Kinetic Roughening with Surface Diffusion: Crossover from Ramified Aggregates to Continuous Films on Liquid Surfaces

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Ramified iron aggregates are fabricated on silicone oil surface by thermal evaporation method at room temperature and the crossover from ramified aggregates to continuous films is studied by atomic force microscopy. It is shown that the aggregates are composed of numerous granules with the average diameter around 34 nm. The dynamic scaling analysis shows that the growth exponent $\beta = 0.23 \pm 0.02$ and the roughness exponent $\alpha$ evolves from 0.65 to 0.42 with the nominal film thickness, indicating a roughening behavior transfer may exist during the growth process. The physical interpretation for the scaling behavior is presented.

KEYWORDS: kinetic roughening, liquid surfaces, ramified aggregation, surface diffusion, crossover, atomic force microscopy

1. Introduction

Thin films and nanostructures deposited on liquid substrates have attracted much attention during the last two decades. The formation mechanism of the ramified metallic clusters on silicone oil surfaces has been found and is described as the two-stage growth model. So far, many interesting topics of the cluster systems on oil surfaces, such as the microstructure, crystallization, stability, etc., have been studied and the results are quite fruitful. Efforts are also focused on the metallic cluster systems on ionic liquid surfaces. Besides, the dynamic microstructure evolution of the non-magnetic nanostructures on liquid substrates have attracted much attention during the last two decades. The formation mechanism of the ramified metallic clusters on silicone oil surfaces has been found and is described as the two-stage growth model. So far, many interesting topics of the cluster systems on oil surfaces, such as the microstructure, crystallization, stability, etc., have been studied and the results are quite fruitful. Efforts are also focused on the metallic cluster systems on ionic liquid surfaces.

During growth, the atomic relaxation on a short range scale is very sensitive on the developing roughness at the film and nanostructure surfaces. Therefore, the dynamic roughening of the surface provides another way to characterize the growth mode of the systems. Generally, the dynamic behavior of a surface can be expressed as $w_{\text{rms}}(h, L) = L^\alpha f(h/L^z)$, where $w_{\text{rms}}(h, L)$ is the surface roughness, $h$ is the average height after deposition, $L$ is the scan length, $\alpha$ is the roughness exponent, $z = \alpha/\beta$ is the dynamic scaling exponent and $\beta$ represents the growth exponent. In the case of $h/L^z \ll 1$, the power-law relation can be simplified as $w_{\text{rms}} \propto h^{\alpha}$, while $w_{\text{rms}} \propto L^{\alpha}$ for $h/L^z \gg 1$. During deposition, the atomic relaxation of the film or nanostructure surfaces, such as the defect movement and atom diffusion, may greatly affect the growth process. As for the conservative growth, the surface diffusion plays an important role, while voids and overhangs are usually introduced in the nonconservative process.

In our previous studies, the growth mechanism and microstructure evolution of the non-magnetic nanostructures on liquid surfaces have been systematically studied. However, to our best knowledge, various magnetic nanostructures on liquid surfaces have been barely investigated so far. In this letter, ramified iron atomic aggregates are fabricated on silicone oil surface and studied by atomic force microscopy (AFM). The experiment shows that the aggregates are composed of numerous granules with the average diameter around 34 nm and the growth process may be traced to the two-stage growth model. It is unexpected that the overlaps of the granules are rarely observed in our experiment, which is quite different from that of the other systems on liquid substrates. Besides, the dynamic scaling analysis of the aggregate surfaces shows that the surface diffusion plays a significant role during the growth process, which is enhanced by the nature of the liquid surface and finally results in a characteristic roughening transfer during the growth process.

2. Experimental

The samples were prepared by thermal evaporation of pure 99.5% iron (Fe) on silicone oil (Dow Corning 705 Diffusion Pump Fluid) substrates at room temperature (300 ± 2 K). The pressure of the vacuum chamber was kept at $2.0 \times 10^{-4}$ Pa. The deposition rate $f = 5.0 \times 10^{-3}$ nm/s. The nominal film thickness $d$ was controlled from 0.05 to 1.40 nm, which was determined by a quartz-crystal balance (ULVAC CRTM-3000) and calibrated by atomic force microscopy (AFM; Veeco DI 3000). The deposition time $t$ is related to the thickness $d$ in the form $d = ft$.

After deposition, the samples were kept in vacuum condition for 30 min and then removed out from the vacuum chamber. The Fe aggregates were then separated from the oil substrate and washed carefully with acetone and ethanol. After that, an immediate AFM measurement was taken in tapping mode with resolution 512 pixels × 512 pixels for the as-prepared samples.

The roughness and growth exponents are two nontrivial elements to characterize the growth mode of the ramified iron aggregates. From the dependence between the average surface roughness $w_{\text{rms}}$ and nominal film thickness $d$, the growth exponent $\beta$ is obtained. Meanwhile, the one-dimensional power spectra density (1DPSD) and spatial frequency satisfy the power-law decay as $f^{\gamma}$ and $\text{1DPSD}(f) = K_d f^{-\gamma}$. The roughness exponent $\alpha$ is related to $\gamma$ in the form...
The area of each aggregate.

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Meanwhile, as $d$ increases from 0.05 to 1.40 nm, the branches of the aggregates gradually grow and extend along the in-plane direction, which results in the increase of the area of each aggregate.

\[
\alpha = \left( \gamma - D \right) / 2, \quad \text{where the line scan dimension } D \text{ equals one. Through the analyses of } \alpha \text{ and } \beta, \text{ the roughening behavior of the aggregate surface can be revealed.}
\]

\section{Results and Discussion}

Figure 1 shows the typical AFM images of the ramified Fe aggregates on silicone oil surfaces with different nominal film thicknesses $d$: (a) 0.05, (b) 0.40, and (c) 1.40 nm. Each image has a size of 10.0 $\times$ 5.0 $\mu$m$^2$.

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\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig1.pdf}
\caption{(Color online) Typical AFM images of the ramified iron aggregates on silicone oil surfaces with different nominal film thicknesses $d$: (a) 0.05, (b) 0.40, and (c) 1.40 nm. Each image has a size of 10.0 $\times$ 5.0 $\mu$m$^2$.}
\end{figure}

For each fixed $d$, more than five AFM images in different areas of the sample were taken with the same scan length in our experiment. It is shown that the morphology of the aggregates in different images remains similar to each other while the apparent Fe coverage of the total area may deviate slightly (i.e., $\leq 3\%$).

In order to further study the microstructure of the aggregates, the high resolution AFM images were taken with the scan length of 2.0 $\times$ 2.0 $\mu$m$^2$ shown in Figs. 2(a) and 2(b). It is found that each aggregate is composed of numerous Fe granules, which is similar to that of the silver systems on oil surface, indicating an experimental evidence that the formation mechanism of the Fe aggregates may also be traced to the two-stage growth model. 1) An interesting phenomenon shown in Fig. 2 is that the Fe granules only stick along the in-plane direction to form the ramified aggregates and, compared with the situations of the Ag, Au, and Cu systems on liquid substrates, 5,25,29 the overlap phenomenon among the granules rarely happens and the percentage of the granule overlap is less than 10%, revealing a characteristic aggregation mechanism of the Fe granules.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig2.pdf}
\caption{(Color online) High resolution AFM images of the iron aggregates. Each image has a size of 2.0 $\times$ 2.0 $\mu$m$^2$. The thicknesses (a) $d$ = 0.05 nm; (b) $d$ = 0.40 nm. (c) and (d) are the corresponding size distributions of the granules in the aggregates shown in (a) and (b), respectively.}
\end{figure}

The diameter distributions of the granules in the aggregates shown in Figs. 2(a) and 2(b) are measured and the results are given in Figs. 2(c) and 2(d), respectively. The Gaussian fittings of the distributions show that the mean size of the granules is around 35.1 $\pm$ 5.0 nm for the samples with the thickness of 0.05 and 0.40 nm, respectively. This result reveals that the mean size of the granules is almost independent of $d$, which is similar to that of the Al system. 6) This interesting phenomenon is quite confusing to the authors. However, two possibilities can still be proposed below: a) the material density of the granules increases with $d$; b) there is a critical size of the granules on the oil surface and with which the granules may possess the lowest free energy and the growth of each granule approaches saturation. Therefore, further study on the microstructure of the granules is still needed.
In order to feature the roughening behavior of the aggregate growth, the dynamic scaling analysis of the Fe aggregate surfaces is performed. Figure 3(a) shows that the surface roughness has a power-law dependence on the nominal film thickness $d$. The slope of the linear fitting in the log–log plot reads $\beta = 0.23 \pm 0.02$, which is consistent with the previous studies on Fe/Fe(001) \(^{30}\) or Fe/Si(111) \(^{31}\) system. However, although the value of $\beta$ is close to these of the epitaxial systems, the growth of the aggregates in our experiment may undergo a different mode which may be described in the following analyses. The 1DPSD spectrum vs spatial frequency $f$ is shown in Fig. 3(b) and it can be clearly seen that each spectra includes two distinct regions. The low-frequency range indicates the present of uncorrelated elements such as white noise, while the high-frequency range contains the correlation information of the rough surface. We find that the value of $\gamma$ varies from 2.22 to 1.73 as $d$ increases from 0.05 to 1.40 nm. According to the relation $\alpha = (\gamma - 1)/2$, the corresponding mean value of $\alpha$ can be derived which is shown in Fig. 4.

As $d$ increases from 0.05 to 0.80 nm, the central value of $\alpha$ seems to increase. After taking the error bars into account, we suggest that $\alpha \approx 0.65$ remains almost no changes, which is similar to the value of Fe/Fe(001) system. \(^{30}\) However, as $d$ further increases, the mean value of $\alpha$ decreases to 0.42 (see Fig. 4), consisting with the ballistic deposition model by Family and Vicsek \(^{18}\) or the KPZ growth. \(^{21}\) The obvious change of the value $\alpha$ indicates that a transfer of the roughening mechanism really happens during the growth process of the aggregates. Compared to the situation on solid substrates, the liquid substrate provides a nearly free sustained surface and both the deposition atoms and aggregates on the surface can diffuse and rotate freely. \(^{1,2}\) Therefore we suggest that the transfer is mainly resulted from the effect of the liquid substrate.

For conservative growth situations, a nonlinear surface diffusion dynamics was presented by Lai and Das Sarma \(^{19}\) and the surface diffusion equation can be described as

$$\frac{\partial h}{\partial t} = -\nu \nabla^2 h + \lambda \nabla^2 (\nabla h)^2 + \eta.$$  \hspace{1cm} (1)

From the simulation result for eq. (1), one obtains $\alpha = 0.66$ and $\beta = 0.2$, which are in good agreement with our results when $d < 0.80$ nm. In our experiment, compared to the situations on solid substrates, the ad-atoms on liquid surfaces may diffuse more freely until they reach the pre-formed aggregates. Meanwhile, the diffusion coefficient of the aggregates on silicone oil surface is much larger than that on solid substrate \(^{1}\) Hence, we propose that the characteristic surface diffusion of the ad-atoms and aggregates dominates the roughening behavior during the surface growth process.

For $d > 0.80$ nm, however, the area of each aggregate goes up quickly, as shown in Figs. 1(b) and 1(c). When $d$ reaches 1.40 nm, a nearly continuous thin film forms and the diffusion coefficient of the aggregates is greatly diminished. Therefore, most of the following deposition atoms may be deposited directly on the pre-formed aggregates. In this case, the growth process of the aggregates and films is similar to the situation on solid substrates. Therefore, the overhangs and voids may be introduced which accords with the growth mode described by Kardar, Parisi, and Zhang and the growth equation of the KPZ mode can be expressed as \(^{21}\)

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \lambda (\nabla h)^2 + \eta.$$  \hspace{1cm} (2)

The simulation result for eq. (2) gives $\alpha = 0.39$ and $\beta = 0.24$, which are in good agreement with our results when $d > 0.80$ nm, as shown in Figs. 3(a) and 4. Therefore, the roughening behavior in this growth stage can be characterized by the kinetic surface roughening mechanism of the KPZ growth.
4. Conclusion

In conclusion, we have studied the growth process and microstructure of the ramified Fe aggregates on silicone oil surfaces at room temperature. The AFM images show that the Fe atoms nucleate to form ramified aggregates and the average width of the branches in each aggregate is in the order of 10\(^2\) nm. The high resolution AFM images reveal that the aggregates are composed of numerous granules with the diameter around 34 nm. An interesting phenomenon is that the Fe granules on silicone oil surfaces only stick together along the in-plane direction while the overlap of the granules rarely happens, which is totally different from those observed in the Cu and Ag systems. Meanwhile, the dynamic scaling analysis shows that the growth exponent \(\beta = 0.23 \pm 0.02\). If \(d < 0.80\) nm, the roughness exponent \(\alpha = 0.65 \pm 0.05\). However, if \(d\) increases and goes beyond 0.80 nm, \(\alpha\) suddenly drops and reaches 0.42 \(\pm 0.02\), indicating a roughening behavior transfer in the growth process.

Compared to the situations of Cu and Ag systems, \(^7\),\(^{25}\),\(^{29}\) we propose that the magnetic behavior of the iron atoms on oil surface does not influence the surface morphology of the ramified aggregates obviously. However, up to now, the underlying physical origin of this phenomenon is still poorly understood. On the other hand, after the magnetic atoms aggregate, the structures of the magnetic domains and its formation mechanism in the ramified aggregates is another interesting topic.

According to the discussion above, for a fixed \(d\), the morphology of the aggregates in each AFM image taken in different regions of the sample remains similar while the apparent Fe coverage of the total area deviates slightly. In this case, if the coverages shown in Fig. 1 are approximately true and may be used to represent the average coverages of the samples, as \(d\) changes from 0.05 to 1.40 nm, one may estimate that the relative mass density increment of the Fe aggregates is more than 100\%. This estimation is simple and approximate, however, it is interesting. Therefore, further study on the mass density evolution of metallic aggregates on various liquid substrates is needed.

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