Atomic Resolution Chemical Mapping via Energy Dispersive X-ray Spectroscopy on an Absolute Scale


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The ability to compare high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images against simulation on an absolute scale [1] has yielded new capabilities, including atom counting [2], composition analysis [3] and determination of dopant depth [4]. We foresee similar advantages for absolute scale energy dispersive X-ray spectroscopy (EDX) STEM imaging: for analysing structure in nanoparticles or nanoprecipitates or interfaces, absolute numbers of dopants are highly relevant whereas relative concentrations may not be.

Absolute scale EDX is more involved than HAADF because X-ray generation and absorption within the specimen introduce further complications. The number of X-ray counts as a function of probe position \( R \) may be expressed as [5]

\[
N(R) = I T F_{\text{ion}}(R, t, X_{\text{abs}}) \omega \left( \frac{\pi}{4 \sigma} \right) D_{\text{eff}}
\]

(1)

with \( I \) the incident beam current, \( T \) the probe live dwell time, \( F_{\text{ion}} \) the fraction of incident electrons causing ionization events (with thickness \( t \) dependent X-ray absorption correction \( X_{\text{abs}} \)), \( \omega \) the fluorescence yield, \( \Omega \) the detector solid angle, and \( D_{\text{eff}} \) the detector efficiency. In particular, quantitative agreement requires correct modelling of the dynamical scattering of the electrons through the crystal when calculating \( F_{\text{ion}} \) [5].

We summarize efforts to achieve absolute scale atomic resolution STEM EDX analysis. Data were recorded from SrTiO\(_3\) using an FEI Titan G2 at 200 keV with a four windowless silicon-drift detector (SuperX) system. To maximise signal-to-noise while minimizing beam damage, data were frame averaged, both during the experiment and in post-processing. Great care was taken in characterizing the sample/holder/detector geometry and calculating X-ray absorption. Figure 1 shows 2D maps at select thicknesses and for column, mean and minimum signals over a wider range of thicknesses for the Sr-K, Ti-K and O-K peaks. (Note: The column and minimum counts constitute the average signal within a radius of 1.0 Å around the atomic column and minimum positions, respectively.) The agreement is generally good, but some discrepancies remain, whose systematic nature suggests some inaccuracy in characterizing multiplicative factors in Eq. (1).

References

[6] This research was supported by the Australian Research Council (Projects DP110102228, DP140102538, DE130100739); the Air Force Office of Scientific Research (FA9550-14-1-0182); the Analytical Instrumentation Facility (AIF) at North Carolina State University, supported by the State of North Carolina and the National Science Foundation; and the National Science Foundation Graduate Research Fellowship (Grant DGE-1252376).

FIG. 1. Quantitative comparison of experimental and simulated EDX signals for the Sr-K, Ti-K, and O-K peaks. Left: STEM images for thicknesses 12.5 nm and 54.7 nm. The probe-forming aperture semiangle is 19.5 mrad. The simulations include a Gaussian incoherent effective source distribution with full-width-half-maximum 2.1 Å. Right: Column, mean and minimum X-ray counts as a function of sample thickness, comparing experiment (symbols) and simulation (dashed lines and symbols). Minor variations in holder orientation at different thicknesses lead to minor variations in effective detector collection angle: the dashed lines guide the eye but do not strictly represent continuity with varying thickness. The experimental error bars represent only the error arising from counting statistics.