Kinetic Monte Carlo Simulation of Thin Film Growth with Void Formation – Application to Via Filling –

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ABSTRACT

In this paper, we study the void formation during via filling as a model of copper damascene plating for LSI interconnects. We developed a new model for crystal growth which enables us to study the void structure in relation to the surface structure depending upon the deposition conditions. Using this model which we call Solid-by-Solid model, we performed the kinetic Monte Carlo simulations of filling V-shaped and flat-bottomed grooves to examine the surface and void structures during the surface growth. It is found that small voids appear successively in the film, being aligned to the growth direction as the V-shaped groove is filled with deposited atoms. In filling the flat-bottomed groove, on the other hand, large voids appear in the middle of the groove which are elongated to the growth direction. The mechanism of filling and void formation and its dependence on the shape of the initial substrate are discussed.

Keywords: Monte Carlo simulation, thin film, voids, via filling

1 INTRODUCTION

In the theoretical studies of crystal growth, Solid-on-Solid (SOS) models have been widely used as a model of vapor depositions as well as the growth from solution. The SOS models are useful for describing the growth process such as the dynamics of kinks and steps, two dimensional nucleation, *etc.* and have been studied both analytically and by computer simulations. The SOS models, however, have an unrealistic assumption that no vacancy is created in the film. In real deposition, lattice defects such as vacancies and dislocations play a crucial role for the physical properties of the film. Therefore, we have extended the SOS model so that vacancies are allowed to be created in the film during the growth.[1], [2] Let us call this new model as Solid-by-Solid (SBS) model. In the SBS model, one can study the surface structure and the void structure simultaneously depending upon the deposition conditions. We developed the program of the kinetic Monte Carlo simulation for the SBS model taking into account three events : adsorption, desorption and diffusion of surface atoms. We related the model parameters with the deposition condition such as overpotential and exchange current density so that the simulation results can be compared with experiments. Using the SBS model, we performed the simulations of the film growth from the flat substrate to study the surface structure, the void structure and the correlation between them for various deposition conditions.[1]

The purpose of the present study is to apply the SBS model to the damascene plating for LSI circuits. The copper damascene electroplating has been widely studied as a new technology for LSI interconnects since the IBM group's announcement to replace the vapor deposition of aluminum with electroplating copper.[3] The dual damascene metallization is the technique to fill the lines and via holes for three-dimensional electronic 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) Planarization (removing excess metals). An important requirement for the success of this process is to fill the via holes and trenches completely without voids. Since the size of the recent LSI chips is of the order of microns or even of shorter scales, it is important to understand the void formation mechanism on an atomic length scale. In this paper we pay attention to the filling process (iii) and investigate the void formation mechanism using the SBS model. We have performed the Monte Carlo simulation of filling V-shaped and flat-bottomed grooves as a model of the damascene plating. The void formation and its dependence on deposition conditions and the influence of the shape of the initial substrate are discussed.

2 SOLID-BY-SOLID MODEL

Our system is a square lattice each site of which is occupied by a liquid atom or a solid atom, otherwise, vacant. The surface solid atoms are defined as the solid atoms of which one of the nearest neighbor sites is a liquid atom. Empty sites surrounded by solid atoms only are regarded as vacancies. We take into account three events : adsorption, desorption and diffusion of surface atoms. The adsorption is to change a liquid atom near the surface to a surface solid atom. The desorption is a reverse process, *i.e.*, to change a surface solid

atom to a liquid atom. The adsorption is not allowed to take place at vacant sites within the film. Surface solid atoms can diffuse to its one of the nearest or the second nearest neighbor sites (liquids or vacancies). Solid atoms of which four nearest neighbor sites are occupied by solid atoms are regarded as frozen atoms. Frozen atoms change to surface atoms when one of the nearest neighbor sites becomes a liquid atom by the process of either desorption or surface diffusion.

The rate constants for adsorption and desorption are denoted as k_n^+ and k_n, respectively, which depend upon the number of the nearest neighbor solid atoms n (the number of bonds). The rate constant for surface diffusion k_{nm} depends upon the number of bonds of the sites before and after the diffusion (denoted as n and m, respectively). Following relations are assumed for the rate constants[4], [5] :

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

$$k_{nm} = \frac{k_n k_m^+}{k_1^+}\exp\left(\frac{\psi - E_d}{k_B T}\right), \tag{2}$$

where ψ is the binding energy for a pair of solid atoms in contact, k_B the Boltzmann constant and μ is the chemical potential which corresponds to the overpotential in electrodeposition. The activation energy of the surface diffusion is denoted by E_d. Equation (1) is derived from the condition of microscopic detailed balance at the kink site in equilibrium (*i.e.*, $k_2^+ = k_2$ for $\mu = 0$).[4] In SOS models, the adsorption occurs only on the nearest neighbor sites to the growth direction. In SBS model, this condition is no longer satisfied and the adsorption occurs on any one of the nearest neighbor liquid sites of the surface solid atoms. As a result of this extension, vacancies are created, which are empty sites surrounded by solid atoms only. We will see that the formation of vacancies reasonably depends upon the surface roughness. In the simulation, the state of each site is changed sequentially using the algorithm of kinetic Monte Carlo method of Bortz *et.al.*[6] In this algorithm, searching the surface atoms is an important as well as time-consuming step of the simulation. [7]

3 RESULTS

We have performed the Monte Carlo simulations adopting the parameters for copper atoms. The binding energy is assumed to be ψ=0.244 eV (the interatomic potential between copper atoms at the nearest neighbor distance 2.55 $\AA$). The temperature is $T = 300K$ (*i.e.* $\psi/k_B T$ =9.45). E_d is assumed as $\psi/2$ and $k_1^+ = k_2^+ = k_3^+$. In our previous work, it was shown that when $\mu/k_B T$ is smaller than $\psi/k_B T$, the surface has a layer structure and point defect appear in the film. The surface becomes rough as $\mu/k_B T$ is increased and large voids with more than one vacant sites appear in the film.[1] Fixing $\mu/k_B T$ and decreasing E_d, the surface becomes smooth since the surface diffusion is enhanced and the surface becomes rough as E_d is increased.[7]

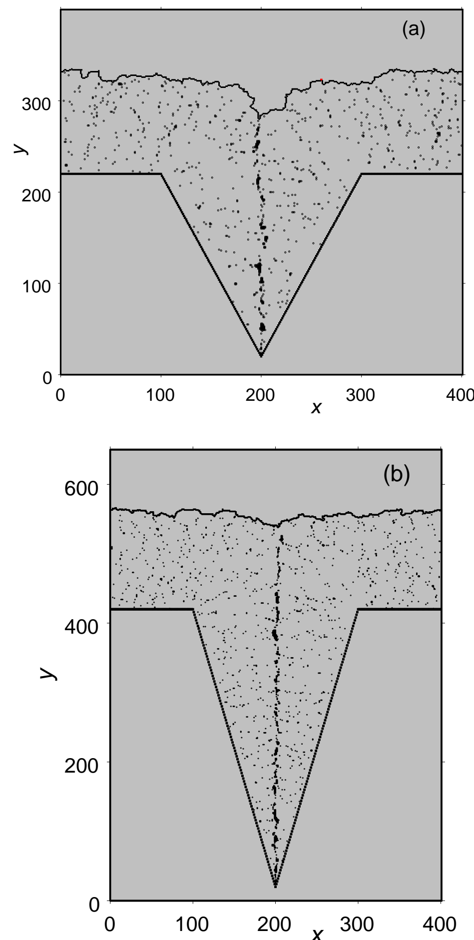

Figure 1: Film structure generated by the kinetic Monte Carlo simulations. The aspect ratios of the initial V-shaped grooves are (a) 1 and (b) 2, respectively. Solid lines show the initial and the final surfaces.

Let us now examine the film growth on a non-flat substrate. Figure 1 shows the results of filling the V-shaped grooves. The aspect ratios of the grooves are 1 (a) and 2 (b), respectively, and $\mu/k_B T = 10.0$. The growth takes place in y-direction and the periodic boundary condition is used in x-direction. Dots denote vacancies. The surface becomes almost flat at the end of the simulation (geometrically leveled). In the middle of the groove, a succession of small voids appears, being aligned in y-direction. These voids are created sequentially from the bottom of the groove. More vacancies are created as the aspect ratio becomes large. If these voids are connected to each other, they form a pinhole which will cause a significant decrease in the corrosion

resistance of the film.

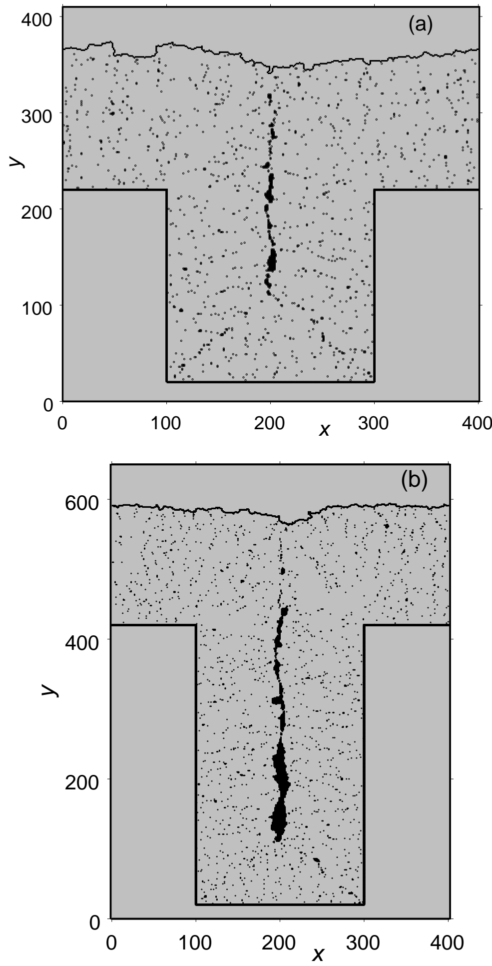

Figure 2: Film structure generated by the kinetic Monte Carlo simulations. The aspect ratios of the initial flat-bottomed grooves are (a) 1 and (b) 2, respectively.

Figure 2 shows the results of filling the flat-bottomed grooves. The aspect ratios of the grooves are 1 (a) and 2 (b), respectively, and $\mu/k_BT = 10.0$. If we assume that the nearest neighbor distance between solid atoms is 2.55 $\mathring{A}$, the widths of the groove is 51nm. Filling is completed and the surfaces are leveled at the end of the simulations. In contrast to filling the V-shaped grooves, large voids are found to appear in the middle of the groove. These voids are elongated in y-direction as the aspect ratio becomes large. Note that the lattice sites are regarded as vacancies in the SBS model when they are surrounded by deposited solid atoms and no liquid atom. Therefore, if parts of the surfaces of both sides of the groove are connected to form a closed shape, the sites inside such a closed shape change to vacancies. (In real plating, these voids may be filled with solvent atoms or impurities, but they are regarded as voids in the present study.)

In order to study the void formation mechanism quantitatively, we calculated the average height and the thickness of the surface defined by

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

and

$$\Delta = \sqrt{\frac{1}{N_s}\sum_{i=1}^{N_s}(y_i - \bar{h})^2}, \tag{4}$$

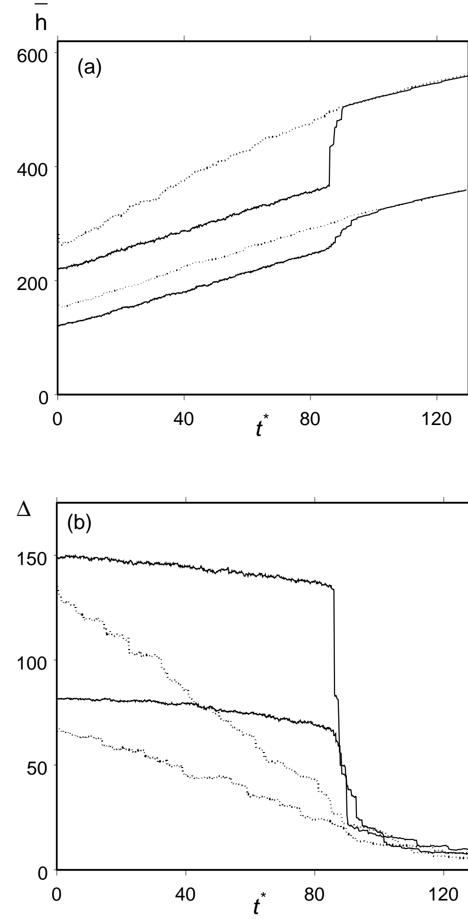

Figure 3: The average height $\bar{h}$ (a) and the thickness of the surface Δ (b). Solid lines are for the flat-bottomed grooves and dotted lines are for the V-shaped grooves.

respectively, where y_i is the y-coordinate of a surface solid atom and N_s is the number of surface solid atoms. Figure 3 shows $\bar{h}$ and Δ as a function of the scaled time $t^* = n \times k_1^+/k_t$, where n denotes the Monte Carlo step and k_t is defines as

$$k_t = \sum_{n=1}^{3} k_n^+ N_{c(n)} + \sum_{n=1}^{3} k_n N_{a(n)} + \sum_{n,m=1}^{3} k_{nm} N_{d(nm)} \tag{5}$$

($N_{c(n)}$, $N_{a(n)}$ and $N_{d(nm)}$ are the numbers of candidate atoms for adsorption, desorption and surface diffusion, respectively). The solid lines show $\bar{h}$ and Δ for the flat-bottomed grooves and the dashed lines for the V-shaped-bottomed grooves. $\bar{h}$ and Δ for the V-shaped grooves change smoothly as a function of time and small steps are observed when voids are created. In contrast to filling the V-shaped grooves, $\bar{h}$ and Δ for filling the flat-bottomed grooves change discontinuously when some parts of the surfaces from two sides are connected and a large void is created. These results clearly show the difference in the void formation mechanism depending strongly on the shape of the initial substrate.

The distribution of the void size is shown in Fig.4. The void size (the number of vacant lattice sites in a single void) is denoted as $n_{\rm v}$ and $N(n_{\rm v})$ denotes the number of voids of size $n_{\rm v}$. Figure 4 shows the log-log plot $\log_{10} N(n_{\rm v})$ vs. $\log_{10} n_{\rm v}$ for filling the V-shaped (open circles) and the flat-bottomed (solid circles) grooves. The aspect ratio of the grooves is 2. The numbers of small voids ($n_{\rm v} < 10$) are almost the same for both the V-shaped and the flat-bottomed grooves. Small voids are created due to local surface fluctuations in short wave lengths and not influenced by the shape of the initial substrate. It is observed that in filling the flat-bottomed groove large voids consisting of more then one hundred vacant sites are created in the film. Large voids tend to appear when the initial grooves are flat-bottomed.

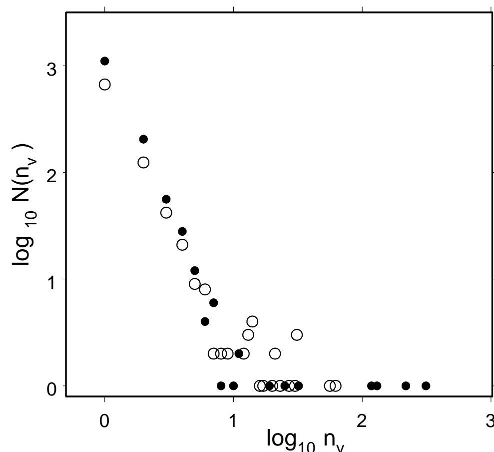

Figure 4: Log-log plot of the void-size distribution $N(n_{\rm v})$ in filling V-shaped grooves (open circles) and flat-bottomed grooves(solid circles). (μ/k_BT=10.0)

4 SUMMARY

In this paper, we applied the SBS model proposed by us to problems of filling grooves as a model of damascene plating to study the void formation mechanism. The main results are the following.

1. When the V-shaped groove is filled with deposited atoms, small successive voids appear during the film growth, being aligned in the growth direction. More voids appear as the aspect ratio becomes larger. The height and the thickness of the surface change almost continuously as a function of time.

2. When the flat-bottomed groove is filled with deposited atoms, on the other hand, large voids with several hundred vacant sites appear in the middle of the groove. The voids are elongated in the growth direction as the aspect ratio becomes large. The height and the thickness of the surface change discontinuously when a large void is created.

In the experiments of via filling for copper interconnections from solutions without additives, similar void structures are observed. It is of interest to introduce additives in the SBS model to control the surface overpotential and to discuss the condition of making void-free depositions.

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