

Experimental Optimization and Data Analysis of In-Situ Electron Energy Loss Spectroscopy

Eoin Moynihan^{*1,2}, Temilade Adegoke^{2,3}, Kevin Ryan^{2,3}, Ursel Bangert¹ and Michele Conroy^{1,4}

¹. Department of Physics, University of Limerick, Co. Limerick, Ireland.

². Bernal Institute, University of Limerick, Co. Limerick, Ireland.

³. Department of Chemical Sciences, University of Limerick, Co. Limerick, Ireland.

⁴. Department of Materials, Royal School of Mines, Imperial College London, London, United Kingdom

* Corresponding author: eoin.moynihan@ul.ie

Through the development of transmission electron microscopy (TEM) techniques it is possible to observe changes in materials at the atomic level. Developments in aberration correctors pushed the spatial resolution of TEM and scanning TEM (STEM) to the sub-Angstrom regime. [1] Monochromators have allowed electron energy loss spectroscopy (EELS) in the TEM to progress to tens of meV energy resolution. [2,3] Direct electron detectors make fast frame-rate high speed imaging possible and has pushed forward the development of in-situ electron microscopy. [4] New hardware can drive electron microscopy forward, but we can also move forward by combining techniques, assessing their procedures, and developing a deeper understanding for the physics and geometry of the system.

This research combines the techniques of EELS and liquid in-situ electron microscopy, optimizing the experimental parameters and data analysis approach. EELS has been successfully used in in-situ microscopy before but there are clear challenges and issues to overcome. [5] A major challenge is the opposing criteria for the two techniques. Most liquid in-situ holders require a SiN membrane to encapsulate the cell where the liquid flows, resulting in a relatively thick sample. However, in EELS experiments it is often easier to use thin samples to avoid the complicated analysis involved with multiple scattering events. Figure 1 demonstrates the effects of collection semi-angle on EELS acquisition in a thick sample of ~200nm SiN and how much useful signal can be discarded due to high angle scattering. Figure 2 shows how fine structure analysis can be used to separate out core-loss EELS signals of different valences. This data required Fourier deconvolution to remove plural scattering, as well as normalizing each spectra by their zero loss peak maximum to compensate for signal lost due to thickness variation. Multiple linear least squares (MLLS) fitting is used to differentiate the different valences.

EELS in the liquid cell also has issues with the liquid itself. Interactions between the electron beam and the liquid inside the cell require smaller beam currents and consequently poorer signal to noise ratio in the EELS spectra. It is possible to work around this by purging the cell with dry nitrogen to remove the solvents while keeping the cell environment inert. [6] We were able to conduct EELS before and after a charge/discharge cycle, while using STEM imaging to capture live changes inside the cell during cycling. The procedures for experiments and analysis we developed, along with the raw and processed data we intend to make publically available, should offer a useful training tool for the in-situ community [7].

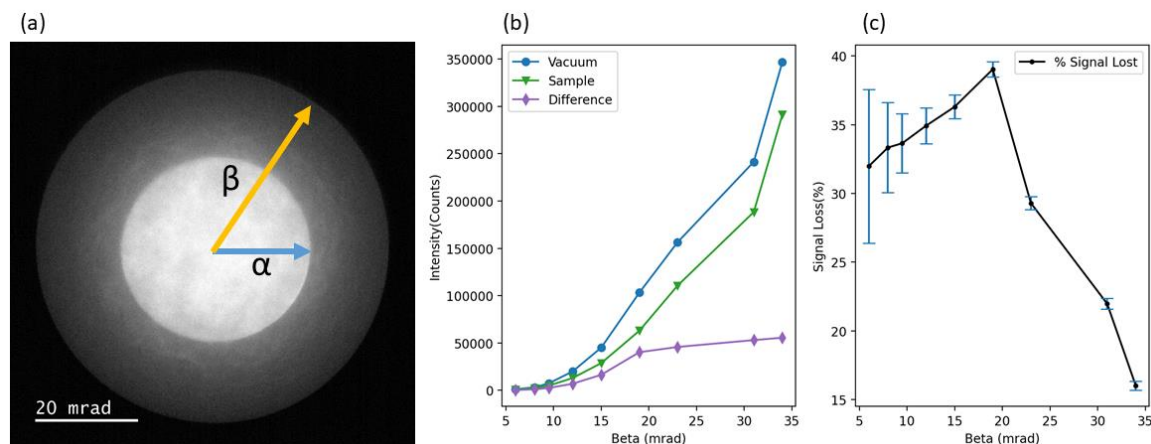


Figure 1. For different GIF collection semi-angles (β) the central CBED disk takes up a different proportion of the GIF entrance aperture in diffraction space. (a) Bright field image of a convergence semi-angle (α) = 18 mrad probe on SiN with β = 37 mrad. (b) The integrated intensity in the detector was recorded when the probe was over vacuum (blue circles) and over a thick 200 nm slab of SiN (green triangles), and then the difference between the two measurements (purple diamonds) showing the amount of signal scattered outside of the GIF entrance aperture by the SiN sample. (c) The proportional amount of signal lost due to electrons scattered outside of the detector by the SiN sample compared to no sample, i.e. vacuum.

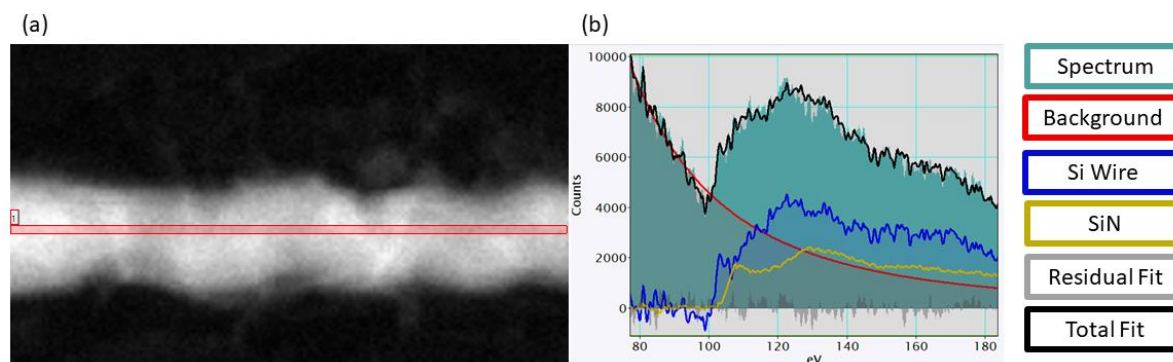


Figure 2. (a) Silicon nanowire sandwiched between two SiN windows in a dry in-situ cell (b) EEL spectra integrated over the red area in (a). The raw spectrum is a convolution of two valence states of Si, one belonging to the SiN windows and the other belonging to the Si nanowire. Plural scattering has been removed using Fourier deconvolution.

References:

- [1] H Müller et al., *Microsc. Microanal.* **12** (2006), p. 442. doi: 10.1017/S1431927606060600
- [2] PC Tiemeijer, MHF Overwijk and AF de Jong, *Microsc. Microanal.* **6** (2000), p. 170. doi: 10.1017/S1431927600033341
- [3] OL Krivanek et al., *Microscopy* **62** (2013), p. 3. doi: 10.1093/JMICRO/DFS089
- [4] ML Taheri et al., *Ultramicroscopy* **170** (2016), p. 86. doi: 10.1016/J.ULTRAMIC.2016.08.007
- [5] ME Holtz et al., *Microsc. Microanal.* **19** (2013), p. 1027. doi: 10.1017/S1431927613001505
- [6] R Serra Maia et al., *Microsc. Microanal.* **27** (2022), p. 2021. doi: 10.1017/S1431927621003925
- [7] E.M. acknowledges funding from Irish Research Council Enterprise Scheme (EPSPG/2017/311) in conjunction with the Ernst Ruska-Centre, Forschungszentrum Jülich. M.C. acknowledges funding from the Royal Society Tata University Research Fellowship (URF\R1\201318). SFI grant 16/US/3344 allowed access to the Titan STEM for these experiments.