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In-situ Oxidation State Mapping by Electron Energy-loss Spectroscopy

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Electron energy-loss spectroscopy (EELS) performed in the scanning transmission electron microscope (STEM) is a powerful technique for probing local electronic structure at high spatial resolution via the spectrum imaging (SI) paradigm. For *in-situ* analysis, the capability to capture spectral data at both high speed and high dose efficiency is critical. Traditional CCD based detectors used for EELS are capable of high spectral rates but give inherently low collection efficiency at high speed due to fixed readout dead time. Spectral quality is further compromised by the need to perform high levels of asymmetric binning to achieve the maximum frame rate. The current generation of CMOS based EELS detectors do not rely on binning for performance gains and utilize rolling shutter readout. With the use of fast electrostatic deflectors, these detectors can achieve nearly 100% live time readout at high spectral rates (> 8 kHz) giving high dose efficiency. Incorporating such a detector into an optimized STEM EELS acquisition system gives a highly efficient platform for *in-situ* STEM EELS experiments.

Here we use a CMOS based EELS spectrometer (GIF Continuum) to demonstrate a novel spectrum imaging acquisition methodology that allows synchronization of an *in-situ* stimulus to the SI data acquisition. The reduction of copper (II) oxide has

been used as a model materials system. Dual-EELS^{TM} multipass spectrum images were acquired using two next generation CMOS detectors, a fiberoptic coupled, indirect detector and an electron counting direct detector (K3). In addition, energy filtered diffraction spectrum images were acquired using the K3 camera in counting mode for some of the data runs. The copper (II) oxide specimens were reduced by *in-situ* heating with both MEMS style (Wildfire, Dens Solutions) or furnace style (Gatan 652 holder) heating holders. Specimen temperature was controlled via scripting during all experiments such that temperature shifts were applied in between spectrum image passes, keeping temperature constant during data acquisition.

Live energy-loss near-edge structure (ELNES) phase mapping was performed on the oxygen K and copper $L_{2,3}$ edges to monitor changes in copper oxidation state during acquisition. Elemental maps were then generated post acquisition for: oxygen, copper [II], copper [I] and copper [0] using standards based quantitative ELNES analysis [1]. This analysis combines measured ELNES with theoretical cross-sections for quantitative phase mapping. RGB composites of these maps at different temperature snapshots are shown in figure (1). The results show a clear trend of gradual decrease in copper oxidation state with increasing temperature. Rapid/spontaneous changes in morphology of two particles (a and b) were also observed over the course of the experiment. Counted diffraction SI results support the EELS results. In this presentation, the advantages of using this novel data acquisition and paradigm for *in-situ* STEM experiments will be demonstrated.

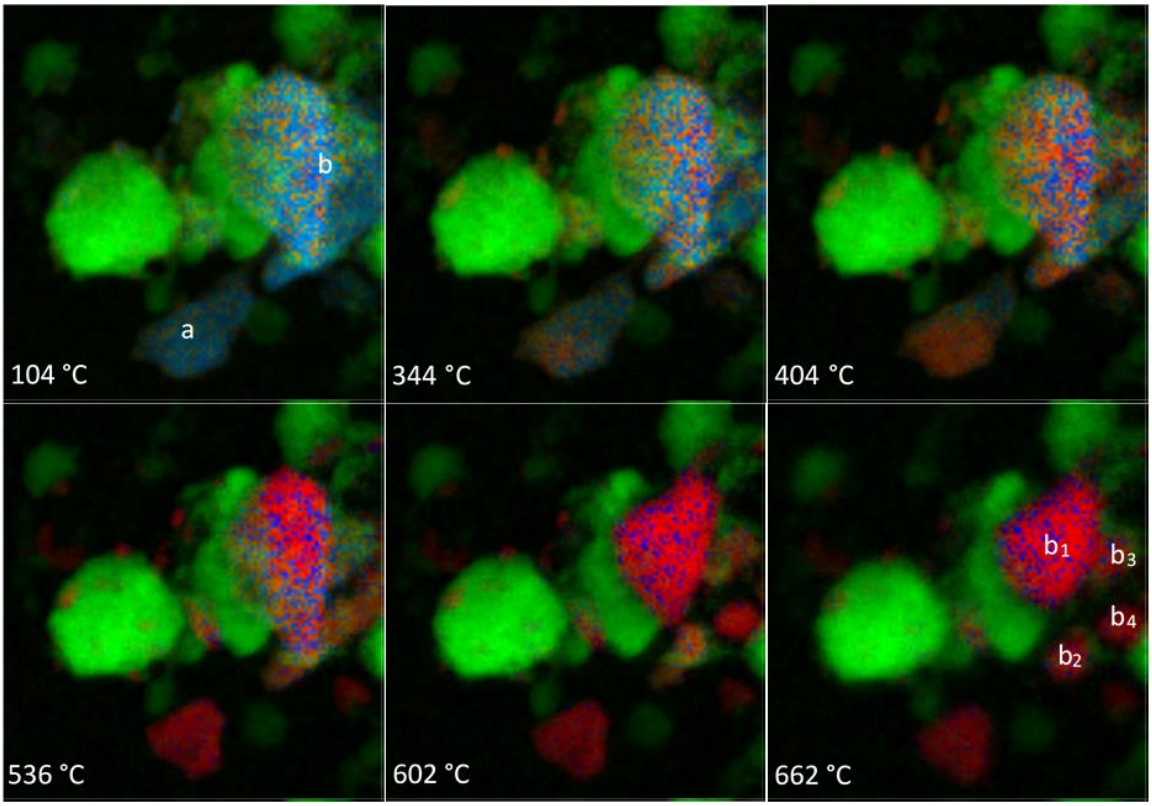

Figure 1. Copper oxide and silica particles at different temperatures throughout a MEMS heating experiment. RGB composite images show: oxygen (green), copper [II] (blue) and copper [I] elemental maps overlaid

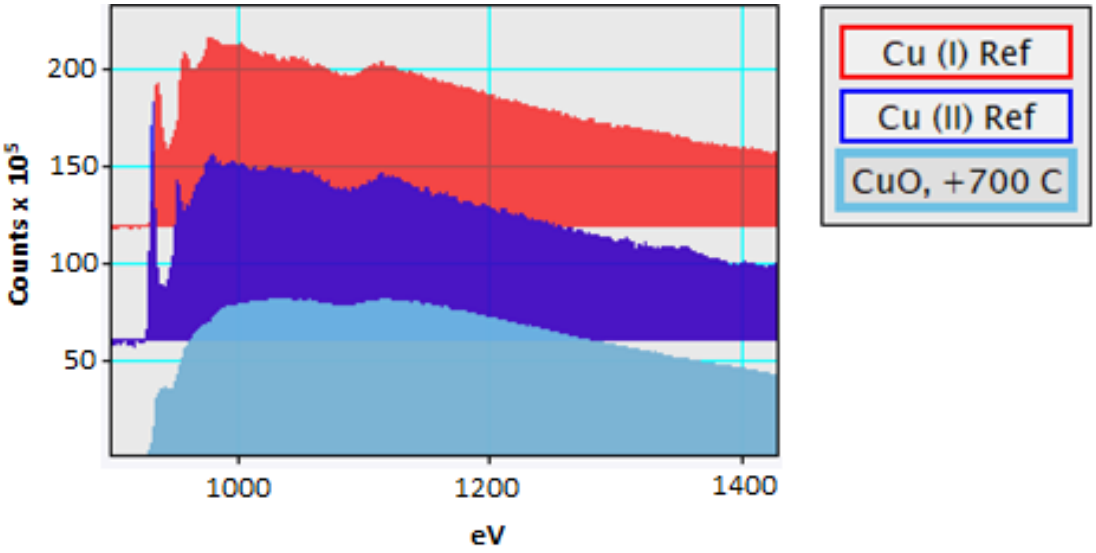

Figure 2. Typical copper L2,3 spectra for Cu [I] and Cu [II] showing ELNES features used to perform phase mapping. An example spectrum from a copper oxide particle heated to 700°C with a MEMS heating holder is also shown for comparison.

References

[1] B. Schaffer, *et al.*, Microsc. Microanal. **25** (suppl 2), (2019)

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