Structural Instability of Ultrafine Particles of Metals

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Dynamic behavior of ultrafine particles of gold around 20 Å in size was examined at the level of atomic resolution by an electron microscope equipped with a real-time video recording system. In real time, it was observed that the shape of the particles changed continually through an internal transformation from a single crystal to a twinned crystal, and vice versa. The transformations were induced to some extent by irradiation by an electron beam. They took place abruptly in less than 0.1 sec.

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A decrease in the size of a solid often leads to anomalies in its physical properties. Takagi first observed the lowering of melting points for small metal particles.[1] More recently, Buffat and Borel confirmed the size dependence of melting points of gold particles.[2] These phenomena would be interpreted by anomalous electronic structures for extremely small metals[3] or lower frequency of thermal vibration of surface atoms.[4] A small cluster of atoms is believed to take a structure which is called the multiply twinned particle (MTP). They were first discovered by Ogawa *et al.*,[5] and the thermodynamical-equilibrium forms and structures of fine particles were theoretically discussed by Ino[6] and later by Marks and Howie.[7]

The present paper deals with morphologies and internal structures of ultrafine particles of gold and the use of a newly developed high-resolution electron microscope. It is emphasized that a structural instability of gold particles smaller than 50 Å in size takes place when they are exposed to intense electron-beam irradiation. The continual change of the outer shapes of the particles accompanying a reorganization of the internal atomic arrangements is disclosed for the first time.

The specimens, clusters of gold, were prepared by *in situ* vacuum deposition onto fine and spherical particles of crystalline silicon or a percolated amorphous carbon film. The details have been reported in previous papers.[8,9] The silicon particles were made by a gas-evaporation method in argon under a reduced atmosphere. They were less than several hundred angstroms in size and were usually covered with SiO_2 layers 10–30 Å in thickness. The gold clusters were initially smaller than 10 Å in size, but they aggregated into larger clusters under the electron-beam irradiation. The size of the clusters was controlled in the range from 10 to 100 Å by adjustment of the electron-beam intensity and the exposure time.

The electron microscope employed, equipped with a real-time video recording and monitoring system, has been specially improved for the present study. The resolution was 2.3 Å at 120 keV and the instrument was operated under ultrahigh vacuum of around 5×10^{-8} Torr. For electron-microscopic observations, metal clusters which were attached on the periphery of the spherical particles of silicon were chosen and observed as projection images along the electron beam. All micrographs presented in this paper were reproduced from pictures each of which corresponds to a single frame of the video-recording tape. The sequence of evolution of a particular gold cluster was studied by examination of a set of picture frames. The video-cassette recorder (Sony BVU-820) has a time resolution of $\frac{1}{60}$ s.

A typical series of electron micrographs of the same particle of gold is reproduced in Fig. 1. These were selected from a video tape recording (VTR) over a period of 5 min. The particle sat on an SiO_2-covered Si substrate and was about 20 Å in size. The shape of the particle itself constantly changed approximately every few tenths of a second. The change was often accompanied by rotational and translational motion of the particle. The center of gravity moved over distances of 30 to 60 Å on the substrate. As mentioned below, the internal structure also changed from a single crystal to a twinned crystal and vice versa. With an increase of the particle size, the movement became slow and no rapid change was observed in the particle if it was more than 100 Å in size.

The momentary change of the particle was promoted by the intense electron-beam irradiation (about 1.3×10^5 $e/\text{Å}^2$ s at the specimen position). The rate of movement was increased by a decrease in the area of the particle in contact with the substrate, which is located at the lower portion of each micrograph. The evolution of the particles, however, became sluggish when an electrically conductive substrate such as amorphous carbon was used. These observations suggest that the instabilities of the particles are affected partly by charge fluctuation on the particles or in their vicinity. This is supported by the fact that some of the particles detached abruptly from the substrate during the observation, as if Coulomb repulsive forces were

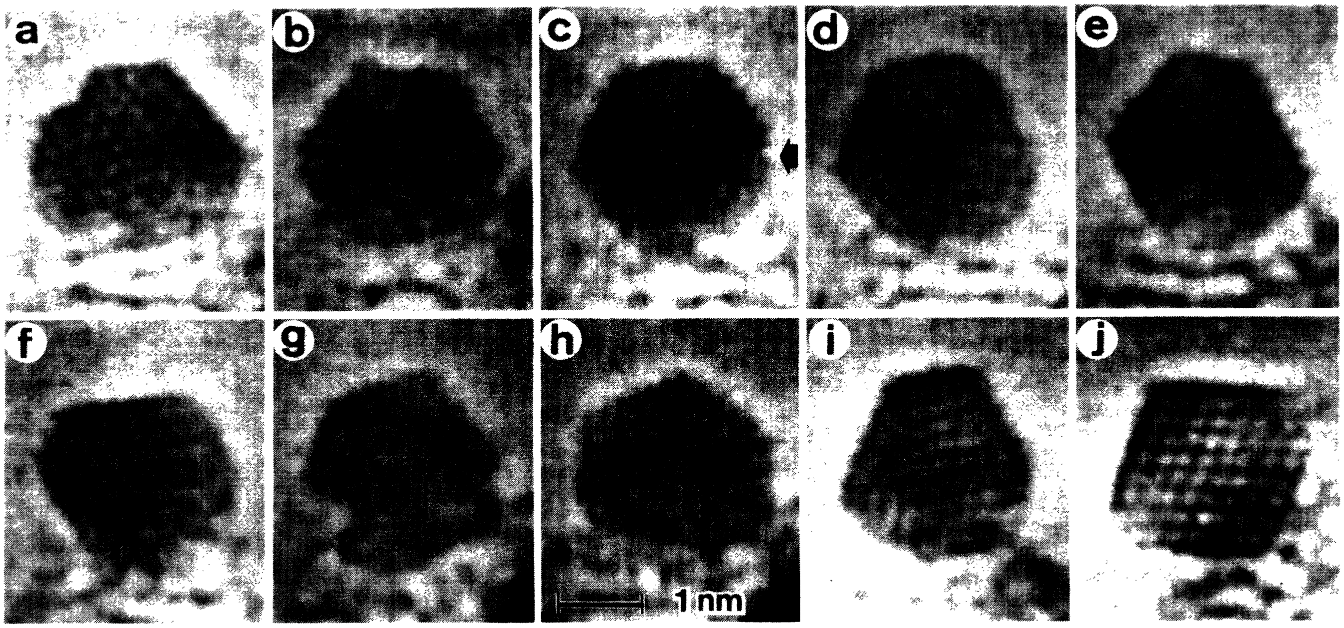


FIG. 1. Electron micrographs showing various shapes of an ultrafine particle of gold 20 Å in diameter reproduced from a VTR. The shape of the particle itself was changing continually under electron-beam irradiation. The lattice fringes appearing in the particles correspond to $d_{111} = 2.35$ Å. The particles in (a), (d), and (i) are single twins. Single crystals with cuboctahedral shape are seen in (e), (f), and (i). From the size of the cuboctahedron (j), the particle theoretically contains 459 gold atoms. The particle also transforms into a multiply twinned icosahedral particle, (b) and (h).

acting on them. Usually metal particles will be charged positively because of the emission of secondary electrons by the electron-beam irradiation.

The particle in Fig. 1(j) is a well-defined cuboctahedron as illustrated in Fig. 2. The two sets of lattice fringes which consist of nine lines correspond to the net planes of $d_{111} = 2.35$ Å and thus the particle is 2.35 Å × 8 = 18.8 Å in thickness. Such an ideal cuboctahedron contains theoretically 459 atoms. Its {100} facet has a dimension of only 3×3 gold atoms (4×4 $Å^2$) [see also Fig. 1(f)]. A similar but larger

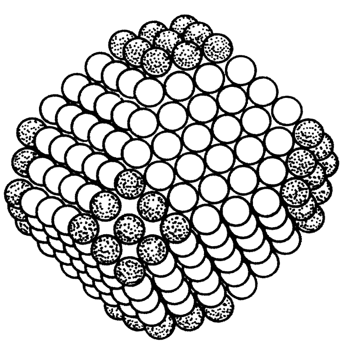


FIG. 2. Clinographic representation of a cuboctahedron consisting of 459 atoms. The model corresponds to the actual gold particle shown in Fig. 1(j). Shaded balls are on the {100} faces and open ones are on the {111}.

cuboctahedron consisting of about 940 gold atoms has been reported by Iijima.[8] Another cuboctahedron in Fig. 1(c) has {100} facets of 4×4 gold atoms. In this case, the number of the atoms is calculated to be 490. The difference can be attributed to an irregularity of the particle shape in the region in contact with the carbon substrate (lower part of the micrograph). An imperfection of the cuboctahedron, where a single row of atoms is missing at the edge [arrowed in Fig. 1(c)] in the ⟨110⟩ direction, is also recognized.

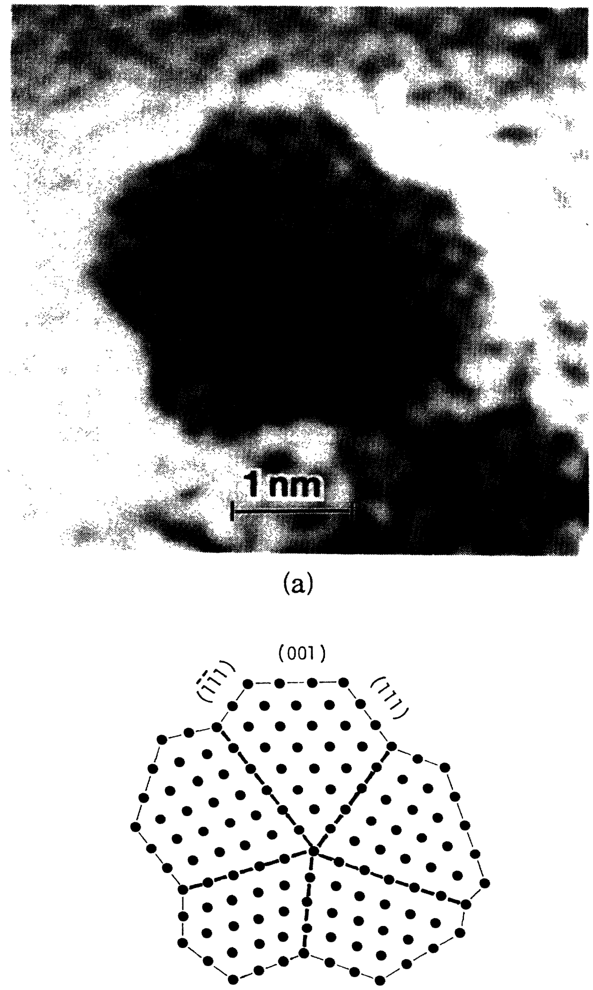
The VTR observation revealed that the particle was not always a single crystal but frequently transformed into a twin. As an example, the reentrant angle appearing at the upper left of the particle of Fig. 1(a) is characteristic of twinning for fcc metals with facetings of {100} and {111} surfaces. The twinning also can be recognized by noticing the {111} lattice fringe systems that are changed in their orientations by 140° [Figs. 1(a), 1(d), and 1(i)]. These twinned particles are oriented with their common [110] axes vertical to the plane of the page. In many cases, twin planes and stacking faults initiated the transformation of a particle which took place with cooperative motion of both external and internal atoms.

In some instances, the particle transformed into an icosahedral MTP, which was identified as the closest packing of twenty tetrahedral units. The particle with a hexagonal shape [Figs. 1(b) and 1(h)] is an icosahedral MTP viewed along one of its threefold axes. The particle in Fig. 1(h) appeared 20 s after the one in Fig. 1(g) had been observed. According to Ino, the iocosahedral MTP is the most stable in the equilibrium state for gold particles smaller than 100 Å in size.[6] For the ideal icosahedral MTP's the number of atoms in the particles are $N = 13$, 55, 147, 309, 561, ...[10] The particle concerned here is close to the one with $N = 561$. The slightly larger number than that of the ideal cuboctahedron of Fig. 1(j) can be attributed to an incomplete shape near the contact boundary with the substrate. In other words, the particle shapes are strongly influenced by the substrate, involving problems with adhesion and wetting.

It has not been confirmed at the moment that there is a particular preference among the particle shapes for a given number of atoms. The decahedral MTP, which consists of five tetrahedra with a common edge, occurred frequently in the present specimens. Figure 3(a) is an electron micrograph from a VTR which is similar to the one reproduced in Fig. 1. It was recorded in an instance during which the particle shape was changing continually. The particle consists of about 940 gold atoms. The decahedral MTP's had {100} surface truncations and reentrant angles without exceptions [Fig. 3(b)]. The {100} truncation seems energetically favorable in reducing surface energy over the regular pentagonal decahedral MTP, which was predicted by Marks and Howie.[7]

The morphological changes of a particle took a spherical form on a few occasions. Such a sphere might be a droplet of molten gold. Study on this subject is now in progress. Finally, it is mentioned that almost the same phenomena described above have been confirmed in other fcc metals such as Pt, Rh, Ni, and Ag.

In order to understand our observation, first it is desirable to know the temperature of the specimen. Since a direct measurement was difficult, it seems sensible to estimate the order of magnitude with the use of available data. The substrate temperature will be fixed primarily by a balance of the heat dissipation through conduction and the heat gain through inelastic scattering events of the incident beam in the substrate. By taking into account the beam intensity, the stopping power of the substrate material (amorphous carbon), and its thermal conductivity, we estimate the substrate temperature to be roughly 100 °C. When a particle size was larger than 100 Å, as was reported previously,[9] surface atoms evaporated slowly during the microscopic observation (a similar observation was reported recently by Borin, Wallenberg, and Smith.[11]) From the rate of evaporation and the vapor pressure of gold, the temperature of such gold particles is estimated to be 800 °C. Whether the evaporation takes place on ultrafine particles or not is experimentally uncertain at present. Nevertheless, the temperature of the ultrafine particles of around 20 Å in size, which we are primarily concerned with in this work, must be much lower than that of 100-Å particles. The temperature of the specimen including the substrate is not extremely higher than 100 °C even under irradiation by a highly concentrated beam as required in the present work.



(a)

(b)

FIG. 3. (a) Electron micrograph showing a decahedral multiply twinned particle of gold. It was viewed along the fivefold axis in the [110] direction. The particle is faceted with the {111} and {100} surfaces. (b) Model for atomic arrangement in the decahedral MTP of (a). The thick lines for fivefold symmetry represent twin planes on {111}. The particle contains about 940 gold atoms.

Another environmental factor is the charging of the specimen system. Some experimental evidence suggested that a gold particle and/or a local area of the substrate deviated *temporarily* from electrical neutrality. If a metal particle is sitting on the substrate, which is an insulator, and the particle has a positive charge, the charge will impose Coulomb repulsive forces on neighboring charged particles or local areas of the substrate, until the particle is discharged. Translational and rotational motion of the particle will be effected by this force. If the Coulomb force becomes larger than the total adhesion force between the particle and the substrate, the particle will become detached from the substrate.

Not only the movement of the center of gravity of the particle but also the morphological shape is abruptly changed in cooperation with the internal atomic arrangement and the creation and annihilation of stacking faults or twin planes. Such phenomena are hardly explained by considerations along the lines of Curie-Wulff theory which predicts only a size effect on crystal habits. It seems that there are various stable forms with subtle energetics under a given temperature. Alternatively, the strain induced through the contact plane with the substrate might be a factor in causing the structural modification.

In this context, a remark will be made regarding the diffraction experiment on the melting of ultrafine particles.[1,2] If the particles continually change their shapes, orientations, and internal structures within a time interval of less than one tenth of a second, the observable diffraction pattern would be considerably diffused, which might give the impression of a liquid phase. As has been seen, however, the individual particles have surprisingly regular atomic arrangements, like bulk crystals. Care must be exercised in studying the size effect of melting through diffraction experiments.

The essence of our observations lies in the unstable behavior of gold particles. It is not straightforward to interpret the observed phenomena in terms of macroscopic concepts such as the averaged temperature, because its fluctuation would be large. It has been proposed that the state of such a small particle should be called "quasi solid state," which is neither solid nor liquid according to the conventional concepts of matter. Although vertices, edges, and surfaces are geometrically defined, the physical roles of atoms located on them in relation to the total system are not clear in such small particles. Whatever is the origin of the structural instability, however, the present observation gives new insight to the study of ultrafine particles and affords a new field in the physics of small atomic assemblies.

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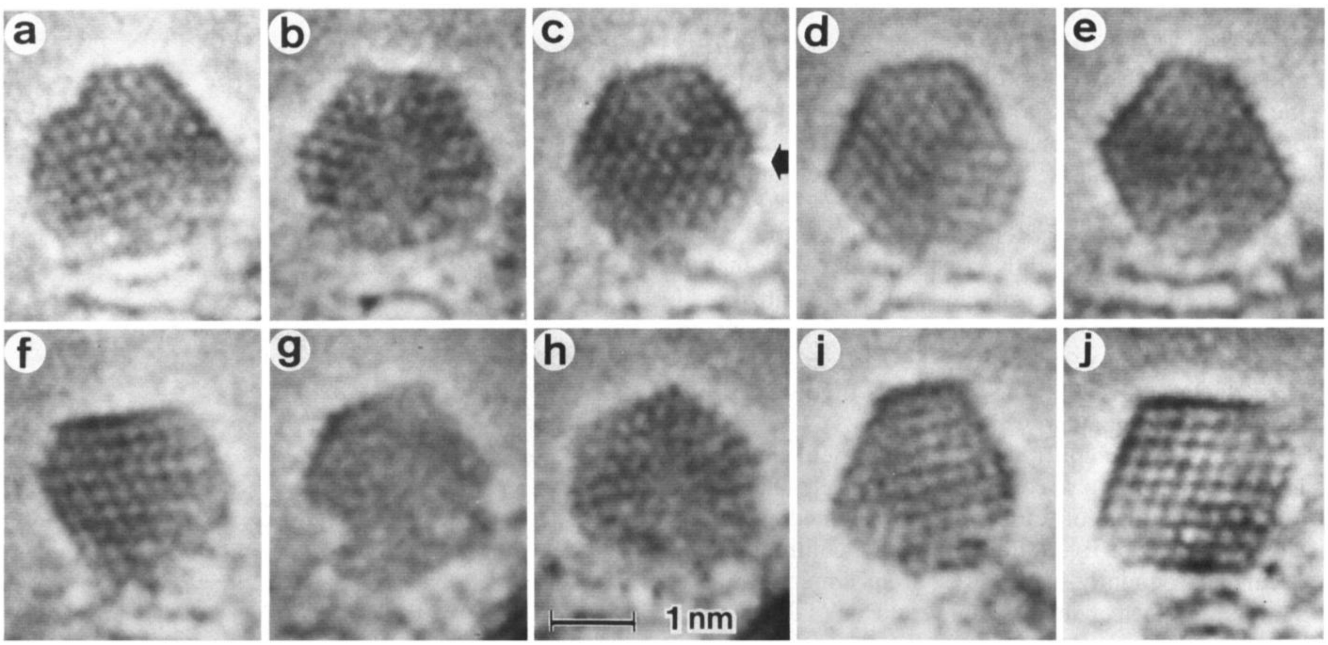

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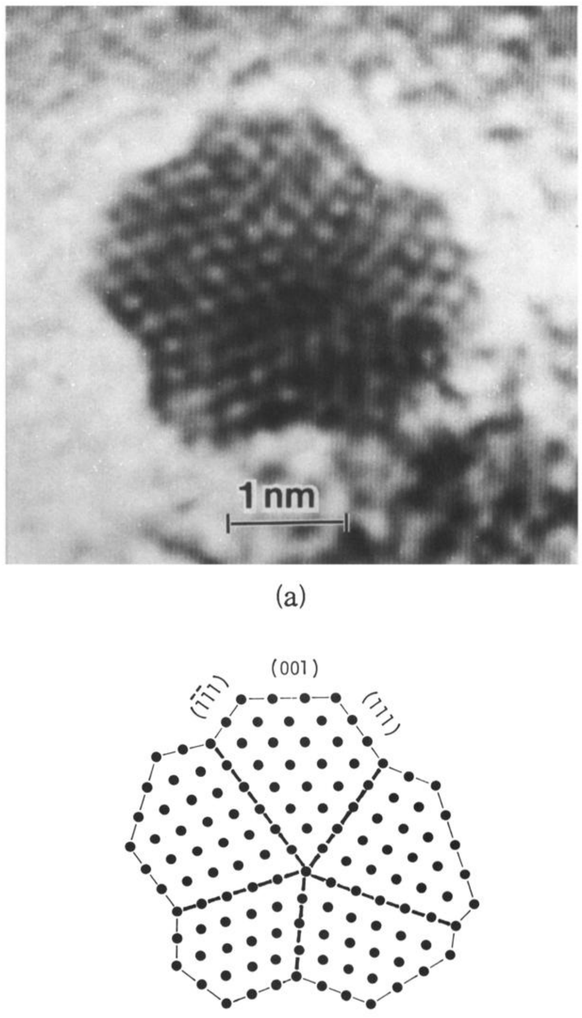

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