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### Original Citation

Ramasse, Q.M., Kepapstoglou, D.M., Hage, F.S., Susi, T., Kotakoski, J., Mangler, C., Ayala, P., Meyer, J., Hinks, J. A., Donnelly, S. E., Zan, R., Pan, C.T., Haigh, S.J. and Bangert, U. (2014) Atom-by-Atom STEM Investigation of Defect Engineering in Graphene. *Microscopy and Microanalysis*, 20 (S3). pp. 1736-1737. ISSN 1431-9276

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

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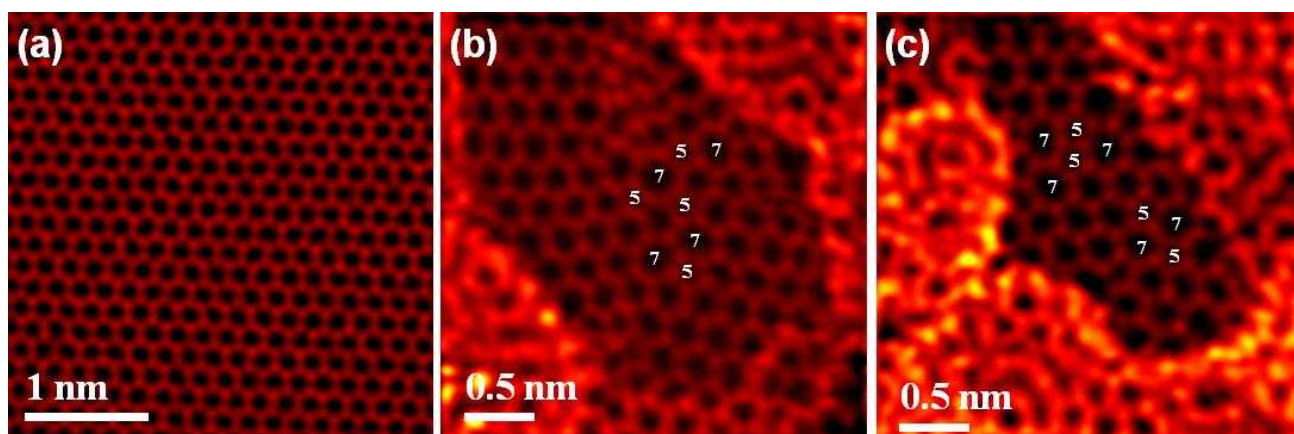
Developing effective practical means of modifying the carrier concentration in graphene in order to create a true p- or n-doped material would represent an essential step towards graphene-based nano-electronics. It was recently shown that this goal could be achieved by means of low energy ion implantation, 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].

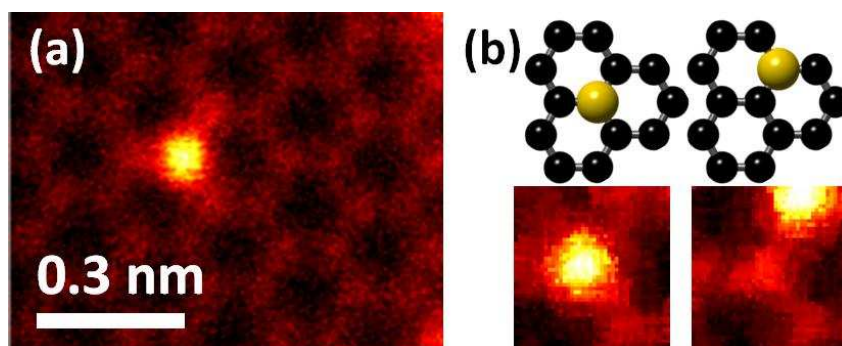
Even though these results represent great strides towards nano-engineering defects in graphene, a full control over the density and nature of the defects is still difficult to achieve. By contrast, the unique structure of graphene nano-cones dictates the presence of a well-defined number of pentagonal 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].

## References

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 [7] SuperSTEM is funded by the UK Engineering and Physical Sciences Research Council (EPSRC). Part of this work was supported by the US Defense Threat Reduction Agency, grant number HDTRA-1-12-0013.



**Figure 1.** HAADF images of single layer graphene irradiated with 30keV He ions at fluences of (a)  $3.0 \times 10^{15}$  ions.cm<sup>-2</sup> and (b-c)  $9.6 \times 10^{15}$  ions.cm<sup>-2</sup>. 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  $\sim 0.45$ s apart. A ball-and-stick model illustrates the atomic jump. [3]