In Situ HREM Observation of Crystalline-to-liquid transition in Nanometer-sized Gold Particles on Graphite

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Interest in nanometer-sized particles (NPs) has grown remarkably for the last decades and a lot of work has been done to understand the origin of the unique structures and properties of NPs. Especially, high resolution electron microscopy (HREM) did a great contribution to the understanding of the phase change in NPs of not only pure substances but also of alloys. It is now well established that not only the surface but also the interface between phases significantly affect the microstructure (or phase stability) of NPs [1,2]. Most of the studies on NPs have been carried out using NPs on typical solid substrates. In this case, the substrate could affect not only the phase stability but also the morphology such as wettability of NPs on the substrate. Actually, regarding to the phase stability, no melting was observed during the sublimation-induced shrinkage of an approximately 9-nm-sized silver particle on a graphite substrate in our previous study [3] although it has been widely accepted as a universal relationship that the melting point has a linear reciprocal relationship with the particle size. On the other hand, the wettability of NPs on typical substrates is also of significant importance from the viewpoint of real application. Based upon these premises, it is of interest to examine the phase and morphology change of NPs. In this study, a series of in-situ HREM experiments to study the solid-to-gas transition (or solid-to-liquid) and the morphology change of Au NPs supported on graphite substrate have been carried out.

For the purpose of keeping the surface of NPs as clean as possible during the experiments, both production and observation of nanometer-sized particles have been carried out in the same vacuum chamber using a unique side-entry TEM holder equipped with an evaporator [4]. Using the holder, we monitored the microstructural and morphological evolution of the particles during slow heating up to 1100 K and also keeping at the temperature.

Remarkable evaporation of gold atoms took place from crystalline Au NPs on the graphite substrate at 1100 K under the vacuum of $5 \times 10^{-7}$ Pa, which resulted in the decrease of the particle size. A crystalline-to-liquid phase transition took place when the particle size decreased down to almost 5 nanometers by sublimation-induced shrinkage of the particle before complete disappearance of the particle from the substrate. On the other hand, the height-to-width ratio (or the contact angle) almost monotonically decreases during sublimation-induced shrinkage of the particle. More surprisingly, the wetting mode has been changed from non-wetting to wetting with decreasing the particle size, which could not be expected in bulk materials.

Based upon these results, the behavior of Au NPs supported on the graphite substrate will be discussed.

References

FIG. 1 A typical change in a nanometer-sized gold particle on the graphite substrate kept at 1100 K. The numbers inserted in each micrograph indicate relative times in seconds. Remarkable sublimation of gold atoms from a crystalline gold particle occurred at 1100 K, and continued until whole the particle disappeared from the substrate. During the sublimation, crystalline-to-liquid phase transition took place at the particle size of approximately 5 nanometers.

FIG. 2. Size dependence of the height-to-width ratio of the gold particle resting on graphite at 1100 K. The height-to-width ratio monotonically decreases with the particle size.