Continuous EELS spectrum imaging of nano-droplet crystallization heterogeneity

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Background incl. aims
Electron energy loss spectroscopy (EELS) is a powerful technique for characterizing nanomaterials; a number of materials properties can be extracted from the information-rich spectra. One application is nano-thermometry, where the local temperature of individual metal nanoparticles can be measured by a precise determination of the plasmon peak position [1]. As thermal expansion increases a particle's volume, the density of electrons decreases, and the energy loss of the plasmon peak shifts to lower energies. This same approach can be used to detect melting and crystallization, which result in even larger changes in the electron density. Continuous acquisition of EELS data enables precise determination of the melting and crystallization temperatures of individual particles. Using the new in-situ EELS spectrum imaging features of the Continuum GIF, a continuous series of drift-corrected spectrum images can be acquired over an ensemble of particles, and the melting and crystallization behavior of each one independently monitored. This would be more difficult or impossible with other techniques such as TEM imaging, diffraction, or 4DSTEM.

Methods
In this work, we show how a series of EELS spectrum images can be acquired and processed along with the temperature data from a MEMS-based heating holder from DENSsolutions. With modern fast detectors and spectrometers, spectrum images with thousands of spectra can be acquired in less than a second, making continuous in-situ spectrum imaging feasible. The holder temperature data is automatically synchronized and correlated with EELS spectrum image data. We also show how the entire series of in-situ EELS spectrum images can be rapidly fit using the built-in NLLS tools in DigitalMicrograph, yielding series of synchronized fit maps, as seen in Figure 1. After summing the EELS spectra over a single nanoparticle, plots of the peak position over time can be generated, and even plotted against the nominal temperature from the holder in scatterplots in DigitalMicrograph. The plasmon peak position within each particle indicates whether the Sn is melted or crystallized at that time.

Results

This new in-situ EELS spectrum imaging capability has been applied to a Sn nanoparticle sample which was oscillated above and below its melting temperature with varying ramp rates. Spectrum images were recorded at a rate of 1 frame every 1.54 s (2000 spectra/s). Watching the maps of plasmon position over time reveals that while all the Sn particles crystallized during most cycles, and most particles crystallized during every observed cycle, some particles occasionally did not crystallize even though surrounding particles did. Images and 4D STEM maps of the particles after the in-situ recording do not indicate a clear difference between a particle that always crystallized and the particles that sometimes did not. Some variation could be the result of random chance, as the nucleation and growth of a crystalline nanoparticle from a nano-droplet is governed by both thermodynamics, which would indicate that the particles should all crystallize at the melting temperature, and kinetics, which stipulates that nucleation times for an ensemble will have some distribution. However, there are only 3 particles (of 11 in the field of view) which don't always re-crystallize, and one of them remains melted during 4 cycles, which seems unlikely to be due only to random statistical fluctuations in nucleation time.

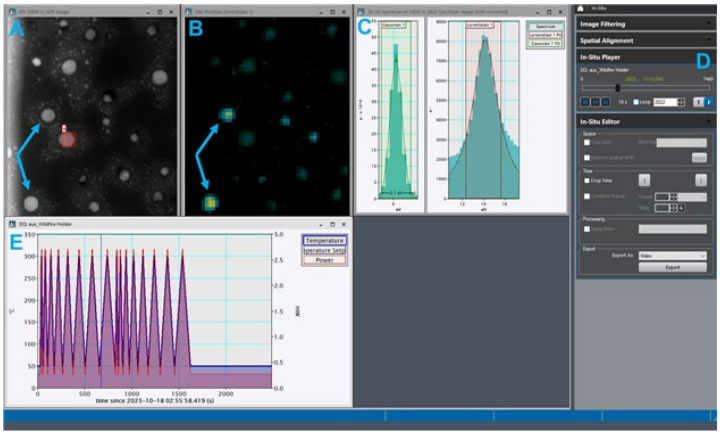
This behavior would be significantly more difficult to observe with TEM or STEM imaging, where the visibility of lattice fringes is dependent on the orientation of the nanoparticles. It would also be challenging with standard diffraction techniques, where the crystallinity of multiple particles could not be independently and simultaneously observed. Continuously acquired 4DSTEM could be used, but this requires more data to be stored, and the analysis is more complex, especially if there are other small crystallites (oxides, etc.) which overlap the droplets, as there are here.

Conclusions

This heterogeneous and stochastic behavior at the nanoscale can only be observed with high spatial and temporal resolution. In-situ electron microscopy, and specifically in-situ EELS spectrum imaging is an excellent technique for exploring these dynamics.

Figure 1: One frame from a screen-capture video showing playback of the in-situ EELS spectrum image dataset. A) Simultaneously acquired dark field STEM images. B) Maps of the plasmon peak position. Arrows indicate 2 particles which have failed to re-crystallize despite super-cooling them to 50 °C. C) Live fit of the zero loss peak and plasmon peaks from the red "picker tool" region indicated in A. D) In-Situ Player which plays back and synchronizes all displayed in-situ dataset components. E) Automatically acquired and synchronized temperature data from the DENSsolutions heating holder used to heat the Sn above and below its melting point of 232 °C.

Graphic:



Keywords:

EELS, In-Situ, nanoparticle, crystallization, melting

Reference:

[1] Mecklenburg, M. et al. Nanoscale temperature mapping in operating microelectronic devices. Science 347, 629–632 (2015).