Aggregation Mechanism of Ag Atoms Deposited on Liquid Surfaces

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We study the aggregation of silver (Ag) atoms deposited on silicone oil surfaces. It is observed that the apparent Ag coverage of the total area, \( \rho \), increases linearly with the nominal film thickness \( h \) for \( h < 0.9 \) nm and its slope \( k \) decreases clearly as the deposition flux \( f \) increases. Our atomic force microscopy (AFM) observation shows that the average thickness of the atomic aggregates first increases with \( f \), and then approaches a saturation value. Then, the aggregation mechanism of Ag atoms is presented.

KEYWORDS: atomic aggregates, aggregation mechanism, surface coverage, liquid surfaces, free energy

1. Introduction

Metallic aggregates have attracted much attention in recent years because of their fundamental importance and potential applications in microelectronic devices, biosensors, catalysts, and other devices.1–7) Recently, considerable theoretical8,9) and experimental10,11) efforts have been made to understand the fundamental aggregation of atomic aggregates, which is related to the fabrication conditions, such as deposition flux, substrate temperature, and substrate properties. As a consequence, it is very important and highly feasible to control the evolution of surface morphology during the growth of the aggregates. A study of the shapes of Pt islands grown on Pt(111) at various surface temperatures and monolayer coverage has been reported.12) Linear, two-dimensional or tenuous fractal aggregates of nanometer dimensions have been studied by exploiting the dependence of the mobility of adsorbed atoms on substrate crystal face and temperature.13) In addition, the effects of temperature and deposition flux on the aggregate size have been investigated recently.14)

Works mentioned above refer to whose aggregates fabricated on various solid substrates, which may strongly affect the morphology and microstructure of the aggregates.15) Meanwhile, several liquid substrates (such as silicone oil and ionic liquid) have been utilized to form metallic aggregates, which have been investigated by many researchers owing to their promising applications and interesting properties. Extensive studies of metallic nanoparticles fabricated at gas-ionic liquid interfaces by Kuwabata and other researchers have yielded a large number of interesting results.16,17) Since 1998, silicone oil has been used successfully as a nearly free-standing substrate to fabricate metallic aggregates by vapor phase deposition.18)

Note that the diffusion coefficients of the large aggregates with \( 10^{10} \) Ag atoms on the oil surfaces are on the order of \( 10^{-11} \) cm/s, which is much larger than the \( 10^{-17} \) cm²/s for the Ag clusters containing about \( 10^2 \) atoms on Ag(100).19) Recently, an AFM study of the microstructures of Ag films on silicone oil surfaces has been performed. It was found that Ag films, including atomic compact and branched aggregates, are composed of grains with a size of the order of \( 10^4 \) nm.20) Unfortunately, to the best of our knowledge, the aggregation mechanism of metallic atoms on liquid substrates has not yet been investigated systematically thus far.

In this research, we study the aggregation mechanism of Ag atoms deposited on silicone oil surfaces, and a physical picture of the formation of Ag atomic aggregates (or islands) is given. We also investigate the relationship between the apparent Ag coverage of the total area of the samples and the deposition flux systematically. The average island thickness is also measured carefully as the deposition flux changes. Finally, the aggregation mechanism of the Ag atoms on oil surfaces is demonstrated.

2. Experimental Methods

Ag (99.999%) island samples were fabricated on commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) substrates by thermal evaporation at room temperature (295 ± 3 K). Silicone oil with a vapor pressure below \( 10^{-8} \) Pa was painted onto a frosted glass surface, which was fixed 135 mm above the filament (tungsten). The base pressure prior to the deposition was \( 3 \times 10^{-4} \) Pa. The deposition flux \( f \) changed from 0.005 to 0.300 nm/s. The nominal film thickness \( h \) was in the range of 0.1–7.0 nm, which was determined using a quartz-crystal balance (ULVAC CRTM-3000) and calibrated by atomic force microscopy (AFM; Veeco D3000).

After deposition, the samples were kept in an evaporation chamber (in vacuum condition) for a time period \( \Delta t = 2 \) h and then removed from the chamber. Optical microscopy (Leica DMLM) was used to take images of the Ag atomic islands on the oil surfaces immediately. For each sample, we took more than seven different images in the homogeneous area of the sample surface randomly, then calculated and averaged the surface coverage \( \rho \) using a computer program (here, \( \rho \) denotes the percentage of oil surface covered by the islands). Subsequently, the atomic islands, including compact and branched Ag islands, were transferred from the oil substrates to glass surfaces and washed carefully with acetone and ethanol. After that, a series of AFM measurements was taken immediately for the as-prepared samples.

3. Results and Discussion

To understand the evolution of the surface coverage \( \rho \) with the nominal film thickness \( h \), a series of samples were prepared over a wide range of \( f \) and \( h \). Figure 1 gives four clear optical microscopy images of the samples for \( f = 0.05 \)
and 0.20 nm/s and \( h < 0.9 \) nm, in which compact and branched islands can be observed clearly.

It is found that, for a fixed \( h \), the island number density \( N \) clearly decreases with \( f \). Generally, as \( f \) increases, the deposited atoms and compact islands may possess a higher kinetic energy and a larger diffusion coefficient. In this case, the coalescence of compact islands and branched islands may occur frequently. This phenomenon may become more distinct for a large \( h \) and a large \( N \) since it will increase the possibility for atoms and atomic islands to meet each other on the liquid surface. Our experimental results show that \( N \) is highly sensitive to \( f \), particularly for the samples with a small \( h \).

The relationship between \( \rho \) and \( h \) is shown in Fig. 2. It can be seen that, for \( h < 0.9 \) nm, the coverage \( \rho \) increases linearly with \( h \), which was reproduced in the inset of Fig. 2. However, if the thickness \( h \) goes beyond the critical value \( h_c \), within the range of \( h \approx 1.0-7.0 \) nm, an unexpected fluctuation behavior appears. Here, the definition of \( h_c \) is shown in the inset of Fig. 2.

For \( h < h_c \) and \( \rho < 0.1 \), most of the deposited Ag atoms may land directly on the oil surfaces. Then compact islands form because of the diffusion and nucleation of the deposited atoms. According to our previous experimental results, compact islands with average diameter \( d \) adhere to each other and branched islands then appear.\(^{18}\) Therefore, the average width of branched islands also equals \( d \). During this process, the percentage of deposited atoms landing on the top surfaces of the existing islands is proportional to \( \rho \), which has no contribution to the increase in the surface coverage \( \rho \). In this case, the increase in the surface coverage \( \rho \) may be written as

\[
d\rho = k(1 - \rho)f \, dt,
\]

where \( k \) is a parameter determined by the island thickness, surface morphology, microstructure, and other factors, \( t \) is the deposition time, and \( ft = h \). Integrating eq. (1) gives

\[
\rho = 1 - e^{-kh}.
\]  \( \text{(2)} \)

On the first order of approximation, for \( \rho \ll 1 \), eq. (2) can be written as

\[
\rho = kh, \quad (kh \ll 1),
\]

which is in good agreement with the linear fit in the inset of Fig. 2 for \( h < 0.9 \) nm. Therefore, a linear increase in \( \rho \) as a function of \( h \) appears and the parameter \( k \) denotes its slope.

According to the two-stage growth model, the geometric shapes of islands on liquid surfaces depend on the deposition...
flux and other experimental conditions.\textsuperscript{18}) To further understand the typical dependence of $\rho$ on $h$ more precisely, a series of investigations for $h < h_c$ were performed systematically. Figure 3(a) shows that, for each fixed $f$, the dependence of $\rho$ on $h$ is linear and satisfies eq. (3) very well. However, as shown in Fig. 3(b), the slope $k$ changes with $f$ non-linearly, indicating that (1) for $0.01 < f < 0.05$ nm/s and $0.15 < f < 0.30$ nm/s, the corresponding values of $k$ exhibit maximum and minimum saturations, respectively, and the maximum $k_{\text{max}} = 0.135 \pm 0.008$ nm$^{-1}$ is approximately double the minimum $k_{\text{min}} = 0.064 \pm 0.006$ nm$^{-1}$; (2) for $0.05 < f < 0.15$ nm/s, $k$ decreases with $f$ monotonically. Therefore, in the range of $0.05 < f < 0.15$ nm/s, the coverage $\rho$ decreases with $f$ at a fixed $h$, suggesting that the corresponding average thickness of atomic islands increases with the deposition flux $f$. Further study of this topic will be discussed later.

The quantitative measurement of the microstructure of Ag atomic islands is another interesting step in studying the relationship between the island thickness $H_{\text{AFM}}$ and $f$. As shown in Figs. 4(a) and 4(b), AFM images indicate that Ag atomic islands are composed of metal grains, which is in good agreement with our previous results.\textsuperscript{20} The distributions of the grain diameter are found to resemble Gaussian distributions approximately and the average diameter of the grains $\Phi$ is approximately 50.0 nm for both images, indicating that $\Phi$ is independent of the deposition flux $f$. The profiles along the lines of the atomic islands in Figs. 4(a) and 4(b) are measured and shown in Figs. 4(c) and 4(d), respectively, and the corresponding average thicknesses $H_{\text{AFM}}$ of the atomic islands are $18 \pm 1$ and $23 \pm 1$ nm.

As shown in Fig. 5, $H_{\text{AFM}}$ increases from $12 \pm 1$ to $23 \pm 1$ nm when $f$ changes from 0.005 to 0.200 nm/s. On the other hand, the average width $d$ of the atomic islands decreases from 780 to 660 nm with increasing $f$, which is consistent with our previous experimental results.\textsuperscript{18} Both phenomena contributes directly to the decrease in the surface coverage $\rho$. From eq. (3), we realize that $\rho = kh \propto (H_{\text{AFM}})^{-1}$. Therefore, the saturation values of $H_{\text{AFM}}$, i.e., $(H_{\text{AFM}})_{\text{max}}$ and $(H_{\text{AFM}})_{\text{min}}$, should correspond to the $k_{\text{min}}$ and $k_{\text{max}}$ obtained in Fig. 3(b), respectively. In other words, the result $(H_{\text{AFM}})_{\text{max}}/(H_{\text{AFM}})_{\text{min}} \approx 2$ shown in Fig. 5 is in good agreement with the result $k_{\text{max}}/k_{\text{min}} \approx 2$ obtained from Fig. 3(b).

In our experiment, as described above, the ratio $H_{\text{AFM}}/d$ increases from approximately $1.5 \times 10^{-2}$ to $4.5 \times 10^{-2}$, which is the interval of the ratio $H_{\text{AFM}}/d$ that we can control in our experiment. Finally, the morphology and microstructure of the atomic islands on the liquid surfaces may be controlled by adjusting the deposition flux $f$, which is quite meaningful for both theoretical and applied purposes in the future.

\begin{figure}[h]
\includegraphics[width=\textwidth]{fig4}
\caption{(Color online) Typical AFM images and AFM line scans across atomic islands on oil surfaces. Each image has a size of $1 \times 1 \mu m^2$: (a) $h = 0.6$ nm and $f = 0.05$ nm/s; (b) $h = 0.6$ nm and $f = 0.20$ nm/s. (c) and (d) are the profiles along the lines in (a) and (b), respectively.}
\end{figure}

\begin{figure}[h]
\includegraphics[width=\textwidth]{fig5}
\caption{Dependence of $H_{\text{AFM}}$ on $f$ for $h = 0.6$ nm. Each data point denotes the average of more than five islands.}
\end{figure}
Theoretically, we suggest that the geometrical shape of Ag compact islands is similar to a disk.\(^{18}\) In this nearly free standing system, the total free energy \(G_{\text{total}}\) of a compact island can be given as
\[
G_{\text{total}} = G_{\text{volume}} + G_{\text{surface}} + G_{\text{side}}
\]
\[
= g \pi \left( \frac{d}{2} \right)^2 H_{\text{AFM}} + (\sigma_0 + \sigma_1 - \sigma_2) \pi \left( \frac{d}{2} \right)^2
+ 2 \pi \left( \frac{d}{2} \right) H_{\text{AFM}} \sigma_0,
\]
where \(G_{\text{volume}}\) is the volume energy stemming from the residual stress and is stored within the island, \(G_{\text{surface}}\) is the surface energy resulting from the upper and lower surfaces of the island, and \(G_{\text{side}}\) is the lateral surface energy of the island. The island area \(S = \pi (d/2)^2\) can be measured from the optical image. The island volume \(V = \pi (d/2)^2 H_{\text{AFM}}\), \(\sigma_0\) and \(\sigma_1\), determined by the microstructure of the island, are the surface energy and interface surface energy, respectively. \(\sigma_2\) is the surface free energy of silicone oil and can be considered constant. The equilibrium island shape is determined by
\[
\frac{\partial G_{\text{total}}}{\partial d} = 0, \quad \frac{\partial G_{\text{total}}}{\partial H_{\text{AFM}}} = 0.
\]
In this case, eq. (5) gives rise to the ratio
\[
\frac{H_{\text{AFM}}}{d} = \frac{1}{3} \left( 1 - \frac{\sigma_2 - \sigma_1}{\sigma_0} \right).
\]
It is well known that the surface morphology and microstructure of the atomic islands depend on the deposition flux \(f\).\(^{21,22}\) However, Michely et al.\(^{21}\) and Lung et al.\(^{22}\) failed to give a systematic theoretical analysis of the relationship between the microstructure of the atomic islands and deposition flux. In the present experiment, the deposition flux \(f\) has essential effects on the surface morphology and microstructure of the atomic islands, and hence the parameters \(\sigma_0\) and \(\sigma_1\) should be closely related to \(f\). Therefore, eq. (6) leads to the conclusion that the ratio \(H_{\text{AFM}}/d\) of the islands on silicone oil surfaces should be determined by the deposition flux and other deposition conditions, which gives a theoretical explanation for the experimental results shown in Fig. 3.

4. Conclusions

We investigated the aggregation mechanism of Ag atoms deposited on silicone oil surfaces and gave a physical scenario of the formation of Ag atomic islands. For \(h < h_c\), a linear increase in \(\rho\) with \(h\) is observed, which is in excellent agreement with our theoretical analysis results. The corresponding slope \(k\) decreases with \(f\), implying that the growth mechanism of Ag atomic islands strongly depends on the deposition flux \(f\). In addition, the AFM measurements show that the average thickness \(H_{\text{AFM}}\) of Ag atomic islands first increases with \(f\), and then approaches a saturation value, which is in good agreement with the experimental behavior of the slope \(k\). Furthermore, the qualitative analysis results give a theoretical explanation for the relationship between the flux \(f\) and the geometrical shape of the islands. However, we also agree that much imperative effort is still necessary to obtain more precise information about the aggregation behaviors of Ag atoms on silicone oil surfaces.

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