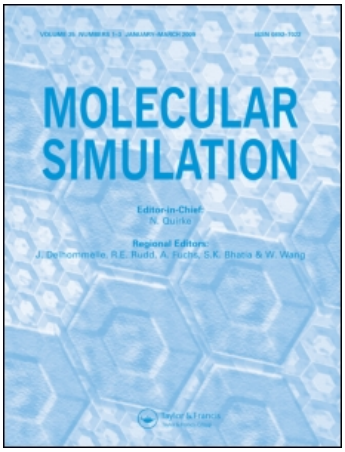

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Molecular dynamics—Monte Carlo hybrid simulation of thin film growth and void formation in electrodeposition process

Yasuaki Hiwatari[a]; Yutaka Kaneko[b]; Takashi Mikami[b]; Katsuhiko Ohara[c]; Fujio Asa[c]
[a] Division of Mathematical and Physical Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, Japan [b] Department of Applied Analysis and Complex Dynamical Systems, Graduate School of Informatics, Kyoto University, Kyoto, Japan [c] C. Uyemura & Co., Ltd, Osaka, Japan

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Molecular dynamics—Monte Carlo hybrid simulation of thin film growth and void formation in electrodeposition process

YASUAKI HIWATARI†, YUTAKA KANEKO‡*, TAKASHI MIKAMI‡, KATSUHIKO OHARA¶ and FUJIO ASA¶

†Division of Mathematical and Physical Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan
‡Department of Applied Analysis and Complex Dynamical Systems, Graduate School of Informatics, Kyoto University, Kyoto 606-8501, Japan
¶C. Uyemura & Co., Ltd, 1-5-1, Deguchi, Hirakata, Osaka 573-0065, Japan

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The surface structure and the void formation during electrodeposition process are investigated using the hybridized method of molecular dynamics and Monte Carlo simulations. In this approach, adsorption and desorption reactions are simulated by means of the Monte Carlo method within the molecular dynamics simulation of solution-electrode interface. The adsorption (desorption) is regarded as the change of metal ions (atoms) to metal atoms (ions). We performed the simulations of crystal growth on FCC (111) and (100) surfaces to study the surface structure depending upon the deposition conditions. The growth mechanism is discussed in relation to the surface diffusion of adatoms. In order to study the void formation in the deposition process, we performed the simulation of filling V-shaped grooves. It is shown that large voids appear in the middle of the grooves when they are filled with deposited atoms and some of the ions are embedded in the film.

Keywords: Electrodeposition; Molecular dynamics; Monte Carlo; Void formation

1. Introduction

Electrodeposition is a technique to plate thin metal film on an electrode surface by reduction reactions from electrolytic solutions [1,2]. It involves physical and chemical processes such as solvation dynamics in solution, electron transfer reaction, surface diffusion of adatoms and crystallization. Molecular dynamics (MD) simulation is a powerful tool to study such a mixture of liquid and solid dynamics. However, the MD simulation of electrodeposition faces a difficulty since the electrodeposition includes electron transfer reactions, which are essentially quantum mechanical processes.

Recently we have developed a hybrid method of MD and Monte Carlo (MC) as a new tool for the simulation of electrodeposition process [3,4]. In this approach, we perform the MD simulation of a solution-electrode interface consisting of metal atoms (an electrode), cations (metal ions), anions and solvent particles. Two reactions, i.e. adsorption and desorption, are assumed to occur in the MD simulation by means of the MC method. These reactions are treated as the changes in the particle species. Adsorption is the change of a metal ion near the electrode to a metal atom. Desorption is the change of a metal atom on the surface to a metal ion. The rate constants for these reactions are the same as those used in our kinetic Monte Carlo simulation of the solid-by-solid (SBS) model [5,6]. The SBS model is a simple extension of a solid-on-solid model for crystal growth to include vacancy formation, which has been developed by our group as a model for electrodeposition. The hybrid simulation is the combination of the MD method and the kinetic MC simulation of the SBS model.

In this paper, we study the surface structure and the void formation during the thin film growth using the MD–MC hybrid method. We performed the simulations of the growth on FCC (111) and FCC (100) surfaces to compare the film structures. The growth mechanism is discussed in relation to the surface diffusion of adatoms. We also performed the simulation of filling V-shaped grooves to study the void formation mechanism during the filling. This paper is organized as follows. In Section 2, we describe the model system and the outline of the method of computation. The simulation conditions and the interatomic potentials are given in Section 3. The results of the simulations of thin film growth and filling grooves are

*Corresponding author. Email: kaneko@acs.i.kyoto-u.ac.jp

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presented in Section 4. Summary and discussion are given in Section 5.

2. Model and method of computation

2.1 Model system of solution-electrode interface

The simulation system is a three-dimensional solution-electrode interface, which consists of the electrode, the solution and the replenishing layer (figure 1). The electrode is composed of metal atoms, frozen substrate atoms and cooling layer atoms. The temperature of the cooling layer is kept lower than that of the upper part of the electrode to remove the latent heat of reactions. The solution part consists of cations, anions and solvent particles. The replenishing layer is located at the top of the solution to replenish the solution with cations when their concentration becomes low. The replenishing layer has two types of particles, i.e. neutral particles and cations. Between the solution and the replenishing layer is a semi-permeable filter to pass cations into the solution. The upper part of the replenishing layer is an elastic wall. The periodic boundary condition is used in x, y-directions. The frozen substrate atoms are fixed at lattice sites, giving the boundary at the bottom of the electrode.

2.2 Hybrid simulation

In the hybrid simulation, we perform the MD simulation of the whole system described in Section 2.1. At every N_r steps, which is regarded as a "reaction step", adsorption or desorption reaction occurs. The adsorption rate $k_n^{\dagger}$ and the desorption rate k_n depend upon the number of the nearest neighbor metal atoms denoted by n. The ratio $k_n/k_n^{\dagger}$ is given by

$$\frac{k_n}{k_n^{\dagger}} = \exp\left\{(n_k - n)\frac{\psi}{k_B T} - \frac{\mu}{k_B T}\right\}, \tag{1}$$

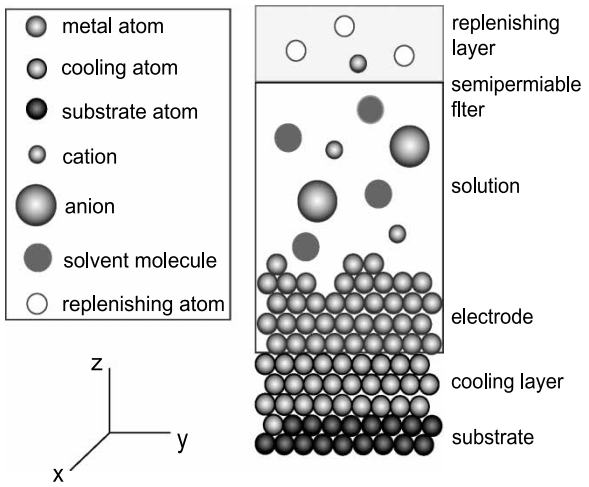

Figure 1. The model system of the electrode-solution interface for the MD–MC hybrid simulation.

where n_k is the number of bonds at a kink site, ψ is the binding energy between the solid atoms and T is the temperature [7]. The chemical potential μ corresponds to the overpotential in electrodeposition. The relation (1) is the same as that used in the MC simulation of the SBS model [5,6]. At each "reaction" step, the surface metal atoms and cations near the surface are searched for to make a list of the candidates for the reaction. One candidate atom (or ion) is selected from the list using a random number. Then, the type of the chosen particle is changed using the rate constant (1) and random numbers, and the MD simulation is continued. The details of the algorithm is described in our previous paper [3].

In the MD simulation, we replenish the solution with cations using the following method. When the concentration of the upper part of the solution becomes lower than the target concentration, we search for the neutral particle which has the smallest z-coordinate in the replenishing layer and change it to a cation. The cation can diffuse and pass through the filter to enter the solution. When a deposition reaction occurs, the filter is moved upward to keep the volume of the solution constant. The width of this movement should be small enough so that the dynamics of the system is not influenced by this movement. In the present simulation, the width is smaller than 0.08[Å].

The temperature of the whole system is controlled by Nosé's method [8,9]. However, when the reactions on the electrode occurs frequently, it becomes difficult to control the temperature only by Nosé's thermostat. Therefore, we put the cooling layer below the electrode. When the temperature of the electrode increases, the velocities of the atoms in the cooling layer are reduced so that the electrode is cooled down by heat conduction.

3. Simulation conditions

We performed the simulations using simple interatomic potentials; Lennard-Jones potential, soft-core potential and soft-core potential + screened Coulomb potential. These potentials are represented by

$$\phi_{ij}(r) = \epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right\}, \tag{2}$$

$$\phi_{ij}(r) = \epsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^{12}, \tag{3}$$

$$\phi_{ij}(r) = \epsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^{12} + \frac{q_i q_j}{4\pi\epsilon_0 r}\exp\left(-\frac{r}{a}\right), \tag{4}$$

respectively, with

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}},$$

where σ_{ij} is the diameter of the particles, ϵ_{ij} is the depth of the energy. q_i and q_j are electronic charges. ϵ_0 is a dielectric constant and a is the screening constant for the Coulomb potential. Equation (2) is used for the

interactions "metal atom–metal atom", "metal atom–cation" and "solvent particle–all the particles". Equation (3) is used for the interactions "metal atom–anion" and "neutral replenishing particle–cation". For the interactions between ions, we use equation (4). We assume that metal atoms are silver atoms and the crystal has the FCC structure. We also assume NO_3^- as anions and H_2O as solvent particles. All the particles are assumed to be spherical. Table 1 shows the values of σ_{ii} and ϵ_{ii} for the pairs of the same kind of particles. The charge is $|q_i| = 1e$ and the screening constant a is 1.50[Å].

The target temperature of all the simulations is $T = 300\,\mathrm{K}$. The time mesh of integration is $\Delta t = 1.0\,\mathrm{fs}$. The simulation without reactions is performed for 10,000 steps to generate the initial configuration. For reactions, we assume $\psi/k_BT = 12.8$, corresponding to the potential energy between metal atoms at the nearest neighbor distance. The reaction interval is $N_r = 3000$. The simulations are performed for several values of μ/k_BT.

4. Results

4.1 Static structure in solution

Figure 2 shows the radial distribution functions (RDF) of the particles in solution obtained by the simulation without reactions. The RDF of cation–cation has a large peak at around 1.5 $\sigma_{\mathrm{Ag-Ag}}$. This means that the cations are surrounded by the anions owing to the Coulomb attractive force. Solvent particles are also distributed around the cations though the peak of the cation-solvent RDF is not so high. Since the Coulomb potential is not included in the interaction between solvents in our simple model, solvent particles are distributed almost uniformly in solution. The dynamics of the cations is expected to be largely influenced by surrounding anions.

4.2 Deposition on FCC (111) surface

Figure 3 shows the snapshots of the simulation with reactions for $\mu/k_BT = 35.0$ at (a) $t = 0.9\,\mathrm{ns}$ and (b) $t = 5.6\,\mathrm{ns}$. The total number of particles at the initial state is 2616 and the initial surface is the FCC (111) surface. The initial concentration of cations and anions is 2.0 mol/l. The solvents and the replenishing layer are not plotted in the figure. It is observed that some of the cations stick to the electrode surface in figure 3(a). These cations are the candidates for the deposition reaction. The electrode becomes thicker as deposition occurs and the surface becomes rough in the final state of the simulation.

Table 1. Potential parameters for the same kinds of particles used in the MD simulations.

	Metal atom	*Cation*	*Anion*	*Solvent*
σ_{ij} [nm]	0.261	0.252	0.528	0.317
ϵ_{ij} [10^{-20} J]	21.21	1.128	3.664	0.108

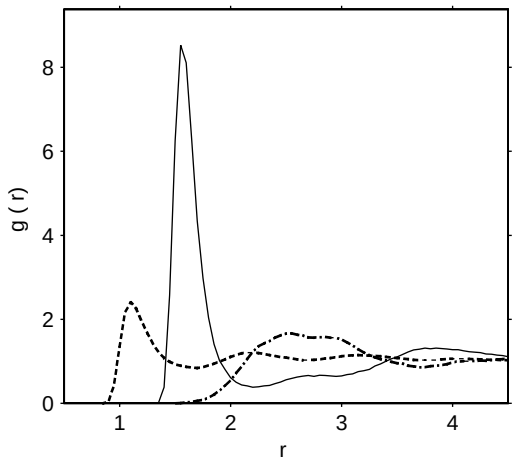

Figure 2. Radial distribution functions of the particles in solution. Cation–anion (solid lines), cation–solvent (dashed line) and cation–cation (dash–dot line). The length is scaled by $\sigma_{\mathrm{Ag-Ag}}$.

Figure 4 shows the contour plots of a series of surface structures for $\mu/k_BT = 32.5$ and $\mu/k_BT = 35.0$. The number of deposited atoms on the surface at $t = 5.5\,\mathrm{ns}$ is 261 for $\mu/k_BT = 32.5$ and 275 for $\mu/k_BT = 35.0$. The growth rate of the surface for $\mu/k_BT = 35.0$ is larger than that for $\mu/k_BT = 32.5$. The surface for $\mu/k_BT = 35.0$ is rough compared to that for $\mu/k_BT = 32.5$. In order to compare the roughness of the surface quantitatively, we evaluated the standard deviation s_h defined by

$$s_h = \sqrt{\frac{1}{N_s}\sum_{i=1}^{N_s}(h - z_i)^2}, \tag{5}$$

where

$$h = \frac{1}{N_s}\sum_{i=1}^{N_s} z_i \tag{6}$$

is the average height of the surface, N_s is the number of surface metal atoms and z_i is the z-coordinate of surface metal atom i. s_h corresponds to the thickness of the

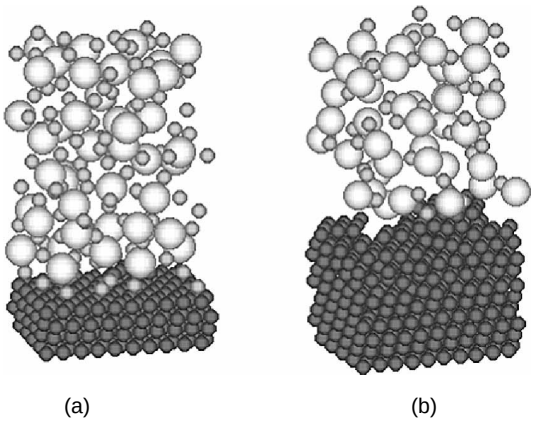

Figure 3. Snapshots of the simulation at (a) $t = 0.9\,\mathrm{ns}$ and (b) $t = 5.6\,\mathrm{ns}$. The initial surface is FCC (111) surface and $\mu/k_BT = 35.0$. Dark circles are metal atoms. Small and large grey circles are cations and anions, respectively.

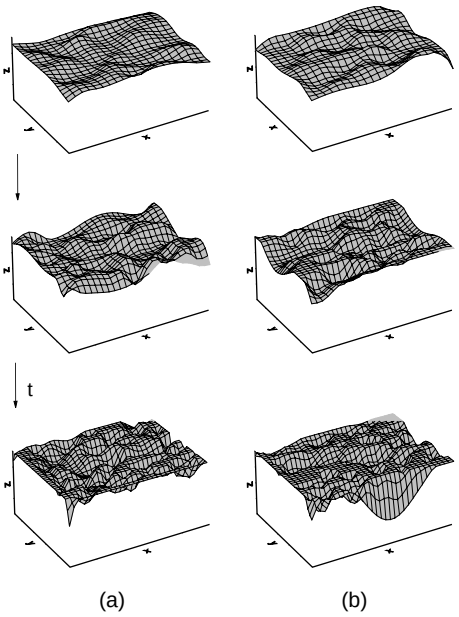

Figure 4. Contour plots of the surfaces for (a) $\mu/k_BT = 32.5$ and (b) for $\mu/k_BT = 35.0$ at $t = 1.8$, 3.7 and 5.5 ns from top. The initial surface is the FCC (111) surface.

surface. Figure 5(a) shows the time dependence of s_h for the simulations corresponding to figure 4. The values of s_h for $\mu/k_BT = 35.0$ are slightly larger than those for $\mu/k_BT = 32.5$. It is observed that s_h for $\mu/k_BT = 32.5$ and 35.0 shows stepwise increase at $1.5 \sim 2.0$ ns and ~ 3.5 ns. This means that the surface shows layer growth, i.e. adatoms diffuse on the surface and crystallize at stable sites. For larger μ/k_BT, the surface becomes rough and adatoms crystallize at the deposited positions without the surface diffusion (continuous growth).

4.3 Deposition on FCC (100) surface

The simulations of the deposition on (100) surface have been performed for $\mu/k_BT = 20.0$, 30.0 and 35.0. The total number of particles in the system is 3814 and the initial concentration of the solution is 2.0 mol/l. The time dependence of the standard deviation s_h of this case is shown in figure 5(b). In contrast to figure 5(a), s_h increases continuously and stepwise increase is not observed for $\mu/k_BT = 30.0$ and 35.0. This is due to the difference in the diffusion of adatoms. Since an adatom on a stable site on (100) surface has four nearest neighbor bonds, while that on (111) surface has three bonds, the former atom is more stable than the latter. The distance between the stable sites on the (100) surface is ~ 0.41 nm, and that on the (111) surface is ~ 0.17 nm. Therefore, the mobility of adatoms on (100) surface is smaller than that on (111) surface. Adatoms on the (111) surface diffuse frequently to a kink site to become stable, while those on the (100) surface tend to crystallize at the deposited sites without the surface diffusion. As a result, the roughness of the surface becomes large when the initial surface is (100) surface. Such a difference is reflected in the standard deviation s_h as shown in figure 5.

4.4 Filling V-shaped grooves

In order to study the void formation during the growth, we have performed the simulation of filling grooves. Figure 6 shows the snapshots of the simulation of filling a V-shaped groove of aspect ratio 2 for $\mu/k_BT = 32.5$. The temporal surfaces at $t = 2.28$ (a), 4.58 (b) and 8.82 ns (c) are plotted. The initial configuration of the metal atoms is arranged so that the [111] direction is parallel to the z-axis. In figure 6, cations and anions located in the groove are plotted as well as the metal atoms. It is observed that large voids appear in the middle of the film and the surface is almost flat after the filling.

Since the concentration of cations near the surface is reduced after the deposition and cations are supplied from above, the growth rate around the upper edge of the groove is larger than that of the lower part. Therefore, the upper part of the groove grows faster and bumps of deposited atoms appear at the edge of the groove. These bumps prevent the cations from diffusing into the groove (shadowing effect). The cations tend to be deposited on these bumps. Finally, the two bumps are connected to each other and the void is created. In figure 6, it is also observed that an anion and some cations remain in the void after the filling. These ions are regarded as impurities in the metallic film.

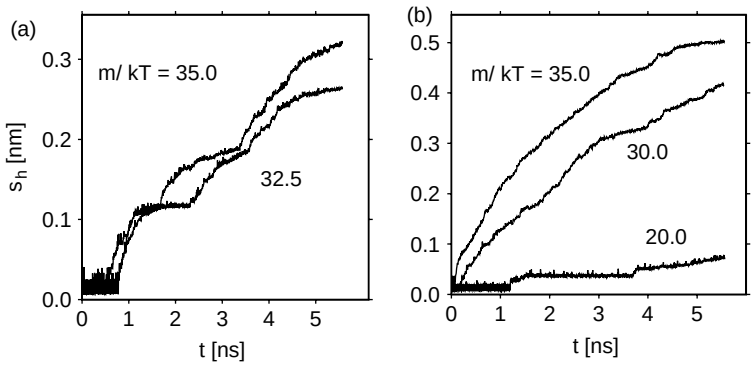

Figure 5. The standard deviation of the surface s_h as a function of time. The initial surfaces are (a) FCC (111) surface and (b) FCC (100) surface.

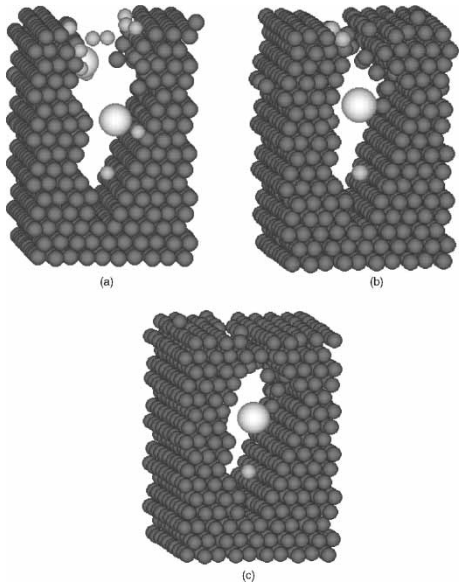

Figure 6. Snapshots of the simulation of filling a groove of aspect ratio 2 with $\mu/k_BT = 32.5$ at $t = 2.28$ ns (a), 4.58 ns (b) and 8.82 ns (c). Dark circles are metal atoms. Large and small grey circles are anions and cations, respectively.

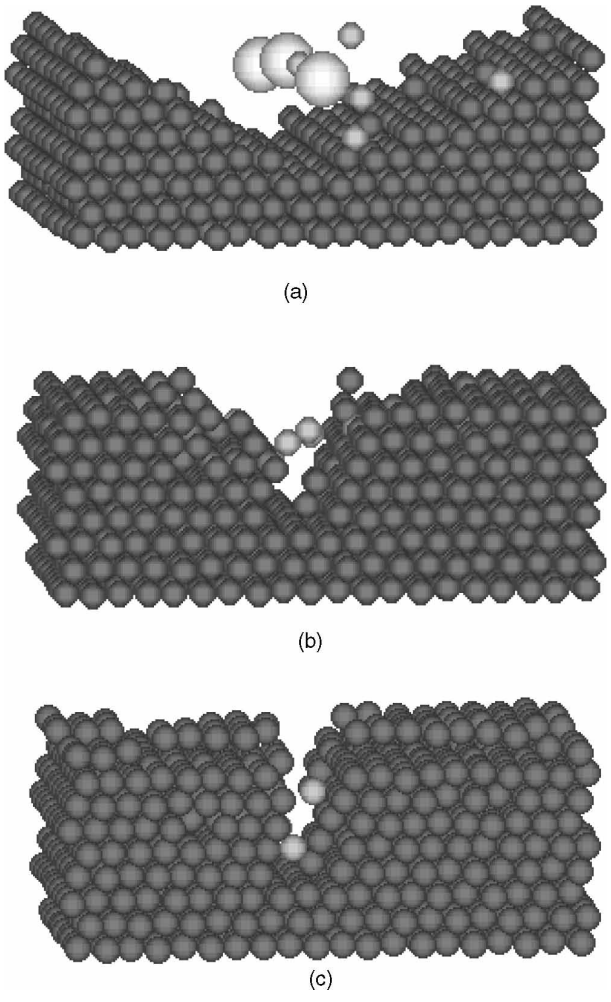

Figure 7. Snapshots of the simulation of filling a groove of aspect ratio 0.5 with $\mu/k_BT = 32.5$ at $t = 0.23$ ns (a), 4.61 ns (b) and 9.00 ns (c). The symbols are the same as those in figure 6.

Figure 7 shows the filling process of the groove of lower aspect ratio (0.5). The initial surface has several steps aligned on the slope of the groove and cations on these steps have more bonds than those on the flat surface. Therefore, deposition occurs more frequently than on a flat surface. These steps grow in horizontal direction and the surface becomes flat as the groove is filled. In figure 7(c), the upper part of the film is a flat surface which grows in the same way as the flat (111) surface. However, it is observed that a narrow groove remains in the middle of the surface. Such a narrow groove could lead to the formation of a large void elongated in the direction perpendicular to the surface. This means that the small roughness with a low aspectratio can cause the formation of large voids.

5. Summary

In this paper, we studied the surface structure and void formation using the MD–MC hybrid simulations for electrodeposition. The main results are as follows.

- We performed the simulations of the deposition on the FCC (111) and (100) surfaces. In both cases, the surface becomes rough as μ/k_BT increases. The adatoms on the (111) surface diffuse more frequently than those on the (100) surface, which leads to the layer growth. On the other hand, the deposited atoms on (100) surface show continuous growth.
- We performed the simulation of filling V-shaped grooves. In filling the groove with high aspect ratio, a large void appears in the film. Some ions are observed to be embedded in the film as impurities. In the case of the groove with a low aspect ratio, a hollow part remains in the middle of the groove though the surface becomes almost flat after the filling.

The solution used in the present simulations is free from additives and impurities. In real electrodeposition technology, additives play an important role to control the surface structure. Since it is straightforward to include additives in the simulation system, the hybrid simulation would be useful to investigate the microscopic behavior of additives on the growing surface.

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