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Atomic Imaging and Spectroscopy of Two-Dimensional Materials

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The introduction of aberration-correction in scanning transmission electron microscopy (STEM) has allowed the realization of Feynman's long sought dream [1], atom-by-atom structural and elemental identification of materials [2], by simply looking "at the thing". Moreover, the higher current in the electron probes achieved with aberration correction has also allowed the identification, by spectroscopic means, of individual impurities [3], as well as the bonding characteristic of individual atoms in two-dimensional (2D) materials [4-6].

In this talk, we will present our ongoing efforts to study 2D materials using STEM analytical techniques combined with first-principles total energy calculations. We will also discuss the new doors that will be opened by advances in instrumentation in analytical STEM. For instance, electron probes with even better spatial and energy resolution of than is currently available (< 0.5 A and < 10 meV, respectively), as well as the combination with *in-situ* measurements, such as heating and biasing.

Figure 1 shows an example of single atom spectroscopy performed in Oak Ridge National Laboratory's aberration-corrected Nion UltraSTEM^{TM} 100, which has a cold field-emission electron source and that can correct 3rd and 5th-order aberrations [7]. The left panel in Fig. 1 shows two Z-contrast images of individual Si impurities in graphene adopting three- and four-fold coordination. However, the images do not reveal if the Si atoms are bonded in or out of plane of the carbon atoms. Atomically resolved EEL spectra (Fig.1 right panel) acquired for the Si impurities reveal different features in their Si L-edges *(i.e.,* the peak at 105 eV), indicating different mixing of the Si *3d* states with the surrounding carbon atoms. First-principles calculations explain the EEL result by showing that for the case of the three-fold coordinated Si atom, the Si *3d* orbitals contribute significantly to the bonding, resulting in a planar sp^{2}d-like hybridization. In contrast, the three-fold coordinated Si in graphene adopts the preferred *sp*^{3} hybridization for Si, with the Si atom out of plane by 0.05 nm [7].

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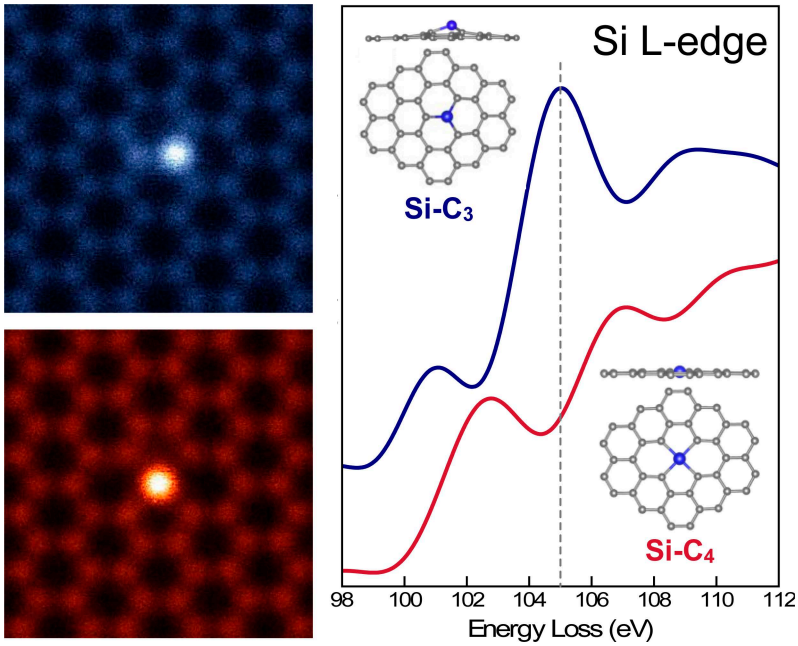

Figure 1. The atomic and electronic structure of individual Si impurities bonded to three or four carbon atoms in graphene are revealed by Z-contrast imaging (left panel), electron energy-loss spectroscopy (right panel) using an aberration-corrected scanning transmission electron microscope in combination with density functional theory calculations. Inset on the right panel; shows the atomic structure formed by the Si impurities obtained by first-principles calculations. Images adapted from Ref. [5].

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