal annealing of the graphene samples may be further applied to reduce the oxygen groups [29].

Furthermore, in the case of N2-Ar plasma, some nitrogen is also incorporated into the graphene scaffold, which further modifies the treated samples. Additionally, collisions with energetic heavy particles and different reactive species result in the physical and chemical sputtering of the sample and consequently the loss of carbon material. Consequently, prolonged treatment destroys the sample and even reduces the amount of incorporated nitrogen. In the following, we analyze the N 1s and C 1s photoelectron lines in order to reveal the nature of the graphene modification by the plasma treatment.

Generally, several nitrogen functional groups in nitrogen-doped graphene are expected. These include pyridinic-N (BE = 398.1–398.3 eV), pyrrolic-N (BE = 399.8–401.2 eV), and quaternary nitrogen N-Q (BE = 401.1–402.7 eV) [28]. Pyridinic-N (labeled as N-6) refers to nitrogen atoms at the edge of graphene planes; each of these N atoms is bonded to two carbon atoms and donates one p-electron to the aromatic \( \pi \) system (see figure 8). Pyrrolic-N (labeled as N-5) refers to nitrogen atoms that are bonded to two carbon atoms and contribute to the \( \pi \) system with two p-electrons, i.e. each N atom is bound with two other C atoms forming a ‘pentagon.’ In quaternary nitrogen structures (labeled N-Q) the \( \text{N}^+ \) ion is bound to four alkyl (aliphatic hydrocarbon) or aryl (aromatic hydrocarbon) groups. It seems that the N-Q structure is 3D, while the first two look more like ‘saturating dangling bonds of graphene-like structure.’ Finally, some oxidized nitrogen can also be formed [30].

Figure 5. (a) TEM image of N-graphene sheets; (b) HRTEM image with the edge of multi-layered sheets consisting of eight layers.

Figure 6. XPS survey spectrum of N-doped graphene.

Figure 7. Evolution of the elemental composition of N-graphene with plasma treatment time (\( P = 600 \text{ W}, \text{N}_2-\text{Ar} \) (10%–90%), \( p = 1 \text{ mbar}, Q_{\text{Total}} = 50 \text{ sccm} \)).
A detailed spectrum of the N 1s line taken from the sample treated for a 5 min exposure time, together with the fitted result, is shown in figure 9. For the peak model each contribution was described by a pseudo-Voigt Gaussian (70%)–Lorentzian (30%) line, and the background was determined using the Shirley algorithm. The constraint that each contribution has the same full width at half maximum (FWHM) was applied. The second (399.7 eV) and the third (401.3 eV) contributions can be attributed to the N-5 and N-Q structures, respectively. Following the results in [30], peak 1 can be clearly interpreted as N-6. It should also be stressed that no oxidized nitrogen was observed.

The dependence of the relative amount of different nitrogen functional groups in N-graphene on plasma exposure time is shown in Figure 10. As seen, the amount of pyridinic-N keeps nearly constant when exposure time increases from 5 to 15 min. Meanwhile, pyrrolic-N decreases and N-Q increases with the exposure time. It should be stressed that the role of the real ‘electrocatalytically active sites’ is still controversial since their contribution to catalytic activity is not well defined. In some studies enhanced electrocatalytic activity is attributed to pyridinic-N and/or pyrrolic-N. As can be seen from the results, these two types are present in the N-graphene analyzed. To this end, an optimal exposure time of 5 min for N-graphene synthesis can be considered.

The peak model for the C 1s line was chosen starting from the well-known fact that highly conductive samples, including different metals and graphite, have asymmetric photoelectron lines. The theoretical consideration yielded the Doniach–Šunjic (DS) profile [31], which then has to be convoluted to some symmetric profiles in order to describe different instrumental broadening effects. Similar to the approach given in [32], we used for the peak model a DS profile with an asymmetry parameter of 0.01, convoluted by pseudo-Voigt GL(70).

Figure 8. Schematically presented nitrogen functional groups: (a) pyridine N-6, (b) pyrrolic N-5, (c) quaternary nitrogen N-Q.

Figure 9. XPS N1s spectrum of N-doped graphene sheets (treatment time is 5 min).

Figure 10. Time evolution of nitrogen functional groups attached to graphene scaffold (P = 600 W, N2-Ar (10%–90%), p = 1 mbar, Q_{Total} = 50 sccm).

Figure 11. XPS C 1s profile modeled using Doniach–Šunjic profiles (asymmetry parameter α = 0.01) convoluted by pseudo-Voigt GL(70).
The detailed spectrum of the C1s photoelectron line taken from the graphene samples exposed to N2-Ar plasma for 5 min is shown in figure 11. The line can be well fitted into 5–6 components interpreted as follows: the contributions at about 284.5 eV and 285.3 eV are usually interpreted as sp² and sp³ hybridized carbon, respectively; the peak at 286.3 eV can be related to epoxide (C-O-C) or C=*O-(C = O) groups; in the range 278–288 eV we expect contributions related to the carbonyl group (C = O) but also to the C-N bond [33]; the peak at 288.7 can be interpreted as the C-O-(C = O) group; the peak at about 289.5 eV is related to the carboxyl (COO) group. Finally, there is a satellite peak due to the π → π* excitation, shifted for about 6.7 eV with respect to the sp² contribution. The results of the fitting of several samples are summarized in table 1.

Several conclusions can be made from these results. Firstly, the Ar plasma treatment increases the number of oxygen bonds, which is fully consistent with the XPS composition analysis. In addition, it also decreases the sp³ intensity, while sp² contribution does not change. Apparently, oxygen bonds were formed at the expense of the sp³ hybridized carbon, which consequently increases the sp²/sp³ ratio from about 3 to 4.3. Adding N₂ to the carrier gas contributes to both an additional decrease of the sp³ component and also an increase of the sp² contribution. After 5 min of N₂-Ar plasma treatment, the sp²/sp³ ratio reaches a value of 5.2. The contribution that was addressed to the carbonyl group and/or C-N bond [33] clearly did not increase when nitrogen was incorporated into the graphene scaffold. Therefore, the increase of the sp² amount could be caused by the formation of N-5 and N-6 structures.

As already mentioned, the energy of the heavy particles from the plasma impinging the graphene does not exceed several eV. These particles are able to recoil only loosely bound atoms in a direct knock-on collision while more stable structures, such as the graphene scaffold, cannot be affected. Consequently, the short-term plasma treatment of the sample increases the relative amounts of sp² hybridized carbon via the etching of less stable sp³-like structures and saturating the dangling bonds by nitrogen and oxygen atoms. It should also be emphasized that the observed increase of the sp²/sp³ ratio is supported by the finding that the D/G intensity ratio increases with the sp² content in the nano-crystalline graphite, as already discussed.

However, prolonged N₂-Ar plasma treatment of the graphene samples contributes to the decrease of the sp²/sp³ ratio, a decrease of the carbon and nitrogen amounts, and an increase of the oxygen amount. The significant damaging of the graphene structure during the long-term exposure has to be caused by another mechanism having a slower etching rate. Chemical sputtering is probably responsible for the latter effect: it could create atoms with dangling bonds in a stable graphene structure, which can then be efficiently etched by collisions with heavy atomic and ionic particles. It should also be stressed that the relative amount of the N-Q contribution in the N 1s line increases with the plasma exposure (see figure 10). This fact supports the assumption that N-5 and N-6 contributions are related to sp² hybridized carbon while an N-Q contribution corresponds to the sp³ structure.

4. Conclusions

We have demonstrated the production of N-graphene using microwave N₂-Ar plasma. Free-standing graphene sheets were subjected to the remote region of the plasma for different exposure times and fixed applied power (P = 600 W), gas composition (0.1 N₂-0.9 Ar), pressure (P = 1 mbar) and total gas flow (Qtot = 50 sccm). Optical emission spectroscopy has been applied to monitor the nitrogen atoms, gas temperature and electron density at the graphene sheets’ positions. Raman and x-ray photoelectron spectroscopy techniques have been applied to characterize the produced N-graphene, along with transmission electron microscopy to study the morphology and structure of the samples. The results demonstrate that the level of doping and type of functional groups attached to the graphene scaffold can be controlled by changing the exposure, with the nitrogen percentage kept constant. The maximum level of nitrogen doping of graphene achieved was 5.6%, which is much higher than that reported for arc-discharge plasma methods [6]. Additionally, a short-term plasma treatment increased the sp²/sp³ ratio, which is apparently related to both C-O bond formation (at the expense of sp³ carbon) and N doping (which increases the amount of sp² carbon via the formation of pyridine- and pyrrol-like structures).

Subsequent work, already in progress, will allow further optimization of the doping process by actively controlling the gas temperature and nitrogen atom fluxes reaching the graphene sheets as well as by applying thermal annealing to reduce the oxygen amount in the graphene samples.

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