What Does Quantitative Mean In Atomic-Resolution EDS STEM?

NR Lugg[1], G Kothleitner[2,3], B Feng[1], N Shibata[1] and Y Ikuhara[1]

[1.] Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Tokyo, JAPAN
[2.] Institute for Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, AUSTRIA
[3.] Centre for Electron Microscopy, Graz, AUSTRIA

Energy-dispersive x-ray spectroscopy (EDS) in scanning transmission electron microscopy (STEM) is quickly becoming ubiquitous in atomic-resolution chemical mapping [1-3] due to increased detector sizes and efficiencies. Much work has been done to try and bring lower resolution EDS mapping to a quantitative scale [4], by carefully calibrating measured x-ray counts so that they represent quantitative information about the specimen – the density of atoms in the area probed for instance. However, at atomic resolution, this is only the first "layer" of quantification. The majority of atomic-resolution EDS mapping to date has been qualitative – identifying in columns specific elements appear. This has been partially due to the lower efficiencies of the detectors available and the inability to obtain significant signal. However a more significant problem exists: the complex elastic and thermally scattering an atomically-sized probe undergoes when interacting with a crystal – i.e., electron channeling – means that the signal detected has a highly non-linear response to the density of atoms that are located under the probe [1,5]. Therefore, in general, even if the x-ray counts have been appropriately calibrated – i.e., we have achieved the first layer of quantification – one still cannot extract quantitative information about the specimen from the atomic-resolution maps acquired. We call this the second "layer" of quantification. In Fig. 1 we see simulated EDS STEM maps, calibrated so that the signal is in units of atoms/nm^3. From these maps we can see that when the STEM probe is on-column, the measured "density" is much higher than the real density. Furthermore, if one considers the average density from the map, we also get a value much higher than the real value. This is due to channeling and, in this presentation, we discuss how this increase occurs in detail [6].

In high-angle annular dark-field (HAADF) STEM imaging, quantification has been achieved by comparing experimental intensities with simulation [7]. This quantification-by-comparison has also been achieved in atomic-resolution STEM electron energy-loss spectroscopy [8] (and by extension, it is possible in EDS STEM) – an impressive effort given the complexity of such calculations. Advanced deconvolution techniques have also been developed which remove the effects of channeling from chemical maps [9]; they are faster to implement then direct simulation and assume nothing about the ionization interactions involved giving them some advantage over direct comparison. However, the biggest drawback of all these techniques is that they requires one to have a model structure to begin with and the information is not directly extracted from the experimental data.

Despite the success of the aforementioned techniques, the best-case scenario would be if one could obtain quantitative information directly from experimental maps. Here we explore how tilting the specimen may help in achieving this [6]. Although the idea of tilting the specimen to reduce channeling is not new, we show here that this rule-of-thumb holds for EDS STEM and that tilting the specimen does indeed reduce the effects of channeling. We show examples of how tilting allows one access to quantitative information using two test cases: single crystal strontium titanate (Fig. 2) and bicrystal yttrium stabilized zirconia with a low-angle grain boundary. The downside of tilting is that one loses atomic resolution in the direction tilted. To ameliorate this deleterious side effect of tilting, we consider

a precession series of tilted images and show that one may retain atomic resolution while also obtaining quantitative information about the specimen.

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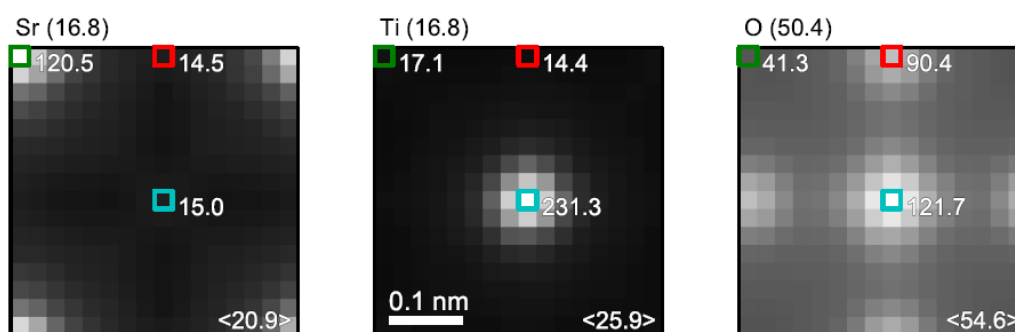[10] The authors acknowledge funding from MEXT and the JSPS.

Figure 1. Simulated EDS STEM maps of the Sr, Ti and O K lines in strontium titanate. Number in parentheses indicates actual density (atoms/nm^3) for specific element. Numbers next to upper-left (green), upper-central (red) and central (cyan) pixels indicate "densities" measured for those probe positions. Number in lower-right corner indicates the "density" measure from averaging an entire map. An accelerating voltage of 200 kV, probe convergence angle of 22 mrad and thickness of 600 Å have been assumed.
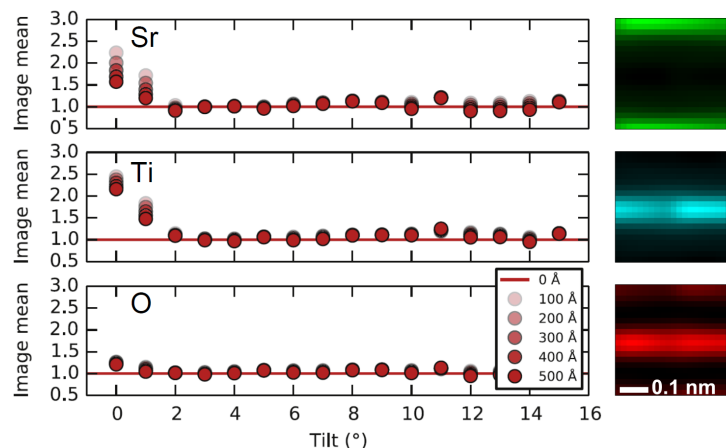

Figure 2. Mean values of tilted EDS STEM maps for the Sr, Ti and O K lines in strontium titanate for a series of thicknesses and tilt angles (along the <100> direction). Units are multiples of the actual density of the respective element. A sample tilted image (300 Å, 3°) is shown next to each plot. An accelerating voltage of 200 kV and probe convergence angle of 22 mrad have been assumed.