AFM study on microstructures of metal films deposited on liquid substrates

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Abstract

We study the formation mechanism and microstructures of silver and gold thin films deposited on silicone oil surfaces by atomic force microscopy (AFM). The growth mechanism of the metallic films obeys the two-stage growth model. We find that the atomic compact clusters and ramified aggregates formed on the oil surfaces are composed of crystal grains with the size of the order of 10^1 nm. The most interesting phenomenon is that, as the nominal film thickness increases, the mean size of the grains in the ramified aggregates does not change obviously. The characteristic difference of the microstructures between the down and up surfaces of the continuous films is measured. The physical interpretation of the results is also presented.

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1. Introduction

Many experimental evidences illuminate that the growth processes and characters of metallic films on solid surfaces can be strongly affected by the fabrication conditions, such as the substrate temperature, surface microstructure of the substrates, deposition flux, etc. [1–5]. Nowadays works in this field have been motivated by the even more stringent requirements on the characters of thin films needed for developing advanced microelectronic, optical and magnetic devices, as well as the nanometer-scale structures.

Since 1998, Ye et al. [6] have presented results on the growth of metallic atom depositions on the silicone oil surfaces by thermal vapor method. Recently, various thin films on liquid substrates are studied in a number of investigations [6–13], in which the nucleation, diffusion and aggregation of the metallic atoms are studied systematically [6–9] and the characteristic surface morphologies of the continuous films are observed [10–13]. However, the details of the microstructures of both the ramified aggregates and the continuous films are rarely studied.

In this Letter, we present an AFM study on the growth mechanism and microstructures of silver (Ag) and gold (Au) films deposited on silicone oil substrates. We find that the compact atomic clusters as well as the ramified aggregates formed on the oil surfaces are composed of crystal grains with the sizes of the order of 10^1 nm. It is quite interesting that the mean sizes of the grains in the ramified atomic aggregates depend on the character of the materials but they do not change obviously as the nominal film thickness increases. The characteristic microstructures of both the down and up surfaces of the continuous films are observed.

2. Experimental method

The samples were prepared by thermal evaporation of 99.99% pure gold and silver in a vacuum of about 6 × 10^{-4} Pa at room temperature [RT = (30 ± 5)]°C]. 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 130 mm below the filament (tungsten). The resulting oil substrate with an area of about 10 × 20 mm² had a
uniform thickness of \(\approx 0.5\) mm. The deposition rate was varied from \(f = 0.01\) to \(0.05\) nm s\(^{-1}\) and the nominal film thickness \(d\) was in the range of \(d = 1–100\) nm, which were determined by a quartz-crystal balance (ULVAC CRTM-8000) located near the substrate.

After deposition, the samples were kept in the vacuum chamber (in vacuum condition) for time \(\Delta t\) and then removed from the vacuum chamber. The films (or atomic aggregates) were then separated from the oil substrates and washed carefully with acetone and ethanol [14]. After that, the AFM (SPI3800N, Seiko Instruments Inc.) measurements were taken immediately for the as-prepared samples. The grain size \(\Phi\) and the size distributions of the samples were measured by the AFM software.

3. Results and discussion

3.1. Microstructure of the ramified aggregates

Fig. 1 shows the typical AFM images of the Ag and Au ramified atomic aggregates deposited on the silicone oil surfaces. Both the insets are the higher-resolution images of the ramified aggregates, respectively. The branch widths of the aggregates in Figs. 1(a) and 1(c) are of the order of \(10^2\) nm and the morphologies of the aggregates are quite similar to that of the Ag or Au aggregates on liquid substrates [6,9]. The experimental results shown in Figs. 1(a) and 1(c) confirm again that the growth mechanism of the thin films in our experiment obeys the two-stage growth model [6]: The first stage of which involves nucleation and growth of the compact clusters during the deposition. In the subsequent stage after deposition, the formed compact clusters continue to diffuse on the liquid surface by Brownian motion and random rotation, then ramified aggregates form. Although, the formation process described above leading to these ramified atomic aggregates appears complex, their shapes resemble the results of computer models for diffusion limited aggregate (DLA) [15] of particles or even more closely to those of cluster–cluster aggregate (CCA) [16] in two dimensions.

An interesting result shown in Fig. 1 is that both the compact and ramified aggregates are composed of metal crystal grains. By means of measuring the grain size \(\Phi\) of all the crystal grains in the aggregates, the grain size distributions are obtained. Figs. 1(b) and 1(d) show the size distributions of the Ag and Au crystal grains in the aggregates presented in Figs. 1(a) and 1(c), respectively. We find that the mean diameter size of the Ag crystal grains, i.e., \(\Phi_{\text{Ag}}\), equals 97.5 nm [see Fig. 1(b)], which is much larger than that of the Au crystal grains (\(\Phi_{\text{Au}} = 39.5\) nm) [see Fig. 1(d)]. This result shows that the mean size distribution of the crystal grains in the aggregates, which contains the information about the nucleation and aggregation mechanism of the atoms, depends on the characters of the metals apparently. However, it is unexpected that, in our experiments, both \(\Phi_{\text{Ag}}\) and \(\Phi_{\text{Au}}\) do not increase with \(d\) obviously and the surface coverage (i.e., the number density of the grains) goes up as \(d\) increases.

3.2. Microstructure of the Au continuous films

As the nominal film thickness \(d\) increases, more and more ramified atomic aggregates appear and the surface coverage increases, finally a continuous film forms. In order to understand
the details of the film surface structure and the size distribution of the crystal grains in the films, the microstructures of both the down and up surfaces of the continuous films are studied by the AFM.

3.2.1. Down surface morphology of the Au film

The typical AFM images of the down surface of the Au film are shown in Figs. 2(a)–2(c). Fig. 2(b) is the higher resolution of Figs. 2(a) and 2(c) is the higher resolution of Fig. 2(b). The vertical distance between the lowest and highest positions of the film is about 100 nm, indicating that the roughness of the film surface is significant with respect to its film nominal thickness ($d = 100$ nm). Similar phenomena are frequently observed in the continuous films on the silicone oil surfaces, but hardly be found in the continuous films deposited on smooth solid substrates. The characteristic surface morphology shown in Fig. 2(a) exhibits a distinct pattern of the obvious loose regions in the film (like a crack), which should be related to the morphology of the ramified aggregates shown in Fig. 1 and the growth mechanism of the films. The grain size distribution in Fig. 2(c) is found to resemble a Gaussian distribution, as shown in Fig. 2(d), from which one finds that the mean diameter of the grains is $\Phi_{Au1} = 40.5$ nm. The size distribution in Fig. 2(d) is quite similar to that of the aggregates shown in Fig. 1(d), indicating that, with the increase of the nominal thickness $d$, the mean diameter of the Au grains does not change obviously. It is suggested that this unexpected phenomenon may be resulted from the characteristic interaction between the metallic atoms and the liquid substrates, and the large diffusion coefficient of the metallic atoms and clusters on the liquid surfaces [6].

3.2.2. Up surface morphology of the Au film

Figs. 3(a)–3(c) show the up surface morphologies of the Au film measured in Fig. 2. Fig. 3(b) is the higher resolution of Fig. 3(a) and 3(c) is the higher resolution of Fig. 3(b). It is noted that the morphologies in both the up and down surfaces of the films resemble each other in appearance [see Figs. 2(a) and 3(a)]. Therefore, the characteristic morphology shown in Figs. 2(a) and 3(a) is the bulk structure of the continuous film. The crystal grain size distribution [obtained from Fig. 3(c)] of the up film surface resemble a Gaussian distribution with the mean diameter $\Phi_{Au2} = 49.5$ nm [see Fig. 3(d)], which is much larger than that of the down film surface mentioned in Fig. 2.

Figs. 2 and 3 present the difference of the grain sizes between the down and up surfaces, mirroring the growth tendency of the crystal grains in the films. It should be noted that, before the continuous film forms, the deposited atoms and aggregates can diffuse randomly on the oil surface with very large diffusion coefficient [6] and then the crystal grains grow on the liquid surfaces freely. In this case, the mean size of the crystal grains is mainly determined by the minimization of the total free energy, including the free energy of each grains, grain boundaries and the interface between the grains and the liquid substrate. Therefore, no obvious difference between the mean size distributions of the Au grains in the ramified aggregates [see Fig. 1(d)] and in the down surface [see Fig. 2(d)] is detected.

Subsequently, as $d$ increases and after the continuous film forms, the ad-atoms are deposited directly on the Au film surface and the liquid substrate effect actually disappears. In this case, the mean size of the grains is determined by the mini-
Fig. 3. AFM images of the up surface of a continuous Au film sample. \( f = 0.05 \text{ nm s}^{-1}, \ d = 100 \text{ nm}, \ \Delta t = 1 \text{ h} \). (a, b, c) The AFM images with different resolutions; (d) the size distribution of the crystal grains on the up surface.

Fig. 4. Comparison of the crystal grain size distributions of different Au film surfaces. \( f = 0.05 \text{ nm s}^{-1}, \ d = 100 \text{ nm}, \ \Delta t = 1 \text{ h} \). (□) On the down surface of the film on silicone oil surface; (✩) on the up surface of the film on silicone oil surface; (△) on the up surface of the film on glass surface.

4. Conclusion

In summary, we have studied the microstructures and growth mechanism of the Ag and Au atomic aggregates and continuous films on the silicone oil surfaces. The nanocrystal grains are newly observed in the large ramified metal aggregates. We find that the atomic compact clusters, ramified aggregates and continuous films are polycrystalline structure and the mean size of the crystal grains is of the order of \( 10^4 \text{ nm} \). The size distributions of the crystal grains in both the aggregates and films depend on the nature of the materials apparently. It is measured that the films exhibit a characteristic surface morphology and the microstructures in the down and up surfaces are obviously distinct, depending on the nominal film thickness.
The above discussion is just confined to the room temperature with atoms deposited on a specific liquid substrate. We hope that the present Letter is intended to help as a guideline for further experimental and numerical studies concerning the crystallization mechanism of thin films on various liquid substrates, which may allow a new class of thin film studies that fabricate various film systems on liquid substrates.

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