

Reaching for atomic-scale quantitative energy dispersive X-ray spectroscopy

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The combined development of silicon drift detectors (SDDs) and aberration correction in the scanning transmission electron microscope (STEM) has significantly advanced the field of microanalysis [1,2]. In particular, the combination of improved detector efficiency and high current densities really opens up the possibilities of quantitative energy dispersive X-ray (EDX) spectroscopy. We can now routinely achieve beautiful EDX maps which reveal atomic-scale features within our materials. However, it still remains to understand exactly where the X-ray signals come from within the specimen and how accurately they can be quantified at these length scales.

For atomic resolution imaging (when a crystal is necessarily aligned along a low order zone-axis), so-called electron channeling makes the beam-sample interactions non-linear and far harder to interpret [1–3]. Channeling occurs when columns of atoms aligned parallel to the electron beam provide an additional focusing effect on the electron beam, increasing the electron density close to the atomic nuclei and thereby producing a higher number of scattering and ionization events [3, 4]. For longer columns this focusing eventually produces a cross-over point within the sample which turns into oscillations of the probe electron density down the length of the column. This variation in probe electron density along atomic columns complicates composition measurements from the EDX signal not only due to the deviation from a linear relationship between atomic density and measured signal but also because it means the atomic ordering along the column can affect the signal.

Excellent quantitative agreement between calibrated experiments and multislice simulations using MuSTEM have been demonstrated [5, 6]. However, the challenge we often face in most interesting materials science applications is that we do not know the atomic-structure well enough to have something to simulate. Therefore, we need an approach that allows us to suppress the channeling and create a first guess of the materials structure using simple linear-based EDX quantification methods. Using SrTiO₃-DyScO₃ multilayers as an example, we will discuss the combined effect of sample tilt [4] and spatial integration for ameliorating the effects of channeling and improving the accuracy of EDX quantification. Figure 1 shows the effect of sample tilt on integrated line profiles of the Ti-K line in both simulations and experiment. In suppressing channeling the peak to background ratio drops significantly, however this brings the absolute values closer to the linear approximation [4]. Therefore, there is a balance to be found between beautiful atomic-scale but only qualitative maps and improving the quantification at a cost of some loss of resolution. Finally, we will also look at the effects of scattering and beam broadening and how this affects our ability to measure the accurate composition profile across an interface. The remaining

limitations and the challenges will be discussed. In particular, the possibility for combining with 4D-STEM will be explored. [7]

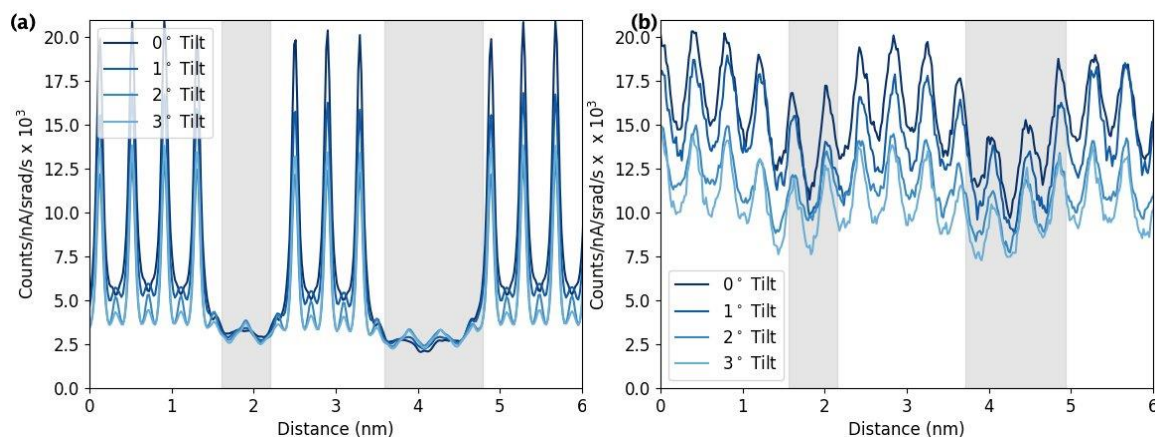


Figure 1. Comparison of quantified X-ray line profiles for Ti-K in a SrTiO₃-DyScO₃ multilayer oxide from simulation (a) and experiment (b) at different sample tilts, the grey regions indicate the approximate location of the DyScO₃ layers. (a) is simulated with a perfectly abrupt interface. Although the match between experiment and simulation is close in average value there is still a significant resolution difference which needs to be understood. (b) There is also no clear distinction between the layers in (b) although this is in part due to beam broadening and scattering occurring.

References

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