Aggregation behavior and microstructure of silver thin films on ionic liquid substrates

Bo Yang, Rui-Rui Ma, Dong-Mei Li, A-Gen Xia, Xiang-Ming Tao *

Department of Physics, Zhejiang University, Hangzhou 310027, PR China

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A silver film system, deposited on ionic liquid substrates by thermal evaporation method, has been fabricated and its structure as well as formation mechanism has been studied. A coexistent phenomenon of quasi-circular and ramified aggregations is observed and both of them are composed of nanograins with the size of the order of 10^{-2} nm, which can be explained in terms of the different diffusion behaviors of the grains during and after deposition. For the nominal film thickness h ≤ 80.0 nm, the average area of the quasi-circular aggregates, namely S_{\text{quasi}} \approx (1 - e^{-H/H_0}) with H = 27 ± 3 nm; for h > 80.0 nm, S_{\text{quasi}} increases quickly with h. The interpretation for this phenomenon is also presented.

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1. Introduction

Thin metal films on the solid substrates have attracted attentions for many years and still do because of their unusual physical and chemical properties. These properties are, to a great extent, determined by the microstructure and morphology, which highly depend on the deposition method and property of the substrates [1–3]. The previous experimental results show that both single atom and atomic clusters can diffuse on the solid substrates, which may sometimes result in ramified islands or compact islands [4–7]. In the past 15 years, unusual phenomena found in metal films on liquid surface have sparked interest in diffusion and condensation of metallic clusters [8–13]. Experimental evidences illuminate that the structure and growth mechanism of these kinds of film systems are quite different from those of metal films deposited on solid substrates. Atoms, atomic compact clusters and ramified aggregates possess large mobility at room temperature and they can diffuse, rotate and aggregate freely on liquid surfaces. The formation of the ramified Ag, Au and Cu aggregates on liquid surfaces can be described by a two-stage growth model [8–12]. The results also demonstrate that the metallic film systems on silicone oil surfaces exhibit polycrystalline structure [9,13]. Recently, the deposition of metal on ionic liquid was researched and has attracted much attention due to their applications and fundamental interests [14–16].

In this paper, we report an aggregation mechanism of Ag atoms deposited on ionic liquid substrate by thermal evaporation method. The experiment shows that, with the increase of the nominal film thickness, the ramified aggregates, the coexistence of the quasi-circular and ramified aggregations and a continuous film are observed in sequence by an optical microscope, which is quite different from those phenomena observed in the metallic films on silicone oil substrate. The dependence between the average area of the quasi-circular aggregates and the nominal film thickness is studied. The microstructures of both the ramified and quasi-circular aggregates are measured by atomic force microscopy (AFM).

2. Experiment

The samples were fabricated by thermal evaporation of 99.999% pure silver (Ag) in a vacuum of 3.0×10^{-4} Pa at room temperature. A drop of ionic liquid ([bmin]BF_4) with a vapor pressure close to zero at room temperature was painted onto a frosted glass surface, which was levelly fixed 250 mm above the evaporating filament (tungsten). The ionic liquid substrate with an area about 12×12 mm^2 had a uniform thickness of ~0.5 mm. The deposition rate f for all the samples was 0.30 nm/s and the nominal film thickness h was in the range of 1.0–150.0 nm, which were determined by a quartz-crystal balance located near the substrate. After deposition, the samples were immediately removed from the vacuum chamber. The film surface morphologies were characterized with an optical microscope (Leica DMLM). Subsequently, the samples were separated from the ionic liquid substrates to glass surfaces and washed carefully with acetone and ethanol. After that, the AFM (Veeco DI3000) measurements were taken immediately for the as-prepared samples. Film surface morphologies were obtained with the AFM operated in tapping mode using an etched single-crystal Si tip with a radius of 10 nm.
3. Results and discussion

Fig. 1 shows the optical morphologies of the Ag thin films deposited on ionic liquid surfaces, with different nominal film thicknesses $h$. The ramified aggregates (darken area in Fig. 1(a)) can be observed. The average branch width of the ramified aggregates is about 0.5 μm. This phenomenon is very similar to the Ag, Au and Cu systems deposited on silicone oil surfaces [8–12]. The two-stage growth process concluded from the experiments of Au and Ag systems on silicone oil substrate can also be used to describe the formation process of the Ag film with $h < 10.0$ nm on ionic liquid substrates [8,11]. The brighter and darker areas in Fig. 1(b)–(d) correspond to the Ag films and the uncovered substrate, respectively. The compact quasi-circular aggregates with diameter $d \geq 0.5$ μm are observed among the ramified aggregates (see Fig. 1(b) and (c) for details). Actually this typical morphology had never been observed on the metallic films deposited on silicone oil surfaces [8–13]. With the nominal film thickness increasing, the diameter of the quasi-circular aggregates increases obviously while the branch width of the ramified aggregates is kept almost unchanged (about 0.5 μm); meanwhile, the number density $n$ of the quasi-circular aggregates in Fig. 1(b) and (c) is almost independent of $h$. For the sample with $h = 80.0$ nm, several large quasi-circular aggregates have been detected, which are attributed to the coalescing of quasi-circular aggregates. In other words, if two of aggregates touch or impact, they will coalesce into a larger one. The gourd-shaped aggregate, (denoted by arrow in Fig. 1(c)), is actually an intermediate stage of the coalescence process. It should be noted here that, when the ramified aggregates encounter the quasi-circular aggregates, they do not coalesce into a more compact shape. The surface coverage increases with $h$, then a continuous film with several quasi-circular holes can be observed and the ramified aggregates can be found in these holes (see Fig. 1(d)). If deposition continues, these holes decrease gradually, and a continuous flat film forms finally.

In order to understand the formation mechanism of the Ag films deposited on ionic liquid substrates, we have kept the samples in the vacuum chamber for time interval $\Delta t$ (varying from 10 min to 24 h). This examination shows that the average diameter of the quasi-circular aggregates and the average branch width of the ramified aggregates are almost independent of $\Delta t$.

Based on the above observations, we suggest that the deposited silver atoms nucleate and form compact clusters during deposition which can diffuse and rotate randomly on ionic liquid surfaces by Brownian motion. Then the compact clusters adhere to each other when they meet and form the ramified aggregates (see Fig. 1(a)). If the deposition finishes, the free ramified aggregates will continue to grow with time due to random motion and adhesion upon impact and large ramified aggregates may be formed (see Fig. 1(a)). If the deposition continues, the substrate temperature may rise because of both the thermal radiation from the evaporation source and the strike by the deposited silver atoms, and then the viscosity $\eta$ of the ionic liquids may be decreased with the temperature [17]. Both the increase of the substrate temperature and decrease of the viscosity $\eta$ result in the changes of the surface and interface free energies. Because the edge diffusion coefficient of the grains in aggregates depends critically on the surface and interface energies [9,18], grains will move along the aggregate edge approximately. In detail, owing to the fewer neighbors of grains located at the aggregate boundaries, such grains are less strongly bound to the aggregate than those in the interior and they are prone to move along the aggregate edges. The aggregate possesses specific edge energy per unit edge length. Diffusion (i.e., grains motion along the edge) will tend to minimize the total edge energy $\delta L$ by minimizing the edge length $L$ [9]. Thus, the ramified aggregates transform into the quasi-circular aggregates. With

![Fig. 1](image-url)

**Fig. 1.** The morphologies of the Ag thin films on ionic liquid substrates. Each image has a size of 100 × 100 μm². (a) $h = 1.0$ nm; (b) $h = 20.0$ nm; (c) $h = 80.0$ nm; (d) $h = 130.0$ nm.
further deposition, the diameter of quasi-circular aggregates increases by capturing the deposited atoms or small compact clusters. If the deposition is over at that moment, the substrate surface temperature and the edge diffusion coefficient decrease, and the grains could no longer move along the aggregate edge. The deposited atoms and small compact clusters, which have not been captured by the compact quasi-circular aggregates yet, adhere to each other when they meet and form the ramified aggregates. Therefore, the ramified aggregates and quasi-circular aggregates can be observed simultaneously in the experiments (see Fig. 1(b) and (c)). If the deposition continues, the quasi-circular aggregates continue to grow. When quasi-circular aggregates touch, they adhere to each other and coalesce into a larger one, which may yield to the formation of holes in the large aggregates. If the deposition finishes at this point, the atoms deposited in the holes aggregate and form the ramified aggregates (see Fig. 1(d)). Otherwise, the holes become smaller as the film thickness increases and finally a continuous and flat film appears.

For further study the growth mechanism of the quasi-circular aggregates, statistical measurements on the diameters of quasi-circular aggregates are performed over a wide range of nominal thicknesses. Fig. 2 presents the related statistical results. For \( h = 50.0 \) nm, the diameter distribution of the quasi-circular aggregates is found to resemble a rough Gaussian distribution, as shown in Fig. 2(a), where one finds that the mean diameter of the quasi-circular aggregates is \( \Phi_m = 2.82 \pm 0.17 \) \( \mu \)m. For \( h = 120.0 \) nm, we find that the number of the quasi-circular aggregates changes with the value of \( \Phi \) and, besides the main peak (peak I), several subordinate peaks marked as peaks II, III and IV in Fig. 2(b), are observed. We found that \( \Phi_2^2, \Phi_3^2, \) and \( \Phi_4^2 \) are about twice, thrice or fourfold as large as \( \Phi_1^2 \), where, \( \Phi_1, \Phi_2, \Phi_3, \) and \( \Phi_4 \) represent the corresponding diameters of the peaks I, II, III and IV (see Fig. 2(b)), respectively. We speculate that the total area of two compact aggregates before coalescence and the area after coalescence, within the error limits, should remain as a constant. Therefore, the average area of the aggregates after coalescence is twice as large as that before coalescence. In addition, it can be found that, some quasi-circular aggregates with a large size are also observed. And the diameters of them are about ten times larger than \( \Phi_1 \). It further proves that coalescence occurs actually in the growth process of the quasi-circular aggregates for the sample with \( h = 120.0 \) nm.

To further confirm the formation mechanism of the coexistent phenomenon and to obtain a more quantitative description of the growth process of the quasi-circular aggregates, a fitting curve between average area \( S_{av} \) of the quasi-circular aggregates and \( h \) is also displayed for our samples (see Fig. 3). Apparently, \( S_{av} \) increases slowly with \( h \) for \( h \leq 80.0 \) nm and then exhibits a rapid increase for \( h > 80.0 \) nm. In general, the diffusion coefficient \( D \) is correlated with cluster or aggregate size as \( D \propto S^{-\alpha} \) [19–21]. Therefore, the diffusion coefficient is very small for the compact quasi-circular aggregates and the average diffusion area of the quasi-circular aggregates is far less than the spacing among the quasi-circular aggregates. In other words, two quasi-circular aggregates meet very rarely in the initial stage of the coarsening process, and the number density \( n \) of the quasi-circular aggregates is almost independent of \( h \) in this case (see Fig. 1(b) and (c)). Therefore, we propose that the quasi-circular aggregates grow gradually by capturing deposited atoms or small clusters during deposition. Then, the increment of the coverage of quasi-circular aggregates \( dC \) can be described by

\[
dC \propto \frac{ft(1-C)}{H} \tag{1}
\]

where \( t \) is the deposition time, \( ft = h \), while \( H \) is the average height of the aggregations. Hence, \((1-C)\) stands for the area percentage of uncovered liquid substrate. It is apparent that \( C \propto n \times S_{av} \), therefore, integrating Eq. (1) yields

\[
S_{av} \propto \left(1 - e^{-h/H}\right) \tag{2}
\]

The experiment data with \( h < 80.0 \) nm in Fig. 3 can be well fitted in the form of Eq. (2) and \( H \) is found to be \( 27 \pm 3 \) nm. With increasing the size of quasi-circular aggregates, the probability of the two quasi-circular aggregates encounters increases and the quasi-circular aggregates grow mainly by coalescing. The average diameter of quasi-
circular aggregates increases rapidly and the experiment data with \( h > 80.0 \) nm in Fig. 3 is not consistent with that of the corresponding fitting curve (see Fig. 3).

In order to identify the microstructure of the Ag films deposited on ionic liquid surfaces, we performed the AFM experiment. The typical AFM images of the ramified and quasi-circular aggregates are shown in Fig. 4(a). It can be found that the edge of the quasi-circular aggregates is very smooth, which agrees with the formation mechanism of coexistence phenomenon we have proposed above. Fig. 4(b) presents the corresponding profiles along the line in Fig. 4(a). It is found that the average height of both the ramified and quasi-circular aggregate is about 30 nm, which is in agreement with our fitting result \( 27 \pm 3 \) nm. The insets in Fig. 5(a) and (b) are the high-resolution images of the ramified and quasi-circular aggregates, respectively. Apparently, one can find that both the ramified aggregates and the quasi-circular aggregates are composed of nanosized grains. Fig. 5(a) and (b) show the size distributions of the nanograins corresponding to the two insets in Fig. 5(a) and (b), respectively. The approximate Gaussian distributions in Fig. 5 indicate a surface having features distributed symmetrically around a mean size. The mean diameters of the nanograins of the ramified aggregates and the quasi-circular aggregates are measured as \( \phi_{m1} = 40.2 \pm 0.5 \) nm and \( \phi_{m2} = 39.0 \pm 0.9 \) nm, respectively.

4. Conclusion

In summary, we have studied the growth mechanism and the microstructure of the Ag films deposited on ionic liquid surface. For \( h < 10.0 \) nm, the ramified aggregates can be found, and the growth mechanism for these objects obeys the so-called two-stage growth model. The typical coexistent morphology of the quasi-circular and ramified aggregates is observed for samples with \( h > 10.0 \) nm. We speculate in this work that the quasi-circular aggregations are formed during deposition and the ramified aggregations are formed after deposition. With the increase of deposition time, the growth of the quasi-circular aggregates is mainly dependent on capturing deposited atoms and small clusters, and the average area \( S_{av} \) of quasi-circular aggregates and \( h \) satisfy \( S_{av} \propto (1 - e^{-h/H}) \) with \( H = 27 \pm 3 \) nm, which accords well with the data obtained from AFM measurement. For \( h > 80.0 \) nm, the growth of the quasi-circular aggregates results from coalescence, which leads to \( S_{av} \) increasing rapidly with \( h \). In addition, AFM tests indicate that both the ramified aggregate and quasi-circular aggregate are composed of nanosized grains.

The phenomena presented in this paper indicate that the physical properties of liquid substrate, such as surface tension, surface energy and kinetic energy of liquid level molecules, severely affect on the morphology, microstructure and formation mechanisms of the silver aggregates and films. We believe that other metallic films deposited on ionic liquid substrates, will also exhibit unusual and rich physical and chemical properties. Meanwhile, the metal film systems deposited on other liquid substrates may also unfold several interesting phenomena. Further experimental and theoretical efforts on this topic are now in progress.

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