In-Situ, Time-Resolved Electron Microscopy of Thermal-Induced Phase Transitions in Nanostructured Materials

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The ability to resist phase transformation over repeated thermal cycling can have important implications on the overall performance of technologically relevant nanomaterials useful in devices such as rechargeable Li batteries, photovoltaic cells, displays, sensors, light emitting diodes, and transparent electronics, for example [1-2]. Recent advances in semiconductor-based MEMS technology fabrication techniques (Protochips Inc., Raleigh, NC) now provide millimeter-sized, disposable MEMS devices that can serve as both heating elements and specimen support grids. These solid-state heaters can be employed in a TEM or SEM holder with electrical feedthroughs for controlled, in-situ heating. The added benefit of miniaturization combined with the dual function configuration of both support and heating surface, permits the full range of imaging and analytical capabilities of e.g. an aberration-corrected electron microscope. Thermal cycling experiments can also be performed with heating/cooling rates that can be varied in-situ, up to $10^6 \, ^\circ \text{C}/\text{sec}$ with virtually instantaneous temperature stabilization [3].

Examples demonstrate high-angle annular dark-field (HA-ADF) imaging of supported ruthenium metal clusters with sub-Ångström resolution, and time-resolved atomic-scale visualization of nucleation events and diffusion of Ru metal particles into thermodynamically stable structures (Fig. 1). Quantitative measures of particle growth scales linearly with particle diameter and is consistent with a sintering mechanism and the linear law of Koch and Friedlander [4]. Surface area reduction of particles toward spherical shapes, as well as the dynamic reordering of crystal structures into predominant (111) surface facets follows the phenomenological macroscopic model that is based on energy balance and surface variations of nanosystems [5].

The stability of the heater devices allows several scenarios for collection of energy-dispersive x-ray spectra and spectrum images. Examples of "hypermaps" collected with a Bruker-AXS silicon-drift detector (SDD), for example Fig. 2, show the ability to acquire data on sample microareas or from nanoparticles at direct magnifications of 5Mx, limited only by the inherent drift characteristics of the microscope's specimen stage [6,7].

References
Fig. 1. HA-ADF images showing growth of Ru metal clusters into thermodynamically stable structures. (31-34 refer to frame numbers from a sequence captured every 20 sec.)

Fig. 2. a) and b) show HA-ADF images of a Au/Fe$_2$O$_3$ catalyst, at 250°C during recording. Panel a) shows the as-received sample, with 1-5nm Au particles both within the support and on the surface; dark features are voids. Panel b) shows the effects of heating for 9min at 500°C, with voids shrunk, surface rearrangement of the oxide, growth of the larger Au nanoparticles, and the very fine Au species coalesced into larger particles. Panels c) and d) are corresponding maps of Au location from the hypermap series.