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Condensation Behavior of Ag Aggregates on Liquid Surfaces *

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We report a condensation behavior of silver aggregates on silicone oil surfaces. The deposited Ag atoms diffuse and aggregate on the oil surface, and then form granular clusters and ramified islands. The apparent Ag coverage of the total area increases linearly with the nominal film thickness h for $h < 0.9$ nm. However, the coverage exhibits a fluctuation behavior for $1.0\,\text{nm} < h < 2.5\,\text{nm}$. It is found that the anomalous behavior of the coverage is resulted from a characteristic material condensation process in the aggregates.

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In the past two decades, metal clusters have given rise to a large amount of studies for both theoreticians and experimentalists, due to their promising technical applications, such as catalysts, biosensors, recording media and nanoscopic devices.[1−10] Compared with bulk materials, the clusters, consisting of ten to a few thousands of atoms, exhibit a rich variety of physical and chemical properties.[1] One of the most important and interesting objects is the magic-numbered clusters,[11−13] which is related to the geometric structure, surface-to-volume ratio and stability of the clusters. It is noted that the studies on metal clusters with cluster size $N < 10^3$, where N denotes the number of atoms in each cluster, are numerous,[5,14] and, however, those investigations with $N > 10^4$ are few, since it is difficult to characterize and calculate the microstructures and physical properties numerically for such large clusters (or nanoparticles) on solid substrates.

A series of experimental and theoretical investigations on Ag clusters was performed and several important results have been obtained. Silver clusters on quartz surfaces with mean diameters below 1 nm are found to be almost spherical whereas larger particles become oblate during growth at room temperature.[15] A two-stage growth process of Ag clusters on the silicon oil surfaces is observed.[16] An empirical formula for the average binding energy of the Ag clusters is given by[17]

$$E_b = \Psi + 2^{1/3}(0.5D_c - \Psi)N^{-1/3}, \qquad (1)$$

where E_b is the average binding energy of the N atom clusters, $\Psi = -2.95\,\text{eV/atom}$ indicates the binding energy of the bulk counterpart, and $D_c = -1.65\,\text{eV/atom}$ expresses the dimer binding energy. From Eq. (1), one sees that the average binding energy monotonously approaches the bulk value with N increasing. In addition, it is reported that the decrease in the film thickness shows the fluctuation behavior after deposition due to a vacancy mechanism.[18] The lattice parameter varying with different cluster sizes is also observed in a recent investigation.[19] These results are quite different from the corresponding bulk values because of the surface effect of the clusters and the strong interaction between the bottom atoms and the solid substrates, such as a pinning effect,[20] which inevitably affect the geometric structure of the clusters.

Self-organized morphologies of the Ag aggregates, including the granular clusters and ramified islands deposited on silicone oil surfaces by vapor phase deposition method, were studied by many researchers.[16,21,22] It has been shown that the formation mechanism of the ramified islands, which are composed of granular clusters, may be described by the two-stage growth model.[16,21] In this Letter we focus on the condensation of the Ag aggregates (i.e., the granular clusters and the ramified islands) on silicone oil surfaces. By means of measuring the apparent Ag coverage of the total area, namely ρ, we find that the coverage ρ does not increase monotonously with the nominal film thickness h, indicating a characteristic material condensation process occurring in the system.

The samples were prepared by thermal evaporation of 99.999% pure Ag in a vacuum of 3.0×10^{-4} Pa at room temperature. Commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) with a vapor pressure below 10^{-8} Pa was painted onto a frosted glass surface, which was fixed at 135 mm above the filament (tungsten). The resulting oil substrate with an area about $8.0 \times 10.0\,\text{mm}^2$ has a uniform thickness of $h \approx 0.5$ mm. The deposition rate $f = 0.05$ and 0.10 nm/s and the nominal film thickness $h = 0.1$–6.0 nm, determined by a quartz-crystal balance, which was calibrated by atomic force microscope (AFM,

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After deposition, the samples were kept in the evaporation chamber (in vacuum condition) for time period $\Delta t = 2\,\mathrm{h}$ and then removed from the chamber. An optical microscope (Leica DMLM) was used to take images for the Ag clusters and ramified islands on the oil surfaces immediately. For each sample, we took more than 7 different images at the homogeneous area of the sample surface randomly, then calculated and averaged the surface coverage ρ by a computer program. Subsequently, the films (or more exactly the Ag clusters and ramified islands) were separated from the oil substrates to glass surfaces and washed carefully with acetone and ethanol.[23] After that, a series of atomic force microscope measurements was taken immediately for the as-prepared samples. The cluster size Φ and its distributions were measured by the AFM software.[22]

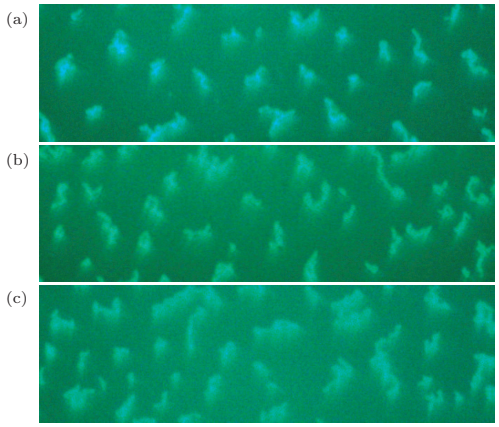

Fig. 1. Three optical microscope images of the samples with different nominal film thicknesses: (a) $h = 0.1\,\mathrm{nm}$, (b) $h = 0.2\,\mathrm{nm}$, (c) $h = 0.3\,\mathrm{nm}$. Each image has a size of $21.0 \times 70.0\,\mu\mathrm{m}^2$. The deposition rate $f = 0.05\,\mathrm{nm/s}$.

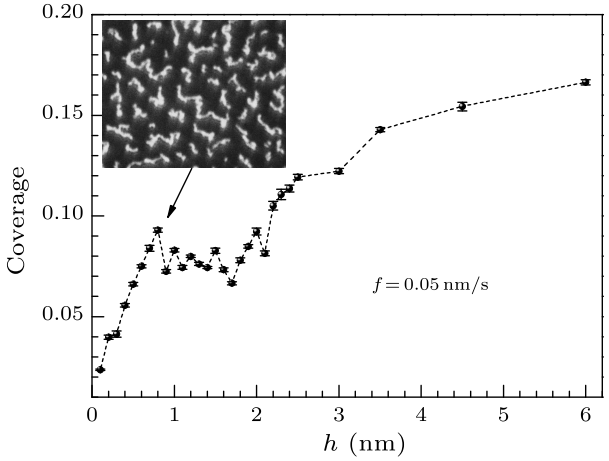

Fig. 2. Typical dependence between the surface coverage ρ and the nominal film thickness h. Each data point represents an average value of more than 7 images. The inset ($34.7 \times 28.8\,\mu\mathrm{m}^2$) gives an example of the images with $h = 0.8\,\mathrm{nm}$.

In order to understand the evolution of the surface coverage ρ with the nominal film thickness h, a series of samples were prepared over a wide range of h. Figure 1 gives three optical microscope images of the samples when $h \ll 1.0\,\mathrm{nm}$, in which granular clusters and ramified islands can be observed. Quantitative analysis shows that the average width of the ramified islands remains nearly unchanged[16] while the surface coverage ρ increases with h obviously.

The characteristic dependence between the surface coverage ρ and the nominal film thickness h is shown in Fig. 2. One sees that, for $h < 0.9\,\mathrm{nm}$, the coverage ρ increases linearly with h. However, if the thickness h goes beyond a critical value h_c and in the thickness range of $h \approx 1.0$–$2.5\,\mathrm{nm}$, an unexpected fluctuation of ρ appears. Here h_c is defined as follows: (1) for $h < h_c$, the coverage ρ increases with h monotonously; (2) for $h > h_c$, the coverage ρ decreases with h first and then exhibits fluctuation behavior.

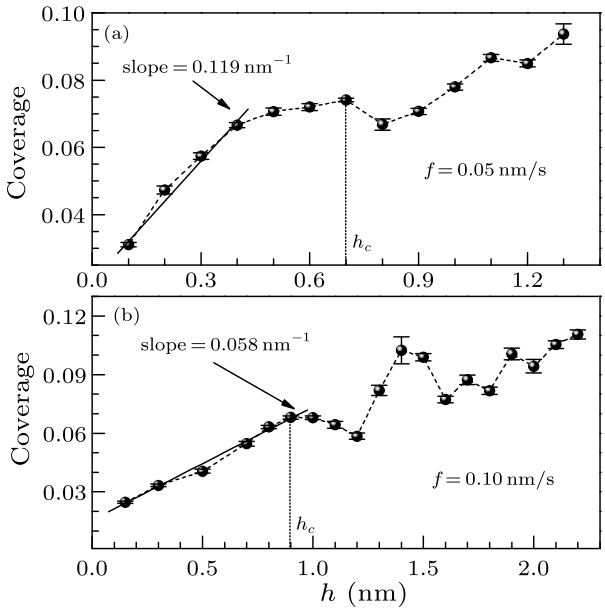

Fig. 3. Dependences between ρ and h for both $h < h_c$ and $h > h_c$ with the solid lines denoting the linear fits to part of the experimental data for $h < h_c$: (a) $f = 0.05\,\mathrm{nm/s}$, $h_c = 0.7\,\mathrm{nm}$, (b) $f = 0.10\,\mathrm{nm/s}$, $h_c = 0.9\,\mathrm{nm}$.

For $h < h_c$, the coverage ρ is smaller than 0.1 (see Figs. 2 and 3) and, in this case, most of the deposited Ag atoms may reach the oil surface. They diffuse speedily and randomly and then granular clusters form. The ramified islands grow by the aggregation of the granular clusters.[16] The percentage of the deposited atoms arriving on the pre-formed clusters or islands is proportional to ρ, which makes no contribution to the surface coverage ρ. For $\rho < 0.1$, most of the aggregates may diffuse randomly and separately on the oil surface, and then the increment of the surface coverage ρ may be given by

$$d\rho = K(1-\rho)f\,dt, \tag{2}$$

where t represents the deposition time, $ft = h$, K is

a parameter related to the average thickness and microstructure of the aggregates. To the first order of approximation, for $\rho \ll 1$, we can assume that K is a constant and then integrating Eq. (2) yields

$$\rho = 1 - e^{-Kh} \approx Kh, \quad (Kh \ll 1). \tag{3}$$

Therefore, for small surface coverage, ρ increases linearly with h and the parameter K represents its slope. It is obvious that, for small h, the experimental data in Figs. 2 and 3 may be fitted by Eq. (3) very well.

In Figs. 3(a) and 3(b), the slope $K = 0.119\,\mathrm{nm}^{-1}$ and $0.058\,\mathrm{nm}^{-1}$, respectively, indicating that the growth behavior of the aggregates strongly depends on the deposition rate f. According to Eq. (2), the linear behavior of ρ indicates that the clusters grow and diffuse separately on the two-dimensional oil surfaces, then ramified islands form. In general, for a fixed h, the decrease of K indicates the increase of the average thickness of the ramified islands. In Fig. 3(a), one sees that $\rho = 5.7\%$ for $h = 0.3\,\mathrm{nm}$. In this case, if the shape of the Ag ramified islands is similar to a flat plate,[16,21] then we find that the average thickness of the Ag ramified islands ranges between 18 and 20 atomic layers. In Fig. 3(b), $\rho = 3.3\%$ for $h = 0.3\,\mathrm{nm}$, then the Ag forms the ramified islands with thickness between 31 and 34 atomic layers.

The number density of the clusters, namely n calculated from the images of the optical microscope, changes with h. The total area of the clusters is $S\rho$, where S denotes the whole area of the image taken by the optical microscope. We assume that all the clusters exhibit a disk shape approximately, thus the average area for each of the disk is $\pi(\Phi/2)^2$, where Φ is defined as the average diameter of the clusters. Thus we obtain the total number of the clusters $\frac{S\rho}{\pi(\Phi/2)^2}$ and the number density $\frac{4\rho}{\pi\Phi^2}$. For $h = h_c$ and $\Delta t = 2\,\mathrm{h}$, the number density n reaches its critical value n_c. For $h > h_c$, more and more Ag atoms are deposited on the sample surfaces, and n goes beyond its critical value n_c. In this case, we propose that a material condensation (such as overlap, coalescence, crystallization etc.) among the clusters may happen, which makes contributions to the fluctuation phenomenon of ρ [Figs. 2 and 3]. In our experiment, it is found that $h_c = 0.7$–$0.9\,\mathrm{nm}$ and its corresponding value n_c equals of the order of $10^6\,\mathrm{cluster/mm}^2$.

In order to confirm the proposal above, a series of AFM measurements for the samples with both $h < h_c$ and $h > h_c$ are made. Both Ag clusters and ramified islands are observed, as shown in Fig. 4. The AFM images shown in Fig. 4 give the local information of the corresponding images taken by the optical microscope. It can be seen clearly that the ramified islands are composed of a great number of granular clusters. The average sizes and morphologies of the granular clusters in both the images are quite similar. Therefore we conclude that the material condensation process among the clusters really happens for $h > h_c$ [Fig. 4(b)]. It should be mentioned that the material condensation and accumulation process exhibits a typical three-dimensional growth characteristics, which may minimize the total free energy of the ramified islands and then increase the average binding energy among the clusters. This process makes contributions to the anomalous fluctuation behavior of ρ shown in Figs. 2 and 3.

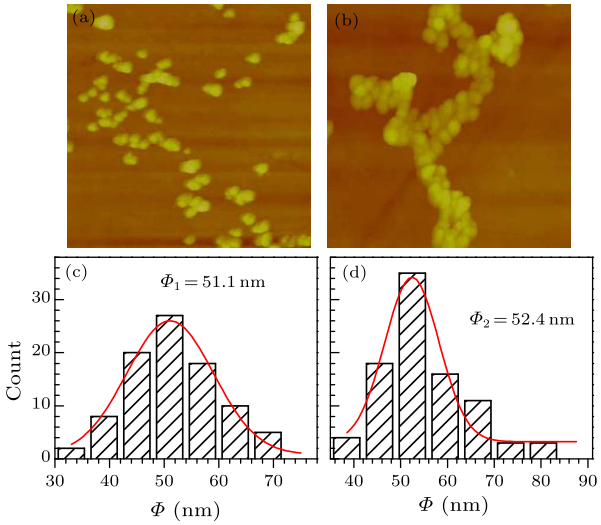

Fig. 4. Typical AFM images and cluster size distributions of the clusters and ramified islands on oil surfaces. Here $f = 0.05\,\mathrm{nm/s}$, each image has a size of $1.5 \times 1.5\,\mu\mathrm{m}^2$. (a) AFM image of the Ag clusters on oil surface, $h = 0.2\,\mathrm{nm}$. (b) AFM image of the Ag ramified islands on oil surface, $h = 1.3\,\mathrm{nm}$. (c) and (d) The cluster size distributions of the clusters in (a) and (b), respectively.

Material density and microstructure are two important factors for characterizing the Ag aggregates. Suppose that the microstructure in the ramified islands is similar to that of the uniform film of bulk Ag covering the whole liquid surface, then statistically the average thickness of the ramified islands may be described by $H = \frac{h}{\rho}$. For example, in Fig. 4(b), $h = 1.3\,\mathrm{nm}$ and $\rho = 7.6\%$, then we can calculate that $H \approx 17.1\,\mathrm{nm}$. On the other hand, by means of the AFM measurement, we can read the average thickness for the island shown in Fig. 4(b) directly from the AFM scan line across the island, i.e., $H_{\mathrm{AFM}} = 32 \pm 4\,\mathrm{nm}$. Then we obtain $\delta \equiv \frac{H}{H_{\mathrm{AFM}}} = 0.54 \pm 0.07$. Similarly, we find $\delta = 0.65 \pm 0.05$ for the sample with $h = 2.0\,\mathrm{nm}$, $\rho = 9.2\%$ and $H_{\mathrm{AFM}} = 36 \pm 2\,\mathrm{nm}$. The above experimental results indicate: (1) the average density of the ramified islands is quite small and it is about 45–70% of the mass density of bulk Ag, which should be resulted from the vacancy mechanism in the clusters, the connection among the clusters [see Fig. 4(b)] and the interconnections between the Ag islands and the silicone oil molecules; and (2) the ramified islands should not exhibit similar polycrystalline structure of the corresponding Ag systems on solid substrates. We propose that, as h increases, the nucle-

ation of the deposited Ag atoms results in the growth of the granular clusters and the aggregation of the clusters results in the ramified islands. First, the densities in both the clusters and islands are small and then increase gradually with h, i.e., $\delta \to 1$ as h increases. Therefore a material condensation process occurs, which also makes contributions to the fluctuation of ρ.

The average material densities ρ_a in the islands are calculated and compared. Generally, the Ag crystal exhibits fcc structure and the lattice constant is $a = 0.409\,\text{nm}$.[24] It can be find that $\rho_a = \frac{\delta}{V_{\text{Ag}}}$, where $V_{\text{Ag}} = 1.71 \times 10^{-29}\,\text{m}^3$ is the volume occupied by each of the Ag atoms in the crystal.[21] Therefore $\rho_a = 29.0$–$35.0\,\text{atom/nm}^3$ for the islands in Fig. 4(b), which are smaller than that in Ag crystals (i.e., $\rho_{\text{cry}} = 58.5\,\text{atom/nm}^3$.[24]). This result indicates again that the aggregates shown in Figs. 4(a) and 4(b) do not exhibit similar structures of the corresponding Ag systems on solid substrates.

Another interesting phenomenon is the average size of the clusters in Figs. 4(a) and 4(b). By means of measuring the cluster size distributions for the samples with $h = 0.2\,\text{nm}$ and $1.3\,\text{nm}$, respectively, we obtain the results shown in Figs. 4(c) and 4(d). As the nominal film thickness h increases, more atoms are deposited on the sample surface, the average number of the Ag atoms in each of the clusters, namely $\overline{N}$, should increase gradually. However, in Figs. 4(c) and 4(d), the size distributions are quite similar and the average cluster size Φ remains nearly unchanged as h increases, e.g., $\Phi_1 \approx 51.1\,\text{nm}$ in Fig. 4(c) and $\Phi_2 \approx 52.4\,\text{nm}$ in Fig. 4(d). This anomalous phenomenon again suggests that, in each of the clusters, a material condensation process really happens and the average binding energy among the atoms increases with thickness h.

In conclusion, we have investigated the material condensation behavior of the Ag aggregates on oil surfaces. For $h < h_c$, a linear increase of ρ with h is observed, which is in agreement with our theoretical analysis. For $h > h_c$, however, a characteristic dependence between the surface coverage and the nominal thickness is detected and ρ fluctuates with h. Our AFM measurement shows that, in order to minimize total free energy of the ramified islands and increase the average binding energy among the atoms in each of the clusters, the self-organized aggregation among the clusters and the material condensation process in each of the Ag islands really happen in our experiment, which are responsible for the fluctuation phenomenon of the coverage ρ.

We note that, for $h > h_c$, the fluctuation phenomenon shown in Figs. 2 and 3 generally exists in the nanosystem. The fluctuation period for $h > h_c$ is not theoretically obvious. However, from the distances between two adjacent peaks shown in Figs. 2 and 3 for $h > h_c$, we believe that the fluctuation phenomenon really exists in our experiment and the fluctuation period can be read to be from 0.4 nm to 0.5 nm approximately. Unfortunately, in order to find all the magic-numbered clusters on the free standing substrates, a more precise measurement is needed. At the moment, a theoretical model, including all the aspects of the average binding energy, surface energy, and correlation length among the clusters, is still lacking. The present study intends to help as a guideline for further experimental and theoretic studies, which may open a new branch of nanoscience for the investigation of the systems containing large metallic clusters on various free standing substrates.

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