Non-destructive method for doping of graphene using the flowing afterglow of microwave plasmas at reduced pressure

L. Vandsburger, G. Robig and L. Stafford

Département de Physique, Université de Montréal, Montréal, Québec, Canada

Abstract: CVD-grown graphene films have been n-doped by downstream plasma-afterglow treatment. In the flowing afterglow of a microwave N2 plasma, metastable species and atomic nitrogen are present in significant densities. XPS and Raman are combined with molecular dynamics simulations to develop a mechanism based on defect localized N-incorporation by a three-body introduction reaction.

Keywords: graphene, plasma-doping, CVD, nudged-elastic band

1. Introduction
Graphene is leading the charge in the drive to develop the next generation of electronics and optoelectronics. Such applications, however, depend on the availability of versatile post-growth processing techniques that can adapt it for implementation in technologies where band gap is necessary, especially in the domain of large-area films grown by chemical vapour deposition (CVD).

The n-type doping of graphene by nitrogen atoms has been addressed as a means either for increasing electron density in graphene films or for inducing a band gap by direct incorporation or carbon replacement [1]. Nitrogen doping is generally realized during growth by various physical and chemical methods [2, 3]. Conventional post-growth methods, which offer more versatility than variation of the growth conditions, are based either on wet chemical or thermal annealing processes [4, 5] or direct implantation of atoms [6-8]. In this work, we explore the potential of the flowing afterglow of microwave plasmas at reduced pressure for non-destructive doping of CVD-grown graphene films [9].

2. Methods
Graphene samples were synthesized by CVD on 25 μm copper foils commercially available from Alfa Aesar (item No. 13382). The foils were first chemically treated with acetic acid and annealed for 30 minutes at 1030 °C under a flow of 12 sccm (standard cubic centimeters per minute) hydrogen gas in order to prepare the copper surface. The temperature was maintained at 1030 °C during a 30 minute CVD growth phase where a gas flow of 4 sccm methane was introduced [10].

The late-afterglow approach was described in detail in a previous paper [11]; it is explained visually in Fig. 1. In Fig. 1a, a surface-wave plasma is produced in a fused silica discharge tube by a surfatron [12], operating at 2.45 GHz. The power injected into the plasma (incident less reflected power) was approximately 30 W, yielding a surface-wave plasma column (zone 1 in Fig. 1a) of about 3 cm. The microwave plasma expands into a stainless steel processing chamber by a flow of ultra-high-purity N2 gas (99.999%). For all experiments reported here, the system operated at 10 torr and a flowrate of 250 sccm. The chamber reached a base pressure of 7×10⁻⁹ torr before gas injection, ensuring a minimal presence of impurities.

Beside the main plasma zone sustained by microwave, two other bright regions appear in the flowing afterglow of nominally pure N2 plasmas: the early afterglow and the late afterglow (see Fig. 1) [13]. Both afterglow regions are linked to the N2 vibration-vibration pumping mechanism, which creates highly energetic N2 vibrational states that are pushed downstream by high gas flows. These highly energetic N2 states can collide to form N2(A) and N2(a′) metastables (at 6 eV and 8.1 eV above ground, respectively) and subsequent ion-electron pairs.
by associative ionization reactions [14]. The number densities of plasma-generated N atoms, $N_2(A)$ metastables, and positive ions in the downstream region was determined in a previous paper by optical emission spectroscopy and Langmuir probe measurements. The results are summarized in Fig. 1d as a function of the parametrized time after the surface-wave discharge in the flowing afterglow. The rise in all quantities at 10 ms corresponds to the early afterglow [15], while longer times can be ascribed to the late afterglow. At the experimental conditions investigated here (dashed line in Fig. 1d), the grounded substrate holder where graphene samples are placed is exposed to the late afterglow. Positive ion number densities in this region are less than $10^7 \text{ cm}^{-3}$, much lower than the values observed in the main plasma region ($>10^{11} \text{ cm}^{-3}$), as well as in other types of low-pressure plasma reactors (typically between $10^{10}$ and $10^{11} \text{ cm}^{-3}$). Furthermore, since these ions are not accelerated towards the grounded substrate, ion bombardment effects can be ignored. As shown in [16], the heavy species temperature is close to 300 K, which further eliminates flux-induced heating of the sample.

For nitrogen to be useful for n-doping, N-atoms must be introduced in pyrrolic (5 member ring), pyridinic (6 member ring), or quarternary (trinary planar) bonded positions in order to participate in the hybridized orbital structure and thus to alter the large-scale electronic structure of graphene films [17]. The basic morphology of these three groups is presented in Fig. 1b. The de-excitation of long-lived $N_2(A)$ metastable species by collision with the surface represents a significant source of energy, at least within a very short time frame (de-excitation time on the order of 1-10 ns), with internal energy 6 eV above the ground state level $N_2(X)$ [18].

3. Results and discussion

Fig. 2 presents the XPS data collected from a representative set of graphene samples treated for 0-5 minutes. Fig. 2 (a) is a high-resolution scan of the N1S peak collected from a sample treated for 30 seconds. The deconvolution focused on identifying aromatic inclusions at 398.7 eV (pyridinic N), 400.1 eV (pyrrolic N), and 401.0 eV (quarternary N) [19]. It is important to note that no N1S peak was observed in untreated samples. The de-convolution of the N1S peaks shows that nitrogen was incorporated into both pyrrolic and pyridinic moieties, with no composition attributed to quarternary-bonded N atoms at 401.0 eV. Considering that incorporation of energetic N atoms typically produces quarternary-bonded N atoms, these findings indicate that N incorporation into aromatic configurations occurs via a different mechanism. Surface chemisorbed amines and amides also appear in the N1S as very broad peaks (FWHM 1.8 eV), typically centered at 399.5 eV [20-22]. These species are known to be present, considering the disparity between the values given for total N composition and the sum of the individual de-convoluted peaks, as shown in Fig. 3. Nitrogen concentration increased during treatment, as shown in both Fig 2 (a versus b) and in the steady increase in the C-N signal (285.6 eV) in the C1S spectrum (Fig. 3).

![Fig. 2. XPS of graphene films: (a) N1S spectrum from high resolution scan of graphene after 0.5 min treatment showing aromatic N bonding, (b) N1S spectrum of graphene on Cu foil after 3 minute treatment. (c) C1S spectra of graphene films for 0, 3, and 5 min treatments.](image)

![Fig. 3. XPS analysis of composition development with treatment duration. The change in signal intensity from C-N bonding in the C1S spectrum and total nitrogen concentration indicates a development of N bonded in non-aromatic groups.](image)

Further analysis of the XPS data, presented in Fig. 3, shows that the N1S signals arising from aromatic N cease to increase soon after the first treatment. This indicates that, over the range of experimental conditions investigated, the dose of plasma-generated species is much larger than the capacity of the graphene to accept aromatic inclusions. N atom bonding, however, continues to increase linearly with treatment time, as shown in Fig. 3. Considering the constant surface flux of N-atoms during late afterglow treatment, these findings strongly indicate that incorporation of atomic N into aromatic
bonding is preceded by surface N adsorption and that the graphene surface is not fully covered by adsorbed N atoms. Published reports indicate that N adatoms are mobile on unsaturated graphene films [23]. Therefore, although adsorption does not necessarily occur at defect sites, adsorbed N species can migrate to defect sites for rapid, defect-guided, N incorporation. In this framework, the density of as-grown defects limits the extent of aromatic inclusions, as seen in the XPS data.

Raman data support the finding that nitrogen atoms are introduced steadily during late afterglow treatment. Raman spectra for three samples are shown in Fig. 4. While as-grown samples show the typical 2D and G peaks resulting from large area sp² bonding, treated samples show the development of the D peak, attributed to out-of-plane sp³-type bonding [24]. By studying the development of the average D/G ratio as shown in Fig. 4c, it can be seen that D peak development increases linearly with treatment time. Considering that the increase in aromatic-bonded N found by XPS ceases early in that period, it is concluded that nitrogen adatoms are attaching on the graphene surface, by converting sp³ bonded graphitic carbon into out-of-plane bonded ternary carbon. The steady development of additional peaks, specifically the D’ and the D+D’ peaks [25], is consistent with sp³ hybridization and corresponds with what has been reported for nitrogenation of graphene. N heteroatoms accentuate the Raman signals originating from point defects [30]. In particular, the development of D’ peaks have been shown to result from defect activation that results from nitrogenation [26].

Fig. 4. Raman resonance spectra of graphene films at 514 nm (a) normalized spectra taken from graphene films transferred onto Si by PMMA transfer. Peaks labeled by ‡ and * are artifacts of the transfer process arising from residual PMMA and the Si/SiO₂ substrate, respectively. (b) Raman spectra of graphene films taken directly on copper foil. The spectra are offset to emphasize that the D peak is induced after plasma treatment. (c) The steady increase of the D:G ratio indicates a near constant rate of surface reactions, corresponding to the steady increase in C-N bonding signals in XPS data. (d) Peak shifts of both the G and 2D peaks from transferred graphene samples as a function of treatment time (min).

Raman data also indicate that in transferred samples, Fig. 3a, the 2D peak was red-shifted up to 1.43 cm⁻¹ after treatment. A red-shift was also measured in the G peak (shift up to 1.15 cm⁻¹ after 5 minutes). The trends, shown in Fig 3d, demonstrate that the shift is not progressive, establishing a stable shift after the first treatment, and is similar in magnitude for both G and 2D peaks. A red-shift in G and 2D peak positions has been found to occur in graphitic nanomaterials after N-doping by aromatic group formation [27], which supports the findings of XPS that nitrogen afterglow treatment results in nitrogen incorporation, and that the incorporation saturates very rapidly during treatment.

The defect-localized formation of aromatic N groups in graphene was examined by computational simulations using density functional theory (DFT) and the nudged elastic band (NEB) method, similar to published analysis of ammonia-based N graphitization reactions [28]. Systems based on single and double-vacancies in graphene were built and were subsequently used to examine the transition state energies of the aromatic N incorporation reaction. The premise of the model approach was to evaluate whether an N adatom could be introduced into a graphene point defect with an activation energy of less than 6 eV. This threshold value of 6 eV corresponds to the de-excitation energy of N₂(A) metastable species present in the late afterglow region. For single-vacancy systems, a graphene cell was created comprising 61 carbon atoms and a single nitrogen atom. This was used to examine the formation of pyridinic N heterocycles in graphene point defects. The cell was larger for divacancy systems, containing 86 carbon atoms and a single nitrogen atom. The divacancy system was used to test incorporation of N adatoms into pyridinic and pyrrolic moieties. Both systems were saturated with hydrogen atoms at the edges. DFT calculations were used both to optimize the molecular images making up the endpoints of the NEB chain-of-states, and to calculate the energy of each image in the chain. Design of the endpoint configurations was based on hypothetical molecular geometries for N adatoms to translate into the heterocycle bonded positions. These images were optimized, with component atoms being free to relax, until the energy change per optimization step dropped below 10⁻¹⁰ eV.

Simulations reveal that aromatic incorporation of adsorbed N atoms in both single and double point vacancies occurs by passing through a transition state with energy less than 6 eV. The reaction paths are shown in Fig. 5a-c. In Fig. 5a, a single vacancy forms a pyridinic N inclusion, with a relative transition state energy of 3.9 eV when starting with adsorbed adsorbed N, while the reverse reaction has a relative energy barrier of 9.2 eV. The same effect is seen in divacancy systems, where pyridinic inclusions (Fig. 5b) are formed at a lower relative energy barrier of 1.3 eV, and are removed only after introduction of at least 8.2 eV. Pyrrolic inclusions (Fig. 5c), which outnumbered pyridinic inclusions in XPS measurements, are formed in divacancy defects with a slightly higher energy barrier of 5.8 eV, with a reverse reaction requiring 9.9 eV. The lower energy of pyrrolic N in graphene provides corroborating evidence to explain its
higher concentration in XPS measurements.

The analysis described above provides further evidence that a single de-excitation collision between an excited N$_2$(A) metastable state could provide sufficient energy to promote a nitrogen adatom into the transition state and allow it to subsequently form an aromatic state. The simulation further shows that the reverse reaction cannot be stimulated in the same way, because the activation energy for the reverse reaction exceeds the de-excitation energy released during the N$_2$(A) third-body excitation mechanism. The prevalence of pyrrole inclusions can be attributed to the proximity of the energy of the transition state in the aromatic introduction reaction to the 6 eV provided by the de-excitation of N$_2$(A) and to the lower overall energy of the pyrrolic configuration, leading to increased overall stability.

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5. References
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