Smart Acquisition EELS

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Abstract.
Electron energy loss (EEL) spectroscopy and high angle annular dark field (HAADF) imaging in aberration-corrected electron microscopes are powerful techniques to determine the chemical composition and structure of materials at atomic resolution. We have implemented Smart Acquisition, a flexible system of scanning transmission electron microscopy (STEM) beam position control and EELS collection, on two aberration-corrected dedicated cold field emission gun (FEG) STEMs located at SuperSTEM, Daresbury Laboratory. This allows the collection of EEL spectra from spatially defined areas with a much lower electron dose possible than existing techniques such as spectrum imaging.

1. Introduction
The STEM is the ideal instrument for combined imaging and analysis because of the potential for multiple signals to be collected simultaneously. For example it is possible to image single atomic columns with the high angle annular dark field signal and simultaneously record EEL spectra to give atomic resolution chemical information [1]. However, this is only possible for radiation insensitive materials because of the large electron doses that are required: for radiation sensitive materials this goal is far off.

It is well known that to attain atomic resolution information from frozen hydrated biological macromolecules, only about \(10e^{-}/\AA^{2}\) can be used [2]. Such a small electron dose requires extensive averaging to increase the signal to noise ratio. The principle of averaging can be applied to EEL spectra, preventing damage by spreading the dose over a large area. However, the systematic noise in charge coupled devices (CCDs) prevents the summation of individual spectra collected from each pixel of a spectrum image taken with low electron doses or at high edge energies, as is also the case with extremely low dose TEM images [3].

Our currently implemented solution is Smart Acquisition. This involves scanning a STEM probe over similar areas of interest while collecting a single spectrum, therefore avoiding readout noise for low electron counts and the time overhead of multiple readouts. This concept is not entirely new, with similar ideas proposed by John Hunt [5; 6]. However, with the successful implementation of aberration correction and improved stage stability, atomically resolved areas can now be defined and analysed.

We have used Smart Acquisition to fabricate nanostructures in aluminium trifluoride AlF₃ and subsequently collect EEL spectra from spatially defined positions. The use of high current...
density STEM probes of $10^7 \text{A/m}^2$ is a promising method of producing nanoscale structures in metal halides and oxides [7]. In particular AlF$_3$ is of interest because its extreme beam sensitivity allows films in the hundred nm range to easily be cut through. A demonstration of the application of AlF$_3$ hole drilling has been the production of electron optical phase plates [8]. The sensitivity to beam irradiation has also made it difficult to define the exposure mechanism[9], though there have been extensive studies [10].

2. Methods
Images were collected on a 5th order aberration corrected Nion UltraSTEM situated at Daresbury Laboratory, UK, with a third generation Nion C$_3$/C$_5$ corrector with 12 quadrupoles and 3 combined quadrupole-octupoles [11]. This uses a cold field emission filament operating at 100kV and is equipped with a Gatan Enfina electron energy loss spectrometer giving a total spectral resolution of 0.4eV, CCD camera, bright field photo-multiplier tube (PMT), medium and high angle annular dark field PMT detectors.

Digital Micrograph (DM, Gatan) scripts have been written to utilize existing beam control commands to control the position of the electron probe on the Nion UltraSTEM, utilising the Digiscan II scanning unit. Shapes to be scanned can be defined in a HAADF image from any combination of regions of interest (ROIs) in DM, or from binary image masks created by thresholding the image itself. This allows the averaging of the EEL signal over defined features.

The beam current was measured by diverting the electron probe onto the drift tube of the Enfina spectrometer connected to an ampmeter. Under standard conditions and after flashing, the beam current was measured to be 100 pA. The beam current was reduced to about 5pA by decreasing the extraction voltage. For a probe size of 1.3Å full width half maximum (FWHM), this gives a current density of $3.8 \times 10^8 \text{A/m}^2$. For a 0.8ms dwell time this gives an electron dose of $3 \times 10^{14} \text{C/m}^2 (7000e^{-}/\text{Å}^2)$.

AlF$_3$ (anhydrous, 99%, Alpha Aesar) was evaporated in a molybdenum boat (modified to prevent the spitting of the powder due to adsorbed water [10]) onto Quantifoil 7/2 square mesh grids covered with 2nm carbon film. The film thickness was monitored using a quartz crystal oscillator and the final thickness measurement was 26.5nm.

3. Results and Discussion
Five positions were exposed to the $\sim1.3\text{Å}$ FWHM STEM probe for 0.6s each to drill holes in the AlF$_3$ (HAADF image following exposure - Figure 1a). Seven sets of pixel positions of circles of radii 5.6nm to 0.7nm around the centre of each hole were generated in DM. The Smart Acquisition script was used to move the beam pixel by pixel (with Digiscan) around the set of points for each radius while using an independent command to collect a single EEL spectrum for each set (Figure 1b).

The EEL spectra are shown in Figure 2. The increasing shoulder of the plasmon peak at 15eV (Al bulk plasmon) suggests that the STEM probe irradiation did not remove all the material, but instead concentrated Al metal.

The threshold current density for AlF$_3$ is $10^7 \text{A/m}^2$, an order of magnitude below the current density estimated for the probe. It is therefore unlikely that metalisation occurred due to a low probe current, but instead due to a constant drilling rate [10] due to the low electron dose of $2.3 \times 10^{14} \text{C/m}^2$, which is also know to cause metalisation [7].

The other mechanism of hole formation often observed is an initially slow drilling rate, followed by sudden mass loss. This is explained by Berger [12] as being caused by bubbles of fluorine/oxygen, which suddenly burst. It was proposed by Macaulay [10] that the two mechanisms of hole formation- a constant drilling rate or sudden mass loss are due to either the diffusion of oxygen/fluorine molecules to the surface and loss to the vacuum or trapping inside
Figure 1. Spatially defined positions of EEL spectra of exposed AlF$_3$ thin films. A) HAADF image of points exposed to STEM probe for 0.6s. B) Sets of positions (red circles) from which EEL spectra were collected from the exposed AlF$_3$ films- from outer to inner radii: 5.6nm, 4.2nm, 3.5nm, 2.8nm, 2.1nm, 1.4nm, 0.7nm. Scale bar is 10nm.

Figure 2. Low loss EEL spectra from each radius. The spectra were aligned vertically to the maximum of the large bulk plasmon signal. This clearly shows a growing shoulder at 15eV- the bulk plasmon of Al metal.

the bulk. Hole drilling by bubble formation was observed with higher doses but holes were larger and less regular.

One of the major problems in our experiments was the inability to control blanking of the electron beam. The movement of the probe was not exactly synchronized with the EELS acquisitions in this application, and therefore an area without specimen (vacuum) was required as a safe position at which the beam could start and end. This did allow the full exposure of the sample to be collected in the EEL spectrum (minimal time taken to move to safe point). However, this was a limiting factor because only areas near vacuum could be studied, and in the loss low region of the spectra, the tails of the zero loss peak had significant intensity. Scripting control of beam blanking has now been implemented on the Nion UltraSTEM. The solution for the first microscope at SuperSTEM, a VG HB501 fitted with second generation 3rd order aberration correctors, was to script control of the printer port to modulate a 5V transistor-
transistor logic (TTL) signal. This is used to directly control the pre-specimen beam blanking and has been incorporated into the Smart Acquisition scripts.

A second issue has been further reducing the electron dose. The Smart Acquisition script takes a list of pixel positions, and requires 0.8ms to move from one position to another. This is largely a communications issue, with 0.8ms being the time required for the computer to communicate with the Digiscan unit over a firewire connection. Further increases of the speed of beam movement could be possible by directly interfacing with the scan unit, as done by Hunt [5], but this may be at the expense of greater inaccuracies in beam position due to the use of electromagnetic scan coils. Further reduction in the extraction voltage appears possible, with an apparent change only in astigmatism, which is easily adjusted in bright field images of amorphous carbon. Another option would be to use the beam blanker to stroboscopically illuminate the sample by fast blanking of the beam during the movement of the beam. A signal generator is already in use at SuperSTEM to attenuate the zero loss peak during the tuning of the Enfina spectrometer and acquisition of loss low spectra, without noticeable drift. The settling time of the blanking plates is in the tens of nanoseconds [13], so a periodic blanking on the order of tens of microseconds could significantly reduce the dose more than 10-fold.

In summary, a flexible system for the recording of low dose EEL spectra, Smart Acquisition, has been developed. EEL spectra can be collected from areas defined at high resolution. We have demonstrated the technique by studying hole drilling in AlF$_3$ thin films. We have now implemented pre-specimen blanking solutions on both microscopes at SuperSTEM, and we are now working on decreasing the minimum dose to extend the range of beam sensitive materials that we can image and analyse.

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