

Name that Atom in 60 Seconds or Less: Energy Dispersive X-Ray Spectroscopy of Individual Heteroatoms in Low Dimensional Materials.

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The feasibility of identification of individual Si atoms on single-layer graphene on the basis of energy dispersive x-ray spectroscopy (EDXS) in a scanning transmission electron microscope (STEM) has been demonstrated [1]. However, the employed measurement conditions, i.e., manual tracking of single Si atoms on single carbon sheets over collections time of 4 to 6 minutes greatly limited the applicability of the method for more wide-spread use. Under such conditions, there is no clear advantage of EDXS over the use of quantitative annular dark field image analysis, or electron energy loss spectroscopy (EELS). To be truly practical for samples such as supported catalyst nanoparticles or other low dimensional materials, single atom EDXS measurement conditions must allow for robust atom identification in seconds, in samples with variable thickness that contain combinations of multiple, unknown heteroatom species.

The collection efficiency of EDXS measurements, which is critical to the practicality of single-atom sensitivity measurements, is a function of multiple instrumental parameters, including: the geometrical solid angle of the detector, the detector window material, the quantum efficiency of the detection electronics, the sample holder material and geometry, and the stability of the host microscope. For our experiments, we used a Bruker XFlash6:100, 100mm² elliptical, windowless silicon drift detector, mounted in a Nion UltraSTEM 200 UHV cold field emission STEM at the Naval Research Laboratory. The calculated solid angle of the detector is ~ 0.7sr, and measurements of NiO standards yield similar values. Additional design considerations of the detector-microscope combination are discussed in more detail elsewhere [2]. We operated the UltraSTEM at 60 keV with ~120 pm probe and a beam current of 50 to 150 pA. The sample investigated was a nanodiamond-amorphous carbon phase mixture extracted from the Murchison meteorite by acid dissolution, and drop cast onto a lacey carbon support film on Cu TEM grid [3].

Multiple methods for atom identification were tested. Regions of interest were first identified as amorphous carbon or nanodiamond through imaging and C K-edge EELS. Heteroatoms of interest associated with either phase were then selected in annular dark field STEM images. These atoms were not robustly incorporated in the carbon lattice, but instead able to diffuse quickly over the surfaces of the sample. Thus, the EDXS signal was collected as either individual spectra during the manual tracking the heteroatom in a live scanning image window (~ 0.25 nm²) in Digital Micrograph, or as long-dwell time single, or short-dwell time, multipass spectrum images with the Bruker Esprit software. In the case of the manual tracking, the live image window was recorded as an image series. For spectrum images, annular dark field images were recorded before and after the spectrum image for single pass acquisition, and with each frame, for multiframe acquisition. In all cases, the acquisitions were terminated when the heteroatom moved out of the imaging area.

Figure 1 illustrates the identification of a Si atom on a few-layer region of amorphous carbon by the manual tracking method. The total acquisition livetime for this spectrum was 55.5 sec at a probe current of 120 pA. The net count yields were 1856 in C and 48 in Si. A second tracking experiment on the same atom yielded similar results, i.e., of order 50 counts in Si in 55 seconds. We estimate that minimum time for reasonable confidence in identifying the heteroatom under these conditions is ~ 10 to 15 sec, limited in part by the amount of overscan area needed to ensure that the atom remained in the field of view. As the atom occupied $\sim 1/10$ the scan area, an immobile atom should be identifiable in ~ 1 sec. Additional experiments revealed heteroatoms of Ca, S, and O, all with total collection times under 60 sec, and ~ 5 net counts/sec of on-atom beam exposure time.

As shown in Fig. 2, it is also possible to identify individual heteroatoms in hyperspectral images. The motion of the atom, in this case S, was recorded as x-ray signal originating from different spatial locations during the acquisition. The 122×96 px map was obtained in total of 1.72 sec by integrating five frames with a $32 \mu\text{s}/\text{px}$ dwell time. Longer dwell-time single pass spectrum images also enabled identification of heteroatoms, but the interpretation was more difficult, because the atoms moved faster than the beam, which resulted in streaked images.

References:

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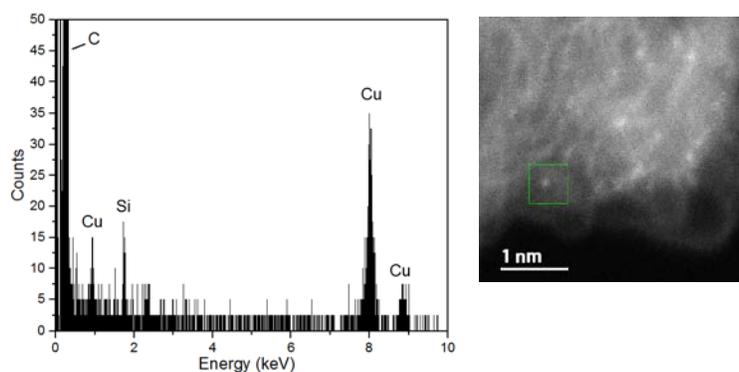


Figure 1. Energy dispersive x-ray spectrum of a single Si atom on amorphous carbon. The green box on the dark field image indicates the area of the tracking window.

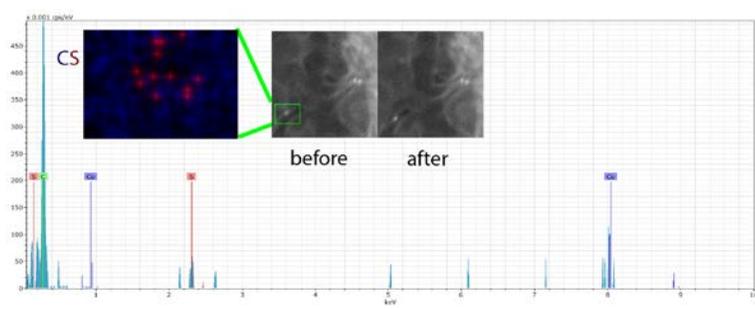


Figure 2. Energy dispersive x-ray spectrum imaging of a S atom on few-layer amorphous carbon. The inset dark field images show the area of interest before and after the spectral acquisition. The green box indicates the $\sim 0.5 \text{ nm} \times 0.4 \text{ nm}$ mapped region. The C and S maps are overlaid in blue and red, respectively.