Surface and Interface Analysis

Self-organization of periodically structured single-crystalline zinc branches by electrodeposition

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We report here the electrodeposition of periodically structured single-crystalline zinc branches from an ultrathin aqueous electrolyte layer of $ZnSO_4$. The main trunk and side branches of electrodeposits are regularly angled, and each branch is made of periodic bead-like structures. Layered morphology has been observed on each bead. During electrodeposition, spontaneous oscillation of electric current occurs when constant voltage is applied across the electrodes, and the oscillation leads to periodic patterns on deposit branches. According to electron diffraction of transmission electron microscopy (TEM), the whole branch of electrodeposits has the same crystallographic orientation despite the fact that the branch looks like an assembly of beads. We interpret this unique growth behavior to the epitaxial nucleation in the transport-limited growth system. Copyright © 2006 John Wiley & Sons, Ltd.

INTRODUCTION

Pattern formation in electrochemical deposition has been studied for many years. Among the many studies, spatiotemporal oscillation in electrodeposition is of particular interest. It has been observed that the electric current/voltage may spontaneously oscillate during electrodeposition of zinc.[1–8] It was suggested that such oscillation is due to repeated charge accumulation and dielectric breakdown in the double layer on the electrode–electrolyte interface.[1] We once reported the correlation between the oscillating concentration field in front of the zinc electrodeposits and the oscillation of electric current/voltage,[4] and proposed a different explanation to the origin of oscillation. We suggested that the oscillatory growth of zinc electrodeposits is due to the competition of mass transfer and nonlinear interfacial growth kinetics.[4] It is known that the material anisotropy of zinc is strong and two-dimensional (2D) nucleation followed by layered growth is the favored interfacial growth mode. For 2D nucleation there exists a critical concentration, which corresponds to the 2D nucleation barrier. Only when the concentration becomes higher than the critical value the nucleation process can take place. Yet, in the thin film electrodeposition system, mass transfer is confined by the thickness of the

electrolyte solution film. For this reason the drop in concentration in front of the growing interface, which is induced by interfacial growth, cannot recover immediately. Hence the nucleation stops until the local concentration becomes sufficiently high. Therefore the electrodeposition process is intermittent. We should point out that the combination of limited mass transfer and nonlinear nucleation process is not the only mechanism that may trigger oscillatory growth. Very recently we demonstrated a unique oscillatory electrodeposition in an aqueous solution film of $CuSO_4$ just a few hundreds of nanometers in thickness.[9–12] In that unique ultrathin electrodeposition system, spontaneously generated Cu_2O played the role to stop the continuous electrodeposition process. So an unexpected spontaneous oscillation of electric current/voltage occurred and periodic nanostructures of Cu/Cu_2O were generated on the deposit filaments. It is noteworthy that in the copper electrodeposition the deposit branches are usually polycrystalline, and there is no strong correlation among crystallites in deposit branches. The material anisotropy of copper is also small. For the electrodeposition of zinc, however, the situation is different. It would be interesting to investigate what will happen to the deposits if electrodeposition of zinc is carried out in a similar ultrathin film system.

We report in this article a unique long-range ordering effect observed in electrocrystallization of zinc from an ultrathin layer of aqueous electrolyte of $ZnSO_4$. The deposition branches are regularly angled and consist of periodic bead-like structures. A layered pattern has been observed on each bead. Spontaneous oscillation of electric current/voltage occurs when a constant voltage/current is applied across the electrodes, which corresponds to the

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generation of periodic patterns on the deposit branches. Further, transmission electron microscopy (TEM) indicates that the crystallographic orientation of each bead is identical. On the basis of experimental observations, we interpret this unusual growth behavior to a model of epitaxial nucleation in a transport-limited growth system (for interfacial growth, mass transfer from ambient to growth site can be controlled by diffusion, convection, and electric migration. For this reason, previously known diffusion-limited growth[13,14] can be extended to transport-limited growth where the way of mass transfer is not restricted to diffusion).

EXPERIMENTAL METHOD AND RESULTS

Electrodeposition of zinc was carried out in a cell made of two cleaned glass plates. The anode was made of pure zinc wire (99.9%, $\phi = 0.5$ mm) and the cathode was a graphite rod ($\phi = 0.5$ mm). Two straight electrodes were placed in parallel and 8.0 mm apart. The electrodes were fixed on the bottom glass plates. The electrolyte of $ZnSO_4$ (0.05 M, pH = 4.5) was confined in the space between the upper and the lower glass plates and the two electrodes. The separation between the upper and the lower glass plates was 70 μm. The geometrical details of the cell for electrodeposition were the same as that reported before.[8,11] The electrolyte solution was prepared by dissolving analytical reagent $ZnSO_4$ in deionized ultrapure water (Milli-Q, electric resistivity 17.8 M Ωcm). To decrease the O_2 concentration in the electrolyte and to suppress the growth of ZnO, the electrolyte solution was heated up and cooled down while N_2 was bubbled into the solution. No special treatments were made on the surface of the glass plates except conventional cleaning. A Peltier element was placed beneath the electrodeposition cell for rapid modification of cell temperature, which is essential to solidify the electrolyte and will be discussed later in this section. Both the deposition cell and the Peltier element were sealed in a thermostat chamber. The electrolyte solution was solidified by cooling the electrodeposition cell from the bottom. Nucleation of ice of the electrolyte usually started from the bottom glass plate. During solidification, $ZnSO_4$ was partially expelled from the solid, a process known as partitioning effect in crystallization.[15–17] Thus the concentration of $ZnSO_4$ in the electrolyte in front of the solid-electrolyte interface increased. On the other hand, it is known that the temperature at which the electrolyte solidifies (melting point/solidification point of electrolyte) depends on the electrolyte concentration. For $ZnSO_4$, the solidification/melting point decreases when the concentration of $ZnSO_4$ is increased. Therefore, when the equilibrium was reached at the set temperature (e.g. $-4\,^\circ$C), an ultrathin layer of concentrated $ZnSO_4$ electrolyte remained in liquid state in the space between the ice of the electrolyte and the glass substrate. The electrodeposition was carried out in this ultrathin layer in which the concentration of $ZnSO_4$ was high and yet did not exceed the saturation concentration at the set temperature. Great care was taken in solidifying the electrolyte in order to keep just one or only a few ice nuclei in the system, and to avoid a cellular or dendritic ice-electrolyte interface. To meet these requirements, several melting–solidification cycles were repeated and a very low solidification rate was applied.

When the equilibrium is reached at the set temperature ($-4\,^\circ$C in our experiments), an ultrathin electrolyte layer is formed. Meanwhile, a constant voltage is applied across the electrodes. Zinc branches initiate from the cathode and develop gradually on the surface of the glass plate toward the anode. Figure 1(a) shows the scanning electron micrograph of zinc deposit branches. One may find that the sidebranches of the electrodeposit possess nearly the same angle with respect to the main trunk. The inset in Fig. 1(a) demonstrates the distribution of the angle between the sidebranch and the main trunk. A distinct peak appears at 60°. Further observation indicates that the electrodeposit branch consists of beads and that the size of each bead is almost identical as shown in Fig. 1(b). The inset of Fig. 1(b) shows the Fourier transform of the intensity distribution along the line on the branch, which indicates that the periodicity on the deposit branch is perfect. Moreover, fine layered structures can be identified on each bead, suggesting that layer-by-layer growth may dominate the electrodeposition (Fig. 1(c)).

For electrodeposition with a constant electric current, the voltage between the electrodes oscillates spontaneously, as shown in Fig. 2(a). The Fourier transform of the voltage signal is illustrated in Fig. 2(b). We also observe that the oscillation frequency increases when the electric current becomes higher. The same tendency occurs by increasing pH of the electrolyte – the oscillation speeds up for higher pH values.[8] Spontaneous oscillation of the voltage signal in zinc electrodeposition has been reported before.[1–8] The difference between our present experimental system and the previous ones is that in this system the thickness of the electrolyte film is restricted to a few hundreds of nanometers, which is much thinner than that used in the previous systems. Therefore the oscillation shown here is unlikely to have been induced by macroscopic thermal convection or buoyancy convection.

To investigate the microstructure of electrodeposits, the branch of zinc electrodeposits is carefully transferred to a sample holder for TEM, as shown in Fig. 3(a). We select the areas labeled as 1, 2, and 3 for electron diffraction, and the achieved electron diffraction patterns are shown, respectively, in Fig. 3(b)–(d). It is noteworthy that there is more than one bead within each selected area. However, Fig. 3(b)–(d) show only one set of single-crystalline diffraction spots. Furthermore, the diffraction patterns in Fig. 3(b)–(d) are essentially identical. All these indicate that the crystallographic orientation of each bead is identical, i.e. not only each bead but also the whole deposit branch is single-crystalline.

Zinc has a hexagonal close-packed structure, with $a = b = 2.66$ Å, $c = 4.94$ Å. Combining Figs 1 and 3, we can determine that the flat facets shown in Fig. 1(c) are (0001) that of zinc, and that the deposit branches develop layer-by-layer. Specifically, the single-crystalline diffraction pattern suggests that during layered growth each newly born layer adopts the same orientation as the existing layers beneath.

DISCUSSIONS

We need to understand why the oscillation of electric signal and the periodic morphology on the deposit branches
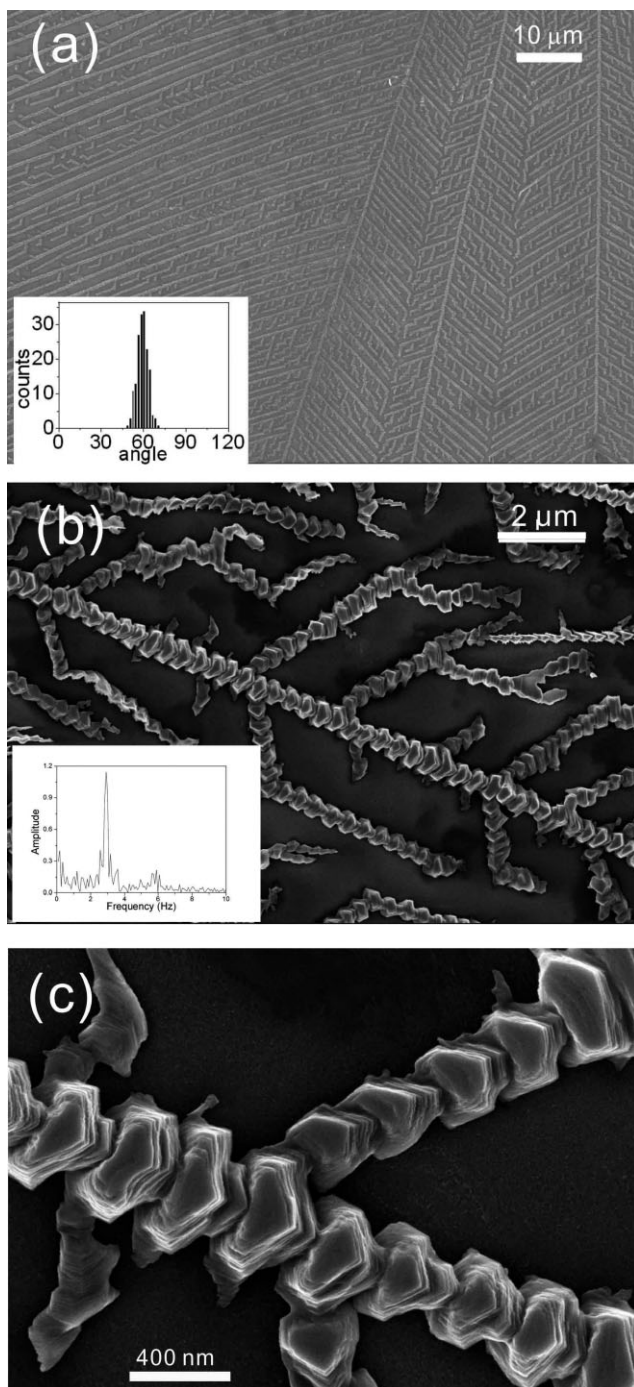
Figure 1. (a) Scanning electron micrograph of zinc deposit branches. The angle between the sidebranch and the main trunk is almost identical. The inset shows the statistics of the angle. A distinct peak appears at 60°. (b) The electrodeposit branch observed with higher magnification. The size of each of the beads on the electrodeposits is almost identical. The inset shows the Fourier transform of the intensity distribution along the dotted line on the branch. (c) The detailed morphology of the bead observed by SEM. Each bead is made of flat crystalline layers.
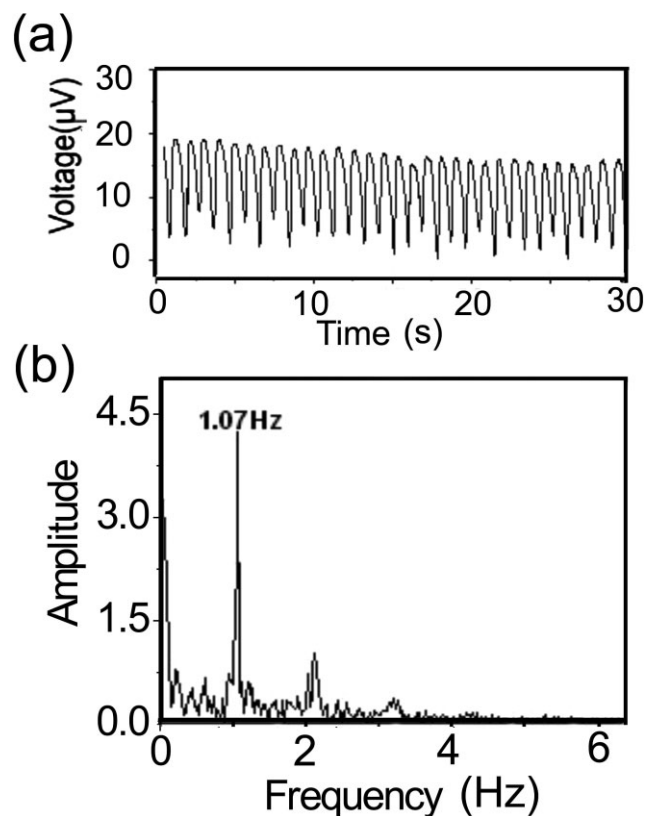

Figure 2. (a) The electric voltage recorded during the electrodeposition when a constant current was applied across the electrodes. Regular, spontaneous oscillation was observed. (b) The Fourier transform of the current signal with distinct peaks.

field, they are then reduced and diffuse on the deposit surface. Nucleation of adsorbed atoms, followed by limited growth, gives rise to a crystallite agglomerate. According to the Nernest equation, equilibrium electrode potential of $Zn|Zn^{2+}$ increases when the concentration of Zn^{2+} ($[Zn^{2+}]$) builds up. Electrodeposition of zinc takes place only when the potential of the cathode is lower than this equilibrium value. The equilibrium electrode potential for ZnO, however, is higher than that for Zn (The standard electrode potential of Zn | Zn^{2+} is −0.76 V *versus* NHE while the standard electrode potential of Zn | ZnO is 0.88 v *versus* NHE.).[18] So, for a wide range of electrolyte concentrations, ZnO deposits with priority. Suppose $[Zn^{2+}]$ is initially high at the growing interface and the equilibrium potential for zinc deposition is also high. By applying a sufficiently low electrode potential, both Zn and ZnO are deposited on the cathode, which follow:

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

$$Zn^{2+} + 1/2O_2 + 2e^- \longrightarrow ZnO$$
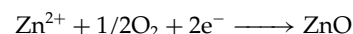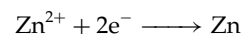
It should be noted that the deposition rate of ZnO is proportional to the product of both $[Zn^{2+}]$ and the concentration of dissolved oxygen in the electrolyte, whereas normally the oxygen concentration in the electrolyte solution is much lower than $[Zn^{2+}]$. Therefore, the mass deposition rate of ZnO is much lower as compared to that of zinc. The electrodeposition consumes Zn^{2+} and at the same time the ion

are generated, and why the electrodeposits have a single-crystalline feature.

Electrocrystallization of zinc can be understood as follows. Zn^{2+} ions are driven to the cathode by the electric
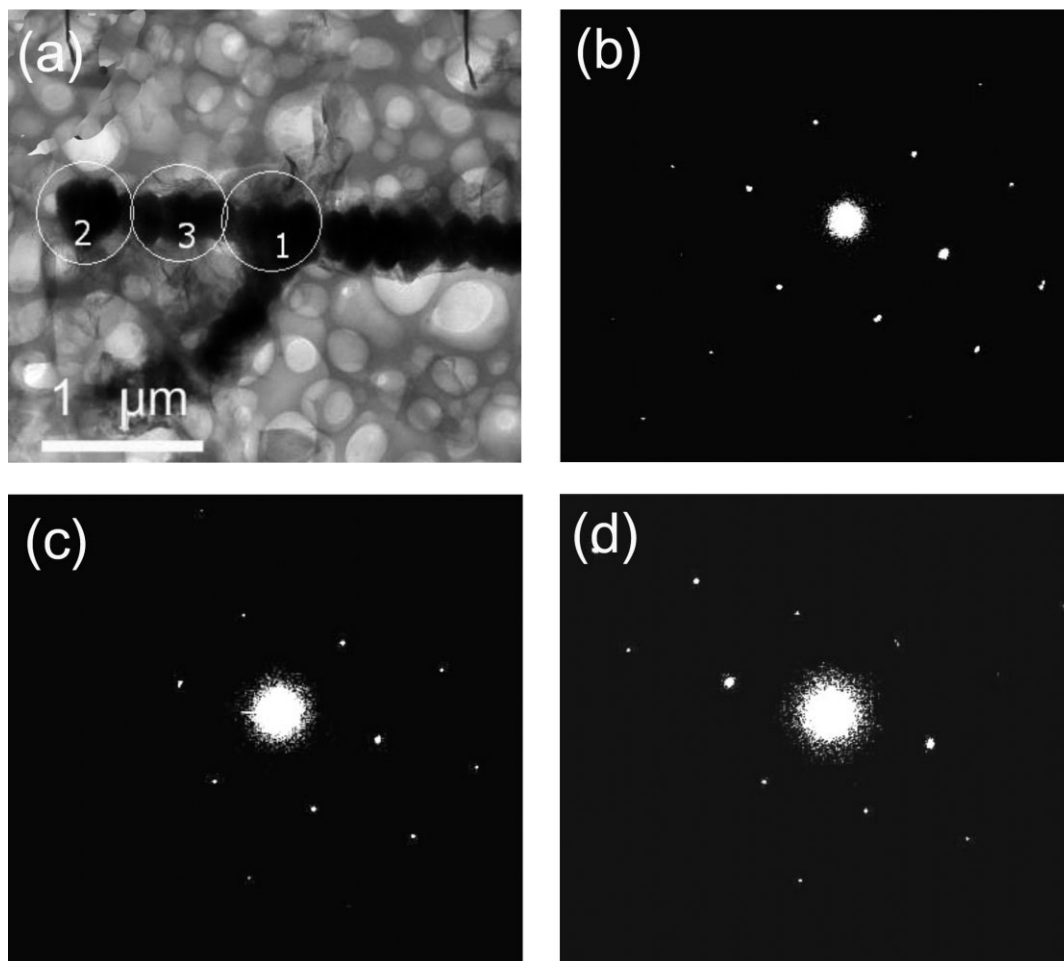
Figure 3. (a) Transmission electron micrograph of the zinc electrodeposits. (b)–(d) show the electron diffraction pattern collected in areas labeled as 1, 2, and 3, respectively, in (a). Note that there are more than one bead within each circle in (a), whereas the diffraction patterns demonstrate a perfect single-crystalline feature.

transport is confined by ultrathin geometry of the electrolyte film. As a result, $[Zn^{2+}]$ decreases in front of the growing interface and it takes time for the Laplacian fields (both the concentration field and the electric field) to compensate this reduction. Meanwhile, the equilibrium electrode potential of Zn drops and it may even become lower than the actual electrode potential. Once this occurs, the zinc deposition stops but the deposition of ZnO continues. Note that the ZnO grows at a very low rate, which allows $[Zn^{2+}]$ in front of the growing interface to be again accumulated during this period. Consequently, the equilibrium electrode potential of Zn^{2+} resumes. When its value exceeds the actual electrode potential, the zinc deposition restarts. In this way the periodic bead morphology is formed.

When we study Fig. 3, however, we do not find any evident diffraction spots of ZnO. This may be because of the fact that the amount of ZnO generated in electrodeposition is very low. If ZnO exists in zinc crystalline layers in the form of nanoclusters and the amount of ZnO is not high, the diffraction spots of ZnO could be too faint to be recognized. As a matter of fact, if the electrolyte solution was not nitrogen bubbled before electrodeposition, even when the pH of the electrolyte is high, a large amount of ZnO nanocrystallites would be generated. In that case, the ZnO crystallites are

plate-shaped and densely stand on the deposit branches.[19] We had carried out the electron diffraction of such a case and found that clear diffraction spots of ZnO appeared together with those from zinc.[19]

Now we try to understand why each layer has the same crystallographic orientation in the electrodeposition of zinc. As shown in Fig. 1(c), we suppose that during the layer-by-layer growth, a new layer initiates on the existing zinc layers as an embryo. According to nucleation theory, the interfacial energy of the embryo of the nucleus and the crystalline zinc layers underneath, γ_{cs}, is contributed by two parts. One part comes from the chemical compositions, γ_{chem}, and the other part is due to the structure of the interface, γ_{str}, i.e. $\gamma_{cs} = \gamma_{chem} + \gamma_{str}$.[15] If the lattice in the embryo of the nucleus matches perfectly with that of the substrate (existing zinc layers), γ_{str} vanishes. If, however, the lattice of the nucleus embryo rotates a degree with respect to that of the substrate, strain is introduced. Meanwhile, an additional elastic energy is added in the formation energy of the misoriented nucleus and the energy barrier for nucleation is increased. This makes nucleation more difficult. Therefore, epitaxial nucleation, in which the nucleus adopts the crystallographic orientation of the existing zinc layers, is energetically favored. Although electrodeposition is not an equilibrium process, we expect

that the principle of minimum free energy is still applicable. It is known that the material anisotropy of zinc is strong and so a layered growth is common in the electrocrystallization of zinc. Therefore, epitaxial nucleation plus layer-by-layer growth lead to a single-crystalline electrodeposit (Fig. 3). This also explains the narrow angle distribution shown in Fig. 1. The sidebranches have the same crystallographic orientation as the main trunk because of the epitaxial nucleation, and the whole zinc dendrite is single-crystalline. The angle between the sidebranch and the main trunk is basically determined by the hcp structure of zinc.

To summarize, we report in this article the formation of periodically structured single-crystalline electrodeposits of zinc electrochemically from an ultrathin aqueous electrolyte layer of $ZnSO_4$. The main trunk and the side branches of the electrodeposits are regularly angled, and each branch demonstrates a periodic bead-like structure. Spontaneous oscillation of electric current/voltage occurs in electrodeposition when a constant voltage/current is applied across the electrodes. Despite the distinct bead morphology on the deposit branches, the whole of the electrodeposits have the same crystallographic orientation. We interpret this unique growth behavior with epitaxial nucleation in this transport-limited system.

Acknowledgements

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