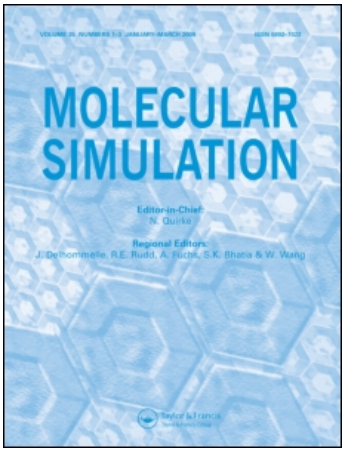

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Monte Carlo simulation of damascene electroplating: effects of additives

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Monte Carlo simulation of damascene electroplating: effects of additives

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The influence of additives on the filling process of via holes in damascene electroplating is investigated with use of a kinetic Monte Carlo method. The basic system is the solid-by-solid model for crystal growth which includes the vacancy formation during the growth of thin film. Three kinds of additives are included in the model to control the local surface growth rate. Inhibitors and levelers have the effect of preventing the deposition, while accelerators increase the local growth rate. Levelers are modeled to stick to the tips of the surface. We performed a series of simulations by changing the parameters which characterize the additives to see their influence on the filling mechanism. It is shown that void-free filling is possible by the combination of the effects of the additives.

Keywords: Damascene electroplating; Void formation; Additives; Monte Carlo simulation

1. Introduction

The copper damascene electroplating has been widely studied as a new technique for the production of LSI interconnections. The dual damascene copper plating developed by the IBM group consists of (i) patterning of the circuits, (ii) seed-layer plating on the patterned materials, (iii) electroplating of copper (filling via holes and trenches) and (iv) planarization (removing excess metals) [1]. In this paper, we focus our attention on the filling process (iii). A crucial point in this process is to fill via holes and trenches completely removing the void formation. The surface roughness and void density of metal films produced by electroplating strongly depend upon the composition and concentration of additives in solution. Different kinds of additives have been used to control the local growth rate. In damascene plating, large voids tend to appear when one uses copper sulfate solution without additives [2]. An important and urgent requirement in semiconductor engineering is to find out the optimal conditions for the additives to establish the complete void-free filling.

Three kinds of additives are commonly used in the damascene plating with copper sulfate solution; polyethylene glycol (PEG), bis (3-sulfopropyl) disulfidedisodium (SPS) and Janus Green B (JGB) [3–7]. PEG is supposed to be an inhibitor which suppresses the deposition of copper atoms when used with Cl^- ions in solution. SPS acts as an accelerator which enhances the deposition. The levelers also have an inhibiting effect and tend to stick to tips and corners of the surface. The inhibitors prevent the growth of the upper part of the hole and the accelerators enhance the bottom-up process. The combination of these effects is expected to realize the complete void-free filling [8].

The purpose of the present work is to study the influence of the additives in the damascene plating by the Monte Carlo (MC) simulation. The basic idea is the solid-by-solid (SBS) model which was developed by our group. In theoretical studies of crystal growth, solid-on-solid (SOS) models have been widely used as a model of vapor deposition and the growth from solution. In the SOS model, vacancy formation is prohibited. In real electrodeposition, however, lattice defects play an important role for the physical properties of the film. Therefore, we extended the SOS model [9] to include the vacancy formation [10–12]. We call the new model as the "solid-by-solid" model since the deposition can occur at any empty sites adjacent to the surface atoms. The characteristics of the SBS model has been investigated

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in detail in relation to the correlation between the surface structure and the void structure [10–12]. The SBS model has also been studied as a model for damascene plating to investigate the void formation mechanism in the case without additives [12,13]. It has been found that large voids appear in the film when the via holes are filled with deposited atoms. The qualitative features of the voids are similar to those found in experiments using additive-free solutions. Recently, we have included inhibitors and accelerators in the SBS model to control the filling process [14]. It has been shown that the void size becomes small due to the effect of additives. However, small voids still appear in the hole and the void formation could not be eliminated completely.

As an extension of these works, we include levelers as well as inhibitors and accelerators in the SBS model. These additives occupy one of the lattice sites of the SBS model and diffuse in the solution by random walk. The surface growth and the diffusion of additives are simulated simultaneously. When the additives are on the surface, they have the effect of decreasing or increasing the deposition rate on the lattice sites around them. The shape of the growing surface is dependent upon the distribution of additives. Therefore, it is expected that the void formation can be suppressed by choosing appropriate parameters for the additives. We performed a series of MC simulations of this combined model of SBS and additives for various parameters for the additives to study their influence on the void formation process. This paper is organized as follows. In sections 2 and 3 we describe the combined system of the SBS model with additives and the method of computations. The results of MC simulations are shown in Section 4. The summary and discussion are given in Section 5.

2. Solid-by-solid model with additives

We used the SBS model with a two-dimensional square lattice, each site of which is a solid atom, a liquid atom or a vacancy. Reactions occur on the surface of solid atoms. Adsorption and desorption are the change of a liquid atom to a solid atom and that of a solid atom to a liquid atom, respectively. The diffusion of surface atoms is also taken into account. The rate constants for adsorption k_n^+, desorption k_n and surface diffusion k_{nm}, are dependent upon the number of nearest neighbor solid atoms n, m and following relations are assumed [9].

$$\frac{k_n}{k_n^+} = \exp\left\{\frac{(2-n)\psi}{k_BT} - \frac{\mu}{k_BT}\right\}, \tag{1}$$

$$k_{nm} = \frac{k_n k_m^+}{k_1^+}\exp\left\{\frac{\psi - E_\mathrm{d}}{k_BT}\right\}, \tag{2}$$

where ψ is the binding energy between atoms, μ the chemical potential and E_d the activation energy for the surface diffusion.

The relation (1) is obtained from the condition of microscopic detailed balance at a kink site in equilibrium ($k_2^+ = k_2$) [9]. The surface growth does not occur in equilibrium since $k_1 > k_1^+$, $k_2 = k_2^+$ and $k_3 < k_3^+$ at $\mu = 0$. For $\mu > 0$, the surface grows towards the liquid side since the adsorption rate becomes larger than the desorption rate. The parameter μ is regarded as the electrochemical potential, which is the control parameter of the growth. The growth rate increases as μ becomes large. We have performed a series of MC simulations for various deposition conditions to study the surface morphology, the void density and their relation to the model parameters. The surface becomes rough and the void density increases as μ becomes large. The details of the results are described in our previous papers [10–12].

Most of the additives used in electrodeposition are polymers which are distributed in solutions. In order to include the effect of additives in the SBS model, we introduce the following assumptions.

1. Additives occupy lattice sites in the solution part and diffuse towards the surface by random walk.
2. Additives have two length scales: the core size and the action range. The core size is defined as the minimum distance between the additives and the surface atoms. The action range is defined as the region in which the rate constants are modified by the additives.
3. When additives are near the metal surface, they stick to the surface. (The sticking probability is introduced.)

The first assumption is to include the diffusive motion of additives in solution. The diffusion is isotropic or biased depending upon the additive species. The second assumption takes into account the fact that the additives are not a single atom but flexible polymers. The action range is regarded as the effective radius of the polymer molecules. It is suggested in experiments that additives tend to stay on the surface during the deposition when some of the atoms in polymer chains are bound to surface metals. This results in the duration of the effect of additives throughout the deposition. The third assumption is to take into account such properties (although no information is available on the sticking probability).

The effects of the additives on the surface are assumed as follows. Here the indices "inh", "lev" and "acc" denote inhibitor, leveler and accelerator, respectively. Inhibitors prevent the deposition on the surface sites within the range l_inh from each inhibitor. That is, the adsorption event is rejected if the surface site is within the action range l_inh of inhibitors in the MC simulation. Here we denote the action range as l_inh. The core size is denoted as $l_\mathrm{inh-c}$, which is smaller than l_inh. When the minimum distance between an inhibitor and surface atoms is $l_\mathrm{inh-c}$, the inhibitor stays at the position with the sticking probability $k_\mathrm{a-inh}$. For levelers, we introduce the action range l_lev and the core size $l_\mathrm{inh-c}$ which are smaller than those of inhibitors. The adsorption is rejected on the sites within l_lev from the levelers. Accelerators also have the action range l_acc and

the core size $l_{\mathrm{acc-c}}$. The adsorption rate $\tilde{k}_n^+$ on the surface sites within the range l_{acc} from the accelerators is set to be larger than k_n^+ of the original SBS model. For levelers and accelerators, we set the sticking probabilities $k_{\mathrm{a-lev}}$ and $k_{\mathrm{a-acc}}$, respectively. The surface growth of the SBS model, diffusion of additives, inhibiting and accelerating effects of additives are simulated simultaneously.

3. Method of computation

The algorithm of the MC simulation of the SBS model is the following [10]. We denote the number of lattice sites with n bonds on which adsorption can occur as $N_{c(n)}$ and the number of surface atoms which can be desorbed as $N_{a(n)}$. The rate of adsorption at any site per unit time and that of desorption are

$$k_c = \sum_{n=1}^{3} k_n^+ N_{c(n)}, \quad k_a = \sum_{n=1}^{3} k_n N_{a(n)}, \tag{3}$$

respectively. The rate of surface diffusion is denoted as

$$k_d = \sum_{n,m=1}^{3} k_{nm} N_{d(nm)}, \tag{4}$$

where $N_{d(nm)}$ is the number of pairs of surface atoms (with n bonds) and their adjacent sites (with m bonds). The rate at which one of the three events occurs is

$$k_t = k_c + k_a + k_d. \tag{5}$$

To start the MC simulation, we make a table of the surface atoms and a table of the lattice sites on which deposition occurs. We also make a table of diffusion events, i.e. surface atoms and their 1st and 2nd neighbor empty sites. We first decide the event (adsorption, desorption or diffusion) from the ratios k_c/k_t, k_a/k_t, and k_d/k_t using a random number. Let R be a random number on [0,1]. We choose "adsorption" if $R < k_c/k_t$, "desorption" if $k_c/k_t \leq R < (k_c + k_a)/k_t$ and "diffusion" if $(k_c + k_a)/k_t \leq R$. Secondly, we decide the type of events (the number of bonds n). In the case of adsorption, for example, the type is determined from $k_1^+ N_{c(1)}/k_c$, $k_2^+ N_{c(2)}/k_c$ and $k_3^+ N_{c(3)}/k_c$ using a random number on [0, 1]. Finally, we select an atom from the table and renew the tables.

We include the effects of the additives in the MC algorithm using the following method. At the beginning of the simulation, the additives are distributed on the lattice sites in the solution part above the surface. We performed the simulation of the random walk of the additives without the surface growth to create the initial distribution of the additives. The mobility of inhibitors is five times smaller than that of accelerators since the inhibitors used in experiments are polymer particles larger than other additives. We performed more than 100,000 random walks for each additive particle.

When additives are distributed near the surface, we start the MC simulation combining the surface growth and the random walk of the additives. The distances between the surface atoms and the additives are calculated at each MC step. If the distance between an inhibitor and the surface sites is smaller than the action range of the inhibitor, the adsorption event on these sites is rejected. If the surface site is within the action range of an accelerator, the adsorption rate is changed to $\tilde{k}_n^+$. If the distance between an additive and the surface sites is equal to the core size of the additive, it sticks to the surface with the sticking probability (i.e. the random walk is cancelled). Since the diffusion of the additives occurs throughout the simulation, the distance between the surface sites and the additives are calculated at every MC step.

4. Results

The simulations of the SBS model have been performed using the same parameters as our previous works [10–12]; $\psi/k_BT = 9.44$, $\mu/k_BT = 10.0$ and $E_{\mathrm{d}} = \psi/2$. Figure 1 shows the results of filling a hole of aspect ratio 2 without additives. The horizontal and vertical directions are denoted as x, and y-directions, respectively. The simulation range is 340 × 1200 (lattice points). At $x = 0$ and $x = 340$, the reflection boundary condition is used. In the figure, the range $0 \leq x \leq 720$ is plotted and the width of the hole is 340 lattice sites. Assuming that the lattice constant a of copper crystal is 0.3 nm, the width of the hole is of the order of 0.1 μm. The solid lines show the initial and final surface structures and dots denote vacancies. In the final stage of the simulation, the hole is filled with the deposited atoms and the surface is almost flat. However, large voids elongated in y-direction appear in the middle of the hole. This is due to the fluctuation of the surface structure.

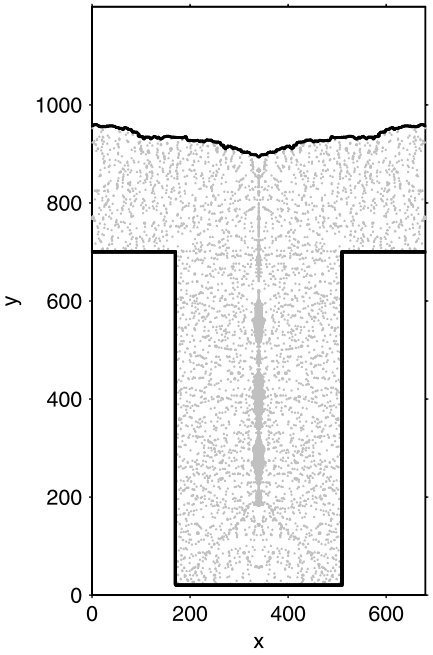

Figure 1. MC results of via filling without additives. The solid lines show initial and final surfaces and dots are vacancies. The labels denote the number of lattice sites.

Although some of the parameters for the additives such as concentrations are available in experiments, their values depend upon the size of the hole and cannot be directly applied to our two-dimensional model. Also, it is difficult to extract the parameters which characterize the influence on the deposition, especially the inhibiting and enhancing effects, from experiments. Therefore, our approach is not to reproduce a specific experimental result, but to investigate the relation between the characteristics of the additives and the filling efficiencies. We referred to some experimental values [6,7] and changed them by try-and-error method. In our previous simulations, we included two kinds of additives and could not succeed in eliminating the void formation [14]. In the present simulations, we include levelers in the model to see their influence on the filling. We have performed a series of MC simulations with three kinds of additives to investigate their influence on the filling process. In some cases the additives have the effects of eliminating the void formation to achieve the superconformal filling. In other cases, however, large voids are formed owing to the presence of the additives in the hole. In the following, we pick up two cases of the simulations and discuss the effects of the additives focusing our attention on the behavior of levelers.

Figure 2 shows the snapshots of the results of the simulation with additives (case A). The concentrations of the additives (defined as the number of additives divided by the number of available sites) are $C_{\mathrm{inh}} = 3.5 \times 10^{-5}$, $C_{\mathrm{lev}} = 3.5 \times 10^{-5}$ and $C_{\mathrm{acc}} = 1.4 \times 10^{-4}$. The core size and the action range of the additives are $l_{\mathrm{inh-c}} = 20$, $l_{\mathrm{lev-c}} = 20$, $l_{\mathrm{acc-c}} = 5$, $l_{\mathrm{inh}} = 50$, $l_{\mathrm{lev}} = 40$ and $l_{\mathrm{acc}} = 40$, where the unit of length is a. The enhancing effect of accelerators is $\tilde{k}_n^+ / k_n^+ = 5$. The diffusion of the additives is assumed to be isotropic. The initial distribution of additives is shown in figure 2(a). The inhibitors and the levelers are distributed around the upper part of the hole, while the accelerators diffuse deep into the hole. The temporal surface and void structures during the filling are shown in figures 2 (b) and (c). It is observed that the inhibitors suppress the growth of the upper surface and the accelerators enhance the growth of the lower part of the hole. Although such distributions seem to be appropriate for the bottom-up filling, large voids appear in the hole. This is due to the inhibitors and levelers which move into the hole. The void size of this case is larger than that of the additive-free case. This means that the void formation is sensitive to the distribution of additives. It is also observed that the growth of the surface around the hole is suppressed by the inhibitors and that of the middle of the hole is enhanced by the accelerators. This results in the bump over the hole shown in figure 2(c). Such an overfilling should be avoided in damascene plating since it makes the planarization (process (iv)) difficult.

Figure 3 shows the results of the simulation for $C_{\mathrm{inh}} = 1.75 \times 10^{-5}$, $C_{\mathrm{lev}} = 1.75 \times 10^{-5}$, $C_{\mathrm{acc}} = 1.4 \times 10^{-4}$, $l_{\mathrm{inh}} = 50$, $l_{\mathrm{lev}} = 40$, $l_{\mathrm{acc}} = 40$, $l_{\mathrm{inh-c}} = 20$, $l_{\mathrm{lev-c}} = 20$, $l_{\mathrm{acc-c}} = 10$ and $\tilde{k}_n^+ / k_n^+ = 5$ (case B). In this case, the concentrations of inhibitors and levelers are smaller than those of case A. Also, the diffusion of the levelers is biased. Most of the levelers used in experiments have positive charges and tend to stick to the tips of the surface. In order to take this into account, we calculate the curvature of the growing surface during the simulation and bias the random walk of the levelers so that levelers move to the site which has the largest curvature. The results clearly show that the levelers are distributed around the edge of the hole, while accelerators are distributed on the surface of the bottom and the side of the hole (figure 3(a)). The growth rate of the edge of the hole is suppressed by levelers and the temporal surface during the filling is

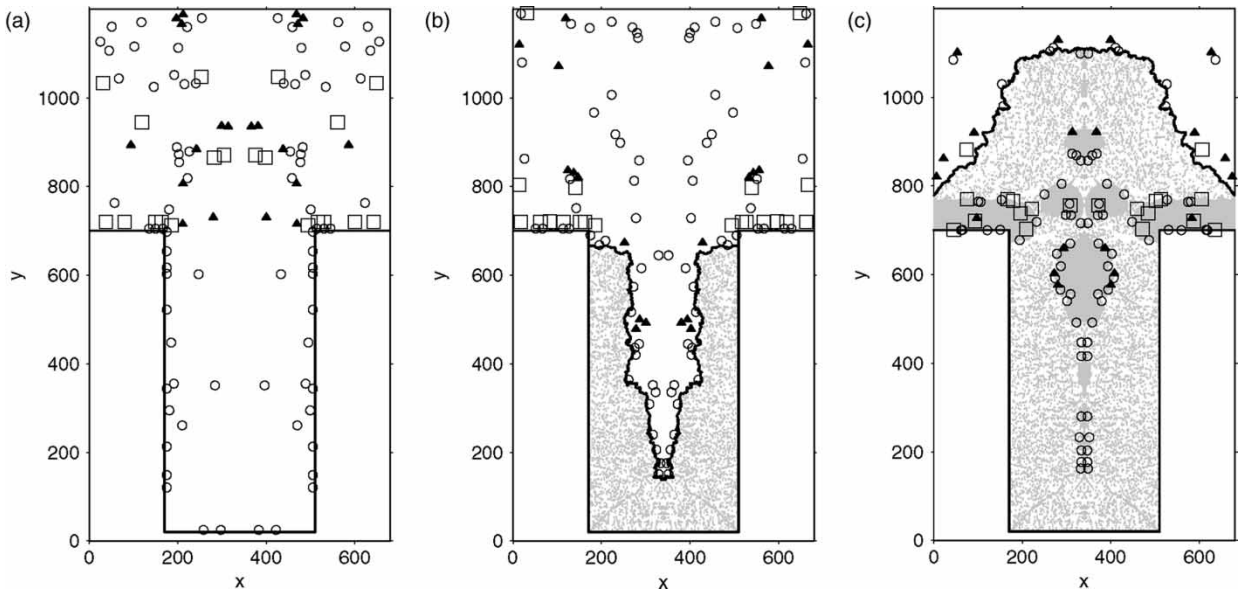

Figure 2. MC results of via filling with additives (case A). Initial distribution of inhibitors (open squares), levelers (solid triangles) and accelerators (open circles) are shown in (a). Temporal surfaces (solid lines) and vacancies (dots) and additives are shown at 2.0×10^5 and 5.0×10^5 MC steps are shown in (b) and (c), respectively.

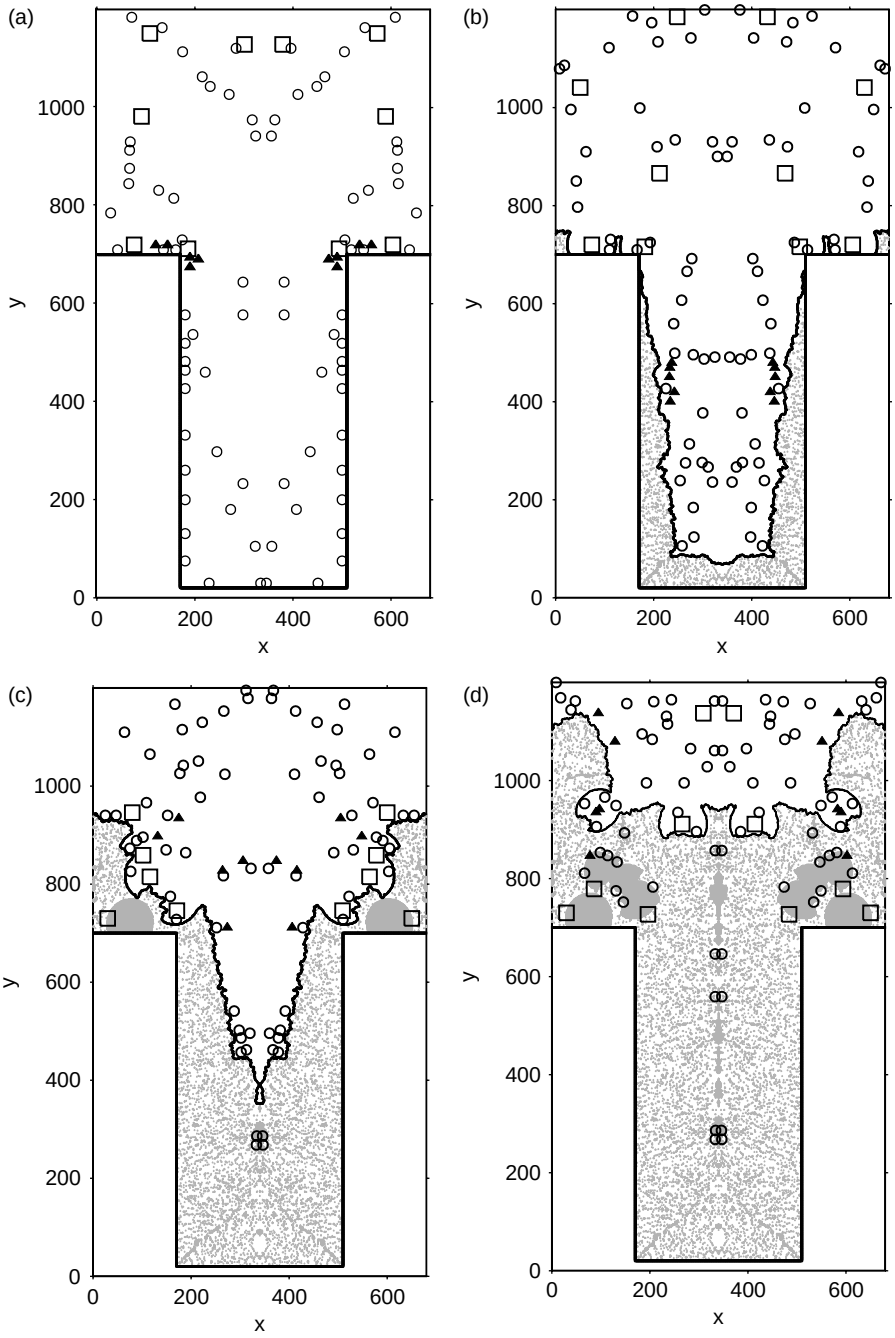

Figure 3. MC results of via filling with additives (case B). (a) Initial distribution of inhibitors (open squares), levelers (solid triangles) and accelerators (open circles). Temporal surfaces (solid lines) and vacancies (dots) and additives are shown at (b) 1.0×10^5, (c) 3.0×10^5 and (d) 5.0×10^5 MC steps.

almost V-shaped. As a result, large voids are not observed in the hole and the filling is almost superconformal. In figure 3, a lot of small voids appear in the film since the surface becomes rough owing to the effect of the additives. In the center of the hole, however, we could eliminate the formation of large voids by making the surface V-shaped using three kinds of additives.

Figure 4 shows the average height of the surface defined by

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

where N_s is the number of surface atoms and y_i is their y-coordinates. In additive-free case, h changes discontinuously when some parts of the surfaces are connected to each other creating voids. The growth rates for case A is larger than that of additive-free case due to the effect of accelerators. The gap in h is still observed corresponding to the void formation shown in figure 2. For case B, h increases almost continuously, which reflects the V-shaped surface profile shown in figure 3. The combination of the suppressing effect of inhibitors and levelers and the enhancing effect of accelerators results in the void-free filling.

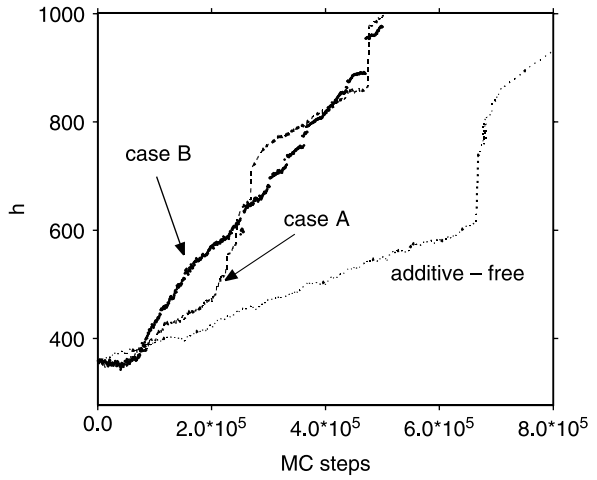

Figure 4. Time evolutions of the average height of the surface h for additive-free, case A and case B.

Finally, let us comment on the reproducibility of the results. We have performed a series of simulations by changing parameters. We also performed the simulations using the same parameters with different initial configuration. It was found that in most cases where the levelers are distributed around the edge of the hole, superconformal filling is achieved as shown in figure 3. However, even with the same parameters, there are some cases where the leveler(s) move into the hole creating a large void. Therefore, the reproducibility of the results is not perfect owing to the stochastic nature of the model. The same problem occurs in the experiments of via filling since the filling is very sensitive to the additive distribution. An important point in the present simulations is that the role of levelers is crucial for the filling. Superconformal filling is possible when the levelers are distributed around the tips to the surface. In order to derive the conclusion on the optimal parameters for the filling, the statistical treatment of the results will be needed.

5. Summary

In this paper we studied the effect of additives in the filling process of damascene plating by the kinetic MC simulations. Three kinds of additives are included, i.e. inhibitors, levelers and accelerators. As discussed in the previous paper, the superconformal filling could not be achieved by using inhibitors and accelerators [14]. By including levelers, we could make the surface V-shaped during the filling, which led to eliminate the formation of voids in the middle of the hole. This confirmsthe fact that three kinds of additives are commonly used in experiments. The combined effects of additives contribute to eliminate the voids in the hole. That is, inhibitors and levelers prevent the deposition on the upper part and the edge of the hole, and accelerators enhance the growth of the bottom.

The drawbacks of using additives are also found in the simulations. When some of the inhibitors or levelers diffuse into the hole, they create the voids around them. Overfilling of the hole was also found in our simulations. The general discussion on the optimal filling condition would be difficult since the distributions of the additives have a stochastic nature and the deposition conditions are dependent upon the size and aspect ratio of the vias in experiments. However, since the results of our simulations correspond qualitatively to the experimental findings, we expect that the MC simulation of the SBS model with additives can used to assist the search for the optimal condition for void-free filling. This will contribute to reduce the number of trial experiments in industries.

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