Morphology and microstructure of Ag islands of aggregated atoms on oil surfaces*

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The morphology evolution of silver islands on silicone oil surfaces is measured and the microstructure of the islands is studied. The deposited Ag atoms diffuse and aggregate on the oil surface and then Ag islands with the width of the order of 10^2-nm form. After the samples are removed from the vacuum chamber, the immediate measurement shows that the apparent Ag coverage of the total area decays with the magnitude up to (23.0±3.8)% in few minutes. In the following two hours, the samples are kept in the ambient atmosphere and several unexpected results are detected: 1) as the topological structure of the islands evolves, the total area of each island decreases gradually and the maximum decrement measured is around 20%; 2) if an island breaks and becomes two small pieces, the total area decreases obviously; 3) however, if two small islands meet and stick together, a sudden increment of the total area is observed. These phenomena, mirroring the evolution process of the island microstructure, are resulted from both the diffusion of the atoms and the combination of the defects inside the islands.

Keywords: liquid substrate, island, microstructure, morphology

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1. Introduction

To know the atomic process in various surfaces is always significant since it may provide us with a possible way to produce desirable atomic islands. The scanning-tunneling microscope (STM) study of homoepitaxial growth of Pt(111) reveals that the island morphologies rely on temperature.[1] Moreover, experiments show that the substrate geometry has great influence on the island shapes, e.g., fractal growth is mainly reported on the triangular or hexagon lattice while the square lattice leads to the compact shape islands in most cases.[2−8] Theoretical calculations by Zhang *et al.* present that the absence of the extended fractal growth regime results in the compact shape island on the square lattice.[9]

It is found that the nature of the substrate plays an important role on the morphology and microstructure of the metallic thin films.[10] The X-ray diffraction (XRD) measurements prove the existence of the 2% concentration of vacancy in the homoepitaxial metallic film system due to the mismatch between the substrate and the thin film. Further researches show that the concentration of the vacancy is temperature-dependent and related to the surface roughness of the thin films.[11,12] Furthermore, previous research showed that the vacancy mechanism leads to the decrease in film thickness and resistivity after deposition in 250 hours.[13] In addition, Tao *et al.* have observed the anomalous electrical conductivity in a gold thin film percolation system. They ascribe this phenomenon to the characteristic microstructure of the Au thin film, which is resulted from the existence of the defects during the quenching process by the oil drop.[14]

Nowadays, the studies on various island shape transitions have attracted much interest because of their applications in controlling the quantum dots and arrays.[15−17] In the initial stage of metal heteroepitaxy, the lattice misfit between the islands and substrate materials leads to strains in the islands. The STM observations by Müller *et al.* showed the island shape transitions from compact to ramified islands during the island growth on the interface with square lattice, which is related to the island size-dependent strain relief.[18] In addition, it is shown that not only

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the strain relief but also the strong inhomogeneous stress distribution in the substrate near the islands can result in the island shape transition.[19] In Pb/Cu(111) system, Gastel *et al.* observed a stress domain pattern with characteristic feature size and a reversible island shape transition is reported in their following experiments.[20,21] It is found that the shape of the island changes from compact to elongated shape when the ratio of the island size to the characteristic feature size reaches a particular value.[21]

To date, both the experimental and simulated studies on microstructure and growth manner of the islands on solid surfaces are fruitful.[22−24] The previous work indicated that the liquid substrate really provided a nonlattice surface for island growth.[25,26] However, systematical studies on the microstructure and its evolution of the metallic islands of aggregated atoms on the liquid surfaces are still lacking. In this paper, we focus on the microstructure evolution of the Ag islands on silicone oil substrate. By means of measuring the apparent Ag coverage of the total area, namely ρ, we find that ρ decays obviously in several minutes as soon as the samples are removed out from the vacuum chamber, indicating that a microstructure evolution process happens in the system. In the following few hours, as the samples are kept in the ambient atmosphere, several interesting phenomena may happen due to the diffusion of the Ag atoms in the islands: (i) the topological structure of the islands may change; (ii) an island may break into two small pieces; (iii) two islands may stick together and become a big one. It is observed that the total area of the islands changes obviously as the above phenomena are in progress.

2. Experiments

The samples were prepared in a vacuum of 2.8×10^{-4} Pa at ambient temperature by thermal evapouration method. The 99.999% pure Ag wires were hung on the filament (tungsten) as the evapouration source. Commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) with a vapour pressure below 10^{-8} Pa was painted onto a frosted glass surface, which was fixed 135 mm below the filament. The resulting oil substrate with an area about 8.0 mm×10.0 mm had a uniform thickness of $d_{\rm u} \approx 0.5$ mm. The deposition rate varied from $f =$ 0.02 nm/s to 0.50 nm/s and the nominal film thickness $d = 0.5$ nm–10.0 nm, which was determined by a quartz-crystal balance and calibrated by the atomic force microscope (AFM, Veeco DI3000).

After deposition, the samples were kept in the evapouration chamber (in vacuum condition) for time period $\Delta t = 0.5$ h and 3 h. An optical microscope (Leica DMLM) was used to take images for the Ag islands after the samples were removed out from the vacuum chamber. A computer programme was used to calculate the coverage ρ of the images and the in-plane area of each single island. Errors caused by optical imaging were carefully calculated and added into the error bars to make the results reliable.

3. Results and discussion

Figure 1 shows the typical optical images of the Ag islands of aggregated atoms on the oil surface, both ramified and compact islands with the width of the order of 10^2 nm can be seen clearly. The apparent Ag coverage of the total area ρ in Figs. 1(a) and 1(b) are (2.7±0.2)% and (2.0±0.2)%, respectively. Our measurement reveals that as the deposition rate f increases, the average width of the islands drops, which is in agreement with the previous finding.[25]

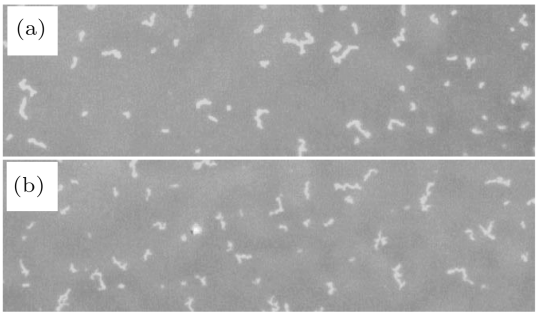


Fig. 1. Typical optical images of the Ag islands on oil surfaces. The deposition rate in panels (a) and (b) are $f = 0.02$ nm/s and $f = 0.10$ nm/s, respectively. Each image has a size of 92.7 μm×26.8 μm. $d = 0.8$ nm, $\Delta t = 3$ h.

Figure 2(a) shows the dependence between the coverage ρ and time t, from which one sees that ρ drops quickly in a few minutes after the samples are removed out from the vacuum chamber. The experimental data in Fig. 2(a) may be well fitted by an equation

$$\rho(t) = A_0 \exp(-t/\tau) + \rho(\infty), \qquad (1)$$

where A_0 is a constant, $\rho(0)$ and $\rho(\infty)$ represent the surface coverage for t=0 and $t \to \infty$, respectively. From Eq. (1) and Fig. 2(a), one reads that the relaxation time constant τ is in the order of 10^2 s. Our further research demonstrates that the decay behaviour

shown in Fig. 2(a) is approximately independent of Δt, indicating that this phenomenon is resulted from the perturbation of the air filling process when the vacuum chamber is opened.

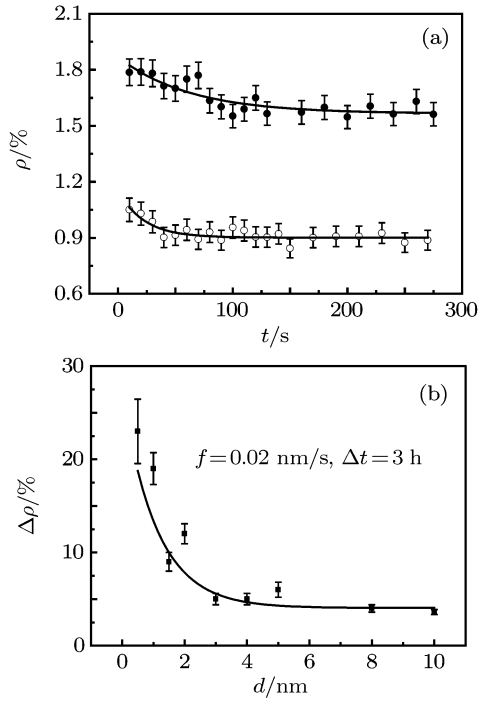


Fig. 2. (a) The apparent Ag coverage of the total area decays with time. $d = 0.5$ nm (open circles), $d = 1.0$ nm (solid circles). The deposition rate is $f = 0.02$ nm/s and $\Delta t = 3$ h. The solid lines are the exponential fits to the experimental data. (b) The amplitude of the coverage decay $\Delta\rho$ as a function of the nominal film thickness d. The solid line is a guide to the eye.

We define the relative coverage decrement $\Delta\rho$

$$\Delta\rho = \frac{|\rho(0) - \rho(\infty)|}{\rho(0)}. \tag{2}$$

Figure 2(b) shows the typical dependence between $\Delta\rho$ and d. One finds that the value of $\Delta\rho$ drops with d from (23.0±3.8)% to (5.0±0.8)% for 0.5 nm $< d <$ 3.0 nm, then it does not change obviously for $d >$ 3.0 nm. The behaviour of $\Delta\rho$ in Fig. 2(b) implies the microstructure evolution process in the islands at room temperature.

Similar decay phenomenon in film thickness and resistivity with time was observed in a copper film system on glass surfaces.[13] However, it should be emphasized that the total relative decrement of in-plane area reads from Fig. 2(b) for $d = 0.5$ nm is $\Delta\rho = (23.0\pm3.8)$ %, while the corresponding value for the copper film in Ref. [13] is around 3.0%. Recently, AFM studies revealed that the material density of the Ag islands on silicone oil surfaces is only 50%–70% to that of the bulk material,[27] therefore the above unexpected result is reasonable.

At the beginning of the deposition process in our experiment, silver atoms are deposited directly on the oil surface. They diffuse and aggregate on the unstable and nonlattice surface and form islands, as shown in Fig. 1. In this case, the liquid substrate effect, i.e., the interaction between the mobile liquid molecules and the deposited atoms, may result in a great number of defects in the Ag islands.[28] As the deposition process is in progress, the coverage ρ goes up gradually and then some of the following deposition atoms may land directly on the preformed islands. Therefore, as d increases, the liquid substrate effect is reduced and the material density of the islands approaches the stable value of the silver bulk, this fact results in the saturation behaviour shown in Fig. 2(b).

During the process of filling the vacuum chamber with air, an air pressure gradient is introduced around the islands. This perturbation provides both the Ag atoms and defects with the energy to migrate in the islands. As a result, in order to reduce the total free energy of the system, the microstructure of the islands is reconstructed in a few minutes at room temperature. In other words, the decay phenomenon shown in Fig. 2(a) gives the information about the evolution process of the average binding energy among the silver atoms in the islands.

It is noted that the behaviour of the coverage ρ, which should be related to the formation mechanism of the islands, is strongly dependent on the deposition rate f. Therefore a series of experiments with $f = 0.02$ nm/s–0.50 nm/s is made, in which $d = 4.0$ nm is fixed, as shown in Fig. 3. It is shown that more than 20% of the total value of ρ is reduced as f increases from 0.05 nm/s to 0.10 nm/s (see Fig. 3(a)) and $\Delta\rho$ drops from about 6.0% to 0 as f increases from 0.02 nm/s to 0.50 nm/s (see Fig. 3(b)).

Simulation study on the island growth reveals that if the kinetic energy of the deposition atoms is large enough and it can overcome the bonding potential between the atoms and the substrate, then the three-dimensional (3D) growth model may be the result for the islands.[29] In our experiment, Ag islands with a flat plate morphology, namely two-dimensional (2D) islands, usually form on the oil surface.[25] It is not difficult to understand that the interfacial bonding between the islands and the liquid substrate is rather weak in comparison with the situation of solid sub-

strates. As f goes up, the total kinetic energy of the deposition atoms and islands increases, then they may overcome the bonding potential to form 3D islands in order to lower the total free energy of the islands, which leads to the decrease of the surface coverage ρ.

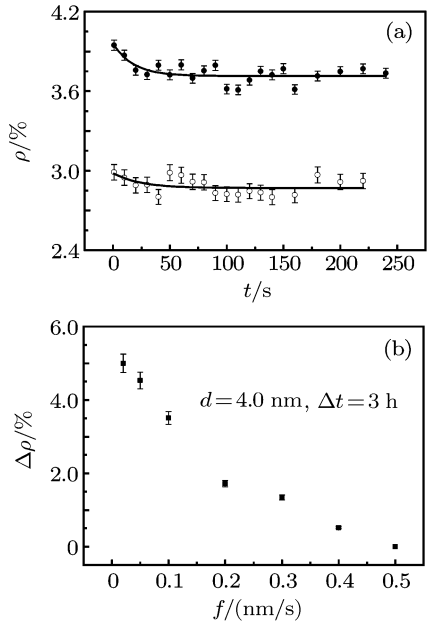


Fig. 3. (a) Time dependence of the apparent Ag coverage of the total area of two samples with different deposition rate. $f = 0.05$ nm/s (solid circles), $f = 0.10$ nm/s (open circles). (b) The dependence between $\Delta\rho$ and f, the nominal thickness is $d = 4.0$ nm and $\Delta t = 3$ h.

During deposition, parts of the deposition atoms land directly on the preformed islands. In this case, the growth model of the islands may also be dominated by the step-crossing diffusion rate with respect to the rates of other kinetic process such as deposition and terrace diffusion.[30] In the Pt/Pt(111) system,[31] for instance, as the substrate temperature is lowered, the kinetic energy of the adatoms is reduced so that they may not be able to jump from upper layer to lower layer, therefore the islands shift their growth model from 2D to 3D. We propose that, as the deposition rate increases, the deposition atoms landing directly on the surface of the preformed islands may not have enough time to diffuse to the edge of the islands before they are captured by the following landing atoms. In other words, the step-crossing diffusion process is suppressed by increasing deposition rate and then a 3D growth manner results. Therefore the total coverage ρ (or the area for each island) is reduced as f increases, which is also in agreement with the previous finding.[25]

The phenomenon shown in Fig. 3(b) gives another explanation for the dependence between f and ρ. As mentioned above, with the increase of f, the possibility for an atom to diffuse to the island edge may be reduced and then the liquid substrate effect, which may result in a great number of defects and then reduce the material density of the islands, may be weakened. That the coverage decrement $\Delta\rho$ decreased gradually with f indicates that the total number of defects in the islands may be reduced and therefore the material density of the islands increases with f, which also results in the decrease of the coverage ρ.

In the following a few hours when the samples are kept in the ambient atmosphere, the Ag islands may change their topological structures gradually. The sequence of the images in Fig. 4(a) shows that a ramified island becomes a more compact one. Figure 5(a) shows that a bar-shaped island evolves gradually and becomes a ring-shaped island. The exact time by taken these images, i.e., capture time, is also shown in Figs. 4 and 5. It should be noted that only 2%–5% of the islands undergo the shape transition which can be obviously detected in our experiment. The random rotation characteristics of the islands can also be observed obviously in both Figs. 4(a) and 5(a).[25]

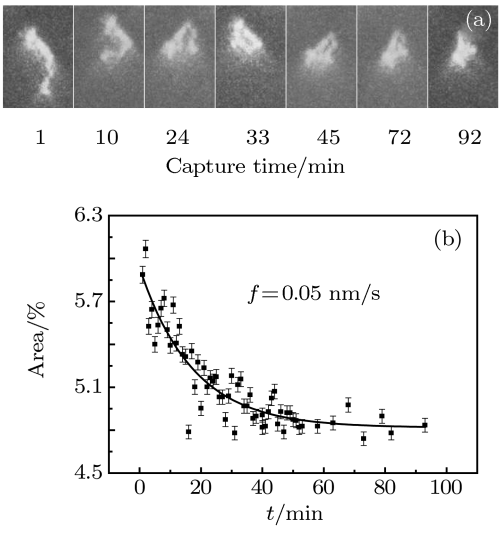


Fig. 4. (a) Sequence of optical microscope images demonstrating the morphology evolution of the island. Each image has a size of 6.5 μm ×9.6 μm; (b) the total area of the island decays with time, $f = 0.05$ nm/s, $d = 0.8$ nm, $\Delta t = 0.5$ h.

It is unexpected that, during the processing shape transition, the total area of each island may change obviously, as shown in Figs. 4(b) and 5(b) and it finally approaches a saturated value, indicating that both the compact and ring-shaped islands are stable structures. We carefully measure the in-plane area of the islands

by a computer programme and the total relative decrements of in-plane areas read from Figs. 4(b) and 5(b) are (20.5±1.6)% and (13.7±1.7)%, respectively. From Figs. 4(b) and 5(b), one also sees that the shape transition generally happens when $t < 60$ min, which suggests that the relaxation time of island microstructure is around one hour. In fact, for $\Delta t > 3$ h or $t > 3$ h, the island shape transition phenomena shown in Figs. 4 and 5 have never been observed on our experimental time scale.

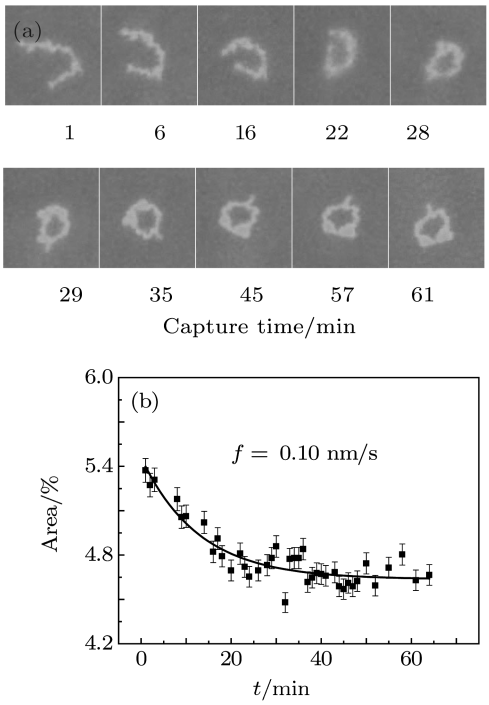


Fig. 5. (a) Sequence of the optical microscope images showing the topological structure evolution of the island, each image has a size of 4.9 μm×6.3 μm; (b) the total area of the island decays with time, $f = 0.10$ nm/s, $d = 0.8$ nm, $\Delta t = 0.5$ h.

In our experiment, the plate-shaped Ag islands form on the oil surface, which is nearly a free standing system.[25] The diffusion manner of the Ag atoms in the islands is proposed to be responsible for the phenomena shown in Figs. 4 and 5. The equilibrium island shape is determined by the total free energy of the island, which can be written as

$$\begin{aligned} E_{\text{total}} &= E_{\text{island}} + E_{\text{surface}} \\ &= \sigma_1 V + \sigma_2 S + \sigma_3 S + \sigma_4 S_{\text{side}}, \end{aligned} \tag{3}$$

where E_{island} is the elastic energy contributed mainly from the residual stress and stored within the island, E_{surface} refers to surface energy contributions from upper surface, down surface and lateral surface of the island, S is the island area measured from the optical image, σ_1, σ_2, σ_3, σ_4, and the island volume V are constants. For a very thin plate-shaped island, S_{side}, the side area of the island, is much smaller than S and then it can be omitted here.[25] Therefore we conclude that, approximately, the total free energy E_{total} is proportional to the island area S.

If an island changes its shape automatically, additional bulk energy ΔE_{island} and surface energy $\Delta E_{\text{surface}}$ are raised. In most cases, $\Delta E_{\text{island}} > 0$ and $\Delta E_{\text{surface}} < 0$. Therefore, in order to minimize the total free energy E_{total}, the final shape of the island is determined by the competition between ΔE_{island} and $\Delta E_{\text{surface}}$. Generally, for $\Delta E_{\text{total}} > 0$, the shape transition of the island may not be detected on the experimental time scale. However, when $\Delta E_{\text{total}} < 0$, the islands become energetically unstable. Then, in order to lower the total free energy, the Ag atoms in the islands may diffuse at room temperature and then the microstructure of the islands is reconstructed, which finally results in the changes of island shape and the decrease of the island area, as shown in Figs. 4(a) and 5(a).

Another two interesting phenomena are observed and described as follows: i) an island may break into several small parts, in this case, the total area of them decreases obviously, as shown in Fig. 6(a). The relative decrement of the total in-plane area read from Fig. 6(a) is (24.3±4.5)%; ii) two islands meet and stick together and form a big one and then a sudden increment of their area is observed (see Fig. 6(b)). The relative increment read from Fig. 6(b) is (22.4±4.6)%.

We attribute the phenomenon in Fig. 6(a) to effect of the free standing substrate. As mentioned above, due to the liquid substrate effect, the material density of the island is small and the interaction among the Ag atoms in the islands is weak in comparison with the case on the solid surfaces. Since the interaction between the Ag islands and the liquid molecules is weak, i.e., the Brownian motion is random and inhomogeneous, so it is possible that some islands deform and then break into several small parts. In this process, the microstructure of the islands near the broken sections may be reconstructed in order to minimize the total free energy, which results in the decrease of the island area.

All the experimental results show that the total area increases obviously when two islands meet and stick together, as shown in Fig. 6(b). This unexpected result is quite confusing to the authors. However, several possibilities can still be proposed below: a) it has

been shown that,[25] when two compact islands meet, they stick together but not coalesce. In fact, a close look shows that a gap area with the width around the order of 10^{-7} m–10^{-8} m between two stick islands may be detected sometimes. However, in most cases, the gap areas may not be resolved by our optical microscope; b) the detailed microstructure and material distribution near the connection between two stick islands are unpredictable and it is beyond the limitation of the optical microscope; c) parts of the islands under the oil surface and the silver atoms combined physically with the oil molecules could not be captured by our optical microscope. Therefore, further study on the microstructure of the island edges is still needed.

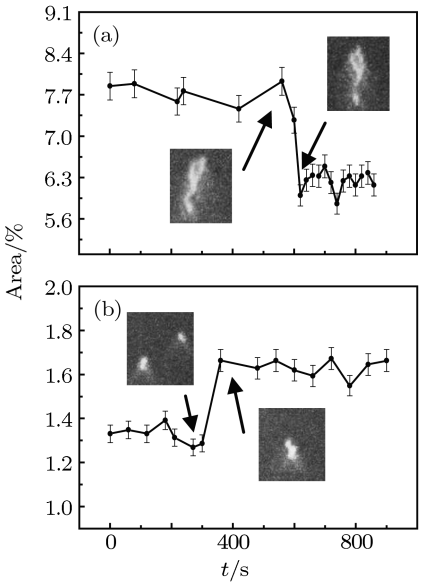


Fig. 6. (a) Area decrement when an island breaks and becomes two small pieces; (b) area increment when two compact islands meet and stick. The sizes of the insets in panels (a) and (b) are 5.6 μm×6.3 μm and 7.1 μm×7.6 μm, respectively. The deposition condition for panels (a) and (b) is $f = 0.05$ nm/s, $d = 0.8$ nm, $\Delta t = 0.5$ h.

4. Conclusions

In conclusion, we have investigated the morphology evolution of the silver islands on silicone oil surfaces. As soon as the samples are moved out from the vacuum chamber, the apparent Ag coverage of the total area decays with time in a few minutes due to the diffusion of the atoms and the combination of the defects inside the islands. The coverage decay $\Delta\rho$ decreases gradually with f and d, which is related to the liquid substrate effect. In the following few hours, as the sample is kept in the ambient atmosphere, the morphology of the islands changes and the area of the islands decreases obviously. These phenomena are also resulted from both the diffusion of the atoms and the combination of the defects inside the islands. The above phenomena mirror the evolution of both the microstructure in the islands and the average binding energy among the Ag atoms in the islands. Another interesting phenomenon is that, if an island breaks and becomes two small pieces, the total area decreases obviously; however, when two islands meet and stick together, a sudden increment of their area is measured, which we attribute to the behaviours of the atoms near the connection between the islands.

Due to the diffusion coefficient of the atoms and islands on the oil surface,[25] it is difficult to trace exactly the microstructure evolution of the islands on oil surfaces with advanced facilities such as XRD, transmission electron microscopy and high resolution electron microscope. For our samples, the islands are approximately composed of 10^{10} or more atoms, which prevents us from studying the system by computer simulations efficiently. By measuring the time dependence of the surface coverage of the islands, we have detected the microstructure evolution of the islands on the liquid substrate successfully. However, further effort on improving the precision of the measurement is still needed.

In our experiment, it is found that the material density of the islands can be easily controlled by adjusting the deposition conditions (e.g., d and f). Therefore, such a kind of island has potential applications on the electronic components. On the other hand, we find that the microstructures of the islands with compact and ring shapes are quite stable, as shown in Figs. 4 and 5, indicating that using the new nanostructures as nanoscopic devices in future is possible.

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