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Substrate and size effects on the coalescence of small particles

Sumio Iijima and P. M. Ajayan

Fundamental Research Laboratory, NEC Corporation, 34 Miyukigaoka, Tsukuba-shi, Ibaraki 305, Japan

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Here we present experimental results, using high-resolution electron microscopy and real time video recording, on the liquid-like coalescence of small gold particles supported on silica.

We report that particles that are few nanometers in size, and decoupled from substrate interactions, coalesce extremely fast, in fractions of a second. When the particles are properly supported on a substrate, coalescence is orders of magnitude slower, depending on the particle size, and influenced by the diffusion of atoms on the substrate surface.

Necks are seen to develop distinctly during coalescence only for particles above certain size.

Solid-state sintering is a practically important process where particles fuse together to form compact structures with better physical properties. During the evolution of the sinter the structure changes in shape and volume depending on how the individual particles bond together. The first stage that involves the growth of individual particles through coalescence is probably the best understood.¹ Nevertheless the exact nature of this coalescence depends on factors such as the material structure, the particle size, temperature, and the mode of matter transport that predominates in specific situations. The coalescence of nanometer sized particles, supported on substrates, can be important in catalysis where coalescence can decrease the activity of the catalyst by decreasing the net surface area exposed. The phenomenon also plays a major role in deciding the structure of nanocrystalline materials, made from the compaction of nanometer sized crystallites.

The driving force for the coalescence of particles and the change of shape is the minimization of surface energy² by elimination of interfaces, grain boundaries, and defects. This is essentially achieved by the flow of matter across particle volumes by mechanisms such as viscous flow, evaporation/condensation, and by volume, surface, and grain boundary diffusion. When particles contact, the bridge between them is filled during coalescence as a result of the chemical potential gradients that exist over regions of varying curvature.¹ Many models have been proposed³⁻⁶ for the coalescence stage of sinter evolution. Most of the above have been theoretical or numerical solutions, except for few early experimental results on the fusion of micron size particles,³ and some indirect electron microscopy observations on smaller metal particles.⁷ Recently some results have been reported⁸⁻¹⁰ on the coalescence of small metal particles, supported on substrates, using high-resolution electron microscopy (HREM). In this letter we present results from a time-resolved study of the coalescence of small gold particles supported on amorphous silica substrates, using real time video recording (time resolution of $\frac{1}{60}$ s) of HREM images. We show that nanometer sized particles, that are almost free from substrate interactions, can fuse together like viscous droplets by the mixing and redistribution of atoms in their particle volumes and report the difference in behavior compared to that of particles anchored properly on substrates.

The coalescence of gold particles on silica was observed in AKASHI transmission electron microscope operating at 200 kV, using current densities of ~ 100 A/cm². The results are presented in Figs. 1–3. Similar results were obtained for platinum particles on silica substrate.

Figure 1(a) shows two small particles of gold (1–2 nm) sitting on narrow protrusions that have formed from the edge of the thin silica (oxidized silicon) substrate layer. In this decoupled state, when the particle-substrate interactions are minimum, the particles start fluctuating between different structures randomly. This phenomenon of substrate growth and decoupling of the particles has been discussed previously.^{11,12} Particles that are extremely small, as in Fig. 1, appear quasimolten without showing well-defined lattice structure. Figures 1(b)–1(d) present consecutive frames that show coalescence when one of the loosely attached particle jumps and coalesces with the neighboring particle. It is seen from the images that the coalescence is completed in a time interval of one frame or $\frac{1}{60}$ s, the video time resolution available. From the size of the coalesced particle (R), it is noted that volume is conserved since $R^3 \sim r_1^3 + r_2^3$, where r_1 and r_2 are the initial particle sizes. Direct fusion of particles occurred in fractions of a second for still larger sizes (~ 2 and 3.5-nm particles coalesced in about $\frac{1}{20}$ s). Note that the observation of such direct coalescence is a rare event since the particles often move randomly and fall on to the substrate plane since they are very loosely anchored. The random motion of particles on the substrate is not purely rigid translation but occurs by the periodic deformation of their particle volumes.

Figures 2(a)–2(f) show the frame by frame sequence of the coalescence of two particles, that are 2–3 nm in size, but sitting firmly on the substrate. Before the bulk of the particles contact, a bridge [contrast marked in Fig. 2(b)] is seen to develop on the substrate between the particles. This feature of a surface (on the substrate) layer formation due to single or monolayers of atom migration on the substrate is typical of particles coalescing on substrates, as observed here and as reported before,¹⁰ and seems to be the initial link for particles to come together. It is observed [Figs. 2(c)–2(f)] that the coalescence seen occurs at least two orders of magnitude slower (order of seconds) than that in

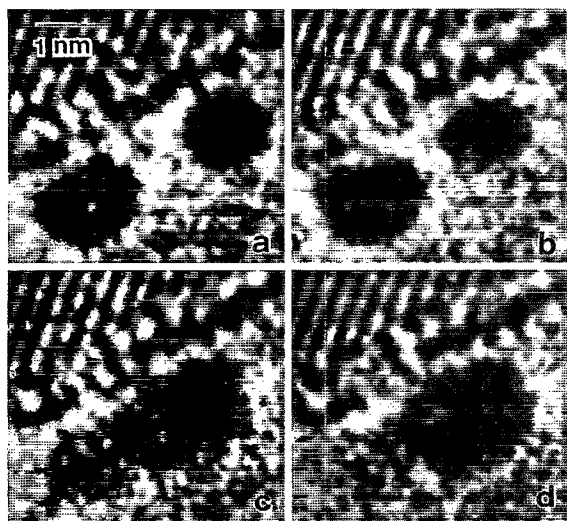


FIG. 1. The direct fusion of two small particles of gold floating on narrow features grown from the thin silica surface layer over a bulk silicon (lattice fringes visible) particle. The time sequence is as follows: (a) before coalescence, (b) frame 0, (c) frame 1; note that overlapping of the ghost image of the frame in (c) can be seen due to the movement of the particles (d) frame 2. Time interval between successive frames is $1/60$ s.

Fig. 1. The lattice fringes of both particles were seen to align even before the particles actually made contact. In both the cases of Figs. 1 and 2 no distinct neck region is developed, as in the sintering of large particles. In Fig. 1 the coalescence occurred by the rapid rearrangement of atoms in both the particles after they made contact and there is a clear and instantaneous penetration of the center of masses. In Fig. 2, rearrangement of atoms have indeed occurred but the movement of the center-of-mass of the particles seemed to be controlled by substrate interactions with some clear migration of surface atoms during coalescence [see Figs. 2(b) and 2(c)]. As the particle size increases or when particle-substrate interactions become stronger (as observed for MgO substrate) the rate of coalescence decreases by orders of magnitude.

Figures 3(a)–3(d) show the nature of coalescence when two larger particles, supported on the substrate, come in contact. Here coalescence occurs during a time interval of minutes and the process occurs in a very similar fashion as in the sintering of micron size particles. A neck is first developed at the plane of contact which is slowly filled by diffusion from the bulk and the surface to the neck region (positive to negative curvature), until a balance of the chemical potential gradients is achieved. As the particle sizes get larger, grain boundaries are formed [Figs. 3(b) and 3(c)] due to the random orientation of the particles before contact and the activation energy barrier for diffusion of atoms in this region prevents any fast plastic deformation or structural rearrangements. But in the long time limit these boundaries also get annealed out, as perhaps discussed in Ref. 4, until the convexity of the neck disappears. The actual movement of grain boundaries during such coalescence was reported before.⁹ It was observed that during the growth and the subsequent annealing of

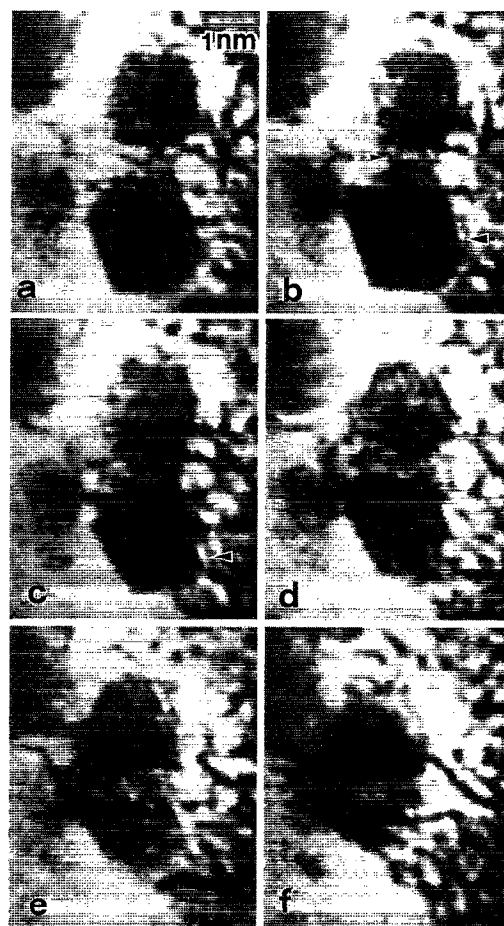


FIG. 2. Time sequence of coalescence of two small particles on silica substrate. (a) Just before the start (0 frames), (b) 32 frames, (c) 56 frames, (d) 2 s and 36 frames, (e) 4 s, (f) 7 s. A bridge of atoms is seen to form between the particles before the particles actually penetrate [thin arrow in (b)]. Also in (d) to (f) the coalesced particle is moving towards a larger particle, which was seen in (a) at the top left corner. Also seen is the transport of atoms from the surface of the particles [thick arrows in (b), (c)].

defects in the neck region, small rotation of the smaller particle was often observed (from the surface profile of the particle) but not by any significant amount as shown in a previous article¹³ where micron size particles were heated to near melting point. The structure in the neck region alone was observed to be changing where as lattice images remained relatively stable at the convex and bulk parts of the coalescing structure. But in smaller particles or at very high temperatures rotation of the particles could indeed be a valid path for boundary elimination.

We have reported in this paper the effects of particle size and substrate on which the particles are deposited, on the coalescence behavior of small particles. For very small particles, less than 5 nm in size, direct coalescence occurs in a similar fashion as two liquid droplets fuse, occurring in a small fraction of a second. But when particles in the same size range are supported on substrates, the substrate interactions control the rate of coalescence, due to the activation energy barrier needed to surmount the substrate friction or particle-substrate contact energy. Initial surface layer migration on substrate surface is seen before the ac-

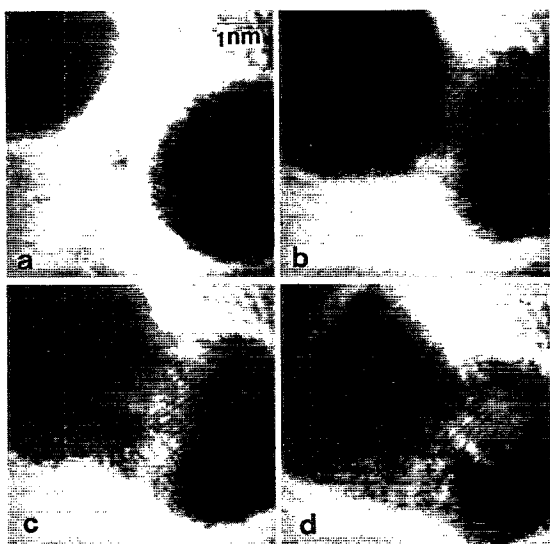


FIG. 3. Time sequence of neck formation and coalescence in two larger particles. (a) before contact (0 s), (b) 1 min, 30 s (c) 1 min, 40 s, (d) 2 min. The structure of the interface (neck) region changes with time with distorted low angle grain boundaries present in (c) and fringes running parallel across the volume of the coalesced particle in (d).

tual contact of the particle takes place, forming a bridge of atoms that serves as the liaison between the particles and realignment of lattice fringes are seen before the particles actually merge. This is followed by the rotation of the particles to bring about the registry between the lattice fringes in their individual volumes. In both, direct and substrate controlled coalescence, since surface atoms constitute a major percentage of the total number of atoms, surface diffusion may be the key during such fast diffusion of atoms.⁴ This might also represent the case where the

diffusion length of the atoms is larger than the particle sizes. As the particle size increases, clear development of necks are seen as in the conventional sense of sintering, which then fill up by the diffusion of atoms to the interfacial region resulting in the annealing out of grain boundaries and other defects.

Since the electron beam provides the activation for the diffusion of atoms, the effect due to the beam may be important in deciding the kinetics of sintering. As discussed by Flueli *et al.*,¹⁰ the beam rather than raising the temperature may be indirectly influencing the diffusion mechanism by electronic transitions. We have in an earlier paper¹⁴ discussed the effect of charging in small particles and have found that when the particles are below ~ 5 nm, charging can increase the vacancy concentrations many-fold and hence affect the diffusion of atoms. Nevertheless these effects should be similar for systems studied under the same conditions inside the microscope.

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