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Vibrational STEM-EELS of Single Si Atom Point Defects in Graphene

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Electron energy loss spectroscopy (EELS) in state-of-the-art monochromated scanning transmission electron microscopes (STEMs) allows for probing the vibrational response of a wide range of materials systems, with high spatial resolution [1]. At the nanoscale, this is showcased by reports on the mapping of bulk phonons and phonon polaritons [2], isotope induced vibrational mode shifts [3] and phonon dispersion measurements [4–6]. Taking full advantage of the ≤ 1 Å sized electron probes available in aberration corrected STEMs, Hage *et al.* [7] recently used a so-called off-axis or dark field (DF) detection geometry to map atomic scale variations in acoustic and optical phonon excitations in a thin flake of hexagonal boron nitride. This approach is equally applicable to non-polar and even atomically thin materials, as we have shown for single layer graphene suspended in vacuum [8]. For graphene, a DF collection geometry is in practice necessary for the acquisition of interpretable vibrational spectra when using our instrumentation; this is due to the EEL spectrum intensity being vanishingly small for momentum transfers near the Brillouin zone centre of graphene [6].

As a next step, we used the experimental geometry of Hage *et al.* [7] to investigate the possibility of probing the vibrational response associated with individual point defects. As a test sample we used single layer graphene with substitutional single Si atom defects. Figure 1a shows the asymmetric Annular Dark Field (aADF) image of a single substitutional tri-valent Si atom in graphene. The corresponding ball-and-stick model is shown in figure 1b. Spectra with signal-to-noise sufficient for meaningful fine structure analysis were acquired by repeatedly scanning the electron beam over small regions of the sample (see Ref. 9). Figure 1c shows a spectrum from a single tri-valent substitutional Si atom "Si" as well as that of the graphene lattice "C", acquired a few atoms away from the Si point defect. From these spectra, and their difference (see figure 1c), it is clear that an individual Si atom point defect drastically modifies the vibrational response of graphene, at the atomic scale. Our experimental results were rationalized by means of density function theory (DFT) calculations which link the observed experimental peaks to characteristic defect-induced pseudo-localized vibrational modes. Atom-by-atom STEM-EEL spectrum imaging shows that, within experimental noise, this effect is localized to the defect atom itself, in excellent agreement with corresponding calculations [8]. The demonstrated approach for vibrational STEM-EELS with single atom sensitivity should be applicable to the study of atomic scale modifications of the vibrational properties of a wide range of materials systems [10].

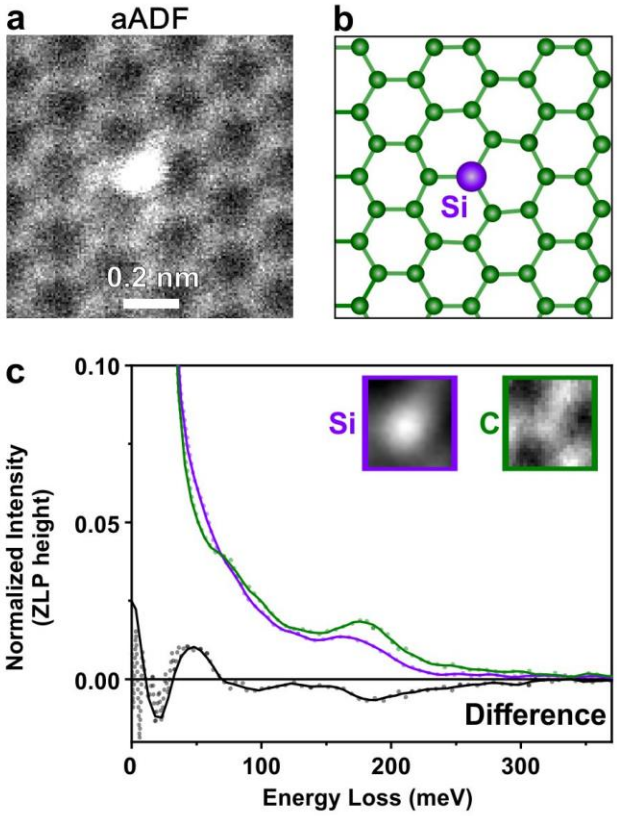

Figure 1. (a) aADF image (thus named due to the asymmetric placement of the ADF detector in angle space, see Ref. 7) and (b) model of the probed single tri-valent substitutional Si dopant in graphene. (c) Vibrational spectrum of the Si atom ("Si") and of a defect-free part of the probed graphene patch, a few atoms away from the Si atom ("C"). The difference spectrum is calculated by subtracting the C spectrum from the Si spectrum. Smoothed spectra (lines) are superimposed on raw data (dots) as guides to the eye. Spectra were acquired by repeatedly scanning the beam over the regions shown in the aADF image inserts.

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