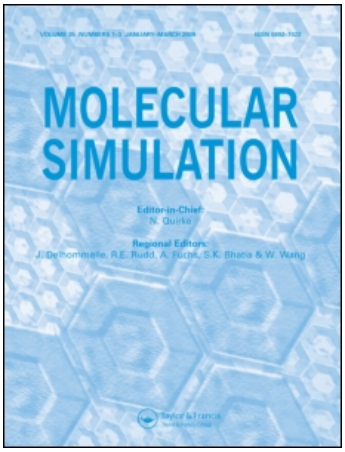

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Monte Carlo Simulation of Thin Film Growth with Defect Formation: Application to Via Filling

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The filling process of via holes in damascene electroplating is investigated with the use of kinetic Monte Carlo method. As a model for damascene plating, we included additives in the Solid-by-Solid model which we developed to study the correlation between the surface and void structures during the crystal growth. Two kinds of additives, inhibitors and accelerators, are taken into account to control the local growth rate and to find out the condition for avoiding the void formation during the filling. A series of simulations have been performed by changing the parameters which characterize the additives to see their influence on the filling mechanism. The distribution of additives, the correlation with the resulting surface and void structures are discussed.

Keywords: Monte Carlo method; Damascene plating; Via filling; Additive

INTRODUCTION

Electroplating is known as a "wet process" to generate thin metal film on an electrode by reduction reaction from electrolytic solutions. Recently copper electroplating has attracted great attention in semiconductor industries for the production of LSI chip circuits. Ever since it was stated by IBM that the conventional vapor deposition of aluminum can be replaced by copper electroplating, the *damascene copper electroplating* has been studied extensively as a new tool in semiconductor engineering [1]. The damascene plating is a technique to fill line trenches and via holes for three dimensional LSI circuits consisting of the following processes: (i) patterning of the circuits, (ii) seed-layer plating on the patterned materials, (iii) electroplating (filling via holes and trenches) and (iv) chemical–mechanical polishing (removing excess metals). In this paper, we pay attention to the filling process (iii). The crucial point for the success of this process is to control the metal deposition so that no void is formed in the film. In experiments, the local growth rate of the surface is controlled by a small amount of additives in solution. The physical properties such as surface roughness and void density of the film depend strongly on the composition of additives. The behavior of additives during the deposition, however, cannot be observed directly in experiments. The optimal condition for the additives has been investigated by the repetition of trial experiments.

Since the line width in recent LSI circuits is as small as several hundred nanometers, it is required to control the deposition mechanism on an atomic length scale. The purpose of the present work is to develop a method of molecular simulation for the damascene plating with the effect of additives. The basic system is the Solid-by-Solid (SBS) model for crystal growth which we developed by extending the conventional Solid-on-Solid model [2] to include the void formation. The characteristic properties of the SBS model have been investigated in detail in relation to the correlation between the surface structure and the void structure for various deposition conditions [3]. Recently, we have applied the SBS model as a model for damascene plating to investigate the void formation mechanism during the filling process (iii) by the kinetic Monte Carlo (KMC) simulations [4,5]. In the simulations, no

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additive was included in the system. As a result, large voids appeared in the film when the via holes and trenches were filled with deposited atoms. The qualitative features of the voids are similar to those found in experiments using additive-free solutions [6]. In this paper, we extend the SBS model to include additives to control the filling process depending upon the distribution of additives. We consider two kinds additives, inhibitors and accelerators, which are commonly used in copper electroplating. We performed a series of KMC simulations to study the effects of additives on the surface structures and the condition to eliminate the void formation.

This paper is organized as follows. In the next section, we describe the combined system of the SBS model and additives. The results of KMC simulations are shown in chapter 3. The summary and discussion are given in chapter 4.

THE SOLID-BY-SOLID MODEL WITH ADDITIVES

We consider a two-dimensional square lattice. Each site of the lattice is occupied by either a solid atom, a liquid atom or a vacancy. Three events—adsorption, desorption and the diffusion of surface atoms—are taken into account to change the state of each site. When an adsorption occurs, a liquid atom adjacent to a surface solid atom changes to a solid atom. Desorption is represented by the change of one of the surface solid atoms to a liquid atom. Vacant sites which are surrounded by solid atoms and have no connection to the liquid part of the model are regarded as vacancies. The rate constants for the reaction; adsorption k_n^+, desorption k_n and surface diffusion k_{mn}, depend upon the number of nearest neighbor solid atoms (the number of bonds) n, m. The rate constants have the following relations [3].

$$k_n/k_n^+ = \exp\{(2-n)\psi/k_BT - \mu/k_BT\}, \quad (1)$$

$$k_{nm} = (k_n k_m^+/k_1^+)\exp\{(\psi - E_d)/k_BT\}, \quad (2)$$

where ψ is the binding energy between atoms, μ the chemical potential and E_d the activation energy for the surface diffusion. The relation in Eq. (1) is derived from the microscopic detailed balance at a kink site [2]. The chemical potential μ is the control parameter of the growth, corresponding to the overpotential in electrodeposition. The state of each site is changed sequentially by the algorithm of the KMC simulation [7].

Here, we include additives in the SBS model. Three kinds of additives are commonly used for copper plating from copper sulfate solution; polyethylene glycol (PEG) as an inhibitor, bis (3-sulfopropyl) disulfidedisodium (SPS) as a brightener and Janus Green B (JGB) as a leveler. Polyethylene glycol is supposed to inhibit the growth of the upper part of the hole, while SPS diffuses to the bottom of the hole to enhance the bottom–up filling. Levelers tend to stick to tips and corners of the surface to prevent the deposition of new atoms. The combination of these effects is expected to realize the (complete) superconformal filling [8,9]. In this paper, we include inhibitors and accelerators to model PEG and SPS, respectively. Each additive takes one of the lattice sites of the SBS model. As an initial condition, additives are arranged in the solution part and diffuse to the surface by random walk. As a result, a concentration gradient following Fick's law is generated in the solution part of the model. Then, the surface growth of the SBS model and the diffusion of additives in solution are simulated simultaneously.

The effects of inhibitors and accelerators on the deposition reaction are the following. Inhibitors which reach the surface reduce the growth rate on the surface sites within the range l_{inh} from the inhibitors. That is, the adsorption on a site in the action range of inhibitors is rejected. The range l_{inh} is regarded as the size of an inhibitor. We also introduce a core size $l_{\mathrm{inh-c}}$ of an inhibitor, which is the minimum distance between an inhibitor and the surface solid atoms. For accelerators, we set up 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, i.e. $\tilde{k}_n^+/k_n^+ > 1$. Inhibitors and accelerators near the surface sites are assumed to stick to the surface. That is, when the distance between an inhibitor (an accelerator) and one of the surface solid atoms is $l_{\mathrm{inh-c}}$ ($l_{\mathrm{acc-c}}$) the inhibitor (the accelerator) is adsorbed to the surface with the probability $k_{\mathrm{a-inh}}$ ($k_{\mathrm{a-acc}}$). The surface growth of the SBS model, diffusion of additives, inhibiting and accelerating effects of additives are simulated simultaneously by the KMC method [7].

RESULTS

We performed the simulation with the parameters for the SBS model fixed as $\psi/k_BT = 9.44$, $\mu/k_BT = 10.0$ and $E_d = \psi/2$. Figure 1 shows the results of filling a hole of aspect ratio 2 without additives (case 1). The width of the hole is 100 lattice sites (about 30 nm). The solid lines show the temporal surface structures and dots denote vacancies. The surface grows at a constant rate depending upon μ and the filling is almost conformal. However, large voids elongated in the growth direction appear in the middle of the hole. This is due to the fluctuation of the surface structure. In the SBS model, vacant sites which are surrounded by solid atoms are regarded

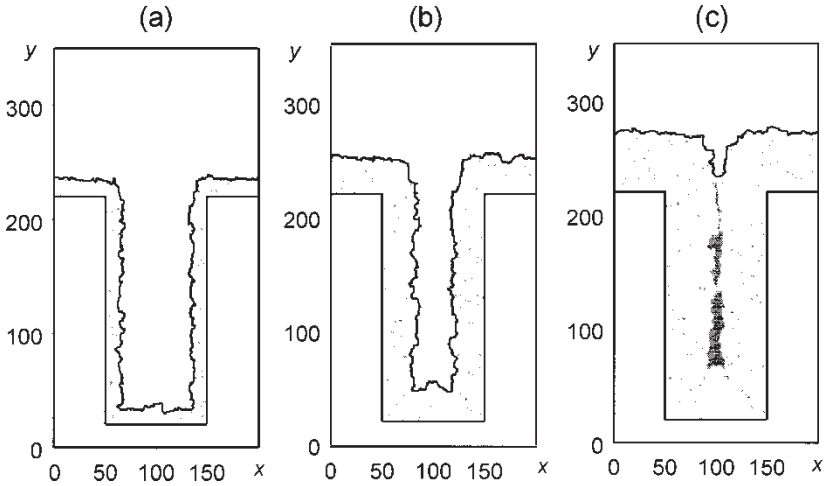

FIGURE 1 Results of via filling without additives. (case 1) temporal surfaces (solid lines) and voids (dots) are shown at (a) 4×10^4, (b) 8×10^4 and (c) 1.2×10^5 MC steps. The labels denote the number of lattice sites.

as vacancies. Therefore, when some parts of the surfaces which grow from two sides of the hole are connected to each other, the liquid sites surrounded by solid atoms change to vacancies. As a result, large voids remain in the film although the surface is almost flat after the filling.

Figures 2 and 3 show the results of via filling with additives. In Fig. 2, the concentrations (the number of additives divided by the number of vacant sites) of inhibitors and accelerators are $C_{\mathrm{inh}} = 0.026\%$ and $C_{\mathrm{acc}} = 0.135\%$, respectively. Other parameters are $l_{\mathrm{inh}} = 10$, $l_{\mathrm{acc}} = 2$, $l_{\mathrm{inh-c}} = l_{\mathrm{acc-c}} = 1$ and $\tilde{k}_n^+ / k_n^+ = 10$. (case 2) To see the influence of inhibitors, the accelerators are assumed not to stick to the surface ($k_{\mathrm{a-acc}} = 0$). The ratio of the mobilities of inhibitors and accelerators in solution is $D_{\mathrm{acc}}/D_{\mathrm{inh}} = 5$, since the molecular weight of inhibitors is assumed to be larger than that of accelerators. The initial distribution of additives is shown in Fig. 2(a). Inhibitors are distributed around the upper part of the hole, while accelerators diffuse to the inner part of the hole. The temporal surface and void structures during the filling are shown in Figs. 2(b) and (c). It is clearly observed that the inhibitors suppress the growth of the upper surface and the resulting void size is smaller than that of case 1 shown in Fig. 1(c). The influence of accelerators on the surface structure is not clearly observed. Figure 3 shows the results of the simulation for $C_{\mathrm{inh}} = 0.026\%$, $C_{\mathrm{acc}} = 0.135\%$, $l_{\mathrm{inh}} = 15$, $l_{\mathrm{acc}} = 15$, $l_{\mathrm{inh-c}} = 10$, $l_{\mathrm{acc-c}} = 4$ and $\tilde{k}_n^+ / k_n^+ = 10$. (case 3) The sticking probabilities of additives are set to $k_{\mathrm{a-inh}} = 0.998$ and $k_{\mathrm{a-acc}} = 0.999$. In contrast to case 2, accelerators are distributed on the surface of the bottom and sidewall of the hole. The growth rate of the bottom surface is increased due to the effect of the accelerators, and the temporal surface during

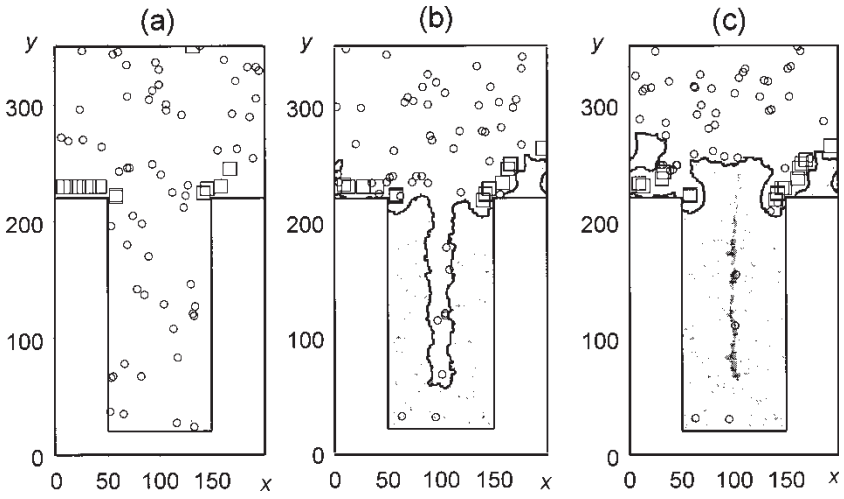

FIGURE 2 Results of via filling with additives. (case 2) (a) initial distribution of inhibitors (open squares) and accelerators (open circles). Temporal surfaces (solid lines) and voids (dots) and the distribution of additives are shown at (b) 7.2×10^4 and (c) 9.6×10^4 MC steps.

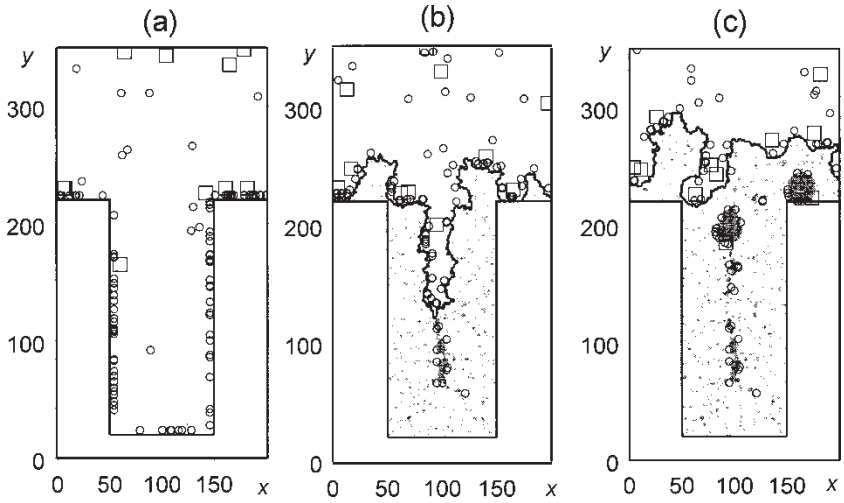

FIGURE 3 Results of via filling with additives. (case 3) (a) initial distribution of inhibitors (open squares) and accelerators (open circles). Temporal surfaces (solid lines) and voids (dots) and the distribution of additives are shown at (b) 4.8×10^4 and (c) 6.4×10^4 MC steps.

the filling is almost V-shaped. The large voids observed in the additive-free case do not appear for case 3 and the filling is nearly superconformal. Figure 4 shows the average height of the surface defined by

$$h = \frac{1}{N_s} \sum_{i=1}^{N_s} y_i, \tag{3}$$

where N_s is the number of surface atoms and y_i is their y-coordinates. The growth rates for case 2 and case 3 are larger than that of case 1, which is due to the effect of accelerators. In case 1, h changes discontinuously at some time when some parts of the surfaces are connected to each other creating voids. The gap in h at this time is small for case 3 and the increase in h is stepwise, which means that the filling is almost continuous. Such a feature reflects the surface profile shown in Fig. 3(b). The combined effect of the inhibitors which prevent the sidewalls from being connected to each other and the accelerators which increase the growth rate of the bottom results in eliminating the formation of large voids in the hole. Such effects are observed in experiments using PEG and SPS [8,9].

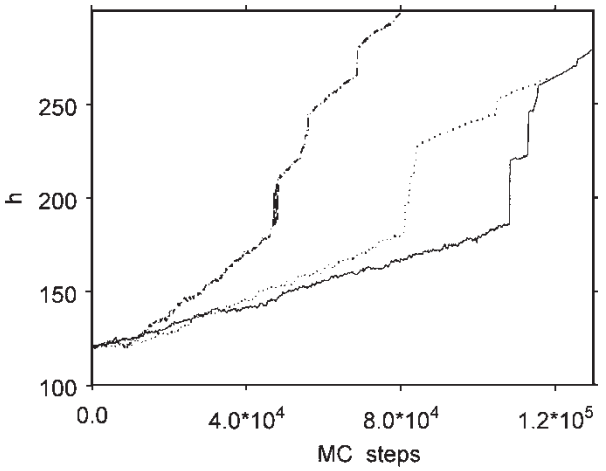

FIGURE 4 The average height of the surface h as a function of MC steps for case 1 (solid line), case 2 (dotted line) and case 3 (dash-dot line).

SUMMARY

In this paper, we developed the combined system of the SBS model and additives. Two kinds of additives, inhibitors and accelerators, are included, which are commonly used in experiments. The combination of inhibitors, which prevent the growth of the upper part of the hole, and accelerators, which enhance the bottom–up process, contribute to eliminating the formation of large voids in the hole. Such effects of additives, which have been expected in experiments, can be realized in our combined model. This model will be used to estimate the deposition condition for void-free filling for various types of via holes and trenches, which will contribute to reducing the number of trial experiments.

Although the void size in the middle of the hole is reduced in the present simulation, the following points should be noticed. Some of the inhibitors remain in the film after the filling, creating large voids in the upper part of the film (Fig. 3(c)). One reason is that the inhibitor is modeled as a rigid sphere while the real additives are polymers. We expect that this point can be dealt with by choosing appropriate values of the core size and the action range of inhibitors. The second point is that a lot of small voids are created in the film in case 3. This is because the surface becomes rough owing to the effect of the accelerators. In recent experiments, the importance of levelers such as JGB has been realized in addition

to inhibitors and accelerators to establish superconformal filling. It is of interest to include levelers in the present simulation as the third additive.

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