

Experimental observation of large ramified Au aggregates on melting glass surfaces

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We report the formation of large ramified gold aggregates after deposition of Au on melting glass surfaces. The growth mechanism of the aggregates is traced to a two-stage process, the first of which involves nucleation and growth of compact Au clusters. The average diameter of the clusters is around $1.2\ \mu\text{m}$, which is approximately independent of the deposition rate. In the subsequent stage, the clusters diffuse randomly on the colloid surface and the diffusion coefficient is in the range between 10^{-7} and $10^{-8}\ \text{cm}^2/\text{s}$. Finally they aggregate. It is found that the structure of the aggregates strongly depends on the aggregation time.

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I. INTRODUCTION

It has been shown that continuous Ag films can be prepared on silicone oil surfaces if sufficient quantities of the metal are sputter deposited.¹ Previous work showed that as the nominal film thickness increases, a percolation structure appears on the oil surface first. The metallic clusters grow gradually and then connect one another. Finally a continuous rough thin film with a characteristic surface morphology at the micrometer scale forms.¹

Recently, Ye and co-workers²⁻⁴ present results on the growth of silver atom deposition on silicon oil surfaces by thermal deposition method in the limit of low coverage, i.e., below a few monolayers. The nucleation, diffusion, and aggregation of the silver atoms are studied. It is observed that large islands, each containing more than 10^6 silver atoms, can diffuse quickly with different diffusion step lengths and rotate obviously with random rotation angles on the liquid surfaces. The experiment also suggests that the formation of the ramified silver aggregates on the liquid surfaces can be described by a two-stage growth model. During the first stage, i.e., during the deposition, the silver atoms deposited on the liquid surfaces nucleate and form compact clusters. Then, during the following stage, the compact clusters diffuse and rotate randomly on the liquid surfaces and finally ramified aggregates are shaped. The average branch width d of the aggregates scales with the deposition rate f according to $d \sim f^{-\chi}$, with $\chi = 0.69 \pm 0.05$. Both stages are dominated by the elastic collision between the liquid molecules and silver atoms on the liquid surfaces.

A number of problems in this field still remain. For instance, the stability of the film structures formed on the liquid surfaces is one of the much concerned problems since it is essential to both theoretical and practical researches. In addition, the nature of the interaction between the metallic atoms and the liquid molecules is also one of the basic problems that we need to face.

We describe in this paper the main features of a new aggregation mechanism of Au atoms deposited on melting glass surfaces. The formation mechanisms, which result in the growth of a web-shaped Au film, compact atomic clusters, and then large ramified aggregates on the colloid substrates, can be understood with the aid of experiments com-

paring different aggregation periods, growth rates, and film thicknesses.

II. EXPERIMENT

The samples were prepared by thermal evaporation of 99.9% pure gold in a vacuum of $1.0 \times 10^{-3}\ \text{Pa}$. A small glass powder disk (about 0.7 g weight and 1 mm thick), shaped with a pressure of $5\ \text{N/cm}^2$, was laid on a piece of commercial slide surface. The melting temperature of the glass powder is $480\ ^\circ\text{C}$, which is much lower than that of the slide. The slide was then mounted on an electrical oven, which was fixed 200 mm below the filament (tungsten) in a level position. Before deposition, we gradually increased the oven temperature T , which was controlled precisely in our experiment, until the oven temperature reached $T = 500 \pm 10\ ^\circ\text{C}$ and the glass powder changed into a colloid substrate supported by the piece of solid slide. Unfortunately, the vapor pressure of the melting glass could not be measured effectively in our experiment. However, during the deposition, no obvious changes of the concerned properties of the melting glass (such as the total quantity and melting temperature) were observed, indicating that the vapor pressure of the colloid substrate is low enough for our experiment. The deposition rate f and the nominal film thickness h were determined by a profilometer (α -step 200 profilometer, TENCOR). When the deposition process finished, we kept the temperature of the oven for time interval Δt , then turned off the electricity. After the oven cooled naturally and its temperature was below $100\ ^\circ\text{C}$, the sample was removed from the evaporation chamber. The Au/glass surface morphologies were characterized with an optical microscope. The crystal structure of the samples was examined by x-ray diffractometry.

III. RESULTS AND DISCUSSION

In order to identify the processes that govern film formation, a series of experiments was performed in which the aggregation time, i.e., the parameter Δt , was varied between $\Delta t = 0$ and 240 s. The phenomenon in our experiment can be understood with the aid of experiments comparing different samples prepared with different aggregation time Δt . The

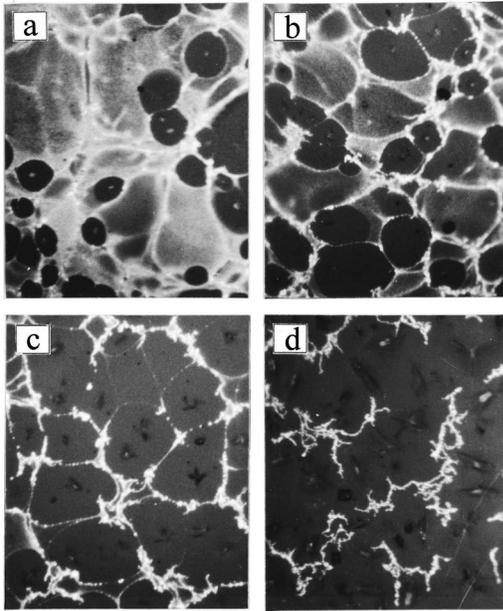


FIG. 1. Aggregating time dependence of the Au film morphology. $f=0.35$ nm/s, $h=42$ nm. The aggregating time t is (a) $\Delta t=0$ s; (b) $\Delta t=60$ s; (c) $\Delta t=180$ s; (d) $\Delta t=240$ s. Each image has a size of $170 \times 140 \mu\text{m}^2$.

most exciting and unexpected result is shown in Fig. 1, where it can be seen that if the substrate temperature is cooled (or, in other words, if the melting glass substrate is solidified) immediately after the deposition, i.e., $\Delta t=0$, then the deposited gold atoms form a characteristic web-shaped Au film [see Fig. 1(a)]. One finds that the web-shaped film becomes tattered as the time Δt goes on [see Figs. 1(a) and 1(b)]. Then compact atomic clusters with an average diameter φ gradually appear on the substrate [Fig. 1(c)]. The compact clusters migrate randomly on the colloid surface and finally they aggregate without coalescing and form large ramified islands [Fig. 1(d)]. This process is also correct if we focus on a given sample and take photographs after different periods Δt (each photograph was taken after the sample was removed from the vacuum chamber), indicating that the structures shown in Fig. 1 really form during the deposition and period Δt and the cooling process does not change the structures obviously.

Indeed, the deposition period and the aggregation time Δt are not independent of each other. We note that among the samples prepared with identical nominal thickness and time Δt , the morphology of the film sample deposited at a lower deposition rate is more branched. This phenomenon is understandable since decreasing the deposition rate implies increasing the deposition period, and therefore the gold atoms could have more time to aggregate directly during the deposition.

The typical ramified aggregates formed on the melting glass surface is shown in Fig. 2(a). The shapes of the aggregates resemble the results of computer models for diffusion limited aggregation⁵ (DLA) of particles or even more closely to those of cluster-cluster aggregation⁶ (CCA) in two dimensions. In Fig. 2(a), the typical size of the aggregates is

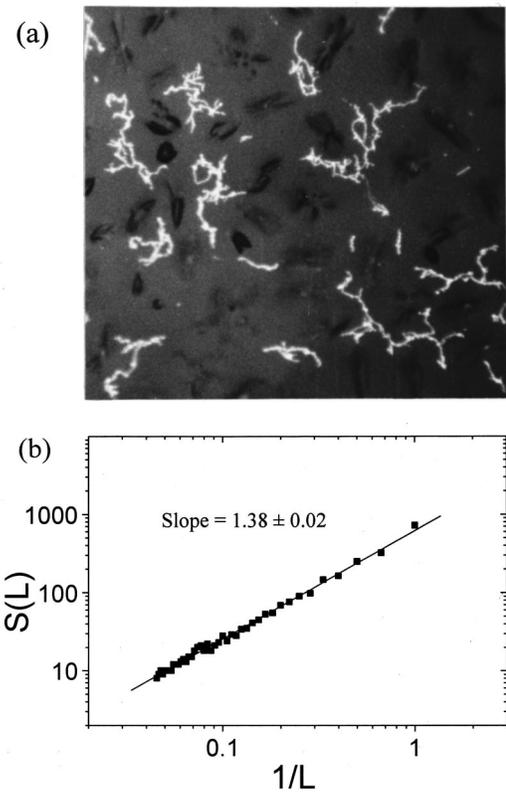


FIG. 2. (a) Au aggregates on melting glass surface. The deposition rate is $f=0.12$ nm/s, the nominal film thickness $h=15$ nm, and the aggregating time $\Delta t=240$ s. The image has a size of $158 \times 148 \mu\text{m}^2$. (b) The fractal dimension of the ramified aggregates as determined for the conditions of (a).

around $50 \mu\text{m}$ and the average branch width is about $1.2 \mu\text{m}$. For the ramified aggregates in Fig. 2(a), we carry out an analysis of the Hausdorff dimension by the box-counting method,⁷ and Fig. 2(b) presents the result obtained for Fig. 2(a). The number S of square boxes needed to cover the ramified aggregates as a function of the inverse of the edge length L of the boxes exhibits clear scaling behavior over more than an order of magnitude, with $S(L) \sim 1/L^{D(H)}$. The Hausdorff dimension $D(H)$ of the aggregates in Fig. 2(a) is 1.38 ± 0.02 . While we generally observe such a scaling behavior of our samples, the values for $D(H)$ range between 1.30 and 1.50, which is quite similar to the result of the Ag aggregates on silicone oil surfaces.^{3,4} The scatter is partially due to differences in the morphology as a function of deposition conditions. In addition, difficulties and ambiguities in digitizing the photographs of the aggregates also contribute to the scatter in the data.

Based on the observations above, we suggest a two-stage description of aggregate formation. At the beginning of stage I, the Au atoms are deposited on the melting glass surface randomly and the nominal film thickness increases with time. Then the film or the atomic layer breaks and forms a web-shaped film due to the inhomogeneous structure on the substrate surface (see the small dark grains on the background of the photographs in Figs. 1 and 2).⁸ The total area of the meshes increases gradually and then the web-shaped film

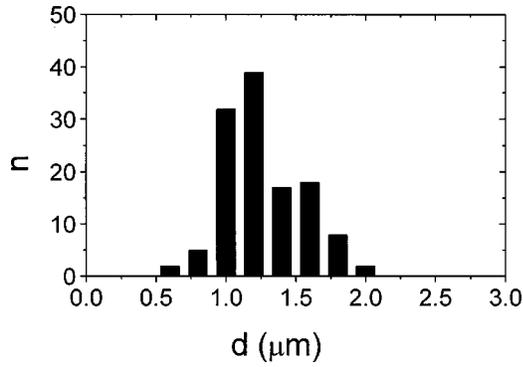


FIG. 3. Diameter distribution of the compact Au clusters. $f = 0.35$ nm/s, $h = 11$ nm; $\Delta t = 240$ s.

becomes tattered. At the end of the stage I, the Au atoms aggregate and form compact clusters. In stage II, the compact clusters diffuse on the melting glass surface randomly due to statistical fluctuations in their momentum by collisions with colloid molecules.^{2,3} They adhere upon impact and finally the ramified aggregates form. We note that the diffusion behavior of the compact clusters is interrupted by the inhomogeneous structure (i.e., the small dark grains in Figs. 1 and 2) on the substrates and therefore the behavior of the clusters is not the exact random diffusion. However, since the compact clusters generally aggregate in small local regions, which are approximately homogeneous areas [see Figs. 1(d) and 2(a)], it is quite reasonable that the Hausdorff dimension $D(H)$ of the aggregates in Figs. 1(d) and 2(a) is close to that of the CCA computer model.⁶

If the description of stage II is correct, the average branch width d of the aggregates must correspond to the average diameter φ of the compact clusters. Comparing the width d with the diameter φ , we find that there is actually no difference between them, indicating that the ramified aggregates really resulted from the random aggregation of the compact clusters.

Figure 3 shows a size distribution of the Au compact clusters. The black bars in the figure represent the result of a statistical measurement. The average diameter of the clusters is $d \approx 1.2$ μm . We then measure the parameter d systematically. In the nominal film thickness range of $h = 5$ –84 nm and for the deposition rate $f = 0.35$ nm/s, we find that d , averaged over a suitable number of locations, remains almost unchanged when h increases [see Fig. 4(a)], which is contrary to both the prediction of the deposition diffusion aggregation (DDA) model⁹ and the experimental phenomenon of the Ag clusters on silicone oil surfaces.³ The result shown in Fig. 4(a) implies that the diffusion coefficient D of the Au atoms and clusters is relatively large. Figure 4(b) shows that d is almost independent of the deposition rate f , which is a totally new result since both theoretical predictions and experimental results suggest the scaling of the branch width d with the deposition rate f of the form of $d \propto f^{-\chi}$, where χ is an exponent.^{2,9,10} The result in Fig. 4(b) indicates that, in the deposition rate range of $f = 0.06$ –3.0 nm/s, the exponent χ approaches zero for the Au atoms and clusters diffusing on the colloid surface at $T \approx 500$ °C. This value of χ is unexpectedly small in view of the fact that in the nucleation

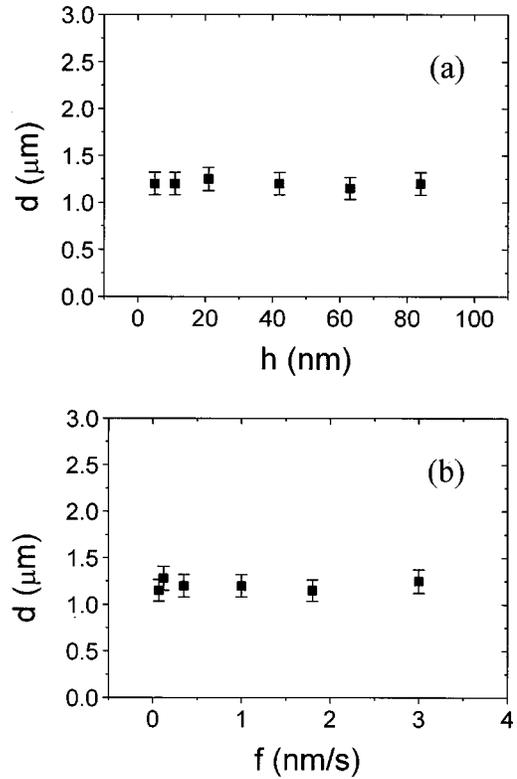


FIG. 4. (a) Average branch width d of the aggregates vs film nominal thickness h . $f = 0.35$ nm/s, $\Delta t = 240$ s. (b) Average branch width d of the aggregates vs deposition rate f . $h = 42$ nm, $\Delta t = 240$ s.

theory χ just approaches 0.5 in the case of large unstable cluster sizes¹⁰ and the DDA model leads to a significant increase in χ .⁹ On the other hand, for the silver atomic aggregates on silicone oil surfaces at room temperature, the value of χ reaches 0.69 ± 0.05 .² Figure 4(b) suggests that, at high temperature, the size of the compact clusters on the colloid substrates approaches a saturated value, which is around 1.2 μm . Supposing the shape of the compact clusters in Fig. 1 resembles a disk,^{2,3} from the apparent Au coverage of 5–10% of the total area, the nominal deposited film thickness of $h = 42$ nm, the volume that each Au atom occupies, and the average cluster diameter in Figs. 1(c) and 1(d), we conclude that each saturated Au compact cluster contains of the order of 10^{10} – 10^{11} Au atoms. To the best of our knowledge, a consistent theory for this saturated size of the compact clusters is still lacking.¹⁰

Unfortunately, we are unable to observe the aggregation process *in situ* in our experiment; therefore the exact value of the diffusion coefficient D of the compact clusters on the colloid surface cannot be obtained directly. However, from Fig. 1, we can approximately estimate the order of it. We note that the average diffusion time for the compact clusters to form the ramified aggregates in Fig. 1 is around 2×10^2 s. This aggregation period is quite short compared with that of the Ag aggregates on silicone oil surfaces.² The typical size of the aggregates in Fig. 1(d) is about 50 μm , which implies that, within about 2×10^2 s, the average diffusion area of each compact cluster before aggregation is about 50×50 μm^2 . Therefore, we obtain the coefficient D is in the

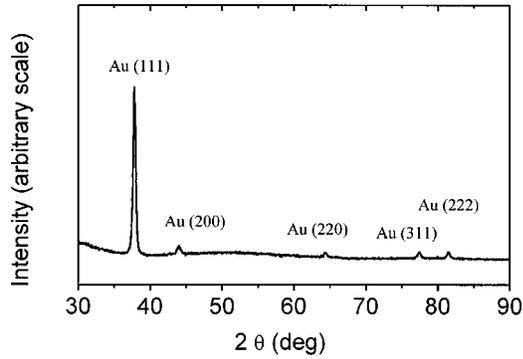


FIG. 5. X-ray diffraction pattern of the sample shown in Fig. 1(a). The shape analysis for the diffraction peaks indicates that the average size of the crystal grains in the film is about 22 nm.

range between 10^{-7} and 10^{-8} cm^2/s , which is a very large value for this huge atomic cluster.^{2,9,11} This result is expectantly consistent with the conclusion obtained from Fig. 4(a), as described above. In fact, according to the theory of Brownian motion,¹² the mean-square displacement $\langle \Delta r^2 \rangle$ is given by $\langle \Delta r^2 \rangle = 4kTF^{-1}\Delta t$ for a two-dimensional motion, where k is the Boltzmann constant and F is the friction coefficient. Compared with Einstein's formula, i.e., $\langle \Delta r^2 \rangle = 4D\Delta t$, one finds $D = kTF^{-1}$. Obviously, the coefficient D is proportional to the temperature T . On the other hand, higher temperature would probably result in a smaller friction coefficient F . Both of the effects above would increase the value of D . Therefore, the formula above gives the explanation for the large diffusion coefficient D since $T \approx 780$ K in our experiment, which is much higher than that of the other systems.^{2,9,11}

The Au film shown in Fig. 1(a) was examined by x-ray diffractometry. The x-ray diffraction pattern of the sample exhibits regular Au peaks (see Fig. 5), providing evidence that the Au film deposited on the colloid substrate still exhibits polycrystalline structure, which is in agreement with that of the Ag films on silicone oil surfaces.¹ Furthermore, by performing the shape analysis of the diffraction peaks in Fig. 5, we find that the average size of the crystal grains in the film is about 22 nm, and it will increase as the time Δt goes on. Therefore, we propose that by using colloid substrates, more film systems with characteristic nanostructures could be fabricated in experiment. Indeed, it is desirable to study the crystalline mechanism of metallic atoms on liquid surfaces.

IV. CONCLUSION

In summary, we have described the formation mechanism of large ramified Au aggregates on melting glass surfaces. The growth mechanism of the large Au aggregates is traced to a two-stage process. During the first stage, the deposition atoms form a characteristic web-shaped Au film on the colloid substrate first, then the area of the meshes increase gradually. Afterwards, the total film becomes tattered and the compact clusters form on the colloid substrate due to the aggregation of the deposition atoms. The saturated diameter of the compact clusters, each containing about 10^{10} – 10^{11} Au atoms, is about 1.2 μm . In the subsequent stage, the huge compact clusters diffuse randomly on the colloid surface and the diffusion coefficient is in the range between 10^{-7} and 10^{-8} cm^2/s . Finally they aggregate.

In our experiment, when the deposition and aggregation periods finished, the electricity of the oven was turned off immediately and the temperature of the sample would drop quickly. Therefore the melting glass was solidified in the next few seconds and the microstructure of the Au film formed on the melting substrate could be preserved stably. The advantages of the deposition of films on melting substrates are obvious: (1) as shown above, since the diffusion time Δt can be controlled effectively in our experiment, it is very helpful for the basic research on the nucleation and aggregation mechanism of the deposition atoms on the melting substrates; (2) nanostructures, metallic compact clusters with diameter of the order of 10^{-6} m, wires or rings composed of the compact clusters [see Figs. 1(b) and 1(c)], and other new structures, which we believe may have various interesting physical properties, can be fabricated in experiment easily; and (3) characteristic microstructures formed on the melting substrates can be studied or utilized after the substrates solidify, which is very convenient for practical purposes. We hope that the results above would contribute to the further research on both theoretical and practical projects in this field.

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does not exhibit such a structure. Therefore, we believe this structure is related to the shortage of oxygen in the vacuum chamber.

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