Electrochimica Acta 100 (2013) 321–328

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Kinetic Monte Carlo simulation of three-dimensional shape evolution with void formation using Solid-by-Solid model: Application to via and trench filling

Yutaka Kaneko [a,*], Yasuaki Hiwatari [b], Katsuhiko Ohara [c], Fujio Asa [c]

[a] Department of Applied Analysis and Complex Dynamical Systems, Graduate School of Informatics, Kyoto University, Kyoto 606-8501, Japan
[b] Toyota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, Japan
[c] C. Uyemura & Co., Ltd., 1-5-1, Deguchi, Hirakata, Osaka 573-0065, Japan

ARTICLE INFO

Article history:
Received 27 December 2011
Received in revised form
22 November 2012
Accepted 15 January 2013
Available online 23 January 2013

Keywords:
Kinetic Monte Carlo method
Solid-by-Solid model
Multi-scale simulation
Damascene electroplating

ABSTRACT

In this paper we present the Kinetic Monte Carlo simulation system for the simulation of three-dimensional shape evolution with void formation as a model for electrodeposition. The basic system is the Solid-by-Solid model which is an extension of the conventional Solid-on-Solid model for crystal growth to include void formation. The advantage of the Solid-by-Solid model is that complex three-dimensional shape evolution accompanying void formation (from point defects to macro voids) can be simulated without the difficulty of treating moving boundaries. This model has been extended to include the solution part in which the migration of ions is simulated by the coarse-grained random walk. A multi-scale method is employed to generate the concentration gradient in the diffusion layer. The extended model is applied to the simulation of via and trench fillings by copper electrodeposition. Three kinds of additives are included: suppressors, accelerators and chloride ions. The mechanism of void formation, effects of additives and their influence on the bottom-up filling are discussed within the framework of this model.

1. Introduction

Electrodeposition is a complex and interesting phenomenon, which has recently been used for the surface finishing and device fabrications in many fields of engineering [1,2]. The surface morphology of the electrode results from the interplay of various physical and chemical processes such as (i) mass transport in solution, (ii) solvation and desolvation dynamics, (iii) electron transfer reaction, and (iv) surface diffusion and crystallization. Additives in solution play an important role to modify the growth process. A small amount of additives (of the order of ppm) can change the surface morphology on macroscopic scales. Electrodeposition has attracted great attention in semiconductor engineering since IBM announced the damascene method to replace the conventional dry process of aluminum with the wet process of copper electrodeposition for the fabrication of LSI interconnections [3]. One of the serious problems in the damascene method is void formation in the filling process of via holes and trenches, which causes high resistance and electromigration. Finding optimal conditions for void-free filling is the key issue for the success of this technique (superfilling).

A lot of theoretical and numerical works have been reported to study the mechanism of superfilling. The superfilling was first studied using the diffusion-consumption theory for suppressors [3–5]. The numerical calculations showed that the bottom-up filling was produced by this theory. However, other conditions for superfilling, i.e. incubation period (conformal deposition at the initial stage) and bump formation after the filling, have not been reproduced by this theory. A new theory for superfilling has been proposed [6–8] and developed by NIST group [9–13]. This theory is now known as curvature enhanced accelerator coverage (CEAC) which focuses on the distribution of accelerators and the change in the area of the surface as a result of the shape evolution. The CEAC model has been shown to realize the superfilling conditions; incubation period, bottom-up and overfilling. This model has been extended to systems with multiple additives (suppressors, accelerators, levelers) [11–13]. The basic concepts and numerical simulations based on CEAC mechanism are summarized in Refs. [11,13]. Akolkar and Landau [14,15] pointed out that the different additive interactions occur in the early stage and the late stage of the filling. In their theory the heterogeneous additive distribution produced by the transport limited nature of suppressors initiates the bottom-up and superfilling is accomplished by the effect of accelerators with the area reduction at the bottom in the late stage. Kinetic Monte Carlo (KMC) simulation is also a powerful tool to study the mechanism of the filling process. The noble combinations of the continuum model for solution and the KMC model for surface reactions have been proposed by Alkire et al. [16–18] and applied to the trench filling.

* Corresponding author. Tel.: +81 75 753 5880; fax: +81 75 753 4923.
E-mail address: kaneko@acs.i.kyoto-u.ac.jp (Y. Kaneko).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.01.076

Most of these studies are based on two dimensional (2D) models. Josell et al. took into account the geometrical factor (curvature of the sidewall of a via) in the 2D model [9]. Buoni and Petzold reported a 3D simulation of dual damascene within the framework of a continuum model [19,20]. The mass balance equation in solution and the reaction equation on the surface are combined and numerically solved under the superfilling condition [20]. However, the direct simulation of 3D shape evolution which accompanies void formation (from point defects to macro voids) is difficult due to the complexity of moving boundary conditions.

The purpose of this paper is to present the KMC simulation system of Solid-by-Solid (SBS) model for 3D shape evolution and the application to via and trench fillings for damascene electroplating. The SBS model is a lattice model for crystal growth developed by our group as a simple extension of the conventional Solid-on-Solid model to include the vacancy formation [21,22]. The correlation between the surface structure and the defect structures in the deposited films has been studied by the 2D SBS model. The 2D SBS model has been applied to the simulation of via filling to study the effects of additives on the void formation [23,24]. The big advantage of the SBS model is that complex 3D shape evolution can be simulated without difficulties. In this paper we present the KMC simulation of the 3D SBS model for electrodeposition with solution part and additives. The core part of the system is the 3D SBS model which can follow the 3D shape evolution and void formation. The solution part is located above the electrode surface and treated by the particle model. The diffusion of the particles representing ions and additives is simulated by the coarse-grained random walk (CGRW). The diffusion layer is located in the upper part of the solution. In order to take into account the difference in the time and length scales between the mass transport in the diffusion layer and the electrochemical reactions occurring on the electrode, the multi-scale method has been employed. The whole system is treated within the framework of the KMC simulation.

We have performed the simulations of via and trench fillings by copper electrodeposition as an application to semiconductor engineering. Suppressors, chloride ions and accelerators are taken into account. We first examined the effects of additives on the surface growth. Then, we performed the simulations of via and trench fillings to discuss the bottom-up mechanism in relation to the additive distribution. Preliminary results were reported in our previous papers [25,26].

The model system and the method of simulations are described in the next section. The simulation results are given in Section 3. Summary and conclusion are given in Section 4. In Appendix we report the algorithm of searching surface atoms, which is an important part in the KMC code of the SBS model.

2. Computations

Fig. 1 illustrates the simulation system of the solution–electrode interface. It consists of the electrode, the solution and the diffusion layer. The whole system is the three-dimensional (3D) cubic lattice. Modeling and the simulation method of each part are described as follows.

2.1. Basic Solid-by-Solid model for crystal growth

The crystal growth on the electrode surface is simulated by the SBS model. In the SBS model, each site represents either of a solid atom, a liquid atom or a vacancy. (In a coarse-grained system, a site represents a superparticle (a group of particles) as described

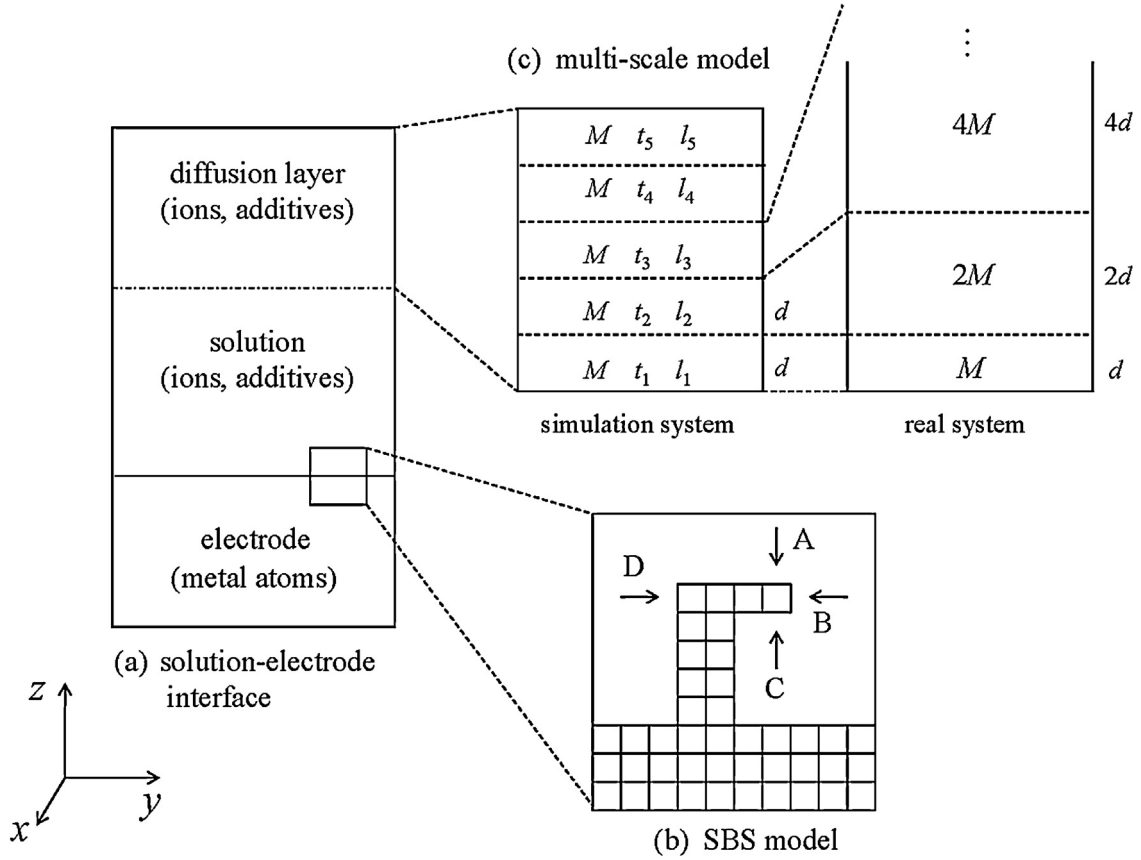

Fig. 1. The image of the simulation system. (a) The whole system of the solution–electrode interface. (b) SBS model for the electrode surface. (c) Multi-scale model for the diffusion layer.