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Atom-by-Atom STEM Investigation of Defect Engineering in Graphene

Q.M. Ramasse¹, D.M. Kepapstoglou¹, F.S. Hage¹, T. Susi², J. Kotakoski^{2,3}, C. Mangler², P. Ayala², J. Meyer², J.A. Hinks⁴, S. Donnelly⁴, R. Zan⁵, C.-T. Pan⁵, S.J. Haigh⁵ and U. Bangert^{5,6}

¹ SuperSTEM Laboratory, STFC Daresbury Campus, Keckwick Lane, Daresbury WA4 4AD, U.K.

² Faculty of Physics, University of Vienna, Strulhofgasse 4, A-1090 Vienna, Austria

³ Department of Physics, University of Helsinki, P.O. Box 43, FI-00014, Helsinki, Finland

⁴ School of Computing and Engineering, University of Huddersfield, Huddersfield HD1 3DH, U.K.

⁵ School of Materials, University of Manchester, Manchester M13 3PL, U.K.

⁶ Department of Physics and Energy, University of Limerick, Limerick, Ireland

Developing effective practical means of modifying the carrier concentration in graphene in order to create a true p- or n-doped material would represent an essential step towards graphene-based nano-electronics. It was recently shown that this goal could be achieved by means of low energy ion implantation, a technique with the great advantage over more conventional chemical routes that it is compatible with current technology for integrated circuit fabrication. STEM-EELS results demonstrate unambiguously that N (for n-doping) and B (for p-doping) ions were successfully implanted into the graphene sheet as pure single substitutional defects, with retention rates consistent with theoretical predictions [2]. The use of a low energy ion source was crucial in avoiding the creation of structural defects by the ejection of carbon atoms under the ion beam, although these combinations of 5-, 7- or 8-member C rings are themselves potentially electronically active. Characterising their formation, using a far more energetic ion irradiation, is therefore essential. A combination of Raman spectroscopy and *in situ* electron diffraction shows that the disappearance of wrinkles in few-layer graphene sheets coincides with a progressive amorphisation of the graphene under ion irradiation [3]. High-resolution HAADF STEM imaging at 60kV reveals indeed that typical arrangements of defected carbon rings are present in samples that have been exposed to a high enough ion dose, while no such topological defect can be observed below a critical dose: fig. 1.

These 'gentle' STEM observation conditions can nevertheless be used to drive the diffusion of substitutional dopants through single layer graphene, one atomic jump at a time [3]. A combined experimental and theoretical study, making use of *ab initio* molecular dynamic calculations, reveals that for Si dopants these jumps are not due to impact on the Si atom, but to sub-threshold impact events on the surrounding C atoms: fig. 2. Similar events were also demonstrated to lead to the transformation of trivalently bonded Si dopants into the tetravalently bonded configuration, both of which have been fingerprinted by STEM-EELS [4].

Even though these results represent great strides towards nano-engineering defects in graphene, a full control over the density and nature of the defects is still difficult to achieve. By contrast, the unique structure of graphene nano-cones dictates the presence of a well-defined number of pentagonal ring defects at their tip and thus offers an ideal test material to study the impact of these defects on the electronic structure of graphene. Momentum-resolved EELS experiments in the STEM show in particular that a high enough pentagon density can lead to the confinement of plasmon modes at the apex of the cones [5], while additional interband states are created in the vicinity of the tip [6].

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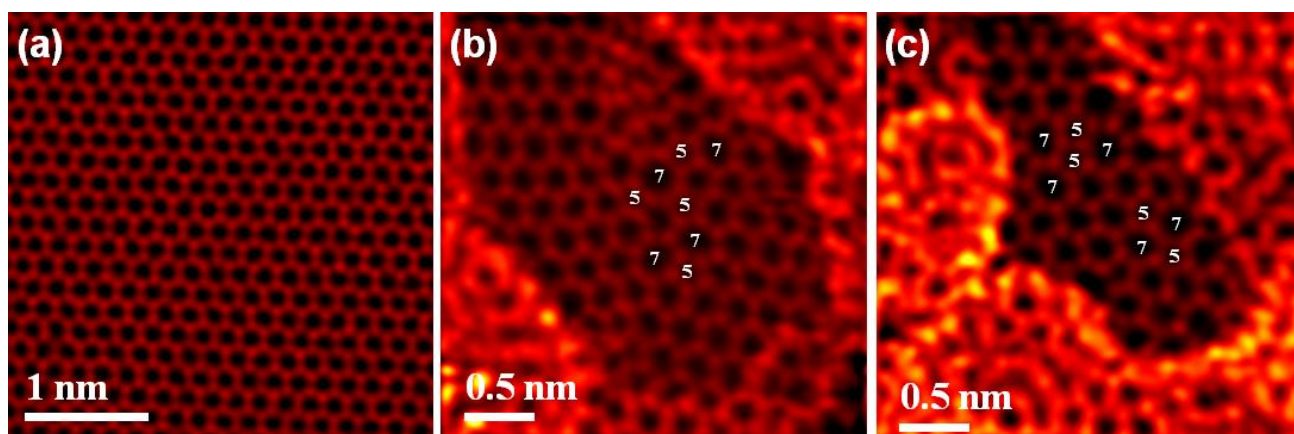


Figure 1. HAADF images of single layer graphene irradiated with 30keV He ions at fluences of (a) 3.0×10^{15} ions.cm⁻² and (b-c) 9.6×10^{15} ions.cm⁻². While no topological defect was observed at low ion fluences, a Haeckelite structure and an inverse Stones-Thrower-Wales defect can be seen in (b) and (c) respectively. The images were low-pass filtered for clarity. [2]

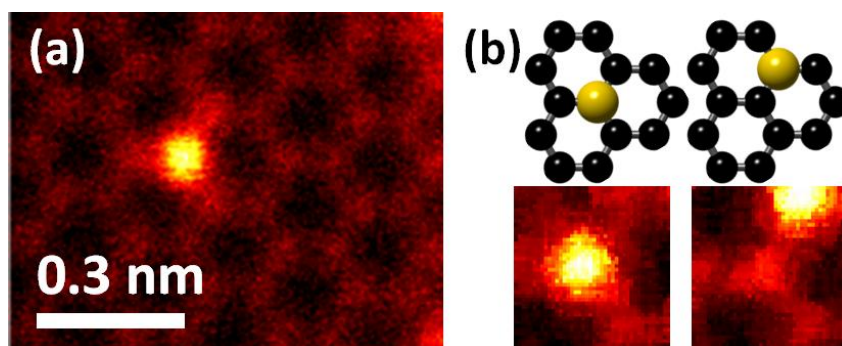


Figure 2. (a) HAADF image of a single Si substitutional dopant in trivalent configuration (fingerprinted with EELS). (b) Sequential MAADF images of a similar Si defect, showing a jump to a neighbouring atomic site: 6 consecutive frames from the original high frame rate movie are averaged (and filtered using a 5x5 Kuwahara filter for clarity), such that the two images presented here were effectively recorded ~ 0.45 s apart. A ball-and-stick model illustrates the atomic jump. [3]