doi:10.1017/S1431927611003175
Microsc. Microanal. 17 (Suppl 2), 2011

A Quantitative Description of Electron Beam Induced Phenomena During *in situ* Fluid Stage STEM Experiments

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Currently there are few generally accepted experimental practices in the field of fluid stage electron microscopy. To obtain consistency in this emerging field, a crucial step is to establish protocols for stage and window cleaning, sample preparation, and microscope settings that minimize contamination and adverse beam-sample interactions. Recently we have observed many unintended phenomena during *in situ* fluid stage STEM experiments, including spontaneous growth of nanoparticles, contamination and aggregation of species on the fluid stage windows, and rapid charging of nanoparticles at high magnification. These undesired phenomena inhibit our ability to use fluid stages for investigation of nanoparticle behavior known to occur without electron beams, such as the aggregation behavior of nanoparticles near charged electrodes [1]. Before any quantitative nanoparticle aggregation experiments can be performed with the fluid stage, the unintended growth, aggregation and charging of nanoparticles must be characterized.

Nucleation and growth of nanoscale clusters was first observed by Williamson *et al.* using *in situ* fluid stage TEM [2]. They observed electroplating of copper with an externally applied electric field, and measured the dynamic growth rate of copper nuclei and film thickness on the fluid stage windows. Using a similar fluid stage enclosure, Zheng *et al.* recently observed electron beam induced growth of platinum nanoparticles in a 200 nm thick fluid stage enclosure [3]. They found that irradiating a solution containing platinum precursor with a 300 kV TEM beam induced spontaneous growth of platinum nanoparticles in the bulk fluid. de Jonge and co-workers have studied in depth the resolution limits of fluid stage STEM in micron thick layers of water [4,5]. By imaging gold nanoparticles above a 3.3 μm layer of water with a 200 kV STEM, they were able to achieve a maximum resolution of 1.4 nm [4]. At high magnifications, they observed dissolution of particles in the fluid by the STEM beam.

Here we provide a quantitative description of fluid stage contamination and particle growth, and analyze their origins towards prescribing methods for controlling their effects during experiments. We have shown that during STEM imaging of nanoparticles in dilute electrolyte, additional nanocrystals were nucleated and grown on the fluid stage windows as well as on the surface of already present nanoparticles. At high magnifications, particles disappeared from the viewing area in a few seconds. A combination of bright field (BF) and annular dark field (ADF) detectors were used to obtain complimentary images simultaneously of nanocrystals in a 50-70 nm thick liquid layer between two SiN_x windows. Significant particle growth occurred above magnifications of 60,000 and happened over time spans of a few minutes. The growth was enhanced with increased amounts of nanoparticle precursor in the liquid, and contamination by the stage tip was found to also

be a contributing factor. Image and chemical analysis techniques were used to describe the behavior of various types of nanoparticles at low and high magnification [6].

References

[1] M. Trau, *et al., Science,* 272 (1996) 706.
[2] M. J. Williamson, *et al.*, *Nature Letters,* 2 (2003) 532.
[3] H. Zheng, *et al., Science,* 324 (2009) 1309.
[4] N. de Jonge, *et al., UltraMicroscopy*, 110 (2010) 1114.
[5] N. de Jonge, *et al., PNAS,* 106 (2009) 2159.
[6] This research was supported by the University of California-Davis Academic Senate and UC Laboratory fee research grant program.

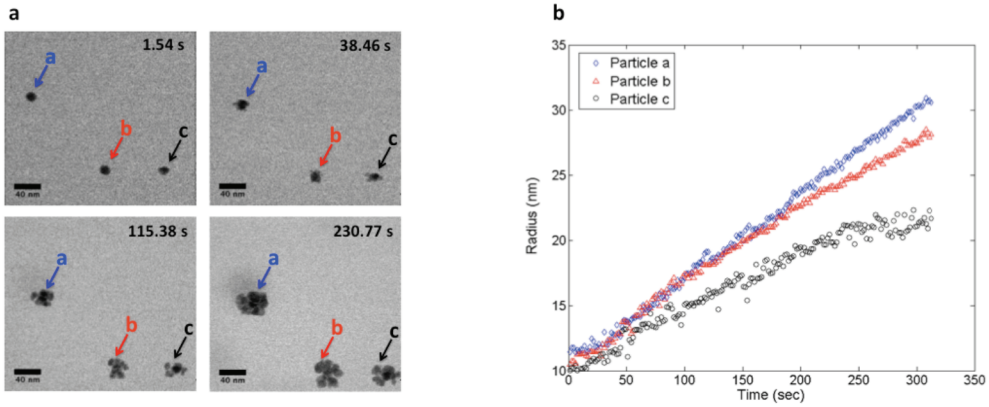

Figure 1. Growth of gold nanoparticles at 400,000 magnification. The scale bar is 40 nm in each image and the current density is ~6 pA/cm^2. **a.** A time lapsed series of images depicting three gold nanoparticles growing in 0.3 mM trisodium citrate. **b.** The radius of each particle is measured over a span of ~300 seconds of electron beam exposure. Note the particles become non-spherical as they grow larger. The radius is approximated as $(A/\pi)^{1/2}$, where A is the projected area of the particle.

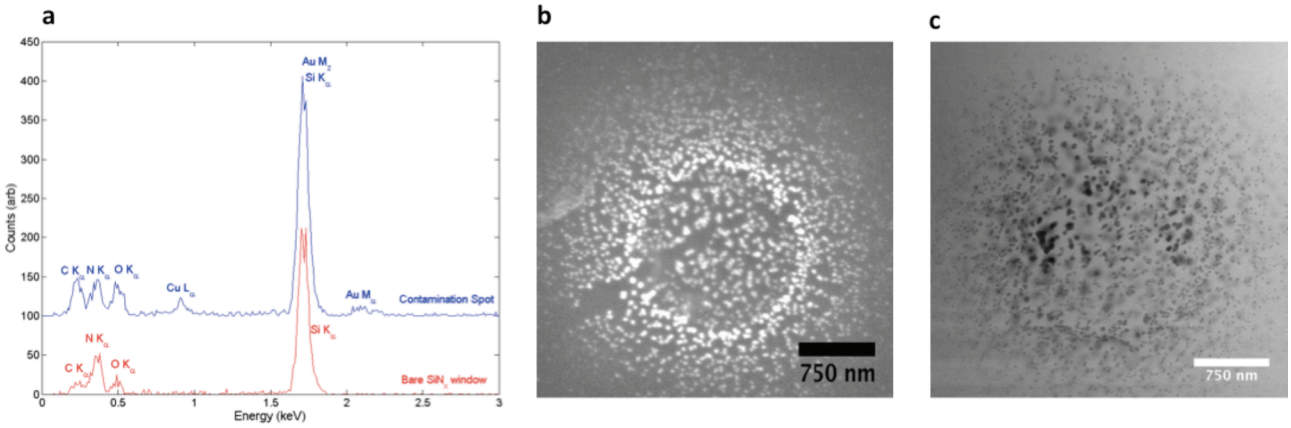

Figure 2. Crystals grown on the SiN_x window during a fluid stage STEM experiment were analyzed *post situ* using SEM and energy dispersive x-ray spectroscopy (EDS). **a.** EDS spectra from the uncontaminated SiN_x window and contamination spot. **b.** SEM image of the contamination spot from which the EDS spectra in **a** was taken. **c.** BF-STEM image of the same contamination spot taken during the fluid stage experiment.

https://doi.org/10.1017/S1431927611003175 Published online by Cambridge University Press