Alternating Morphology Transitions in Electrochemical Deposition

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Alternating morphology transitions between dendrite and dense-branching morphology have been studied for the first time in electrochemical deposition of $FeSO_4$ aqueous solution film. We suggest that the observed alternating transition is caused by the interchange of anisotropy in interfacial growth, which arises from the periodic accumulation and depletion of impurities in front of the growing interface in our experimental system. The selection problem in pattern formation is discussed.

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Pattern formation and pattern selection in nonequilibrium growth has been a fascinating problem for a long time and has received considerable attention recently [1–3]. It has been demonstrated that anisotropy in either surface tension or growth kinetics is required to produce stable tip behavior in dendritic growth [4]. In the absence of sufficient anisotropy, tip splitting dominates interfacial growth and a dense-branching morphology (DBM) will be formed. In the electrodeposition of $CuSO_4$ aqueous solution, the deposit usually possesses DBM, which has no evident main stem and consists of random tiny crystals [5]. In this case, it is suggested that additional kinetic effects may be involved and lead to a reduction of the effective anisotropy [2]. In a $ZnSO_4$ aqueous solution system, however, a dendritic pattern with a well defined main trunk on the scale of several tens of microns to even several centimeters can be observed [6,7], which may be ascribed to the influence of higher material anisotropy of zinc, or a kinetic mechanism on the growing interface which causes long-range crystalline order [8]. However, because of the complexity of the electrodeposition system, the pattern formation therein is still far from being fully understood. Up to now, several efforts have been made to study the relations between the morphology and the growth conditions near the growing interface [9,10]. It has been found recently that growth morphology is very sensitive to impurities [9,11], which may influence surface tension, increase the nucleation rate, or change the effective anisotropy on the boundary. With this background, we suggest that during dendritic growth, if interfacial dynamics is periodically modulated for some reason, and hence local anisotropy is changing accordingly, then periodic morphology transitions between dendrite and DBM may be observed. In this Letter, we present our experimental findings of the alternating morphology transitions between dendrite and DBM in electrochemical deposition in $FeSO_2$ aqueous solution film.

An *in situ* observation technique is employed to study the alternating morphology transitions. The cell for electrochemical deposition consists of two closely spaced glass microscope slides, sandwiching a layer of $FeSO_4$ aqueous

solution. The thickness of the solution film is controlled by mica spacers. The spacer thickness varies from 10 to 100 μm. Two straight parallel electrodes, which are made of iron with a purity of 99.997% (anode) and a pencil core with rectangular cross section (cathode), are fixed on the bottom slide 22 mm apart. The detail structure of the growth cell is the same as that reported previously [7]. Analytical grade $FeSO_4$ is used and the concentration of the electrolyte solution is 0.5 mol/l. During deposit growth the voltage across the two electrodes is fixed at 4.00 ± 0.01 V (the voltage should not be high, otherwise too many hydrogen bubbles will be generated and the growth will be hindered). The electrodeposition is performed at room temperature ($\sim 20\,°C$). The growing process of the deposits is observed under a microscope (Leitz, Orthoplan-pol) and recorded by either a microscope-matched video system or a camera.

The observed alternating morphology transitions are shown in Fig. 1. By a dendritic pattern we mean a branch with a central trunk decorated with side branches. As the dendrite grows, its tip retains integrity. The DBM, however, grows in a tip-splitting way and usually
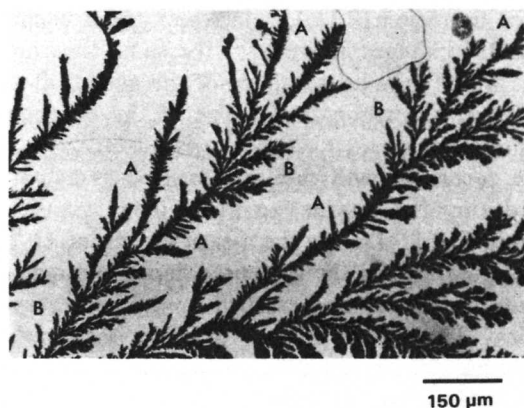

150 μm

FIG. 1. The alternating morphology transitions observed in our system, in which dendrite and DBM regimes are labeled A and B, respectively. On the upper right corner of the figure, a hydrogen bubble hinders the dendrite growth.
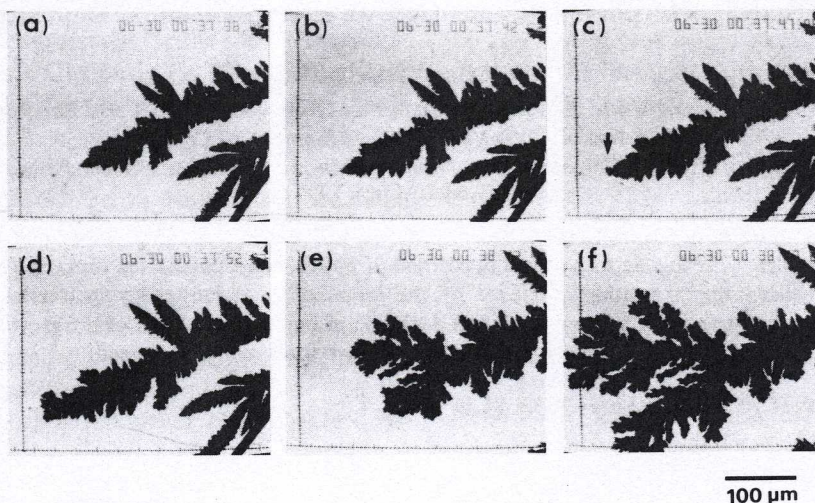
100 µm

FIG. 2. Snapshots to show morphology transition from a dendrite to a dense-branching morphology. The tip splitting is responsible for the transition, as indicated by the arrow in (c). Meanwhile, the thickness of the solution film is ~50 µm, the initial concentration of the $FeSO_4$ solution is 0.5 mol/l, and the voltage across the two electrodes is 4 V and kept constant during the whole process. The last three figures in the time scale on the upper-right corner of each picture represent a minute, a second, and $\frac{1}{100}$ second, respectively.

does not maintain a main stem. In Fig. 1 the morphologies of dendrite and DBM are labeled A and B, respectively. One can find that dendrite and DBM appear alternatingly on the deposit branches. The pattern transitions have a typical scale in the range 100–200 µm. Figure 2 illustrates the pattern transition process from dendrite to DBM. At first, the morphology of the deposit is dendritic [Figs. 2(a) and 2(b)], then, as indicated by the arrow in Fig. 2(c), the tip begins to split. Just before the tip of the dendrite splits, the growth rate of the dendrite drops sharply. Thereafter, the deposit grows in a tip-splitting way and a DBM is formed [Figs. 2(d)–2(f)]. In situ observations indicate that the morphologies appearing on the neighboring branches are independent; i.e., when a branch is growing in dendritic form, the neighboring branches may be growing in DBM concurrrently. This character is different from the previously reported Hecker transition [9,11,12], in which the branching rate of a DBM changes abruptly at the same time on an envelope which mimics the shape of the anode. Besides, in the Hecker transition the change of the branching rate does not alternate.

The deposit growth rate is measured as a function of time during the alternating morphology transitions, as shown in Fig. 3. During the measurement, no H_2 bubbles are detected around the measured deposit branch. So the measurements are not disturbed by the generation of H_2 bubbles. The growth rate of a DBM is defined as the average envelope moving rate. One can find that dendrite grows faster than DBM under the same applied voltage, and there are steplike jumps in the growth rate corresponding to the morphology transitions. Just before the morphology varies from dendrite to DBM, the deposit growth rate decreases sharply, then it increases, with the

tip split and the morphology changed. During DBM growth, if one or several tips grow faster than the others, for a reason that will be discussed later, the most outward tip(s) will develop into dendrite(s). The second growth rate jump in Fig. 3 (as indicated by the arrow) corresponds to a DBM → dendrite transition.

In our thin film deposition system, we take the deposits as two dimensional. Meanwhile, deposit growth can be characterized by either the envelope growth rate, or the deposit area increasing rate on a single branch. Corresponding to the first morphology transition (dendrite → DBM) in Fig. 3, the average increasing rate of deposit area of a single branch, $\Delta S/\Delta t$, is measured as a function of time by image processing (Fig. 4). Δt is chosen to be 3 s. Figure 4 indicates that $\Delta S/\Delta t$ is almost a constant be-
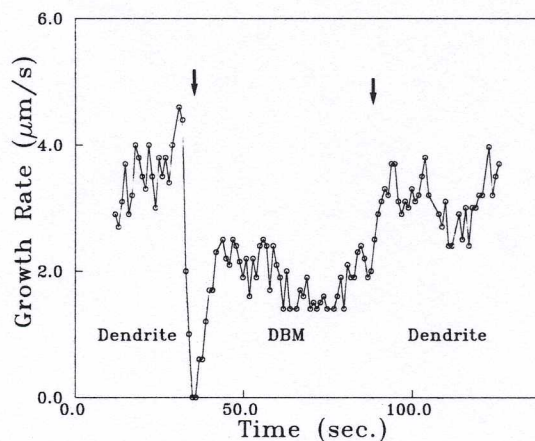

FIG. 3. The interfacial growth rate measured as a function of time during the morphology transitions. The arrows indicate the positions where a morphology transition occurs.
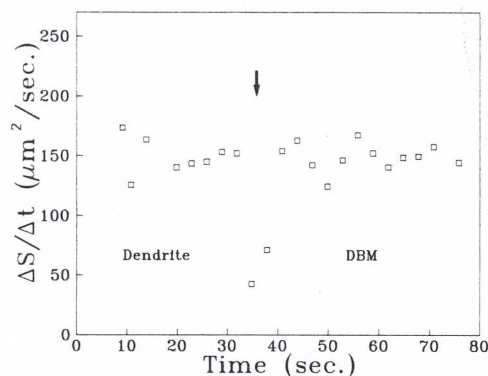
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FIG. 4. The average deposit area increasing rate of a single branch, $\Delta S/\Delta t$, measured as a function of time during the morphology transition from dendrite to DBM. The transition process corresponds to the first arrow in Fig. 3. One can find that although there is a steplike jump in envelope growth rate, $\Delta S/\Delta t$ is almost a constant before and after the transition.

fore and after the morphology transition. Because the thickness of the growth cell is fixed and homogeneous, $\Delta S/\Delta t$ is actually proportional to the mass deposition rate onto a single branch. So, Fig. 4 implies that the mass deposition rate is almost a constant, although both growth morphology and interfacial growth rate vary evidently.

In an electrodeposition system, macroscopic interfacial dynamics and macroscopic electric field and diffusion field are the competing components which decide the growth morphology. When electrodeposition begins, all cations are driven towards the cathode by the electric field. However, a higher Fe^{2+} concentration lets the deposition rate of Fe^{2+} be much higher than that of impurities, so impurities are gradually accumulated near the growing interface. At the very beginning of electrodeposition, impurity concentration in front of the growing interface is low; the material anisotropy of iron is strong enough to maintain dendritic growth. As the dendrite grows, the concentration of impurities increases gradually, which may have two effects. One is that a layer of concentrated impurity ions around the growing interface may influence growth dynamics by decreasing the interfacial anisotropy. The possible mechanism might be that the random deposition of impurities on the growing interface decreases the local nucleation barrier. The second effect is that the accumulated impurities generate a screen layer, which hinders Fe^{2+} from depositing on the cathode. So the interfacial growth rate will decrease. The decrease of both interfacial anisotropy and the growth rate may be responsible for the transition of deposit morphology from dendrite to DBM (Fig. 2). Actually, according to the microscopic solvability theory, dendritic growth will not be stable when the growth lacks sufficient anisotropy [2,4]. The theory also suggests that the selected stable dendritic pattern is the one with the largest growth rate. If the tip velocity is decreased, there

might be a morphology transition from a dendrite to a DBM [13]. In our experiments, as DBM grows forward, the larger active growing interface consumes more impurities (meanwhile, the impurity deposition rate becomes higher because of the higher local impurity concentration). As a result, the local impurity concentration is decreased and the screen layer is weakened. When the concentration of the impurity becomes lower than a certain threshold, we suppose impurity deposition will become negligible. Meanwhile, the effective anisotropy on interfacial growth will enhance again. The higher anisotropy, together with the influence of diffusive instability (Mullins-Sekerka instability), which encourages the growth of the most outward tip, will eventually regenerate a dendritic pattern out from the DBM. Thereafter, as the dendrite grows forward, impurities in front of the dendrite tip will accumulate again, so the process described above will repeat. Our studies show that the impurities in our system are quite possibly H^+ in an aqueous solution of $FeSO_4$ [14]. In a $FeSO_4$ aqueous solution there is an abundance of H^+. Actually, if the concentration of H^+ in front of the growing interface exceeds a certain value, sudden nucleation and growth of the H_2 bubble can be observed. In this case, the growth of the deposit branch will soon be blocked. Therefore, we suggest that the alternating accumulation and depletion of H^+ near the growing interface change the anisotropy on the growing interface alternatingly, so the growth morphology is changed accordingly.

So far, great progress has been achieved in understanding the pattern selection problem. The microscopic solvability criterion indicates that the selected dendrite (needle crystal) should be the one with the largest growth rate, which is stable against the diffusive instability. Furthermore, Ben-Jacob et al. proposed that the dynamically selected morphology is the fastest growing one [3,15]. That is, if more than one morphology is possible, only the fastest growing one is nonlinearly stable and can be observed (no matter whether it is a dendrite or a DBM). In our experiment, we find that DBM and dendrites coexist and can be observed on the same deposit branch alternatingly; the growth rate of a dendrite is higher than that of a DBM. Moreover, it is noteworthy that a DBM has a larger growing interface (longer growing boundary in the two-dimensional case) than a dendrite. Although DBM grows slower than a dendrite under the same applied voltage, the average increasing rate of deposit area is almost the same before and after the morphology transition. This means that there might exist a constant mass deposition rate corresponding to specific growth conditions, which is possibly governed by both the diffusion field and the electric field. Meanwhile, if the active growing boundary is long (the case of DBM growth), the envelope growth rate will be slow; in dendritic growth, the active growing boundary is relatively short (far from the tip, the growth rate is negligible because of the screen effect in

diffusion field), then the growth rate of the dendrite tip will be higher. The evidence has been found that the growth rate of a deposit adjusts itself according to the branch density [11]. It should be mentioned that in previous studies of the pattern selection problem more attention was paid to the interfacial growth rate. However, the observed phenomena in our experiment imply that the growth rate seems not a perfect parameter to describe the selection process. If we only consider the main stem growth of a dendrite, because the shape of the main stem usually remains the same, a one-dimensional growth rate is sufficient to describe the interfacial movement [2]. However, if dense-branching morphology is involved, the interfacial growth rate is no longer the same over the entire interface. Meanwhile, a one-dimensional growth rate is not sufficient to describe DBM growth and the transition process between dendrite and DBM. There should be a parameter which gives out more information than a one-dimensional growth rate does. According to our experimental results, we suggest that the previously proposed "fastest growth rate" selection role [3] might be a one-dimensional approximation of a more general one, say, the "largest mass deposition rate" selection role. That is, if more than one morphology is possible, only the one with the largest mass deposition rate is stable and can be observed; if more than one morphology possesses this highest mass deposition rate, then these morphologies may coexist. Meanwhile, the microscopic growth dynamics plays the decisive role of selecting specific morphology. On the other hand, it is possible to relate the mass deposition rate to the entropy production rate. In this way, a more general thermodynamic principle underlying morphology transitions may be reflected. However, direct evidence of such a "largest mass deposition rate" should be found before a conclusion can be made.

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[14] We intentionally add drops of diluted H_2SO_4 into the 0.5 mol/l $FeSO_4$ solution, to a final $pH \sim 2.50$. We carry out electrodeposition in this acidified solution. Although more H_2 bubbles are generated and hence deposit growth is easily disturbed, we are still able to study the morphology of the deposit branch during the time between the generation of two bubbles. We find that the growth morphology of the deposit is DBM (tip splitting occurs frequently). A dendrite with an evident main stem cannot be observed in the early stage of electrodeposition. Besides, we also dilute the $FeSO_4$ solution from $0.5M$ to $0.06M$ (meanwhile H^+ concentration is decreased); then dendrites become the dominant morphology and no evident dendrite-DBM transitions have been found. However, if drops of diluted H_2SO_4 solution are added (pH value decreases from 3.32 to about 2.50), then the growth morphology changes to DBM evidently. If we let the DBM deposit grow continuously, several minutes later we find the growth morphology changes back to dendrite again, and alternating dendrite-DBM transitions can also be seen. Meanwhile, the average pH value of the electrolyte solution in the cell is checked. We find that it has increased to about 4.0. The increasing of the pH value is ascribed to the consumption of H^+ by DBM growth and H_2 generation. The above phenomena suggest that H^+ may be the major impurity to influence the growth morphology. The detailed effects of H^+ on pattern formation in electrodeposition will be discussed separately.

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