Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Nanoscale Imaging of Freestanding Nitrogen Doped Single Layer Graphene

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The nitrogen ion bombardment of LFG was carried using an inductively coupled plasma (ICP) generated in a 20 L stainless steel vacuum chamber ICPII-600 (base pressure < 10^{-6} Torr) fed by N_2 feedstock gas. The plasma discharge was generated via a 13.57 MHz radiofrequency (RF) power supply (SEREN Industrial Power Systems R601) coupled to a multi-turn flat RF coil *via* a tuned capacitor matching network (controlled by a SEREN MC2 Matching Network Controller). The coil was separated from the discharge by a quartz window (8 inch diameter) and a Faraday screen to prevent capacitive coupling. During operation of this system plasma parameters are measured using standard swept-voltage Langmuir probe techniques. This ICP plasma system is described in more detail in reference.[1] For our experiments the plasma discharge was operated with 100 W forward RF power and < 2 W reflected RF power. The plasma parameters for the experimental conditions used (N_2 input flow rate = 20 sccm and 100 W RF power) were as follows: plasma density $n_0 = 4 \times 10^9$ cm^{-3} and electron temperature $T_e = 4.3$ eV. The ionic composition was approximately ~ 86% molecular ions (i.e. N_2^+) and 13% atomic ions (i.e. N^+),[2] with the remaining 1% being other ion species.

High voltage plasma ion implantation is commonly used to drive energetic ions deep into target substrates. However, even without high voltage biases applied, electropositive plasmas float to positive potentials relative to the grounded chamber walls and targets.[3] In the graphene doping experiments performed here the plasma potential was approximately +20 V relative to the grounded target holder on which the graphene sample was mounted. Thus ions from the plasma bombarded the graphene target with energies ~ 20 eV. For the majority species (N_2^+ molecular ions) this is equivalent to 10 eV energy per N atom.

The mean penetration depths of ion implantation ("projected ranges" R_p) are commonly calculated using the well-calibrated public domain code SRIM.[4] For a graphite target [ICRU-906] the results given by SRIM-2013 are graphed in Fig. S1. It can be seen that at a mean bombardment energy of ~ 10 eV, atomic nitrogen has a projected range R_p ~ 2 Å, comparable to the thickness of single-layer graphene (SLG or 1LG).[5] The penetration depth of the nitrogen dopant atom in the plasma discharge used to modify the LFG is consistent with nitrogen ion bombardment energy. This validates the low defect doping observed in the NLFG samples and proves the efficacy of our nitrogen ICP exposure technique as a suitable method for the preparation of low defect n-doped graphene.

Figures:

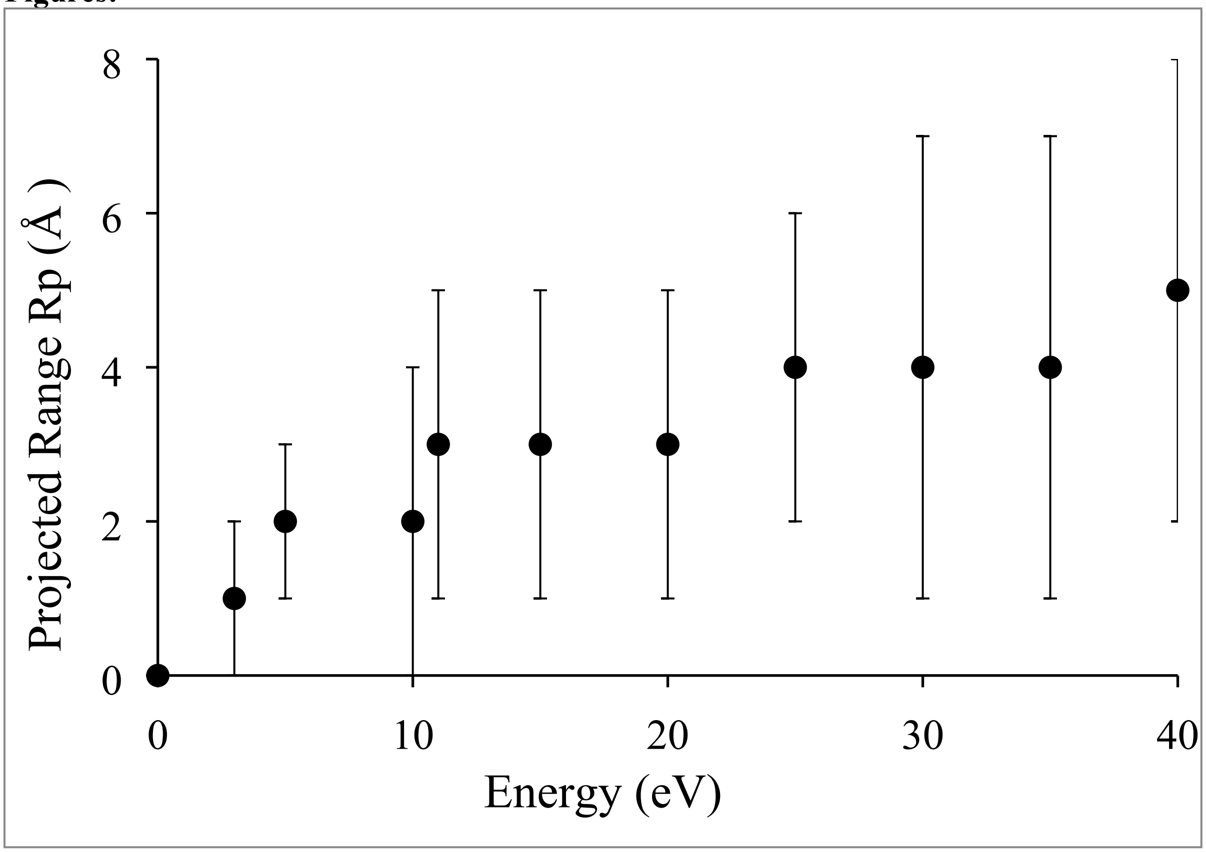

Figure S1: Projected range for atomic N ions in ICRU-906 graphite, as calculated by SRIM-2013 [4]. The projected range is the mean penetration depth of the ions along the direction of the incident beam; as such it corresponds to the penetration depth of the ions into the target material. The error bars on the data points correspond to the values of "longitudinal straggle", which is the standard deviation of the projected range.

References

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[2] M. Risch and M. Bradley, "Predicted depth profiles for nitrogen-ion implantation into gallium arsenide", *physica status solidi (c)* 2008**, 5**, 939–942.

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[4] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, "SRIM – The stopping and range of ions in matter", *Nucl. Inst. Meth. B,* **2010**, *268*, 1818-1823.

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