

USE OF *IN SITU* TEM TO STUDY NANOMATERIALS

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A burgeoning interest in nanoscale materials has initiated a world-wide investigation of the unique properties that materials in this size range tend to exhibit. The inherent size of the materials of interest makes the transmission electron microscope (TEM) an indispensable characterization tool. When coupled with *in situ* sample holders, it is possible to heat, strain and even compress nanoscale samples [1-4]. *In situ* TEM techniques, typically through unique sample holders, allow for direct observation of the phenomena in question even at this small scale. Here, several *in situ* techniques are used to investigate the properties of nanoparticles, nanowires, and thin films. These studies utilize the Tecnai T12 TEM at the University of Minnesota and the JEOL 3010 TEM at Lawrence Berkeley National Labs.

Typically, high-temperature experiments are limited to characterization of a sample prior to heating and after cooling, leaving the experimentalist to determine what has occurred in between. Heating a sample in the TEM allows the entire process to be observed, though careful sample design must be considered. In this work a support was made by dimpling and ion-milling a three-millimeter sapphire disk. The thinned disk was then chemically cleaned and heat treated to remove any amorphous material introduced during ion milling. This method produces an electron-transparent sample with a surface consisting of well-defined facets [5]. A thin film of NiO was then deposited onto the sapphire by means of pulsed-laser deposition (PLD). The film was observed in the TEM at room temperature and then heated *in situ* to 1200°C. Using this method it was possible to observe the dewetting of the film, a phenomenon typically only speculated about after cooling. Figure 1 shows a dewet film on the surface of a sapphire substrate. Similarly, *in situ* heating was used to observe the evolution of catalyst particles in nanowires. In this case the wires were grown directly on a TEM grid. Figure 2 shows a nanowire at room temperature (a) and at 300 °C (b), where the catalyst particle is visibly smaller.

Another *in situ* holder has been designed to indent, or compress in the case of small particles, a sample and observe the deformation event in the TEM as it occurs [6]. In this work the compression of individual nanoparticles is described. Typically, the particles are deposited on a sapphire substrate and are compressed by the diamond indenter, which is very large compared to the particle. Using this technique elastic contact, plastic deformation and even particle fracture were observed. Figure 3 shows a nanoparticle after compression where the particle has fractured into two pieces, where a portion of the particle has pulled away from the substrate upon retraction of the diamond tip.

In situ experiments in the TEM have become essential tools for characterizing nanomaterials. Through the development of new holders and the design of novel experiments the properties of these materials can be characterized through direct observation. This work describes the use of several *in situ* techniques to examine the properties of nanomaterials.

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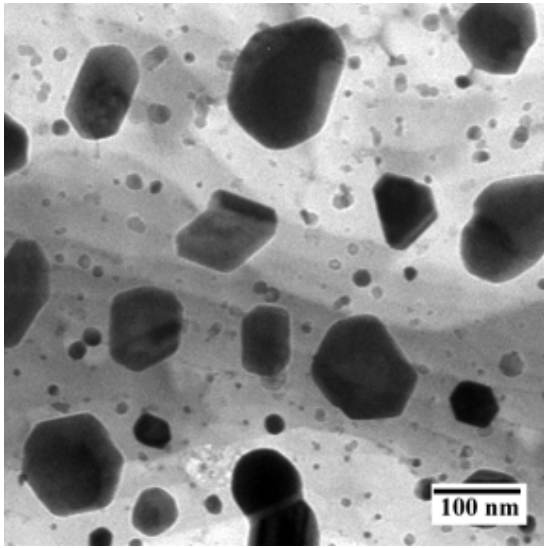


Figure 1 (above): *In situ* dewetting of a film on the surface of an electron-transparent sapphire substrate. The temperature is 1020°C.

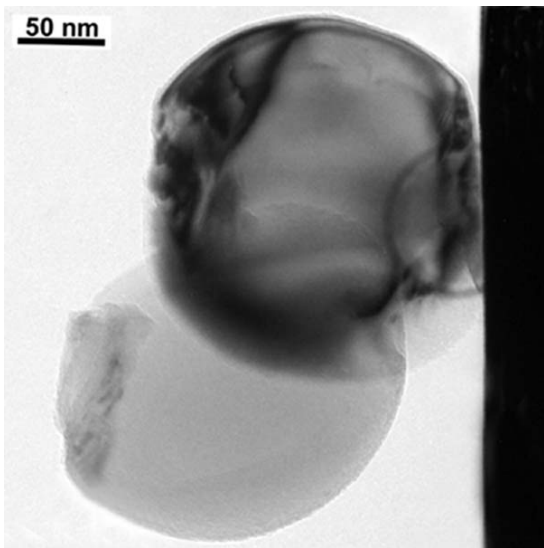


Figure 2 (above): Silicon nanosphere after fracture. One portion of the particle has pulled away from the substrate upon retraction of the tip. The nanosphere has sustained significant plastic deformation at both the top and bottom contact.

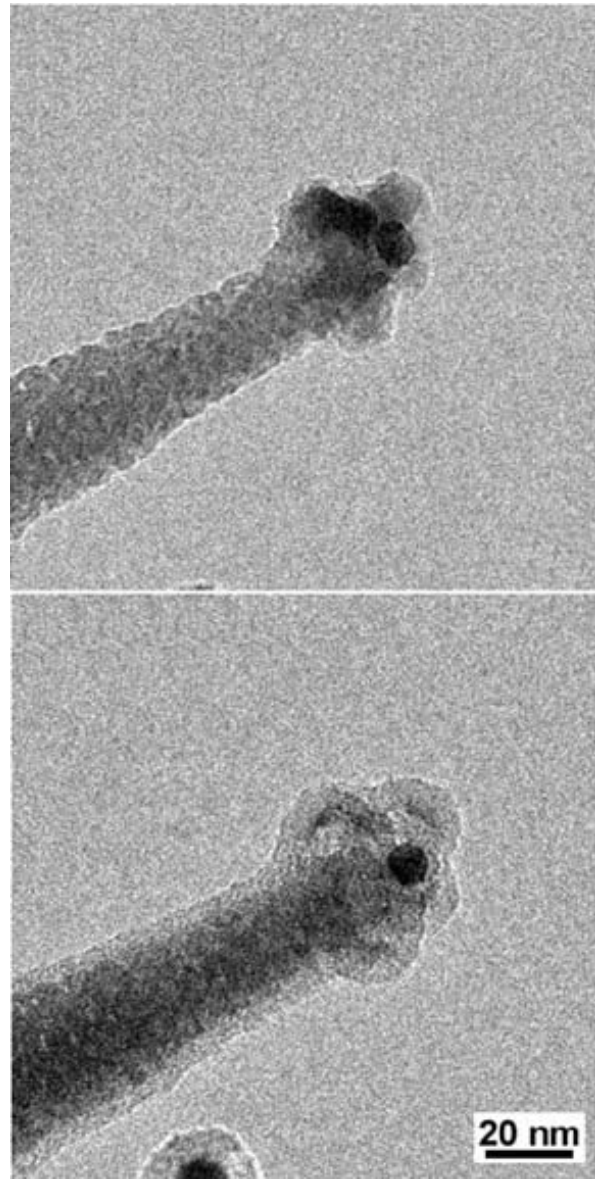


Figure 3 (above): *In situ* heating of a nanowire. The top image shows a ZnSe nanowire with a Au catalyst particle at 100°C. The bottom image shows the same nanowire after heating to 300°C. The change in the catalyst particle suggests nanowire growth occurring below the reported ternary eutectic temperature of Zn-Se-Au.