Defect Controlled Addition of Nitrogen into Aromatic Configurations in CVD-Grown Graphene by Microwave Late Afterglow Plasma Exposure

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Abstract

Statement of background and motivation:

The tuning of graphene electronic properties via a fine and controlled Nitrogen doping is promising for multiple domains including: digital electronics, optoelectronic and bio-sensors. Using variable-bias ion bombardment on graphene enables a controlled formation of reactive defects and therefore the tuning of the number of sites where chemical bonds can be formed by Nitrogen [1,2]. The cleaning and reconstitution of graphene achieved by Nitrogen plasma treatment in combination to annealing processes allows the formation of surface engineered defect free Nitrogen doped graphene sheets [3]. Unlike wet-chemistry treatment, the plasma approach requires no acidic environment, is less time consuming, easily adapted to clean-room conditions in addition to being more eco-friendly.

Methods:
A dual source plasma system was developed to examine the role of defect density in determining aromatic nitrogen content in graphene films, shown in Fig. 1. A primary plasma source, consisting of a 600 MHz surface wave generator (surfatron) was used to produce an ion-rich argon plasma. A secondary source consisting of a 2.45 GHz surfatron was used to produce the nitrogen plasma flowing afterglow used for downstream treatment. In this system, samples were mounted in direct electrical contact with a biased sample holder, which was biased at -100 VDC during exposure to Ar plasma. Based on literature published on defects in Ar ion treated graphene, a timeframe of 1-10 seconds of treatment under Ar bombardment conditions was investigated. All nitrogen treatment parameters where held constant to isolate the effect of ion bombardment treatment defect density. These comprised 6 torr operating pressure, 0 VDC substrate bias, 300 sccm N_2 flowrate, 30 W dissipated power, and 3 min exposure time to the nitrogen flowing afterglow. Following treatment, samples were analyzed by XPS and compared to data collected from untreated samples.

Results:
High resolution XPS analysis demonstrated that treatment by ion bombardment prior to N_2 flowing afterglow exposure had a significant and dramatic effect on aromatic content as shown in Fig. 2. The calculated relative atomic percent values are presented in Fig. 3. In particular, there was a 300% increase in pyridinic N content, while amine and pyridinic N content was relatively unaffected by Ar ion treatment. The largest change was seen in adsorbed N_2 content in films. This phenomenon is explained by activation of the graphene film by ion bombardment, as has been shown to occur in literature [ref], leading to an increase in the sticking coefficient and stabilization of N_2 chemisorption processes. Over the first two seconds of Ar bombardment, the content of aromatic pyridinic N increases relatively linearly, which supports a hypothetical hypothesis of incorporation at point defects. The stability of amine bonding is explained by the fact that N_2 treatment parameters were held constant.

Conclusions and Implications:
These data represent a conclusive demonstration of defect-limited low energy incorporation of N into graphene by downstream plasma treatment. Adsorbed and amine nitrogen content can be removed selectively by substrate transfer and thermal treatments, respectively. This allows the approach to produce a graphene film with significant aromatic N content as well as tightly controlled composition, through a completely integrated post-growth process. In addition, a fundamental understanding of the plasma physics involved in the process allowed for its development based on physical principles, a characteristic that has thus far been absent from downstream plasma treatment work.

References

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Figures

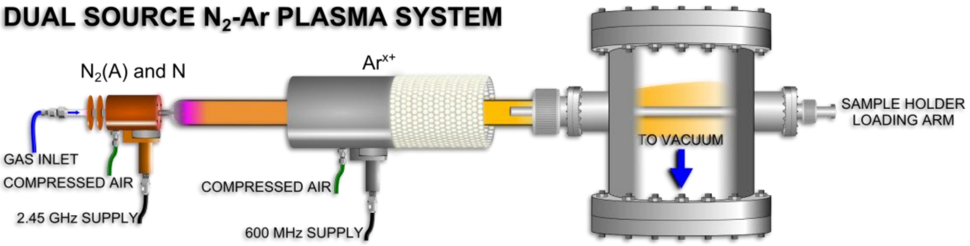

Figure 1. Plasma treatment vacuum system comprising two sources and a movable sample holder arm

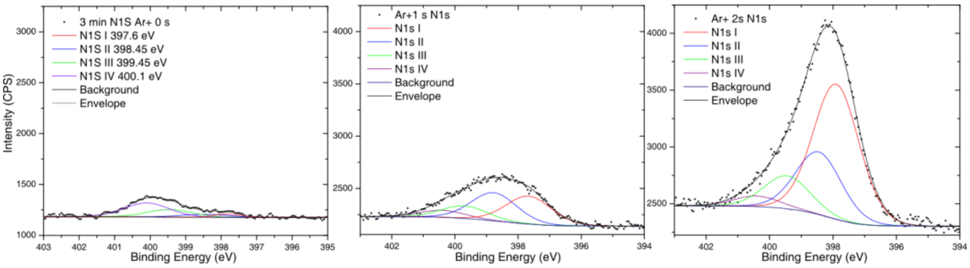

Figure 2. XPS spectra for graphene films treated by 0-2 second Ar+ bombardment treatments. The peak assignments are as follow: N1s I is attributed to adsorbed N_2, N1s II to pyridinic N (aromatic), N1s III to pyrrolic N (aromatic), N1s IV to amines and other C-N-C bonds (non-aromatic).

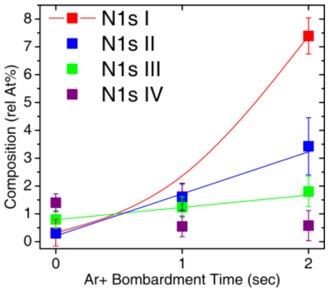

Figure 2. XPS relative atomic percentages calculated from high resolution scans of N1s peaks. The peak assignments are as follow: N1s I is attributed to adsorbed N_2, N1s II to pyridinic N (aromatic), N1s III to pyrrolic N (aromatic), N1s IV to amines and other C-N-C bonds (non-aromatic).