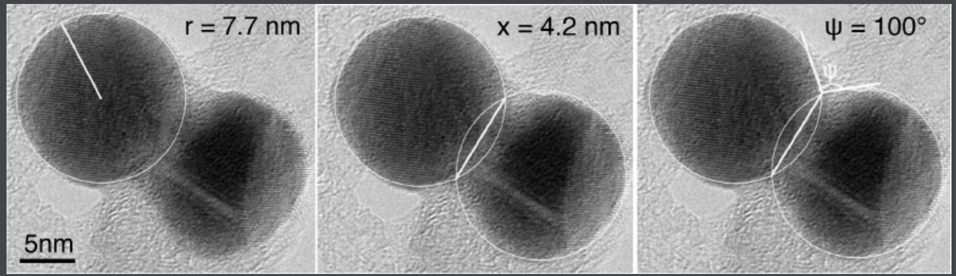
APPLICATION NOTE

Aduro™

Melting and Sintering Behavior of Silver Nanoparticles in the TEM



Introduction

Metal nanoparticles possess enhanced properties at the nanoscale, and are extensively investigated for applications in fields such as plasmonics, catalysis and nanoelectronics. Their properties are highly dependent on the surface-to-volume ratio, which, on the nanoscale, is much higher than bulk materials. This dramatically increases the surface's influence on nanoparticle properties and behavior.

Understanding these properties is critical when using these materials in new and existing applications. The increased surface-to-volume ratio and particle curvature impact sintering behavior and melting, significantly decreasing the melting point of nanoparticles relative to bulk.

Direct observation of the melting and sintering behavior of metal nanoparticles in the TEM using in situ heating experiments can uncover important characteristics on a nanoparticle by nanoparticle basis, which bulk techniques cannot resolve.

In this application note, the Aduro in situ heating and electrical biasing system was used to analyze the melting and sintering behavior of silver nanoparticles in the TEM.

Aduro uses semiconductor devices, called E-chips™, which have a ceramic heating membrane that acts as the active area and sample support. The small size and monolithic design of the E-chips, significantly reduces thermal drift, enabling high resolution imaging at temperatures up to 1200 °C.

Users can effectively compensate for thermal drift and analyze the same particles over a large temperature excursion, room temperature to 1200 °C, while maintaining the same field of view. Each E-chip is individually calibrated to ensure the temperature of the material being heated is accurately known, making quantitative interpretation and explanation of results easier than ever.

Experiment

In this experiment, silver nanoparticles were analyzed to determine sintering characteristics as well as melting and vaporization temperatures as a function of size. Silver was chosen for its resistance to oxidation. The nanoparticles were dispersed directly on the heating membrane of an E-chip, which had a thin layer of carbon for added support.

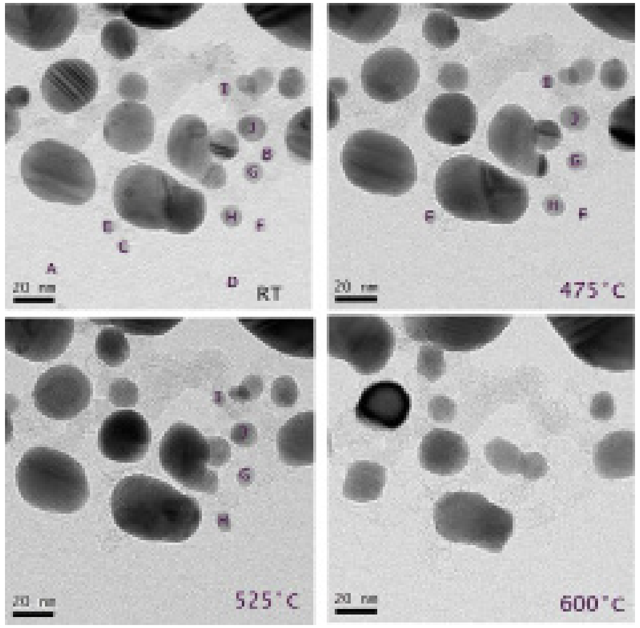
The melting and vaporization characteristics of silver nanoparticles with sizes ranging from 4 to 50 nm were investigated in the first experiment. Sintering characteristics of nanoparticles with sizes ranging from 15 and 40 nm were investigated in the second experiment. Sintering parameters measured included neck radius and dihedral angle. Surface diffusion coefficients were calculated from these measured parameters.

The silver nanoparticles were purchased from Nanotechnologies, Inc. with an organic layer to prevent agglomeration at room temperature. The experiments were done in a JEOL 2010F in Dr. Paulo Ferreira's laboratory at the University of Texas at Austin. The microscope was operated at 200 kV in bright field mode.

Discussion

In the first experiment, the melting and vaporization points were measured as a function of size. The figure below shows a sequence of images at increasing temperature from room temperature to 600 °C. The smaller particles are observed to melt and vaporize before the larger particles.

Shrinkage was also observed along specific crystallographic planes in the nanoparticle, which was likely due to surface energy



anisotropy or interactions with the carbon support film.

In the second set of experiments the sintering behavior of the silver nanoparticles was observed. The figure at the top of the previous page shows two 15 nm diameter nanoparticles in the process of sintering. The temperature was held at a constant 200 °C during this experiment. In the middle figure the neck radius was measured to be 4.2 nm, and in the right figure the dihedral angle was measured to be 100°.

From these parameters the surface diffusion coefficient can be measured (see references), and depends on the change in neck radius over time, the particle radius and the temperature. In this case it was in the range of 1.04 - 1.55 x 10^{-21} m^2/s. The organic capping layer likely also plays a role in this process, and is believed to decrease the surface diffusion coefficient.

Applications

Metal nanoparticles are an important material used in many applications. It is crucial to understand their behavior at elevated temperatures, especially when nanoparticles are used in catalysis. The Aduro heating and electrical biasing system is ideal for measuring the behavior of small particles from room temperature to 1200 °C on a particle-by-particle basis, at resolutions down to the atomic scale.

Contact us to discuss the full range of capabilities of Aduro with Thermal and Electrical E-chip sample supports. We can be reached at (919) 341-2612 or contact@protochips.com.

References

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