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doi:10.1017/S1431927614010411

Microsc. Microanal. 20 (Suppl 3), 2014

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

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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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[7] SuperSTEM is funded by the UK Engineering and Physical Sciences Research Council (EPSRC).

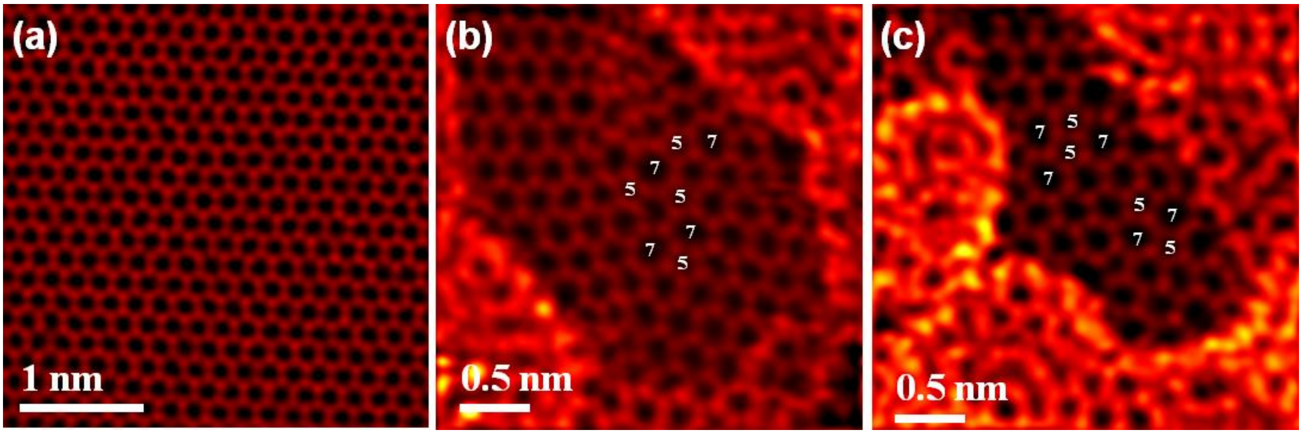

Figure 1. HAADF images of single layer graphene irradiated with 30keV He ions at fluences of *(a)* 3.0×10^{15} ions.cm^{-2} and *(b-c)* 9.6×10^{15} ions.cm^{-2} While no topological defect was observed at low ion fluences, a Haeckelite structure and an inverse Stones-Thrower-Wales defect can be seen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

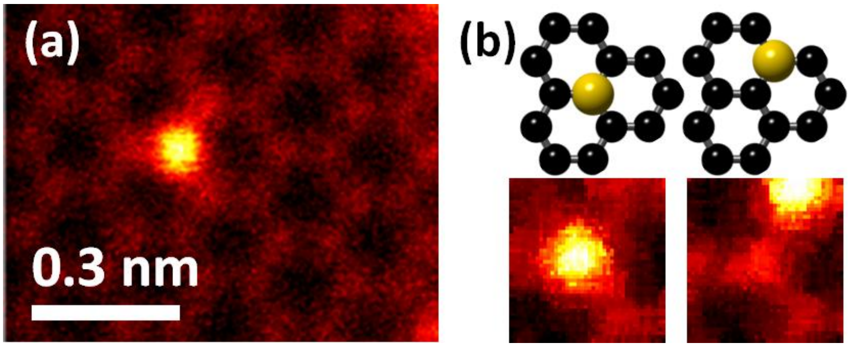

Figure 2. *(a)* HAADF image of a single Si substitutional dopant in trivalent configuration (fingerprinted with EELS). *(b)* Sequential MAADF images of a similar Si defect, showing a jump to a neighbouring atomic site: 6 consecutive frames from the original high frame rate movie are averaged (and filtered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