PHYSICAL REVIEW E VOLUME 50, NUMBER 1 JULY 1994

Electrodeposition of a two-dimensional silver dendritic crystal under Langmuir monolayers

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(Received 7 July 1993; revised manuscript received 28 December 1993)

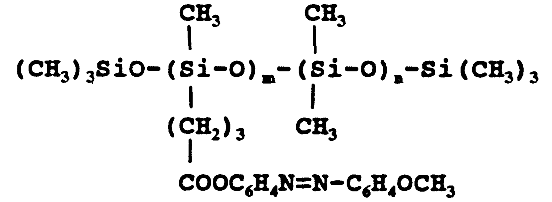
Two-dimensional silver films, which grew along Langmuir monolayers, were obtained by electrodeposition. A transition from a dense morphology to a dendritic crystal is found when the applied voltage through the cell was reduced rapidly from a higher value (2–3 V) to a lower one (0.4–0.6 V). The morphology of the dendritic crystal is related to the surface pressure of the Langmuir monolayer and the difference of the applied voltage.

PACS number(s): 61.50.Cj, 68.70.+w, 05.70.Ln

Electrodeposition of metal aggregations has been widely studied in the past ten years [1–8]. These investigations were triggered by the introduction of fractal theory [9], especially by the proposition of the diffusion-limited aggregation (DLA) model [10].

Recently, some experimental results in the diffusion-limited aggregation indicate that there are several qualitatively different growth morphologies: DLA-like, homogeneous, and dendritic crystal, which can be observed by changing the parameters (concentration and applied voltage) [2,3]. To grow first at one overpotential and then continue at a lower overpotential, Hibbert and Melrose have found a distinct change in microstructure from irregular to dendritic microcrystalline from high to low potential, respectively [11]. With the development of the Langmuir technique, some authors [12] used a kind of organic material to form a Langmuir monolayer on the solution's surface and have deposited two-dimensional silver films along the monolayer. In this article, we report some observations of the growth of dendritic silver at an interface defined by a Langmuir monolayer. We also apply the tactic of switching down the growth voltage, which has been used in Ref. [11], and we have generated a more open growth on top of a denser deposit.

Our electrodeposition cell consists of a silver ring anode 9 cm in diameter set into a taper vessel with 0.2 mm exposed above the surface. Aqueous silver nitrate ($0.001M$, $p\mathrm{H}=7$) is poured into the reservoir. The cathode and growth site is a fine silver with a tip of 0.2 mm, held upright at the center of the anode ring by a micromanipulator which controls the vertical movement of the tip. Using the Langmuir technique, a polymer liquid crystal solution (PLC, $0.001M$, dissolved in chloroform)



$$(CH_3)_3SiO-(\underset{\underset{COOC_6H_4N=N-C_6H_4OCH_3}{|}}{\underset{(CH_2)_3}{\underset{|}{\overset{\overset{CH_3}{|}}{Si}}}}-O)_m-(\underset{\underset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Si}}-O)_n-Si(CH_3)_3$$

is injected into the clean aqueous surface to form an ordered monolayer. The surface pressure (SP) of a Langmuir monolayer can be controlled by injecting different amounts of PLC solution (shown in Fig. 1). We can see from Fig. 1 that the surface pressure is limited to around 7.0 dyn/cm because the diffuse force of PLC is limited and the domain will appear on the surface if more than 30-μl PLC solution was injected into the solution. A larger surface pressure (10 dyn/cm, for example) can be obtained by lowering the level of solution in the vessel, which makes the surface area decrease. As soon as the cathode needle is just on the monolayer, a voltage is applied across the vessel and silver ions migrate along the monolayer to the central cathode silver needle where they accrete. To obtain two-dimensional silver deposit, we find that the surface pressure larger than 0.2 dyn/cm is needed and the vessel is Ohmic by measuring the I-V characteristic.

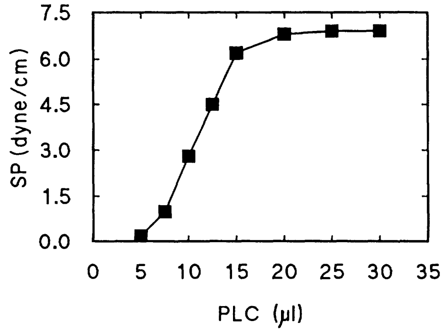


FIG. 1. Surface pressure against the amount of PLC.

Although two-dimensional silver films can be obtained within a certain scale of applied voltage (1–3 V), dendritic crystals will grow at the boundary of dense silver film when the applied voltage decreases rapidly from a higher value to a lower one. By changing the SP and the difference of the applied voltage (ΔV), three different kinds of dendritic growth were observed (shown in Figs. 3–5).

In Ref. [13], a transition boundary of silver film was observed when a constant current was applied. To study the role of the transition boundary of silver film, we first deposit under a lower applied voltage and find that no transition happens in the growth of the silver film boundary. Figure 2 shows the pattern of the growth. The surface pressure of PLC is about 2.8 dyn/cm and the applied voltage is 0.4 V. Although the growth velocity decreased with the increase of the SP, the silver film can grow larger and thicker along the PLC monolayer. Why can

FIG. 2. Growth pattern under a low voltage deposit.

silver ions be deposited two dimensionally along the interface of a Langmuir monolayer? We believe that it is because there is a negatively charged monolayer, which forms a thin layer of higher concentration and conductance than in the bulk solution layer of silver ions.

In spite of the fact that silver film deposits in a thickness about 200 μm below the Langmuir film, the main growth is still along the radial of the monolayer. The potential under the deposited thin film was somewhat screened, which makes the growth under the film limited. For deposition below the Langmuir monolayer, the PLC and silver crystals both are induced to grow by the monolayer. These formations are attracted to each other by Coulomb electrostatic force, which prevents them from sedimenting.

At a higher applied voltage (1.5 V for instance), silver ions deposit and grow larger in two dimensions with dense morphology for a few minutes. At this time we rapidly (in less than 2 sec) reduce the applied voltage to a lower one (0.6 V for instance). Many dendrite crystals then grow outside the boundary of the silver dense film [shown in Fig. 3(a)]. The dendrite's morphology can be related to the changes of ΔV and the surface pressure.

When the change of the applied voltage ΔV is small (0.9 V) and the SP is high (10 dyn/cm), the pattern of the dendritic crystal is a high degree ordered with a low frequency of side branches. The angles between the side branches and the main branch are about 60° [shown in Fig. 3(b)].

When the voltage changes ΔV is large (1.7 V) with a middle SP (5.6 dyn/cm), the regularity of the dendritic crystal decreases, more side branches appear, and the angle of them to the main branch varies over a large scale. The growth branches are curved (shown in Fig. 4).

At a lower SP (2.8 dyn/cm) and middle ΔV (1.1 V) the main branches are winding and have a high frequency of side branches (shown in Fig. 5). Figure 6 shows the curve of measured current against time through the first growth of high voltage (2.1 V) and then down to a lower one (0.4 V). It is clear that after lowering down to a new voltage there is a steep drop in current over a period of 2 sec, followed by a steady decline and leveling off. The current eventually rises again after a few seconds.

The growth velocity of dense silver films was tested with different SP monolayers at a constant applied voltage. Figure 7 gives the curve of growth velocity against SP and the applied voltage. We find that the velocity of the growth decreases as the SP increases; this means the mobility of the silver ions within the layer decreases with the density of the Langmuir layer, perhaps because the ions are more tightly bound to the Langmuir layer. If the SP is too small (less than 0.2 dyn/cm) we cannot obtain a steady two-dimensional deposition. So there exists a largest velocity growth (shown in Fig. 7). The growth velocities of the dendrite crystal outside the silver films shown in Figs. 1–3 are about 3.4 μm/min (SP = 10 dyn/cm), 6.2 μm/min (SP = 6.8 dyn/cm), and 8.4 μm/min (SP = 2.8 dyn/cm), respectively. We conjecture that the morphology of the dendritic crystal may be related to the velocity of the growth.

A kinetic theory of electrochemical deposition indicates that the growth of dendritic crystal results from the difficulty of the transmission of metal ions [14]. The transmission of metal ions is difficult due both to the low voltage after it has been reduced and the resistance of the monolayer. Silver film grows first at a higher voltage, the current through the vessel increases almost linearly in time, and silver ions drift to the cathode where they are deposited. The silver film continues to grow until the voltage is changed. When the voltage is reduced rapidly, the drift velocity of the silver ions is slower and diffusive transport may become significant. The film boundary is uneven and a spherical surface diffuse field will exist in the protruding part. The Mullins-Sekerka instability [15] may play an important role at this time and protrusions into the diffuse field will grow faster. But as the tip of a dendrite crystal becomes needlelike, the surface energy and surface kinetics may also be important. As shown in Figs. 4(b) and 5(b), the higher the growth velocity, the smaller the radius of curvature of the tips. It may be that

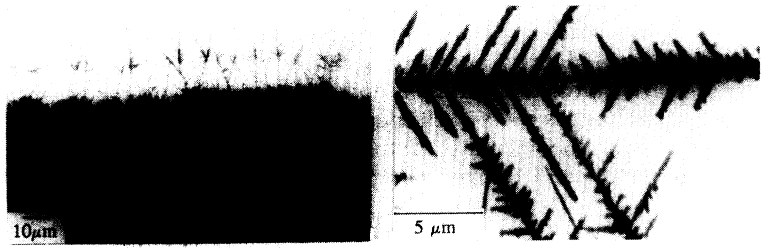


FIG. 3. Two-dimensional ordered dendritic growth outside the dense silver film. (a) The applied voltage is reduced from 1.5 to 0.6 V, SP = 10 dyn/cm, grown in 10 min. (b) Magnification of the ordered dendritic crystal pattern in Fig. 1(a).

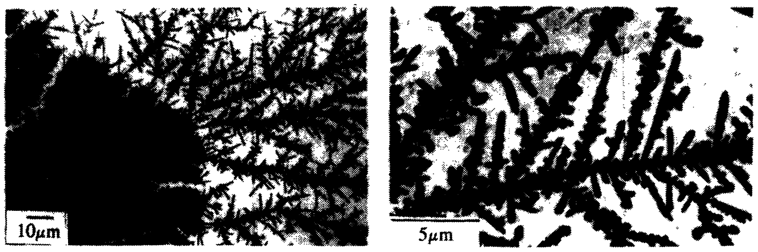


FIG. 4. Disordered dendritic pattern surrounding dense silver film. (a) The same as Fig. 1(a), except that the applied voltage is reduced from 2.1 to 0.4 V, SP=6.8 dyn/cm, grown in 90 min. (b) Magnification of Fig. 2(a).

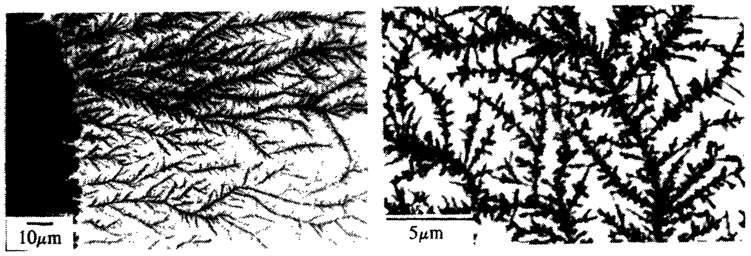


FIG. 5. Ramified dendritic crystal pattern growth. (a) The same as Fig. 1 except that the applied voltage is reduced from 1.5 to 0.4 V, SP=2.8 dyn/cm, grown in 20 min. (b) Magnification of (a).

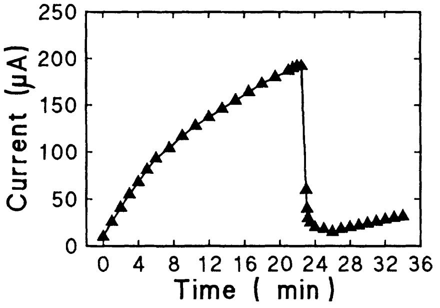


FIG. 6. Current against time, for the growth at 2.1 to 0.4 V, of Fig. 4.

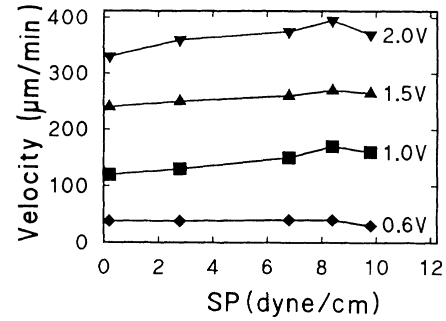


FIG. 7. The curve of growth velocity vs the SP at different applied voltage.

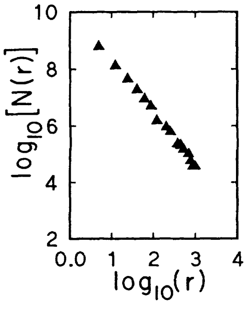


FIG. 8. A plot of $\log_{10}[N(r)]$ against $\log_{10}(r)$ for the pattern of Fig. 5(b).

to grow at the largest velocity an optimum radius of curvature is selected. Although an extensive study of the role of anion migration is reported in Refs. [6] and [11], we suspect the cation transmission is important in our system.

This kind of silver deposition is a nonequilibrium growth. The microstructure of the dendritic crystal morphology is effected strongly by the characteristics of the PLC Langmuir monolayer. With a large SP, a dense ordered monolayer of PLC can be obtained and the anisotropy of the Langmuir film is strong and stable on the solution's surface. An ordered dendritic crystal can grow along such a film. With a lower SP, the Langmuir film on the surface is not in dense structure and will move on the surface with the growth. At this time the dendritic crystal will grow curvedly with the moving of the Langmuir film, which makes their pattern more ramified.

Compared with the ordered dendritic crystal shown in Fig. 3(b), the morphology of the dendritic crystal in Figs. 4(b) and 5(b) is disordered. We analyzed these disordered patterns by digitization with a resolution of 250×170 pixels. The fractal dimensions were measured by dividing the pattern into boxes of size r, and then counting the number of boxes $N(r)$ containing occupied pixels as a function of r. Taking the best-fit slope of $\log_{10}[N(r)]$ vs $\log_{10}(r)$, we measured the fractal dimension of $D=1.83\pm0.03$ in Fig. 4(b) (shown in Fig. 8) and $D=1.66\pm0.03$ in Fig. 5(b). Why is the fractal dimension in Fig. 4(b) larger than that in Fig. 5(b)? We can consider it as follows. In a same scale length, the dendritic crystals in Fig. 4(b) are thicker than those in Fig. 5(b), which results in its fractal dimension increasing nearly to 2. Conversely, because the surface pressure for the growth pattern Fig. 5(b) is lower, the growth does not form on a dense ordered PLC monolayer; this makes the growth pattern more ramified.

In conclusion, dendritic crystals can grow at the boundary of a dense silver film as the applied voltage is reduced rapidly. Under different SP of Langmuir monolayers, silver aggregations with ordered, disordered, and ramified morphologies can be obtained. The patterns of disordered and ramified dendritic crystal are fractal. To understand this kind of transition clearly, the growth kinetic course should be studied in further experiments. Instead of using a box counting fractal dimension, multifractal theory is needed to explain the kinetic course of the growth.

The authors acknowledge Y. M. Zhu and G. J. Jing for discussions and the Department of Chemisty, Wuhan University, for supplying the polymer liquid crystal. This work was supported in part by the National Natural Science Foundation of China through Grant No. 9689010.

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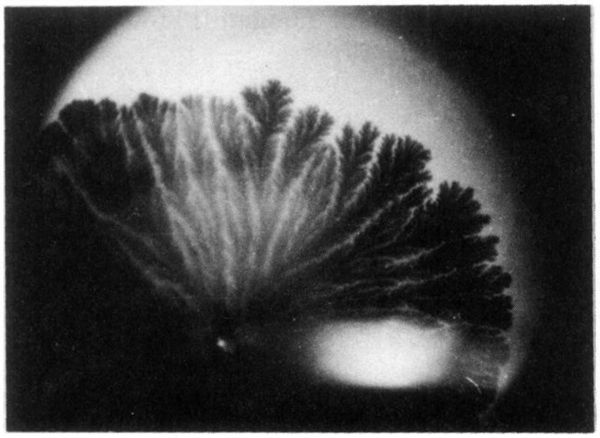
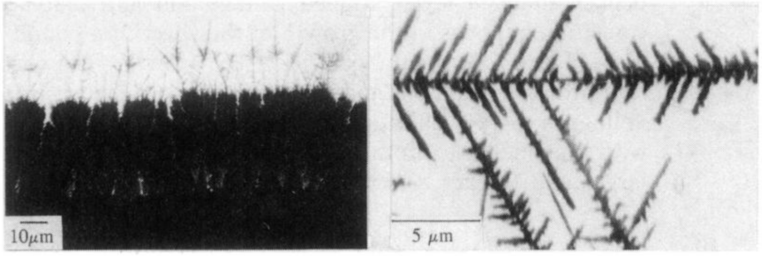


FIG. 2. Growth pattern under a low voltage deposit.



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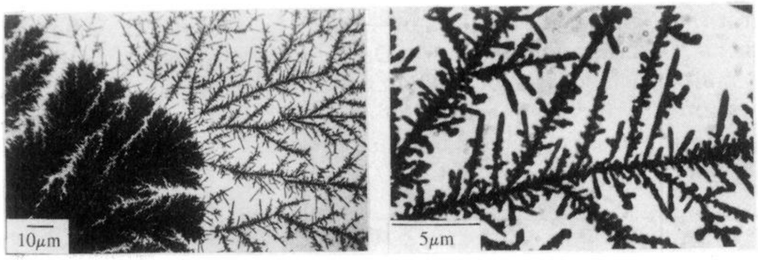

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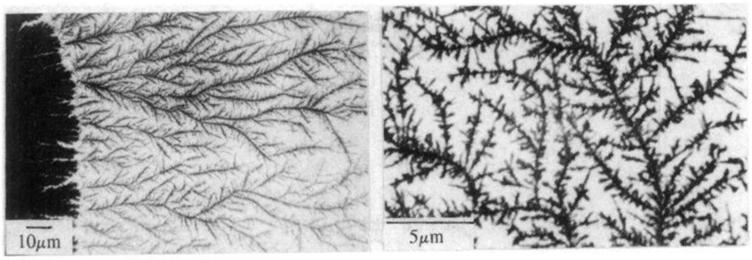

FIG. 5. Ramified dendritic crystal pattern growth. (a) The same as Fig. 1 except that the applied voltage is reduced from 1.5 to 0.4 V, SP=2.8 dyn/cm, grown in 20 min. (b) Magnification of (a).