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Spontaneous dissolution at room temperature of gold nanoparticles

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We have studied gold nanoparticles evaporated on NaCl. We examined the sample before and after an annealing at room temperature for seven months. We found that most of the small particles with square shape disappear after the annealing. Many of the particles remaining correspond to multiple twinned particles (MTP), i.e., particles with icosahedral or decahedral shapes. We also found that the size of the icosahedral and decahedral particles did not change with the room-temperature annealing. The only consistent explanation is a spontaneous dissolution of the square-shaped nanoparticles at room temperature. This indicates that the binding energy of the atoms in such particles is much lower than the bulk value. The reason why such a particle would rather be dissolved instead of undergoing quasimelting is not clear. Room-temperature dissolution of square-shaped particles is another example of nanoparticles instability.

In recent years there is increasing evidence that metallic clusters of nanometer size present structural instabilities. In a theoretical work, Hoare and Pal[1] found that a particle with a small number of atoms does not need to have a fixed structure at room temperature but it can fluctuate dynamically between different structures. That means that in a free floating situation the particle behaves as a liquid. This state was termed quasimelting by Marks, Ajayan, and Dundurs.[2] Experimental evidence for quasimelting of nanometer-sized gold particles was given by Ijima and Ichihashi,[3] who found that particles change continuously between cuboctahedra and icosahedra shapes under the influence of a microscope electron beam. Several other reports confirmed these findings.[4-6]

Some theoretical work suggested that the observed quasimelting, in particles of the order of 10 nm, was due to violent events such as core excitations[7] or Coulomb explosion[8] induced by the intense electron beam. However recently, Ajayan and Marks[6] have presented experimental evidence that the gold particles that are not strongly coupled to the substrate are indeed in a fluctuating state at room temperature.

In the present work we report experimental evidence that suggests the existence of particle instabilities at room temperature. In our experiment we produce small particles in the nanometer size range by sputtering of gold onto a NaCl substrate. The vacuum during deposition was 10^{-6} Torr. Samples were covered with carbon and mounted on a microscope grid after flotation on water. Observations were carried out in the JEOL-100CX and JEOL-4000FX transmission electron microscopes (TEM). The observations reported in this paper were independent of the type of microscope used on the observations. A typical aspect of the sample is shown in Fig. 1(a). The main particles morphologies observed are: multiple twinned particles (MTP) either of icosahedral or decahedral shape (marked with *A*), square or rectangular particles (marked with *B*), and single twinned particles (marked with *C*). Square and rectangular particles are often found in deposits of metals on alkali halides. It has

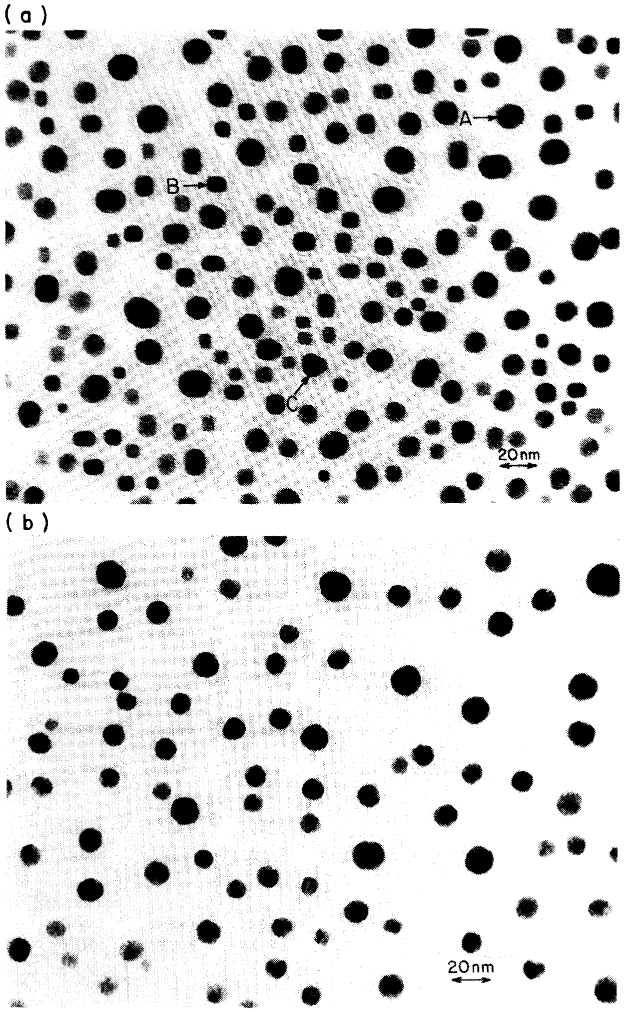

FIG. 1. (a) TEM image of gold particles showing multiple twinned (*A*), square (*B*), and single twinned (*C*) particles. (b) The same sample observed after seven months' annealing at room temperature. Note that the square-shaped particles have almost disappeared.

TABLE I. Particle density for samples as deposited and after seven months' annealing at room temperature.

Sample	Particle density (10^8 particles/cm^2) MTP	Square	Others	Total
As deposited	257	442	1186	1885
	363	835	1074	2271
	538	716	1060	2314
Average	386	664	1107	2111
(Standard deviation)	116	165	57	185
After annealing	520	47	708	1275
at room temperature	432	31	589	1051
for seven months	445	11	654	1111
	512	19	562	1093
	410	22	741	1173
	367	87	646	1100
Average	447	36	650	1134
(Standard deviation)	54	25	62	73

been shown that they correspond to a half-octahedron or a whole octahedron which is composed by (111) faces.[9]

In the case of the half-octahedron or pyramid the base corresponds to a (100) face and it is often truncated by a (100) facet.[10] Even in some cases this type of particle has been found containing planar defects.[11,12]

After the TEM observations some of the grids containing the gold sample, and some of NaCl substrates containing the film were stored for a period of seven months. Samples were placed on plastic capsules and stored in a dry box which was left in a clean room. No increase on the temperature of the samples was produced during the storage period. Therefore the particles have remained at room temperature for 7 months. Samples were reexamined on the TEM. The results are shown in Fig. 1(b).

When these samples were observed in TEM the most surprising effect is that the density of particles has been reduced greatly. This is shown in Table I for a number of areas. Moreover, we can easily note that the number of square particles has been dramatically reduced from more than 30% to about 1%. An histogram of the relative populations of particles is shown in Fig. 2.

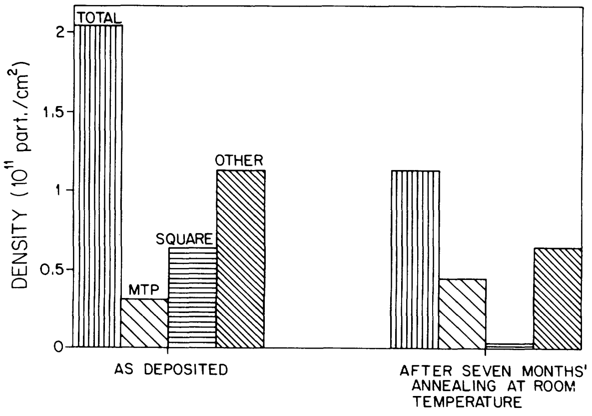

FIG. 2. Histogram showing the relative population of particles before and after annealing during seven months at room temperature.

In addition we found that the mean MTP particle size and the size distribution do not suffer an important change as shown in Fig. 3. The average multiple twinned particles size has changed from 12.5 nm to 12.6 nm over a period of seven months. We found this behavior to be observed very consistently in different areas and samples. The only explanation that arises from these observations is that the square particles are unstable and they dissolve away spontaneously at room temperature. This evapora-

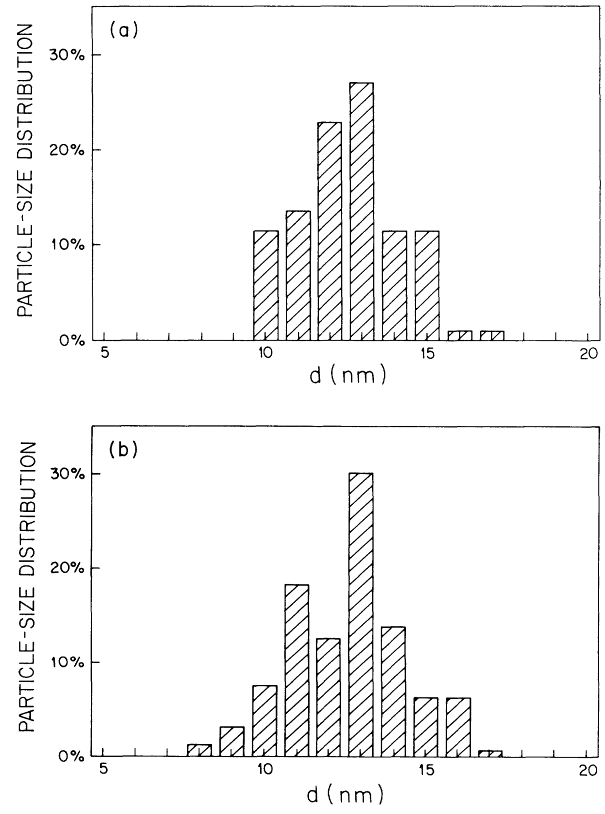

FIG. 3. MTP particle size distribution. (a) At the initial stage. (b) After seven months' annealing at room temperature.

tion dissolution process is very slow but fast enough to be observed in a seven-month period. We expect that atoms dissolved away from the particle will diffuse on the carbon surface and eventually will be incorporated on more stable particles, such as the icosahedral or decahedral particles, or will evaporate from the substrate or be dissolved into the substrate. Because of the temperature this phenomenon will be very slow and the situation of Fig. 1(b) will be an intermediate of the growth sequence.

In order to confirm this mechanism we annealed the sample *in situ* at the TEM using a heating state, for 24 h at 282 °C. The results for the case of the MTP particles are shown in Fig. 4. We clearly see that the mean particle size increases by more than 20% after 6 h of annealing, then it stays almost constant. As expected the particles have been growing incorporating the gold atoms (or perhaps dimers) that were located on the carbon surface. It was observed that the annealing temperature did not induce coalescence between particles that will increase the particle size. These kinds of events were observed at larger temperatures ~600 °C and always produce a reduction on the particle density. This is in contrast with the annealing at 282 °C that did not change the mean density. We also check that contamination was not present on the sample before and after both annealing.

It can be concluded from our results that the square particles (octahedral) are highly unstable and they tend to evaporate. In a recent work Bertsch *et al.*[13] studied the evaporation of metal clusters. They found using both a microscopic and macroscopic approach that the rates of evaporation are extremely sensitive to the binding energy (E_0) of the emitted atom. In the case of clusters this effect is greatly magnified because E_0 can be reduced significantly due to surface and magic number effects. The same concepts can be applied to the present case. In the case of octahedral clusters one would expect that the binding energy would be reduced in the corners along the $\langle 110 \rangle$ directions. This fact can explain the results. Avalos[14] found that during high density irradiation of electrons the square particles tend to dissolve and evaporate rather than undergo quasimelting. This is in contrast with the multiple twinned particles that under irradiation start to fluctuate. On the other hand the particles of square shape become triangular after evaporation indicating the preferential removal of atoms along the $\langle 110 \rangle$ direction. It is straightforward to calculate the predicted dissolution rate at room temperature using classical theory. The results indicate that in gold particles of 100-Å, size, atoms will dissolve from the particle at a rate of $\sim 10^6$ sec^{-1}. Therefore seven months of annealing will be time enough for the square cluster to evaporate completely. It is therefore clear that the MTP and single twinned cluster are more stable and most likely have a larger binding energy.

We have also studied pieces of the sample that were not stripped from the NaCl substrate but left annealed at room temperature for seven months. A typical image is shown in Fig. 5. As it is possible to see in this case not all the square particles have disappeared but some of them have changed to a more rounded, probably octahedral, shape. Although the less pronounced density reduction indicates that the particle-NaCl substrate interaction reduces the possibility of dissolution, in the case of the particles stripped from the NaCl substrate the particle–amorphous-carbon interaction is weaker than the former and did not play an important role. Another possibility is that the metal particles are dissolved into the carbon substrate. This will be less likely to happen on the NaCl substrate.

We therefore can conclude the following points.

(i) Square-shaped nanoparticles dissolve after room-temperature annealing for seven months. This indicates that the binding energy of the atoms in such particles is much smaller than the bulk value.

(ii) The MTP and single twinned particles are not dissolved; however, the change on their relative populations after seven months' annealing suggests the possibility of quasimelting.

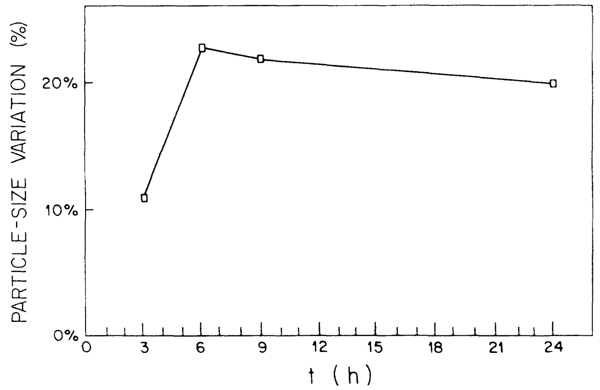

FIG. 4. Variation of the mean MTP particle size as a function of annealing time. Annealing *in situ* at the TEM at 282 °C.

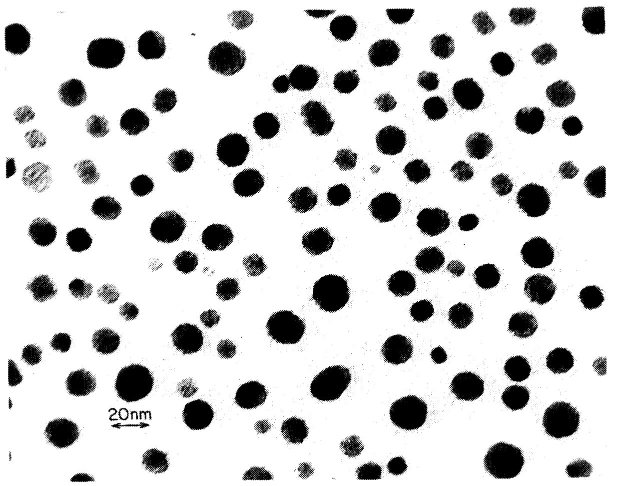

FIG. 5. Image of the same sample of Fig. 1 but left on the NaCl substrate during the annealing at room temperature. Note that square particles have become rounded.

(iii) The phenomenon of room-temperature dissolution is another example of instabilities on nanoparticles. At the present time, the conditions under which a particle will undergo dissolution rather than quasimelting are not known.

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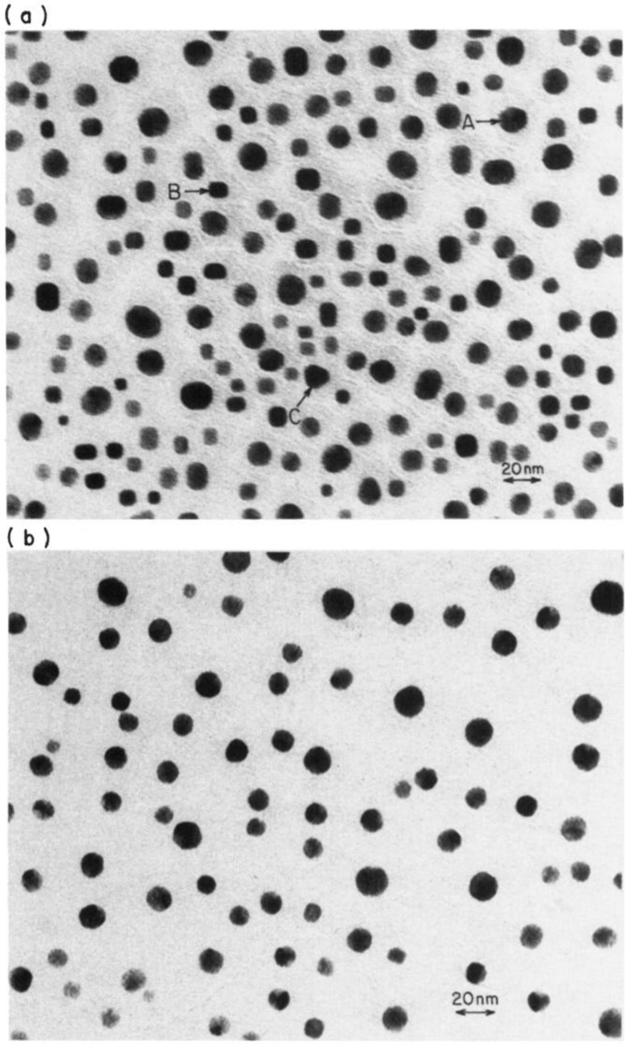

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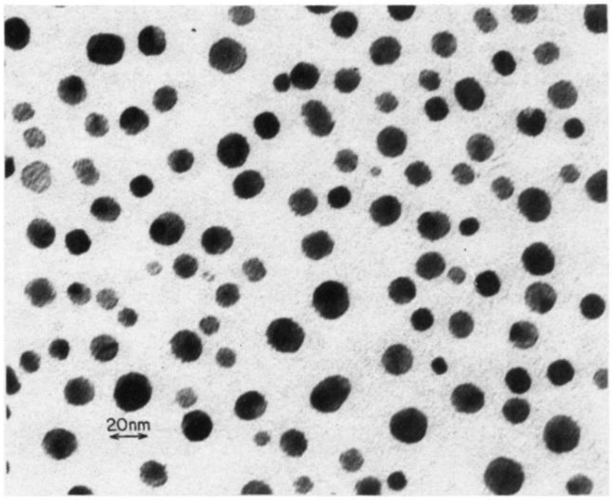

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