Dynamic Atomic-Level Rearrangements in Small Gold Particles

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Small metal particles (<5 nanometers), which are widely used in catalysis, have physical and chemical properties that are markedly different from those of the bulk metal. The differences are related to crystal structure, and it is therefore significant that structural rearrangements in small particles have been observed in real time by using high-resolution electron microscopy. A detailed investigation at the atomic level has been made of the factors affecting the dynamic activity of small gold crystals that are supported on thin films of amorphous carbon, silicon, and germanium. The rate of activity depends mainly on the current density of the incident electron beam and the degree of contact of the particle with the substrate, but this rate decreases rapidly as the particle size is increased. The activity of the particles is very similar on either carbon or silicon, but it is generally less marked on germanium because of increased contact between the particle and the substrate. The electron beam effectively heats the particles, and it appears that their dynamic behavior depends on their thermal contact with the substrate.

Developments in instrumentation for the high-resolution electron microscope (HREM) have facilitated the observation and recording of dynamic events at the atomic level directly within the microscope. Processes recorded include the motion of defects in gold foils (1), the annealing of defects in cadmium telluride (2), and atomic rearrangements on the surfaces of small gold particles and extended gold foils (3–6). Rapid structural rearrangements also occur in gold crystals smaller than about 5 nm (4–7), but to our knowledge, no detailed study of the various factors affecting these activities has been reported. In an attempt to understand these processes, and also because of the possible links and similarities between these electron beam–induced rearrangements and those that occur during thermal annealing treatments of small particles (8), we have carried out further systematic studies on small gold crystals.

The small gold crystals were originally prepared as cluster complexes containing 55 gold atoms (4). Under electron irradiation, the attached ligands were evaporated, leaving the gold clusters randomly distributed on the supporting substrate. Further irradiation led to the development of bigger crystals, as documented previously (4), and our observations were then concentrated on those particles that were protruding over holes in the support film. For comparison purposes, the holey amorphous substrates were made of silicon and germanium as well as the traditional carbon. Samples were also prepared by direct evaporation of gold. Most of the observations were made with an HREM (JEM-4000EX) that was operated primarily at 400 kV, although some studies were also made at 200 and 350 kV. The microscope was equipped with a TV system (Gatan 622), fiber optically coupled to an yttrium-aluminum-garnet screen, and this was used both for image viewing and for video tape recording. Typical electron optical magnifications were 600,000 or 800,000 times, with electron current densities at the sample usually ~20 to 25 A/cm², although these values ranged from ~10 to ~80 A/cm² for those particular experiments designed to investigate the dependence on beam current density. Some of the videotapes were later processed with a digital video processing unit (Quantex DS-30) to reduce noise and to improve image contrast. Some observations were made with a 100-kV electron microscope (Philips 400ST) that was equipped with a specimen heating holder.

The images shown in Fig. 1 provide a graphic representation of the structural changes that occurred in the small gold crystals. Each image is a photograph of the monitor screen showing two to four averaged frames from a video tape recording, and the total elapsed time of the sequence is only 20 seconds. The images show the particles, supported on a thin film of amorphous silicon, near to a [110] orientation; they were taken at close to the optimum defocus (an amount out of focus at which one can directly interpret the image), so that the atomic columns appear black.

The sequence of images shown in Fig. 2 is

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Fig. 1. Series of high-resolution electron micrographs showing some of the structural rearrangements of a small gold crystal (diameter, 4.8 nm), supported on an amorphous silicon substrate, during 20-second time span. Imaging conditions: 400 kV; 40 A/cm²; electron-optical magnification, ×800,000. (a) The particle contains one twin plane (indicated by arrow) with a notch. (b) Four seconds later, the twin plane is displaced. Atomic columns are in an anomalous position at A, the notch is at B, and two are missing atom columns at C. (c) The crystal is rotated slightly away from the well-aligned condition, so the two-dimensional lattice structure is not readily visible. The twin plane is still discernible (arrow) if one tilts the image and looks along the various lattice directions. A column of atoms has hopped away from the site at C. (d) The twin is again clearly visible with good contrast but with a pronounced notch. A stacking fault appears at D; there are no missing columns at C. (e) The upper twin is still visible. The stacking fault visible in (d) has disappeared, and another stacking fault (arrow) parallel to the other set of (111) planes has appeared. An anomalous surface structure appears at A, and there is severe lattice distortion at E.

of another gold crystal on an amorphous silicon support. This sequence was recorded under imaging conditions identical to those in Fig. 1 except that the overall particle “diameter” was considerably smaller (~3.5 nm compared with ~5.0 nm). In this case, the structural changes occurred more rapidly, and it was difficult to obtain good contrast photographs from the monitor since many individual frames showed a blurred image of the particle because of its motion. The contrast in Fig. 2, a and c, suggests that the particle has an icosahedral multiply twinned shape (9), whereas in Fig. 2, b and f, it appears to be a single crystal, and in Fig. 2, d, e, and g, it contains, respectively, a stacking fault, a twin plane, and both a stacking fault and a twin plane. Depending on size and contact with the support, the particles were often observed to rotate on the substrate, and it was difficult in some cases to be certain whether a structural change had really occurred or whether the change observed in the image of the particle was simply a result of rotation.

In the very small crystals (diameter, <2 nm), motion was extremely rapid, making it unclear whether rotations or shape changes were taking place. Such particles would behave like pulsating liquid globules that could momentarily “freeze” in a particular shape and then “melt” into motion several fractions of a second later. A good example of a gold crystal on an amorphous carbon support is shown in Fig. 3. Similar behavior was also seen in larger particles that had minimal contact with the support, such as the gold crystal (diameter, ~4 nm) on amorphous silicon shown in Fig. 4. Single-frame images cannot convey the fascinating dynamic behavior of these rearrangements. The two twin planes meet at an angle in Fig. 4b, and Fig. 4c shows the dodecahedral multiply twinned shape, with pronounced reentrant notches at the separate twin boundaries. This latter configuration is expected because of minimization of the surface free energy (10).

From many observations similar to those
they were located in such positions a drastic curtailment of their activity was observed.

The behavior documented here has been observed in other microscopes at 200 kV (4) and 120 kV (7). The threshold for exit surface sputtering in gold is around 400 kV (11), and direct "knock-on" from the bulk occurs at even higher voltages. This dynamic activity of the particles at lower voltages implies that an explanation for the motion of the particles and their rearrangements in terms of atomic displacement mechanisms is unlikely.

The observations suggest that the quasi-fluidic behavior of the gold particles is explicable in terms of local heating of the particles by the electron beam, with more substrate contact providing greater opportunity for heat dissipation and thereby reducing the dynamic behavior. The TV system attached to the microscope was not equipped with an image intensifier, so the electron current densities at the sample could not be varied over a wide range. At 1 million times magnification and 60 to 80 Å/cm², the rate of activity noticeably increased after a short period (presumably as the particle warmed up). At 500,000 times magnification and 10 Å/cm², when the crystal lattice structure was just visible on the monitor, it was still possible to tell that the motion was considerably, though not entirely, reduced.

Since small metal particles are extensively used to catalyze chemical reactions at elevated temperatures, it was interesting to study the behavior of the gold crystals as the substrate was heated. We expected the structural rearrangement to occur for increasing larger particle sizes and for lower current densities as the temperature was increased. Moreover, given the studies of Wang et al. (8), where a threshold annealing temperature of 480°C was established for structural alterations in small platinum particles, it seemed reasonable to expect that structural changes in the smallest gold particles would occur spontaneously at sufficiently high temperatures. Observations were made with evaporated particles on an amorphous carbon substrate in the heating holder of the 100-kV microscope. The resolving power of this machine is limited to ~0.35 to 0.40 nm, which excluded the possibility of lattice plane or atomic resolution, and thus thermal drift prevented satisfactory image recording. Nevertheless, at a temperature of ~470°C, some particle motion was visible on a TV monitor, even when the electron current density at the sample was kept to a low level (~1 Å/cm²). At a temperature of 520°C, many particles were moving rapidly, and several appeared to change shape.

These preliminary, low-resolution results provide a crucial link between particle rearrangements that are beam-induced and those that occur naturally at elevated temperatures. Moreover, rearrangements in small crystals of platinum, rhodium, cadmium, and zinc have also been observed under high current density conditions (12). HREM observations could therefore represent a valuable alternative method for duplicating and characterizing the behavior of small metal particles, in particular those structural changes that occur during the annealing treatment. Further studies on other metals might assist in establishing the real structure of catalyst particles, particularly their surfaces, and might also help to elucidate the perplexing changes in physical and chemical properties that occur in small particles.

REFERENCES AND NOTES
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