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Electron-Beam Manipulation of Lattice Impurities in Graphene and Single-Walled Carbon Nanotubes

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The recent discovery that covalently bound impurity atoms in crystal lattices can be manipulated with focused electron irradiation has unveiled new perspectives for top-down atomic engineering, with the potential to surpass existing techniques in both versatility and capabilities. This has been made possible by advances in electron optics and instrument stability, but also in the incorporation of impurity elements into the materials using techniques such as ion implantation [1].

Arguably the first system where this potential was fully realized was incidental silicon impurities in single-layer graphene. Although typically not purposefully introduced, Si are often found as covalently bound substitutional impurities in the lattice. After discovering how the Si can exchange places with one neighboring C atom via an out-of-plane displacement (*bond inversion* or *direct exchange*) [2], caused by the elastic backscattering of an energetic probe electron from a moving C nucleus, first us [3] and then others [4] demonstrated the possibility to control such dynamics by directing the focused electron beam.

The initial experiments were limited in scope, moving the impurities by just a handful of lattice sites [3,4]. Now, we can demonstrate greatly improved control over the movement of silicon in graphene [5] (Fig. 1). Our manipulation rate is already nearly on par with any atomically precise atom manipulation technique including fully automated scanning probe microscopy, although there are also crucial differences due to the stochastic nature of electron scattering [5]. I will additionally show how such manipulation is possible in large-diameter single-walled carbon nanotubes [6].

Besides Si impurities, we are able to manipulate P dopants in graphene [7], although this appears to be much more challenging. First principles modelling allows us to both understand the reasons for such differences, as well as to potentially enhance the probability of desired outcomes. However, at least for the out-of-plane displacement mechanism, it seems there are physical limits on what is feasible, demonstrated by the fact that significantly heavier Ge impurities cannot be thus manipulated [8].

However, there are many possible lattice impurity atoms whose atomic dynamics under electron irradiation have been observed, including N and B, although the possibility of their manipulation has not been confirmed yet and the quantitative modelling of their dynamics is still a challenge [9]. Nonetheless, it is already clear that electron-beam manipulation of lattice impurities has opened an exciting new frontier for atom manipulation, nanotechnology and materials science [10].

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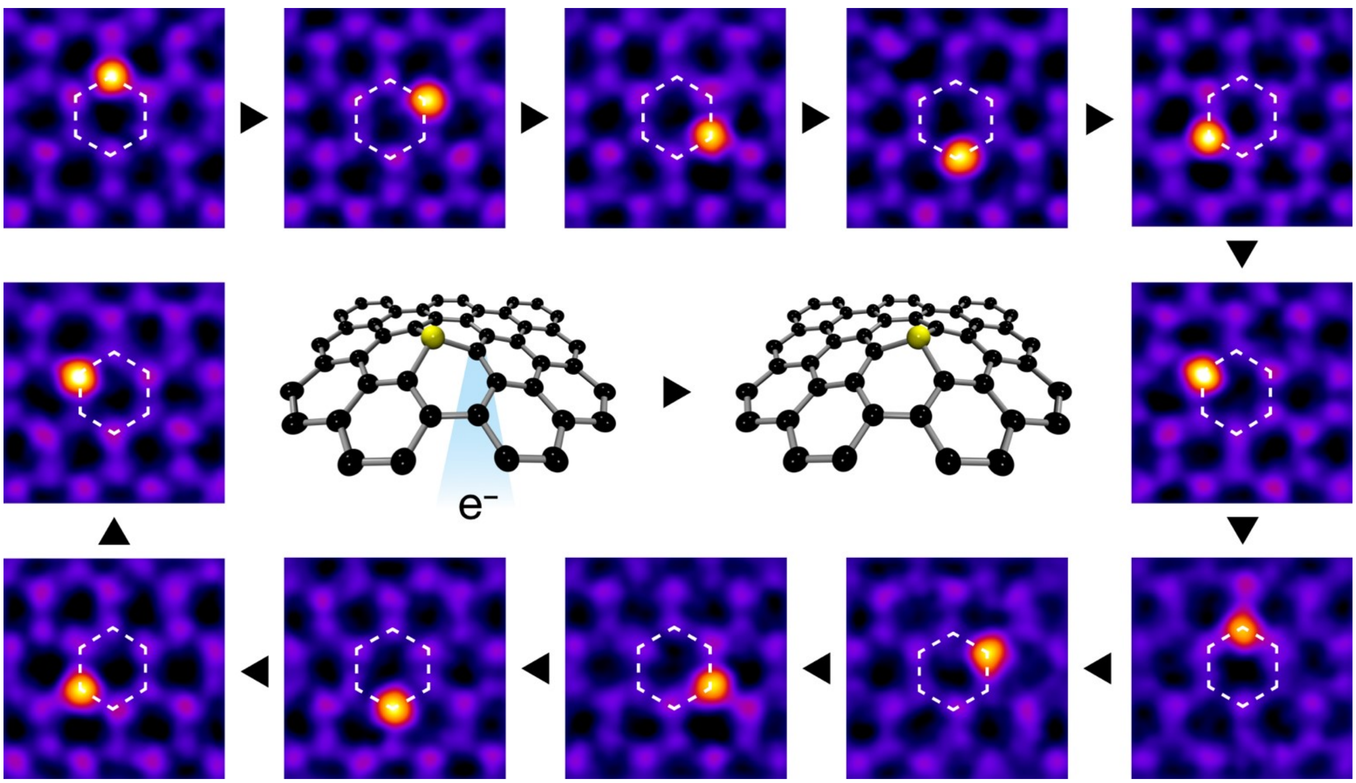

Figure 1. Electron-beam manipulation of silicon impurities in graphene. The schematic in the middle illustrates how selectively irradiating one chosen carbon neighbor by directing the focused electron beam causes it to switch places with the silicon impurity (*bond inversion* or *direct exchange* mechanism [2]). The surrounding panels show filtered and aligned STEM/MAADF frames acquired between the spot irradiations, demonstrating how the Si can be iteratively moved around a carbon hexagon in the graphene lattice with essentially perfect control [5].

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