Graphene re-knits its holes

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The development of graphene devices has entered a new era: increasing effort is being put into achieving devices that employ suspended membranes as well as graphene of defined geometries, e.g., nano-ribbons and quantum dots, because of their predicted novel, exceptional electronic properties [1]. It has been recently shown that in the presence of metals, following a sequence of point defect reactions, graphene can be etched on the nano-scale [2] under exposure to an electron probe in a scanning transmission electron microscope (STEM), a process different from previous attempts at graphene etching. In earlier studies, graphene and graphite had been etched or tailored in a gas environment, e.g. through exposure to hydrogen or oxygen, at high temperatures [3, 4].

A number of papers have previously discussed defects in graphene, either following experimental TEM studies [5, 6] where defects were introduced by the electron beam, or by simulations based on Density Functional Theory (DFT) calculations [7,8]. Defects studies in all those papers are based on reconstruction of the graphene lattice as a result of knock-on of carbon atoms from the graphene lattice (mono- and multi- vacancy) or/and as a result of bond rotations, e.g., the formation of Stone-Wales (55-77) and 8-ring defects. Here we present the first observations of reconstruction, i.e., the mending and filling of many-vacancy holes (100 vacancies or more) in graphene in the STEM where the holes are created as a result of metal-graphene interaction.

To show atomic arrangements we employ high angle annular dark field (HAADF) imaging in an aberration-corrected STEM operated at 60 keV [10]. TEM samples were obtained by transfer of graphene membranes grown by CVD on copper substrates, to TEM grids. Various metals were deposited by electron beam (Au, Cr, Ti and Pd) and thermal (Ni and Al) evaporation. There is normally no damage inferred to pristine graphene with a 60 keV electron beam, in so called ‘gentle STEM’ conditions. However, as we have recently observed at atomic resolution [2], if transition-metal or silicon atoms are present and in direct contact with the graphene lattice, hole formation can occur in pristine graphene sheets. These holes are enlarged as long as metal atoms are present at the hole’s edges. The nature of the metal atoms was identified by single-atom-sensitive energy loss spectroscopy (EELS). It is believed that the process occurs due to metal-catalysed dissociation of C-C bonds, perhaps in association with O atoms initially adsorbed onto nearby patches of carbon-based contamination. This leads to point defect formation. The role of the electron beam in this is mainly to mobilise the metal atoms on graphene, and not to initiate the hole formation in the first place, i.e., by carbon atom displacement. When the reservoir of metal atoms is exhausted, the process stops and the hole remains of almost the same size, although the edges undergo repeated reconstruction in consecutive scans. If metal-impurities are not present and, at the same time, carbon atom supply is warranted, e.g. through near-by hydrocarbon contamination attracted towards the hole by the scanning probe, ‘filling’ occurs and the hole mends itself by non-hexagon arrangements, which are 5-, 6-, 7- and 8-ring members, shown in Figure 1. However, if no hydrocarbon contamination is present, healing occurs via reconstruction of the perfect graphene hexagon structure.
The incorporation of 5-, 6-, 7- and 8-member ring structures, called Haeckelites, into highly defected graphene was suggested by theory [7] but had never been observed experimentally hitherto. Figure 1 shows clearly that this kind of structure can exist in suspended form and provides a remarkable glimpse into the atomic arrangements of amorphous carbon structures [11].

References


Figure 1. Atomic resolution HAADF images (raw data) from consecutive scans of suspended graphene, showing a) a hole created at the border of hydrocarbon contamination b) complete reconstruction with incorporation of 5-7 rings and two 5-8 rings, and c) redistribution of defects in the ‘mended’ region, by 5-7 rings. Images d-e have been processed using the maximum entropy deconvolution algorithm to a-c with their contrast optimised to visualise the C atoms. The carbon atom positions are highlighted by light green dots and polygons numbered according to atom number in the rings.