## Atom-by-atom defect engineering and characterisation in graphene and other 2-dimensional materials using scanning transmission electron microscopy

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## Abstract

Modern aberration-corrected scanning transmission electron microscopes (STEMs) have been optimised to provide improved data collection ability and greater flexibility even at low acceleration voltages, to the great benefit of the field of graphene and two-dimensional materials. By reducing the acceleration voltage to overcome knock-on damage limitations, many of these structures can be imaged directly at atomic resolution, revealing for instance the successful low energy ion implantation of single N or B dopants in graphene with retention rates consistent with theoretical predictions, a technique commonly used by the modern semiconductor industry and which has the potential to revolutionize graphene technology [1]. Furthermore, the sensitivity of complementary analytical techniques such as electron energy loss spectroscopy (EELS) is such that it also possible to study precisely how these atoms bonded to one another and how minute structural differences affect their electronic configuration [2,3]. In particular, EELS fine structure differences can distinguish unambiguously between tri- and tetravalent bonding configurations of single Si contaminants in graphene [2], while a clear signature in the near-edge fine structure of the B and N EELS K edges but also that of neighboring C atoms and their EELS K edges (Figure 1) provide evidence of electronic structure modifications due to presence of the dopants. Ab initio calculations are used simulate experimental spectra and to rationalize the experimental observations, thus providing further insight into the nature of bonding around the foreign species [3]. Finally, these otherwise 'gentle' STEM observation conditions can also be precisely tailored to engineer and modify defects in 2-dimensional materials: the electron beam can thus drive the diffusion of substitutional Si dopants through graphene (Figure 2), one atomic jump at a time [4].

## References

[1] U. Bangert, W. Pierce, D.M. Kepaptsoglou et al., Nano Lett. 13 (2013), p. 4902.

- [2] Q.M. Ramasse, C.R. Seabourne, D.M. Kepaptsoglou et al., Nano Lett. 12 (2012), p. 3936.
- [3] D.M. Kepaptsoglou, C.R. Seabourne, R. Nicholls *et al.*, Submitted (2015)
- [4] T. Susi, J. Kotakoski, D. Kepaptsoglou et al., Phys. Rev. Lett. 113 (2014), 115501

## Figures



**Figure 1.** Atomically resolved EELS map (b), showing a single N dopant in the graphene lattice (a-b). C K edge spectra (d) from neighboring C atoms, show changes in their near-edge fine structure.



**Figure 2.** A single Si substitutional impurity in graphene can undergo a bond inversion with its neighbouring C atoms under a 60kV electron beam.