Phase-field modeling for electrodeposition process

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Abstract

A novel phase-field model for electrochemical processes, in which cations were driven by an electrostatic potential coupled with a thermodynamic potential, was formulated from a variation of the Ginzburg–Landau free-energy functional. Using this model, an electrodeposition process of copper deposits from copper-sulfate solution was studied using a phase-field simulation. The dependence of the growth velocity of the electrode on the applied voltage was examined in a one-dimensional system. Then, the morphological transition of the electrodeposits as functions of the applied voltage and the composition ratio of copper ion in electrolyte was examined using a two-dimensional system. Thin and dense branches were observed at a low applied voltage. The shape of the branches became more complicated as the composition ratio was lowered.

Keywords: Phase-field modeling; Electrochemistry; Electrodeposition; Pattern formation

1. Introduction

The electrochemical deposition of metals has been studied for a long time since it is important to control the morphology of deposits. The morphology has much variety; for example, homogeneous, dendritic, fractal, open-ramified, finger-like and other complex structures appear depending on applied voltage and electrolyte concentration [1–9]. For instance, Sawada et al. [1] showed the transition from dendritic to disordered ramified patterns with decreasing electrolyte concentration in the electrodeposition of Zn from a thin layer of ZnSO₄ solution confined between Plexiglas disks. Sagués et al. [2] presented a diagram summarizing the morphologies for Zn electrodeposition from a non-deaerated ZnSO₄ solution in a parallel cell. The diagram showed that the morphology changed from homogeneous to dendritic and open fractal with increasing concentration. López-Salvans et al. [3] examined the morphological transition in thin-layer electrodeposits from CuSO₄ solution and the dependence of the growth velocity of electrodeposits on the applied voltage. Gonzalez et al. [4] studied the effect of viscosity of the electrolyte on the electrodeposits from the viewpoint of fluid dynamics (i.e., Navier–Stokes equation). In addition to the above studies, pattern formation in electrodeposition has been studied experimentally [5–9].

In conjunction with the experimental results, theoretical and numerical approaches [9–14] have contributed to our understanding of such complex phenomena. Details of the internal structures from the experimental results were analyzed using the correlation function [9] or fractal dimension [10]. Chazalviel [11] conducted a macroscopic analysis of the growth process of electrodeposits on the basis of ion transport equations. As an example of the study of a pattern-formation process, diffusion-limited aggregation (DLA) [12], which was developed for the growth process of soot, dendrites and other random structures, was applied to the electrodeposition process. In the DLA model, random walkers stick to the growing aggregate resulting in dendritic or other random structures. The morphologies of the deposits in the electrodeposition were compared with the DLA model [10]. In addition, a mean-field model, which is based on the lattice-gas model, has been developed to describe the evolution of instability in the electrochemical process [13,14].

Other than that in electrochemical deposition, pattern formation has been widely studied in the area of
solidification. Among various numerical techniques, a phase-field model [15,16] is one of the powerful tools for understanding the pattern formation in solidification processes. It enables us to obtain the direct solution of the evolution of the interface pattern constrained by a free boundary condition. This method can be applied to other problems including biphasic materials. Hence, the application of the phase-field model to the electrodeposition process is reasonable [17]. However, the formulation of the phase-field model related to the electrodechemical process is not straightforward since a model of the electric field in the phase-field model has not been established.

Geyer et al. [18,19] developed a diffuse-interface model for an electrochemical process and examined the equilibrium distribution of components with electrostatic potential in a one-dimensional (1-D) system. In this model, Poisson’s equation was solved for the electrostatic potentials arising from the charge density of the components. However, it is complicated to solve Poisson’s equation for the electrostatic potential from the component itself since it is numerically difficult to solve the equation coupled with a time-dependent partial differential equation. Hence, the model is bound to use quite a small time scale and spacing of the mesh point for numerical solution. Moreover, the definition of free energy density in the model results in the sharp-interface limit. It also restricts the model to be suitable at a small space. Though it is a nice model for investigating the scale of the interfacial double-layer, it may not be suitable for morphological analysis during electrodeposition.

Pongsaksawad et al. [20] developed a phase-field model under assumptions of transport-limited operation and rapid charge redistribution, and examined the electric-field-enhanced smelting and refining process using a binary Fe–FeO system. This model is applicable to the system in which an interfacial double layer can be negligible. It is a suitable model for analyzing processes including the flow during electrochemical processes. On the other hand, we have developed a phase-field model [21] in which one of the components is charged and driven by an electrostatic potential caused by an external charge. This model is similar to Pongsaksawad’s model, but uses an order parameter field with thin-interface limit parameters, which describe the motion of the interface quantitatively. This model can also capture both deposition and dissolution processes due to the thermodynamics-based nature of the phase-field method. Using this model, the process of bridge formation and disappearance in a nanometer-scale switch [22,23] was studied. In our previous study [21], we assumed the components of the electrode and electrolyte as an ideal metal, M, and an ideal sulfide, M2A, instead of the real materials, Ag/Ag2S or Cu/CuS, for simplicity.

In this study, a phase-field model with an electrostatic potential caused by an external charge was modified and new thermodynamic parameters were developed for the electrodeposition process of Cu with CuSO4 solution. Using this model, first, we checked the dependence of the growth velocity of the electrodes on the applied voltage in a simple 1-D system. Next, the growth process of dendritic deposits of Cu was calculated in a two-dimensional (2-D) system. The dependence of morphology on the applied voltage and the electrolyte concentration was examined.

2. Formulation of a phase-field model for an electrochemical process

2.1. Variation of a Ginzburg–Landau free-energy functional

The state of the phase is represented by an order parameter $\xi$ (the phase field) in the phase-field model. In this study, $\xi = 1$ and 0 represent the electrode and electrolyte, respectively. The electrode/electrolyte interface is defined by the distribution of the region, $0 < \xi < 1$. The changes in time of the phase field and molar concentration are assumed to be proportional to the variation of a Ginzburg–Landau free-energy functional, $F_{GL}$:

$$F_{GL} = \int \left( f_V(\xi, C_i) + \frac{k}{2} | \nabla \xi |^2 + \rho \phi \right) dV,$$

(1)

where $f_V$ is the free-energy density, $k$ is a gradient term coefficient that is related to the interfacial energy, and $C_i$, $V$, $\rho$, and $\phi$ represent the molar concentration, volume, electric charge density and electrostatic potential, respectively. Hence, governing equations are derived from Lagrange’s method for an undetermined multiplier with constraints described below:

$$\int_V C_i dV = CV \tilde{C}_i,$$

(2)

$$\sum_{i=1}^{n} \tilde{V}_i C_i = 1,$$

(3)

$$F \sum_{i=1}^{n} z_i C_i = \rho,$$

(4)

where $\tilde{C}_i$ is the average molar concentration, $\tilde{V}_i$ is the partial molar volume, $z_i$ is the valence of species $i$ and $F$ is the Faraday constant. Eqs. (2)–(4) represent the conservation of the total number of moles of each species in the entire system, the conservation of moles in each element and the conservation of charge in each element, respectively. From the variation, we can derive following equations:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{J}_i,$$

(5)

$$\mathbf{J}_i = -M_i \sqrt{\frac{\partial f_V}{\partial C_i} + F_{z_i} \phi} - \tilde{V}_i \left( \frac{\partial f_V}{\partial C_n} + F_{z_n} \phi \right),$$

(6)

$$\frac{\partial \xi}{\partial t} = -M_\xi \left( \frac{\partial f_L}{\partial \xi} - \kappa_\xi \nabla^2 \xi \right),$$

(7)

where $M_i$ is the mobility of species $i$ and $M_\xi$ is that of the phase field $\xi$. 

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2.2. Definition of free-energy density

It is simply assumed that the electrode consists of $M^+$ and $e^-$, and the electrolyte consists of $M^+$ and $A$, which is the summation of other elements such as $\text{SO}_4^{2-}$ and $\text{H}_2\text{O}$. Hence, the ternary system consisting of $M^+$, $A$ and $e^-$ is considered. This system reduces to the binary system of $M-A$ in the case of $\phi = 0$. Assuming an electroneutrality condition, it is not necessary to consider the motion of the electron explicitly because the electron follows the component $M^+$. Therefore, it is sufficient to define the free-energy density as a function of the volumetric molar concentrations of $M^+$ and $A$ as in the case of a binary alloy [16]. Hence, the free-energy density $f_V$ is defined as follows:

\[ f_V = p(\xi)\bar{f}^\alpha(C_{M^+}^\alpha, C_A^\beta) + (1 - p(\xi))\bar{f}^\beta(C_{M^+}^\beta, C_A^\beta) + Wg(\xi), \]  
\[ p(\xi) = \xi^3(10 - 15\xi + 6\xi^2), \]
\[ g(\xi) = 30\xi^2(1 - \xi)^2, \]
where $g(\xi)$ is a double-well potential function $W$ is the height of the double-well function, and $p(\xi)$ is a function that monotonically changes from $p(0) = 0$ to $p(1) = 1$. The superscripts $\alpha$ and $\beta$ represent the electrode and electrolyte, respectively. On the basis of the KKS model [16], the concentration at the interface is defined as a mixture of the concentration of each phase with equilibrium conditions described by Eqs. (13) and (14)

\[ C_{M^+} = C_{M^+}^\alpha p(\xi) + C_{M^+}^\beta (1 - p(\xi)), \]
\[ C_A = C_A^\alpha p(\xi) + C_A^\beta (1 - p(\xi)), \]
\[ \frac{\partial f^\alpha}{\partial C_{M^+}^\alpha} = \frac{\partial f^\beta}{\partial C_{M^+}^\beta}, \]
\[ \frac{\partial f^\alpha}{\partial C_A} = \frac{\partial f^\beta}{\partial C_A}. \]

The molar volumes of $M^+$ and $A$ are assumed to be the same. Hence, the free-energy density $f_\xi$ is expressed using the composition ratio of $M^+$ and the phase-field parameter $\xi$ as in case of a binary alloy system [16]. Hence, the flux of the component $M^+$ results in

\[ \dot{J}_{M^+} = -M_{M^+} \nabla \left[ \frac{\partial f^\xi}{\partial C_{M^+}^\alpha} + Fz_{M^+} \phi \right]. \]

The mobility $M_{M^+}$ is obtained by comparing Eq. (15) with a diffusion equation of the composition ratio of $M^+$ in a single phase of the electrode or electrolyte:

\[ M_{M^+} = \frac{D_{M^+}^\alpha p(\xi) \left( \frac{\partial^2 f^\alpha}{\partial C_{M^+}^\alpha} \right)^2 + D_{M^+}^\beta (1 - p(\xi)) \left( \frac{\partial^2 f^\beta}{\partial C_{M^+}^\beta} \right)^2}{2 \left( \frac{\partial^2 f^\alpha}{\partial C_{M^+}^\alpha} \right)^2 + \left( \frac{\partial^2 f^\beta}{\partial C_{M^+}^\beta} \right)^2} \cdot \]

2.3. Governing equations

For simplicity, a dilute-solution approximation and an ideal-solution approximation are adopted to define the free-energy densities of the electrode ($\xi$) and the electrolyte phase ($\beta$), respectively. On the basis of the above conditions, governing equations are given by

\[ \frac{\partial \xi}{\partial t} = M_\xi \left[ k_\xi^2 \nabla^2 \xi + \frac{\partial p(\xi)}{\partial \xi} \frac{RT}{V_{M^+}} \ln \frac{C_{M^+}^\alpha e C_{M^+}^\beta}{C_{M^+}^\beta e C_{M^+}^\alpha} - W \frac{\partial g(\xi)}{\partial \xi} \right], \]
\[ \frac{\partial C_{M^+}}{\partial t} = \nabla \left[ D(\xi) \left( p(\xi) C_{M^+}^\alpha (1 - C_{M^+}^\alpha) + (1 - p(\xi)) \right) \times C_{M^+}^\beta (1 - C_{M^+}^\beta) \right] \left( \ln \frac{C_{M^+}^\beta}{C_{M^+}^\alpha} + \frac{z_{M^+} F \phi}{2RT} \right). \]

As described above, $C_{M^+}$ represents the composition ratio of $M^+$. Superscript $e$ represents the equilibrium composition ratio. The coefficient of the phase-field gradient energy term, $\kappa_\xi$, the height of double-well potential, $W$, and the mobility of the phase field, $M_\xi$, are employed from the KKS model as follows [16]:

\[ W = \frac{3\gamma_x \sigma}{\lambda}, \]
\[ \kappa_\xi = \sqrt{\frac{6\sigma_x}{z_x}}, \]
\[ M_\xi = \frac{\sigma}{\kappa_\xi} \left( \frac{RT}{V_{M^+}} \left( 1 - \kappa^e \right) \beta + \frac{\kappa_\xi}{D_{M^+} + \sqrt{2W}} \left( C_{M^+}^\alpha - C_{M^+}^\beta \right) \right)^{-1}, \]
\[ \kappa^e \left( C_{M^+}^\alpha - C_{M^+}^\beta \right) = \frac{RT}{V_{M^+}} \left( C_{M^+}^\alpha - C_{M^+}^\beta \right)^2 \times \int \frac{p(\xi)(1 - p(\xi))}{p(\xi) C_{M^+}^\alpha (1 - C_{M^+}^\alpha) + (1 - p(\xi)) C_{M^+}^\beta (1 - C_{M^+}^\beta)} \right]. \]

A dilute solution approximation was used to derive the mobility of the phase field as Eqs. (21) and (22) [16]. $\gamma_x$ is the coefficient used for the definition of interface thickness $2\gamma_x$. Here, the coefficient $\gamma_x$ is set to 2.2, which fits the interface thickness $2\gamma_x$ to the width of the phase field between 0.1 and 0.9 [16].

In addition, the equation of charge conservation in its simplified form is solved for the distribution of the electrostatic potential:

\[ \nabla \cdot [\sigma_\xi(\xi) \nabla \phi] = 0, \]
\[ \sigma_\xi(\xi) = \sigma_\xi^e p(\xi) + \sigma_\xi^e (1 - p(\xi)), \]
where $\sigma_{e}(\xi)$ is a total electrical conductivity that is defined as a mixture of the electrical conductivity of each phase, $\sigma_{e}^{a}$ and $\sigma_{e}^{b}$. The simplified form of the equation is employed by assuming rapid charge distribution (i.e. neglecting the term of time variation of the charge) and electromigration as a dominant factor for current (i.e. neglecting the diffusion term) based on Pongsaksawad’s model [20], in which the equation of charge conservation was simplified by comparing the timescale of charge buildup relative to diffusion, current driven by diffusion relative to electromigration and flux due to convection relative to current. The ratio of electrical conductivities is set to 100 assuming a conducting electrode.

2.4. Thermodynamic parameters

The thermodynamics parameters for the calculation of the electrodeposition process of Cu from CuSO$_4$ solution were determined from the equilibrium concentration of Cu$^{2+}$ in electrolyte. The saturated concentration of Cu$^{2+}$ in 100 grams of water is given as

$$m_{\text{CuSO}_4} = \frac{S_{T}}{M_{\text{CuSO}_4}} + 100 \frac{M_{\text{H}_2\text{O}}}{M_{\text{CuSO}_4}} \text{(mol)}.$$  (25)

where $S_{T}$ is the solubility of CuSO$_4$, which is defined as a solute mass in 100g of water, and $M$ represents the atomic weight ($M_{\text{CuSO}_4} = 63.55$, $M_{\text{SO}_4}^{2-} = 96.07$ and $M_{\text{H}_2\text{O}} = 18$ amu). The other elements SO$_4^{2-}$ and H$_2$O are lumped into A for simplicity in this model as described above. Hence, the number of moles of A is given as

$$m_{A} = \frac{S_{T}}{M_{\text{CuSO}_4} + M_{\text{SO}_4}^{2-}} + 100 \frac{M_{\text{H}_2\text{O}}}{M_{\text{CuSO}_4}} \text{(mol)}.$$  (26)

Then, it is transformed into the following composition ratios:

$$\epsilon C_{\text{CuSO}_4}^{b} = \frac{m_{\text{CuSO}_4}^{b}}{m_{\text{CuSO}_4}^{b} + m_{A}}.$$  (27)

$$\epsilon C_{A}^{b} = \frac{m_{A}}{m_{\text{CuSO}_4}^{b} + m_{A}}.$$  (28)

The equilibrium composition ratio of Cu$^{2+}$ in the electrolyte depends on the temperature since solubility varies with temperature. $\epsilon C_{\text{CuSO}_4}^{b}$ at 293K is 0.018 as obtained from $S_{293\text{K}} = 16.8$. In this study, we used the equilibrium composition ratio as a ‘fictional’ phase diagram for thermodynamic parameters. The equilibrium composition ratio of Cu$^{2+}$ in the electrode is set to 0.98 assuming that the electrode consists almost entirely of copper. Hence, the melting point, liquidus slope and partition coefficient of the fictional phase diagram are determined as 4051.79 K, 3828.86 K/mol and 0.023, respectively. The parameters determined above are listed in Table 1.

In addition, there are no reports on parameters such as interfacial energy, anisotropy and kinetic coefficient for the electrode/electrolyte interface. Hence, other parameters are taken from our previous studies [21] with minor modifications. The diffusion coefficients of Cu$^{2+}$ in the electrode and electrolyte are set to be $3.0 \times 10^{-13}$ and $7.2 \times 10^{-8}$ m$^2$/s, respectively. The relative permittivities of the electrode and electrolyte are set to 200 and 2, respectively. The kinetic coefficient determines the system as ‘transport-limited’ or ‘kinetic-limited’ based on thin-interface limit theory. In this study, the kinetic coefficient was tuned empirically for assuming transport-limited growth based on our previous simulation for solidification of binary alloy by the thin-interface limit theory. Other parameters are listed in Table 2. For a better understanding of these parameters, they should be discussed from the viewpoint of their physical meanings in the next stage. The Galvani potential, which is the difference between internal potential of the electrode and that of the electrolyte, is neglected in this model since it is much smaller than the applied voltage. When it is considered, the ratio of equilibrium composition ratios in the fictional phase diagram moves as follows owing to the effect of the Galvani potential, $\Delta \phi$:

$$\frac{\epsilon C_{M+}^{b}}{\epsilon C_{M+}^{b}} = \frac{\epsilon C_{M+}^{b}}{\epsilon C_{M+}^{b}} \exp \left( \frac{z_{M+}F\Delta \phi}{RT} \right).$$  (29)

This equation is derived from the equilibrium condition of the electrochemical potential. It is consistent with Nernst’s equation, which is for the electromotive force in terms of the composition ratio [24].

2.5. Simulation methodology

A finite-difference scheme is employed for the solution of the differential equation for the phase, $\xi$, and composition ratio, $C_{M+}$, with a time step of $2.78 \times 10^{-7}$ s. The spacing of the mesh points is set to $1.0 \times 10^{-7}$ m. The equation of charge conservation for the electrostatic potential is solved at each time step using the Gauss–Seidel method. A Dirichlet boundary condition is used at the right
The composition ratio of Cu\(^{2+}\) in electrolyte was varied from 0.001 to 0.0183 (equilibrium composition ratio). Growth velocity was determined by the combination of two opposing driving forces: (1) the migration of the cation caused by a positive applied voltage, which shifts the interface to the electrolyte area, and (2) the diffusion of the cation from the electrode to electrolyte, which restores the system back to the equilibrium composition ratio. Without the applied voltage, the interface shifted to the electrolyte area (characterized by negative values of the velocity), which indicates electrode dissolution. The growth velocity of dissolution increased with increasing difference between the actual composition ratio, \(C_0\), and the equilibrium composition ratio, 0.0183. By definition, the interface did not move in the case of \(C_0 = 0.0183\) without applied voltage.

The growth velocity increased with increasing applied voltage. The interface did not move when the values of the two driving forces were equivalent. The applied voltages at the equilibrium point with the composition ratios of 0.0183, 0.015, 0.01, 0.005 and 0.0001 were 0, 79, 239, 505 and 1130 V/m, respectively. The applied voltages at the equilibrium point increased with increasing difference between the equilibrium and actual composition ratios of Cu\(^{2+}\) in electrolyte. The equilibrium composition ratio of Cu\(^{2+}\) in electrolyte defined by the fictional phase diagram is 0.0183. Hence, the liquidus line of the fictional phase diagram is thought to shift to lower composition ratios due to the applied voltage from another point of view.

When a larger voltage was applied, the interface shifted to the electrolyte area (positive values of the velocity), which indicates electrodeposition. Pattern formation in the electrodeposition process is examined in this range in the following session.

**3.2. Morphology of the electrodeposits in the 2-D system**

Pattern formation in the electrodeposition process of Cu deposits from CuSO\(_4\) solution was examined using a 2-D system. The system size was set to 70.0 \(\times\) 50.0 \(\mu\)m, expressed by 700 \(\times\) 500 mesh points, and the electrode/electrolyte interface was set 1.0 \(\mu\)m away from the left boundary as an initial condition. The left boundary was maintained at 0 V and the electric potential gradient at the right boundary was maintained at constant values of 2500, 5000 and 7500 V/m. Fig. 2 shows snapshots of the growth process of Cu electrodeposits with the composition ratios of 0.015, and applied voltages of 2500 and 5000 V/m. After planar growth occurred in the initial stage, the disturbance of the interface caused by the noise developed a bump, which is subsequently followed by an evolution to branches. Then, some of the branches protruded preferentially and second-order branches developed perpendicular to the growth direction not only from the protruding branches but also from the late-developing branches. Several parts of small sub-branches flaked away by local dissolution. In the case of the applied voltage of 2500 V/m, tip splitting was observed, although it was not observed in the branches from the electrolyte with the applied voltage of 5000 V/m. As in the case of the 1-D calculation, the
Fig. 2. Snapshots of the growth process of copper electrodeposits with composition ratios of Cu²⁺ in electrolyte of 0.015, and applied voltages of (a) $C_0 = 0.015, 2500$ and (b) $C_0 = 0.015, 5000$ V/m.

Fig. 3. A morphological diagram of the electrodeposits as functions of the applied voltage (2500, 5000 and 7500 V/m) and composition ratio of Cu²⁺ in electrolyte (0.015, 0.01 and 0.005). The snapshots taken when the most protruding branch reached 60.0 µm were compared (except for the condition of $C_0 = 0.005, 2500$ V/m due to the computational limit).
lower applied voltage offered the slower electrode growth for the same composition ratio. Hence, a more complicate structure was observed in the case of the lower applied voltage (2500 V/m) since electrodeposits required much time to develop the second-order branches before reaching the other boundary.

Fig. 3 shows a morphological diagram of the electrodeposits as functions of the applied voltage and the composition ratio of Cu$^{2+}$ in electrolyte. The snapshots taken when the most protruding branch reached 60.0 µm were placed in the diagram. Thick branches were observed at a higher applied voltage, whereas thin and dense branches were observed at a low applied voltage. In addition, the shape of the branches became more complicated at a lower composition ratio of Cu$^{2+}$ in electrolyte. Although both the lower composition ratio and lower applied voltage resulted in a low growth velocity, their effect on the morphology was different. In addition, the thickness of planar growth in the initial stage increased with increasing applied voltage. It was independent of the composition ratio of Cu$^{2+}$ in electrolyte.

The growth velocity of deposits in the 2-D system was compared with an experimental result [3], although the time–space scale was different due to a limit in the computation. Fig. 4 shows the average growth velocity of the electrodeposits during planar growth in the case of the composition ratio of 0.005. The experimental data were obtained from Ref. [3], in which the electrodeposition of Cu from CuSO$_4$ solution was examined. The electrolyte concentration of CuSO$_4$ in the experiment was $1 \times 10^{-1}$ mol/l, which corresponds to a composition ratio of 0.0004. The size systems for our calculation and the experiment in Ref. [3] were 70 µm and 40 mm, respectively. Hence, our calculation corresponds to the region very close to the interface in the experimental condition since the composition ratio of Cu$^{2+}$ in electrolyte increases near the interface due to electromigration with applied voltage for electrodeposition [20]. That is, the composition ratio of Cu$^{2+}$ in electrolyte near the interface was much higher than the bulk composition ratio. However, a detailed quantitative discussion is not presented in this paper since our calculation remains in the qualitative stage.

4. Conclusion

A novel phase-field model was proposed to analyze the electrodeposition process of Cu from CuSO$_4$ solution. Cations were driven by an electrostatic potential coupled with thermodynamic potential in the model, which was formulated from a variation of Ginzburg–Landau free-energy functional. First, the dependence of the growth velocity of the electrode on the applied voltage was examined using a 1-D system. The growth velocity was determined from the balance of the diffusion and electromigration of cations. The applied voltages for the stationary interface increased with increasing difference between the equilibrium and actual composition ratios of Cu$^{2+}$ in electrolyte. Next, the morphological transition of the electrodeposits as functions of the applied voltage and the composition ratio of Cu$^{2+}$ in electrolyte was examined using a 2-D system. Thick branches were observed at a higher applied voltage, whereas thin and dense branches were observed at a lower applied voltage. In addition, the shape of the branches became more complicated as the composition ratio of Cu$^{2+}$ in electrolyte was lowered. Flakes of small sub-branches brought about by local dissolution were observed.

The proposed model enables us to treat both the deposition and dissociation processes to represent electrodeposition. Both processes are important to reproduce such as the flaking away of the small sub-branches. This model may provide a good hint in understanding what factor predominantly determines the morphology of the electrodeposits. In this study, several parameters are employed empirically. For example, different anisotropy will result in different morphological diagram. Higher anisotropy will result in more finger-like structures since the main branches will be slim and sharp. In the next stage, the physical meaning of the parameters should be described for quantitative discussions.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.stam.2007.08.001.
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