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Research paper

Numerical modeling and experimental verification of copper electrodeposition for through silicon via (TSV) with additives

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ABSTRACT

Since voids and seams are easily formed during the process of filling TSVs with high aspect ratio, good methods that can achieve the superfilling of TSVs are eagerly needed. This paper presents the numerical modeling of TSV filling concerning the influence of three additives (accelerator, suppressor and leveler). By changing the additives' doses and current density, the following three different simulation results were obtained: the pinch-off effect, seam-inside filling model and "V" shaped filling model. The corresponding distributions of the current density along the cathode surface were analyzed to investigate the filling mechanism. Moreover, TSV filling experiments in the presence of additives were also conducted to validate the proposed numerical model. The simulation results matched well with the experimental results. TSVs with a diameter of 20 μm and depth of 200 μm were fully filled in the appropriate conditions.

1. Introduction

3D integration with through silicon vias (TSVs) has been widely known as a promising technology for future electronic systems. It provides the shortest vertical interconnections with a series of significant advantages, such as a wide bandwidth, lower energy consumption, higher density, smaller form factor, and improved electrical performance [1–4] compared with the conventional 2D integration approach. The vertical interconnects are formed through the wafer to enable communication among the stacked chips. Its applications are also quite wide, which include MEMS sensors, CMOS image sensors (CIS), memorizers, hybrid memory cubes (HMC), radio-frequency circuits and so on. For most TSV development, copper electrodeposition is one of the most important technologies for implementing the 3D interconnection [5,6]. However, since most TSVs are of high aspect ratios [7–9], and the TSVs filling experiment is a complex physicochemical dynamic process, it is really a difficult and challenging task to fill these TSVs with no voids or seams.

To accomplish void-free filling, several additives such as bis disulfide (SPS), poly (PSG) and chloride ions (Cl^-) are usually added to the plating bath [10–15]. At the same time, the bottom-up superfilling has been achieved as the join of these additives. On the other hand, numerical modeling for TSV filling has also been presented. The bottom-up superfilling model was first proposed by Moffat et al. and explained by the curvature enhanced accelerator coverage (CECA) [16]. Some other numerical models of TSV filling have also been developed to explain the superfilling process [17–22]. Among these models, a general diffusion-adsorption theory has been widely used in explaining the superfilling phenomena [23–28]. However, numerical modeling and experimental verification for high aspect ratio (H:D = 10:1) TSV filling with three additives(accelerator, suppressor and leveler) have not yet been closely combined to deeply investigate the filling mechanism. In addition, experiments of filling high aspect ratio TSVs with a diameter of 20 μm and depth of 200 μm in the presence of additives have not yet been systematically conducted from published papers.

In this paper, a new numerical model that is based on the Butler-Volmer equation and considers the process of adsorption, desorption and diffusion of the three additives (accelerator, suppressor and leveler) on the cathode surface is proposed for copper electrodeposition of TSVs. Three different simulation results for TSV filling were obtained by changing the additives' doses and current density: the pinch-off effect, seam-inside filling and "V" shaped filling. The corresponding distribution of current density along the cathode surface was also analyzed to help us better understand the filling mechanism of copper electroplating. Moreover, TSV filling experiments with additives were also conducted to validate the proposed numerical modeling. The simulation results match well with the experimental results.

2. Numerical model

Fig. 1 shows the planar model and boundary conditions of the TSV filling. The diameter (D) of the TSV is 20 μm and the depth (H) is

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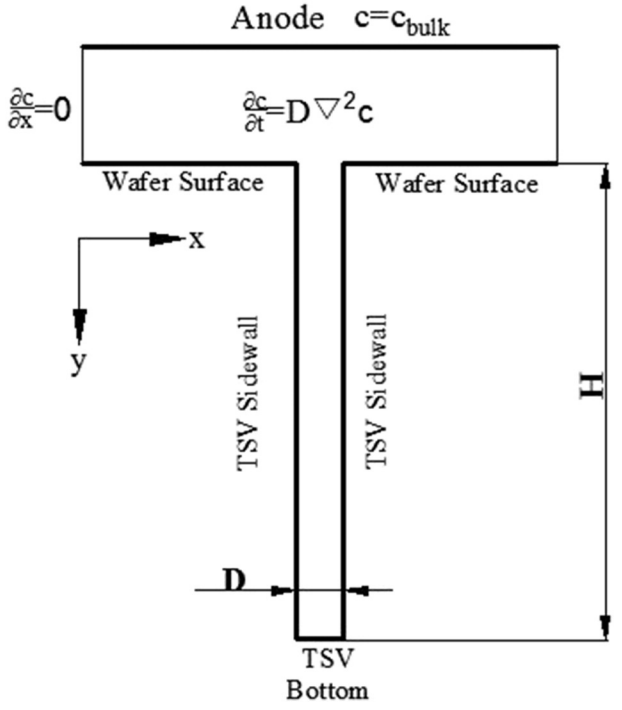

Fig. 1. Schematic illustration of the mathematical model used in the TSV copper electroplating.

200 μm. The symmetrical boundary of the electrolyte is 50 μm in height and 200 μm in distance. The cathode includes the wafer surfaces, the TSV sidewalls and the TSV bottom, which are all marked as shown in Fig. 1. It's assumed that the mass transport is dominated by diffusion and electromigration. Convection is neglected. The concentration of ions (c) on the anode surface, including copper and additives ions, is defined as equal to that in the bulk solution (c_{bulk}). The concentration of ions between anode and cathode varies with time, which is defined as $\frac{\partial c}{\partial t} = D\nabla^2 c$. The ion concentration remains steady in the x direction, which is defined as $\frac{\partial c}{\partial x} = 0$. The main parameters used for the numerical modeling are shown in Table 1.

The plating bath of the model consists of copper ion, sulfate ion and additive ions. The ion flux is given by the Nernst-Planck equation:

$$N_i = -D_i\nabla c_i - z_i u_i F c_i \nabla\phi_l + c_i\vec{u} \tag{1}$$

where N_i is the ion flux, D_i is the diffusion constant, c_i is the ion concentration, z_i is the valence (charge number), u_i is the mobility constant, ϕ_l is the electric potential inside the electrolyte solution, $\vec{u}$ is the flow velocity of the electrolyte and F is Faraday's constant.

Table 1
Parameters used for the numerical modeling.

Symbols	Values
$c_{Cu^{2+}}{}^{\infty}$	500 mol/m^3
k_{Acc_ads}	7.9×10^{-3} m^3/(s·mol)
k_{Sup_ads}	0.158 m^3/(s·mol)
k_{Lever_ads}	9×10^{-3} m^3/(s·mol)
k_{Acc_des}	1×10^{-3} 1/s
k_{Sup_des}	0.01 1/s
k_{Lever_des}	0.3×10^{-3} 1/s
$D_{Cu^{2+}}$	2×10^{-8} m^2/s
D_{Acc_s}	3.24×10^{-4} m^2/s
D_{Sup_s}	3.92×10^{-5} m^2/s
D_{Lever_s}	1.46×10^{-5} m^2/s

The effect of accelerator (Acc for short), suppressor (Sup for short) and leveler (Lever for short) on TSV filling are all considered in the model. The three additives can affect the distribution of current density along the cathode, which can affect the deposition rate in different parts of the via and the final filling result. The distribution of the three additives in the electrolyte can be shown by the concentration diffusion field. The equation of the concentration field is:

$$\nabla^2 c_i = 0 \quad (\mathrm{i} = \mathrm{Acc}, \mathrm{Sup}, \mathrm{Lever}) \tag{2}$$

where c_{Acc} is the concentration of accelerator, c_{Sup} is the concentration of suppressor and c_{Lever} is the concentration of leveler.

Considering the adsorption, desorption and diffusion of the three additives(accelerator, suppressor and leveler) on the cathode surface, the time-dependent surface coverage of the three additives can be shown as:

$$\begin{cases} \dfrac{\partial\theta_{Acc}}{\partial t} = k_{Acc\_ads}c_{Acc}(1-\theta_{Acc}-\theta_{Lever}) - k_{Acc\_des}\theta_{Acc} - D_{Acc\_s}\nabla_{\nabla}^2\theta_{Acc} \\ \dfrac{\partial\theta_{Sup}}{\partial t} = k_{\mathrm{Sup}\_ads}c_{Sup}(1-\theta_{Acc}-\theta_{Sup}-\theta_{Lever}) - k_{Sup\_des}\theta_{Sup} - D_{Sup\_s}\nabla_{\nabla}^2\theta_{Sup} \\ \dfrac{\partial\theta_{Lever}}{\partial t} = k_{Lever\_ads}c_{Lever}(1-\theta_{Acc}-\theta_{Lever}) - k_{Lever\_des}\theta_{Lever} - D_{Lever\_s}\nabla_{\nabla}^2\theta_{Lever} \end{cases} \tag{3}$$

where θ_{Acc} (θ_{Sup},θ_{Lever}) is the surface coverage of accelerator (suppressor, leveler) on the cathode, k_{Acc_ads}(k_{Sup_ads},k_{Lever_ads}) is the adsorption coefficient of accelerator (suppressor, leveler), k_{Acc_des}(k_{Sup_des},k_{Lever_des}) is the desorption coefficient of accelerator (suppressor, leveler), D_{Acc_s}(D_{Sup_s},D_{Lever_s}) is the diffusion coefficient of accelerator (suppressor, leveler), and ∇_T is the mathematical operator of the vertical edge interface. Since every area in the via has four different states (covered by accelerator, covered by suppressor, covered by leveler and covered by basic solution), based on Butler-Volmer equation and considers the process of adsorption, desorption and diffusion of the three additives (accelerator, suppressor and leveler) on the cathode surface, the current density on the cathode surface can be then calculated as:

$$\begin{cases} \mathrm{i}_{Acc} = \dfrac{c_{Cu^{2+}}}{c_{Cu^{2+}}^{\infty}}\left[\mathrm{i}_{0\_\mathrm{Acc}}\theta_{Acc}\ \exp\left(\dfrac{-\alpha_{Acc}F\eta}{R_gT}\right)\right] \\ \mathrm{i}_{\mathrm{Sup}} = \dfrac{c_{Cu^{2+}}}{c_{Cu^{2+}}^{\infty}}\left[\mathrm{i}_{0\_\mathrm{Sup}}\theta_{Sup}\ \exp\left(\dfrac{-\alpha_{Sup}F\eta}{R_gT}\right)\right] \\ \mathrm{i}_{Lever} = \dfrac{c_{Cu^{2+}}}{c_{Cu^{2+}}^{\infty}}\left[\mathrm{i}_{0\_Lever}\theta_{Lever}\ \exp\left(\dfrac{-\alpha_{Lever}F\eta}{R_gT}\right)\right] \\ \mathrm{i}_{Basic} = \dfrac{c_{Cu^{2+}}}{c_{Cu^{2+}}^{\infty}}\left[\mathrm{i}_{0\_basic}(1-\theta_{Acc}-\theta_{Sup}-\theta_{Lever})\ \exp\left(\dfrac{-\alpha_{basic}F\eta}{R_gT}\right)\right] \end{cases} \tag{4}$$

where $\mathrm{i}_{0\_\mathrm{Acc}}$($\mathrm{i}_{0\_\mathrm{Sup}}$,$\mathrm{i}_{0\_Lever}$) is the exchange current density of the electrolyte containing accelerator(suppressor, leveler), i_{0_basic} is the exchange current density of the basic solution without any additives, $c_{Cu^{2+}}$ is the concentration of copper on the cathode surface, $c_{Cu^{2+}}{}^{\infty}$ is the concentration of copper in the bulk electrolyte, and α_{Acc}(α_{Sup},α_{Lever}, α_{basic}) is the electrochemistry transmission coefficient. The total current density on the cathode surface is the sum of $\mathrm{i}_{\mathrm{Acc}}$, $\mathrm{i}_{\mathrm{Sup}}$,$\mathrm{i}_{Lever}$and i_{basic}, which can be shown as:

$$\mathrm{i} = \mathrm{i}_{Acc} + \mathrm{i}_{\mathrm{Sup}} + \mathrm{i}_{Lever} + \mathrm{i}_{Basic} \tag{5}$$

Substituting Eq. (4) into Eq. (5), we can achieve:

$$\begin{aligned} i = \frac{c_{Cu^{2+}}}{c_{Cu^{2+}}^{\infty}}\Bigg[&\mathrm{i}_{0\_\mathrm{Acc}}\theta_{Acc}\ \exp\left(\frac{-\alpha_{Acc}F\eta}{R_gT}\right) + \mathrm{i}_{0\_\mathrm{Sup}}\theta_{Sup}\ \exp\left(\frac{-\alpha_{Sup}F\eta}{R_gT}\right) \\ &+ \mathrm{i}_{0\_Lever}\theta_{Lever}\ \exp\left(\frac{-\alpha_{Lever}F\eta}{R_gT}\right) \\ &+ \mathrm{i}_{0\_basic}(1-\theta_{Acc}-\theta_{Sup}-\theta_{Lever})\ \exp\left(\frac{-\alpha_{basic}F\eta}{R_gT}\right)\Bigg] \end{aligned} \tag{6}$$