Atom-by-Atom Analysis and Lithography in the Electron Microscope

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A modern, aberration-corrected Scanning Transmission Electron Microscope (STEM) equipped with an efficient Cold Field Emission Gun (CFEG) such as the Nion UltraSTEM [1] can form a probe of 60-200 keV electrons that is ~1 Å in diameter and contains ~160 pA of current. This means that a single atom in a sample can be "illuminated" by ~10^9 medium-energy electrons per second, and that many different analytical signals can be collected from the single atom. Optimized post-sample optics and detectors allow the various signals to be captured efficiently, often with single particle sensitivity and close to 100% collection efficiency. The signals include forward scattered (bright-field) electrons as well as medium-angle and High-Angle Dark Field (HADF) electrons, which carry information about the types of atoms present in the sample and their locations; energy-loss electrons, which carry information about electronic states of the sample, the types of atoms present and their bonding arrangements, and also the sample's vibrational (phonon) energies; and further emitted X-rays, which carry simple-to-interpret information about the types of atoms present in the sample. The cross-sections for some of these signals are rather large, allowing the signals to be collected in 10^{-6} to 10^{-3} seconds per examined atom.

When the energy of the primary electrons is below the knock-on threshold in materials that do not suffer ionization damage, there is essentially no radiation damage and data with very high signal-to-noise ratios becomes available. In graphene and monolayer BN this means operating at ~60 keV or lower primary energy. By raising the primary energy to ~100 keV, it becomes possible to knock out individual atoms from the structure, thereby creating single vacancies and more complicated defects. Some of the defects subsequently trap atoms diffusing on the surface [2, 3]. If the diffusing atoms are introduced deliberately, it becomes possible to select the dopant atom for a specific site.

Figure 1 shows a 60 keV HADF image of graphene containing substitutional Si atoms in two different configurations: a one-Si-for-one-C substitution with 3-fold coordination, and a one-Si-for-two-Cs substitution with 4-fold coordination. Figure 2 shows Electron Energy Loss Spectra (EELS) collected from the two types of silicon atoms with a dose of about ~10^{10} electrons. The dose was large enough to capture EELS fine structures that allowed the detailed electronic state of the single Si atoms to be determined. This showed that the 3-coordinated Si atom sticks out of the graphene plane [4, 5].

Planned modification of the Nion UltraSTEM will allow different atomic species to be introduced in-situ while the sample is being observed, thus enabling defects such as those shown in Fig. 1 to be created and patterned into new types of structures and devices.

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[4] W. Zhou et al., Phys. Rev. Lett. **109** (2012) 206803.
[5] Q.M. Ramasse et al., Nano Lett. **13** (2013) 4989–4995.

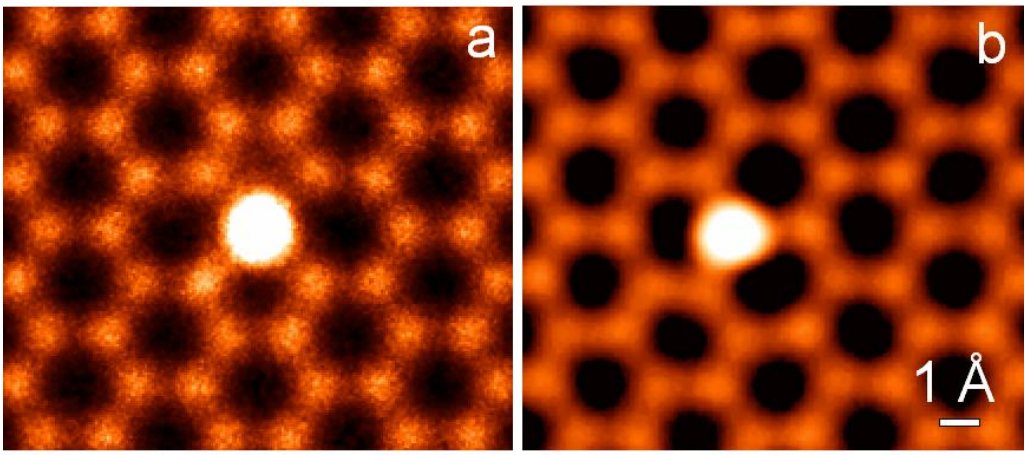

Figure 1. 60 keV HADF STEM images of a) Si substituting for two C atoms in monolayer graphene, b) Si substituting for one C atom.

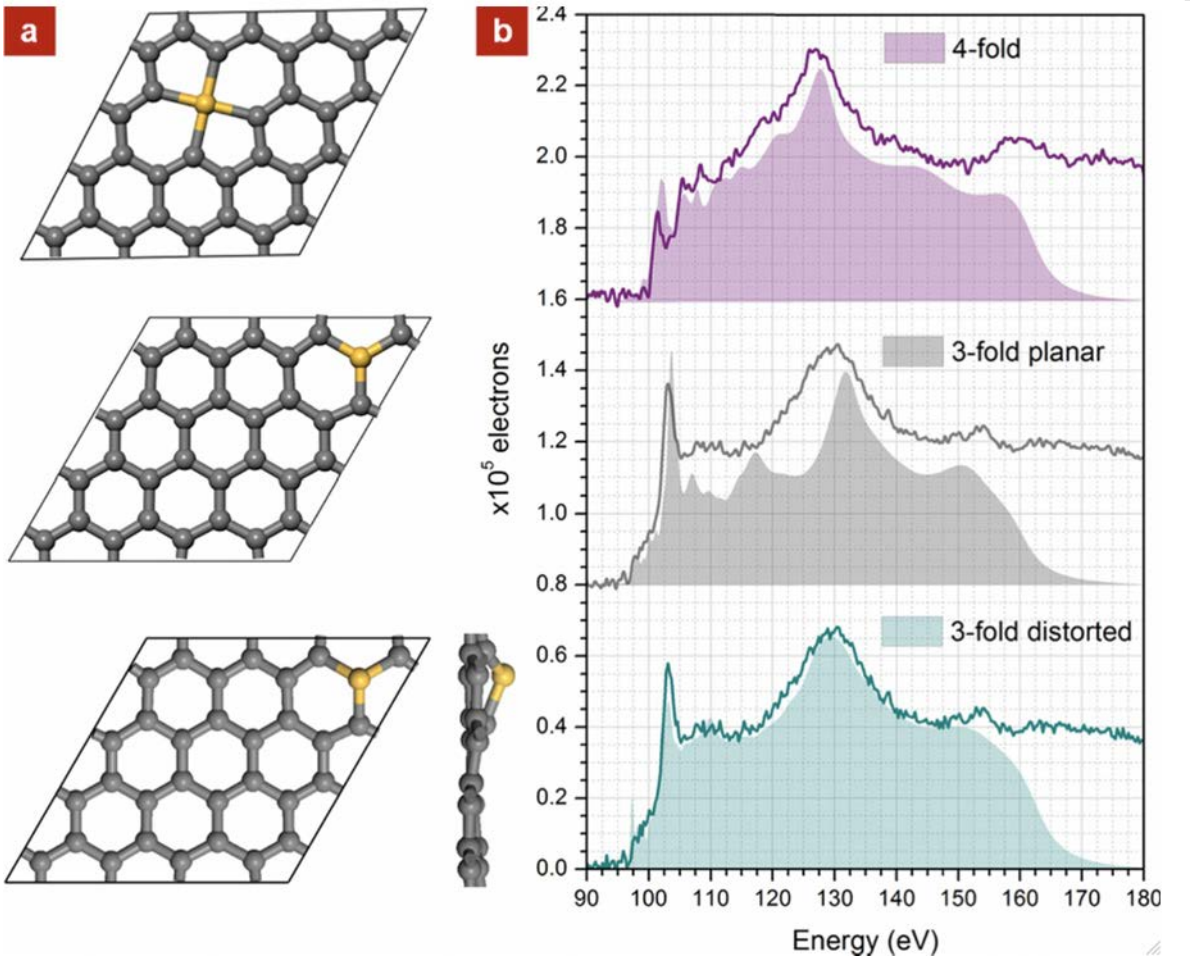

Figure 2. EELS data and atomic models for the two types of Si substitutional atoms shown in Fig. 1. a) Atomic models. b**)** Fine structure of Si $L_{2,3}$ edge EEL spectra from individual Si atoms (lines) and CASTEP simulations for the models shown in (a) (solid spectra).