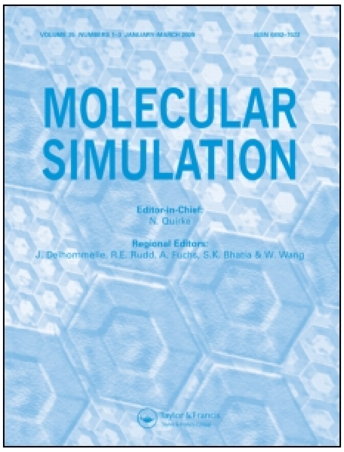

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Computer simulation of electrodeposition: hybrid of molecular dynamics and Monte Carlo

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Computer simulation of electrodeposition: hybrid of molecular dynamics and Monte Carlo

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In this paper, we propose a hybrid method of molecular dynamics (MD) and Monte Carlo (MC) for the simulation of thin film growth with electrodeposition. In this method, we simulate the dynamics of particles by the MD method, while the reactions of the deposition are realized by the MC method. Two reactions are taken into account, that is, adsorption and desorption, which are treated as changes in the species of the particles. When adsorption occurs, one of the metal ions near the surface changes to a metal atom. Desorption is the reverse process. We performed the simulation using a simple model for the solution–electrode interface, consisting of metal atoms, metal ions, anions and solvent particles. The correlation between the surface structure and the deposition condition is investigated.

Keywords: Molecular dynamics; Monte Carlo; Hybrid simulation; Electrodeposition

1. Introduction

Electrodeposition is a popular technique to plate thin films onto metal surfaces, which has been used in various fields of electrochemical engineering [1]. The electrodeposition consists of the following four steps:

1. Diffusion of solvated metal ions in solution towards an electrode.
2. Desolvation in the double layer.
3. Electron transfer reaction (adsorption).
4. Surface diffusion of adatoms and crystallization.

Although a lot of advanced experimental techniques, such as scanning tunneling microscope and atomic force microscope, have been developed to observed the surface structure of the film on an atomic length scale, it is not yet fully understood how the deposition conditions, for example, how overpotential, solution structures, etc. influence the resulting film structure.

Molecular dynamics (MD) simulation is a powerful method to investigate the relationship between the surface structures and the deposition conditions on an atomic scale. There are a lot of MD simulations performed for crystal growth such as vapor deposition, growth from melts and growth from supersaturated solutions. These simulations can be performed within the framework of classical mechanics. However, the conventional MD method cannot be used for the reactions of electrodeposition. Monte Carlo (MC) simulation is also a useful tool to study crystal growth. In most of the MC studies of crystal growth, solid-on-solid (SOS) models have been used as a model of vapor deposition and crystal growth from solution [2,3]. Recently, Kaneko *et al.* extended the SOS model to the solid-by-solid (SBS) model which allows creation of vacancies in the film [4–6]. In the SBS model, rates of adsorption and desorption are given as input parameters. These parameters are related to experimental parameters such as the overpotential and the exchange current density [4].

In this paper, we propose a new method for the simulation of crystal growth with electrodeposition, which is a hybrid of MD and MC methods. In the hybrid method, the processes that depend on the dynamics of particles, i.e. steps 1, 2 and 4 listed above, are simulated by the MD method. Step 3, which depends upon the reactions of

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deposition, is performed by the MC method. The deposition rate is the same as that used in our MC simulation of the SBS model. We apply this method to a simple model of the solution–electrode interface to study the relationship between the film structure and the desorption conditions.

In Section 2, we describe the model system of the solution–electrode interface. The details of the method of computation are described in Section 3 and the results of the simulations are shown in Section 4. Summary and discussion are given in Section 5.

2. Model

We consider a three-dimensional model which consists of six types of particles as shown in figure 1 [7]. These particles form the solid–liquid interface, which represents an electrode in the electrolytic solution. This model is divided into three parts; the electrode, the solution and the replenishing layer, which is set to add metal ions to the solution when the density of metal ions in the solution becomes low. In the electrode part, the particles of the bottom layers are substrate atoms. These atoms are frozen to prevent other particles from going across the lowest boundary. The solution consists of three types of particles; metal ions, anions and solvent particles. In the replenishing layer, there are replenishing particles and metal ions to control the concentration of metal ions in solution. We put a semipermeable filter between the solution and the replenishing layer. In x- and y-directions, we use the periodic boundary conditions.

Reduction and oxidation are important processes in electrode reactions. In our model, we assume two types of "reactions", adsorption and desorption, to represent the above reactions. Adsorption is regarded as a change of a metal ion near the surface to a metal atom. Desorption is the reverse process, i.e. the change of a metal atom on the surface to a metal ion. We introduce the adsorption rate $k_n^{\dagger}$ and the desorption rate k_n, which depend upon the number of bonds n (the nearest neighbor metal atoms). We assume the ratio of the adsorption rate $k_n^{\dagger}$ and the desorption rate k_n using the formula [2,3]:

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

where n_k is the number of bonds at the kink site, ψ is the binding energy between the solid atoms and T is the temperature. μ is the chemical potential, which is regarded as the overpotential in our simulation. We use μ as the control parameter of the growth. The relationship between these rate constants and the experimental parameters is described in our previous paper [4].

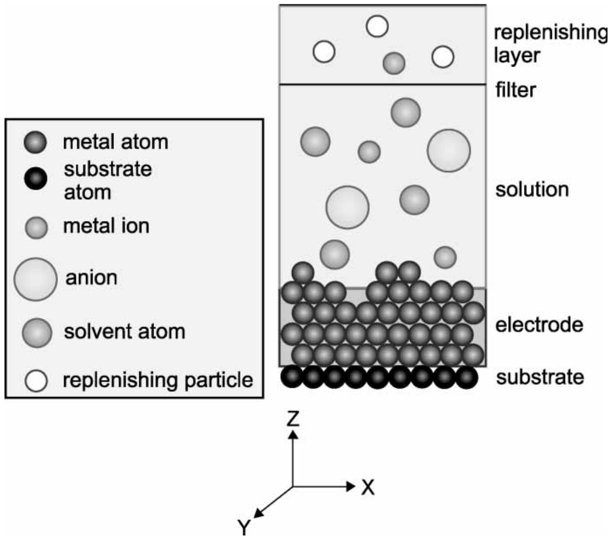

Figure 1. Schematic picture of the model.

3. Method of computation

3.1 Hybrid of molecular dynamics and Monte Carlo

We simulated the trajectories of all the particles by the MD method and at the same time we realized the deposition process by the MC method. The outline of the combination of the MD and MC methods is as follows.

1. Solve the equations of motion of the particles by the MD method for N_{r} steps. The N_{r}th step is regarded as the "reaction" step.
2. At every "reaction" step, the reaction is performed by the MC method.
    (a) Assume that the "reactions" occur only on the surface of the metal crystal. Therefore, at the "reaction" step, first search the surface particles.
    (b) Carry out the reaction (adsorption or desorption) by the MC method.
3. Repeat 1 and 2.

3.2 Reactions: Monte Carlo method

Adsorption and desorption are regarded as changes in the species of the particles. That is, we change the interaction potential of the selected particle at the "reaction" step. In the simulation, we decided which reaction occurs by the MC method. We assumed that the adsorption rate per unit time does not depend on n,

$$k_1^{\dagger} = k_2^{\dagger} = \cdots = k_{11}^{\dagger} = k^{\dagger}. \tag{2}$$

If we assume that the electrode forms the FCC structure, the possible number of bonds n is $1 \sim 12$. Then, the adsorption per unit time k_{c} and the desorption per unit time

k_a are written as

$$k_c = k^{\dagger} N_c, \tag{3}$$

$$k_a = \sum_{n=1}^{11} k_n N_{a(n)}, \tag{4}$$

where N_c denotes the number of cations near the surface and $N_{a(n)}$ denotes the number of metal atoms with n bonds that can be desorbed from the surface. Using equation (1), the probabilities of desorption and adsorption are given by the following equations, respectively.

$$\frac{k_a}{k_a + k_c} = \frac{\sum_{n=1}^{11} N_{a(n)} k_n}{\sum_{n=1}^{11} N_{a(n)} k_n + N_c k^{\dagger}} = \frac{\sum_{n=1}^{11} N_{a(n)} \frac{k_n}{k^{\dagger}}}{\sum_{n=1}^{11} N_{a(n)} \frac{k_n}{k^{\dagger}} + N_c}, \tag{5}$$

$$\frac{k_c}{k_a + k_c} = 1 - \frac{k_a}{k_a + k_c} \tag{6}$$

At the "reaction" step, we performed the following processes.

1. We searched the surface metal atoms on the metal surface and the metal ions near the surface. These particles are the candidates for reactions.
2. At the "reaction" step, only one reaction can occur. We decided which reaction occurs with the use of equation (5) and a random number on [0,1]. If the random number is smaller than the probability of desorption, $k_a/(k_a + k_c)$, the desorption reaction occurs. Otherwise the adsorption reaction occurs.
3. When the adsorption occurs, we selected a candidate particle by using a random number. When the desorption occurs, we selected the number of bonds by using equation (4) and a random number, then we decided which particle is desorbed.
4. We changed the species of the chosen particle. When the adsorption reaction is selected, we changed a metal ion to a metal atom, and when the desorption reaction is selected, we changed a metal atom to a metal ion.

3.3 Replenishing metal ions

If the simulation is continued for a long time, the number of metal ions in the solution is reduced by the reactions of deposition. In order to keep the concentration of metal ions constant, we set the replenishing layer in the model to add metal ions to the solution. We regard this operation as supplying metal ions from the bulk solution. We put a semipermeable filter between the solution and the replenishing layer. This filter allows only metal ions to pass towards the solution from the replenishing layer, and other particles and metal ions in solution cannot pass through the filter. This filter acts as an elastic wall for other particles and metal ions in solution.

We replenished the solution with metal ions using the following method. First, we checked the concentration of the upper part of the solution, which is regarded as the bulk liquid. If the concentration of this part is lower than the target concentration, we searched for the replenishing particle that has the smallest z-coordinate in the replenishing layer, and changed the species of the chosen particle to a metal ion. The metal ion can pass through the filter and enter the solution by diffusion. We checked the concentration again after a while, and if the concentration is still lower than the target one, we searched for another replenishing particle, and changed the species of that. When a metal ion passes through the semipermeable filter, we moved the filter upward to keep the volume of the solution constant. Here, the width of the movement at one time is small enough to prevent this movement from influencing the dynamics of the system. In our simulation, the width is smaller than 0.018 Å.

4. Results

4.1 Simple model for solution–electrode interface

We tested the above algorithm using a simple system of solution–electrode interface. We assumed three types of potential $\phi_{ij}(r)$ between particles i and j depending upon the species of the particles. That is, 12-6 Lennard–Jones potential, soft core potential, soft core potential + screened coulomb potential, which are represented by

$$\phi_{ij}(r) = \epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right\}, \tag{7}$$

$$\phi_{ij}(r) = \epsilon_{ij} \left(\frac{\sigma_{ij}}{r} \right)^{12}, \tag{8}$$

$$\phi_{ij}(r) = \epsilon_{ij} \left(\frac{\sigma_{ij}}{r} \right)^{12} + \frac{q_i q_j}{r} \exp\left(-\frac{r}{a} \right), \tag{9}$$

respectively, where q_i and q_j are the effective charges and a is a screening constant of the Coulomb potential. For the interactions between a metal atom and a metal atom, a metal atom and a metal ion, a solvent particle and all kind of particles, we use equation (7). For the interaction between a metal atom and an anion, a replenishing particle and a cation, a replenishing particle and an anion, we use equation (8). For the interaction between ions, we use equation (9).

We assumed metal atoms as silver atoms. We choose NO_3^- as an anion and H_2O as a solvent particle. The shapes of these particles are assumed to be spherical. The parameters are the following: $\sigma_{M-M} = 2.609$ Å, $\sigma_{c-c} = 2.52$ Å, $\sigma_{a-a} = 5.28$ Å, $\sigma_{s-s} = 3.167$ Å and $\epsilon_{M-M} = 21.29$, $\epsilon_{c-c} = 1.128$, $\epsilon_{a-a} = 3.664$, $\epsilon_{s-s} = 0.108$. (The unit of ϵ is 10^{-20} J). Here the suffices M, c, a and s denote metal, cation, anion and solvent, respectively. We assumed $|q_i| = 1e$ and the screening constant a is 1.50 Å. Also, we assumed

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}. \tag{10}$$

The initial concentrations of cations and anions are 2.0 mol/l and $T = 300$ K. The initial surface of electrode is

8 × 8 (111) surface. As the parameter for the MC simulation, we assumed $\psi/k_BT = 12.8$, corresponding to the potential energy of a metal atom at the nearest neighbor distance. We used μ/k_BT as a control parameter and $N_r = 5000$. The initial system contains 23 cations, 23 anions, 598 solvents, 192 metal atoms and 241 replenishing particles.

4.2 Results

Figure 2 shows the surface structures for $\mu/k_BT = 35.0$ (a) and 50.0 (b) at the final state of the simulation. It is observed that the surface for $\mu/k_BT = 50.0$ is rough compared to the case for $\mu/k_BT = 35.0$. This is because, the growth rate for $\mu/k_BT = 50.0$ is larger than that for $\mu/k_BT = 35.0$. The number of metal atoms deposited on the surface is 20 for $\mu/k_BT = 35.0$ and 40 for $\mu/k_BT = 50.0$. Figure 3(a) shows the average height of the surface atoms

$$h = \frac{1}{N_s}\sum_{i=1}^{N_s} z_i, \tag{11}$$

where N_s is the number of surface atoms and z_i is the z-coordinate of the ith surface atom. h for $\mu/k_BT = 35.0$ does not increase in the first part of the simulation. A metal ion near the surface is adsorbed, but a single metal atom (adatom) is unstable on the surface and is easily desorbed. As a result, adsorption and desorption occur repeatedly and surface growth does not occur. Once a nucleation core is formed (i.e. two deposited atoms are combined), the surface growth starts at around $t = 550$ ps. For $\mu/k_BT = 50.0$, on the other hand, the surface growth occurs in the early stage of the simulation. This means that the nucleation occurs rather easily due to the high value of the deposition rate. The variance of the surface fluctuation

$$\Delta = \sqrt{\frac{1}{N_s}\sum_{i=1}^{N_s}(z_i - h)^2} \tag{12}$$

is shown in figure 3(b). This corresponds to the thickness of the surface. The overall feature of Δ is the same as that of h. These results show that the deposition and nucleation processes can be simulated by our method using μ/k_BT as a control parameter.

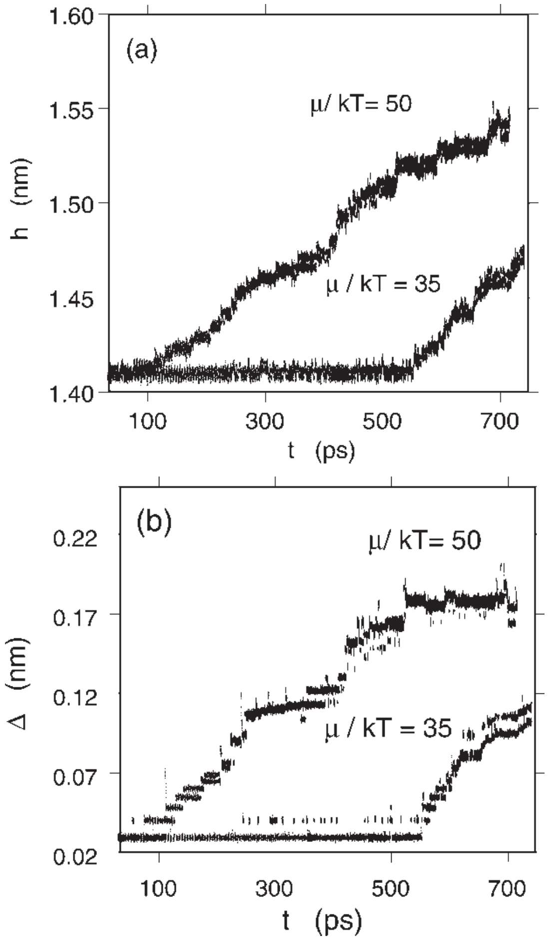

Figure 3. (a) The average height of the surface h as a function of time. (b) The thickness of the surface Δ as a function of time.

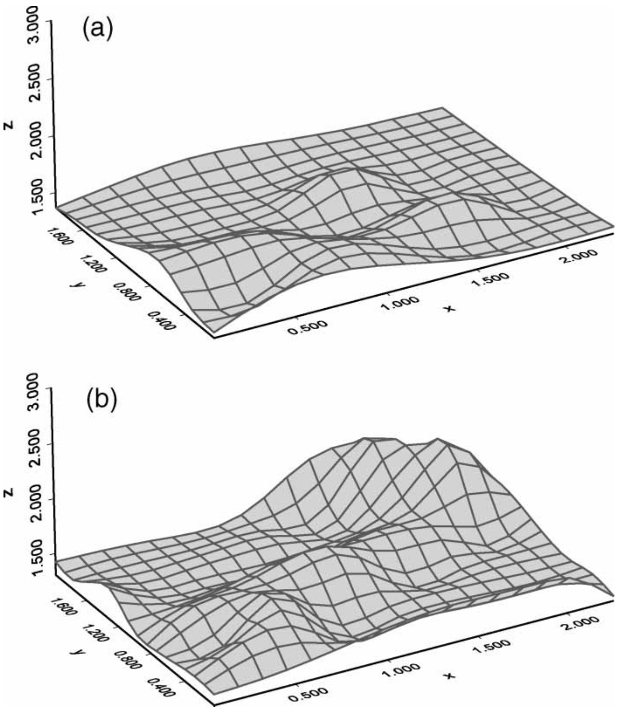

Figure 2. The surface structures for (a) $\mu/k_BT = 35.0$ at $t = 740$ ps and (b) $\mu/k_BT = 50.0$ at $t = 688$ ps. The unit of labels is nm.

5. Summary

In this paper we developed the hybrid method of molecular dynamics and Monte Carlo for the simulation of electrodeposition. Using this method, we simulated the trajectories of particles by the MD method.

During the MD simulation, we realized the electrodeposition by the MC method, and using this method, we performed the simulations to study the relation between the structure of thin film and the conditions of electrode and solution. Although the present simulations are small ones with simple interaction potentials, we succeeded in simulating the deposition process and showing the difference in the nucleation process depending upon the control parameter $\mu/k_{\mathrm{B}}T$. Since more than 23 atoms (the initial number of cations) are deposited, the replenishing process works well. We expected that the concentration overpotential, which is hard to be evaluated in experiments, can be estimated separately using our simulation method.

Since the size of the system is small in the present work, it is difficult to compare with the experiments quantitatively. It would be of interest to perform the simulations for large systems.

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