Simulation of produced cuprous ion concentration distribution during periodic reverse pulse current waveform

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1. Introduction

3D chip stacking realize high-density packaging and high-speed performance. High-aspect-ratio through-silicon via allow short interconnects and reduced signal delays. Copper electrodeposition in high-aspect-ratio via is one of the key technologies for 3D packaging. Voids or seams formed in the via may causes serious problems in reliability.

We already have reported that 4 μm diameter via of aspect ratio of 7.5 is perfectly filled within 25 minutes by changing the reverse current of periodical reverse current(1). Additionally, we have reported the advantage of via filling performance with purging oxygen gas in the bulk electrolyte (2). In this study, we simulated produced cuprous ion concentration during electrodeposition by using COMSOL Multiphysics.

2. Numerical Analysis

Simulation of cuprous ion concentration profile by the numerical computation of fluid dynamics will be compared with the electrodeposits profiles in the via. The equation of continuity, Navier-Stokes equations, and mass transfer equation is shown below.

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0 \qquad (1)$$

$$\rho\left(u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}\right)=-\frac{\partial P}{\partial x}+\mu\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}\right) \qquad (2)$$

$$\rho\left(u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}\right)=-\frac{\partial P}{\partial x}+\mu\left(\frac{\partial^2 v}{\partial x^2}+\frac{\partial^2 v}{\partial y^2}\right) \qquad (3)$$

$$u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}=D\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}\right) \qquad (4)$$

Butler-Volmer equation is shown below (3). Boundary condition is shown Fig.1.

$$\begin{aligned} i_{Cu} = & -Fk_1 c_{Cu^{2+}}(1-\theta_{Cu^+})\exp\left[-\frac{\beta_1 n_1 F}{RT}\phi_M(t)\right] \\ & + Fk_{-1}\theta_{Cu^+}\exp\left[\frac{(1-\beta_1)n_1 F}{RT}\phi_M(t)\right] \\ & - Fk_2\theta_{Cu^+}\exp\left[-\frac{\beta_2 n_2 F}{RT}\phi_M(t)\right] \\ & + Fk_{-2}\exp\left[\frac{(1-\beta_2)n_2 F}{RT}\phi_M(t)\right] \end{aligned} \qquad (5)$$

The reaction equations of cuprous ion is

$$Cu^{2+}+e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu^+ \qquad (6)$$

$$Cu^{+}+e^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Cu \qquad (7)$$

Kinetic parameters k_1, k_{-1}, k_2, k_{-2} are 2×10^{-4} m/s, 8×10^{-3} mol/(m^{2}s), 130 mol/(m^{2}s), 3.9×10^{-7} mol/(m^{2}s), respectively (3).

3. Results

1. We measured produced cuprous ion concentration during electrodeposition by using rotating ring disk electrode (RRDE). From the electrochemical measurement by RRDE, cuprous ion concentration on the reactive surface was markedly increasing with the increasing $i_{rev}/|i_{on}|$ ratios (Fig. 2). Cuprous ion is the accelerators which are accumulated and accelerates the via bottom (4, 5, 6).
2. We simulated produced cuprous ion concentration at the via bottom with changing $i_{rev}/|i_{on}|$ ratios. From the simulation results, produced cuprous ion concentration was increasing with the increasing $i_{rev}/|i_{on}|$ ratios.

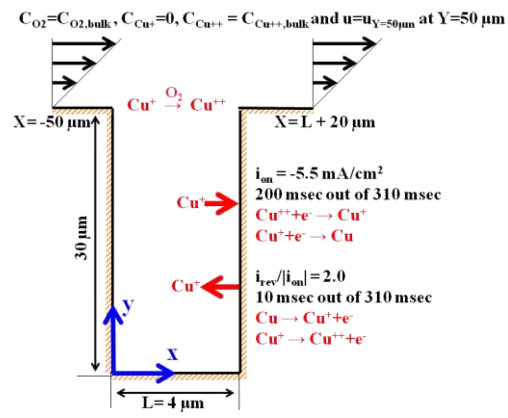

Figure 1. Boundary condition of cuprous ion distribution by the numerical computation.

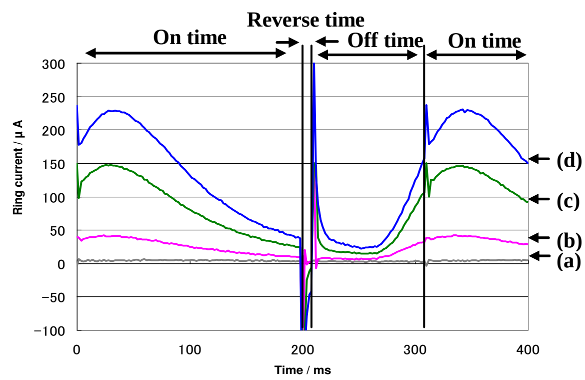

Figure 2. Ring current and time curves for different reverse current. (a) $i_{rev}/|i_{on}|=0$, (b) $i_{rev}/|i_{on}|=2.0$, (c) $i_{rev}/|i_{on}|=4.0$, (d) $i_{rev}/|i_{on}|=6.0$.

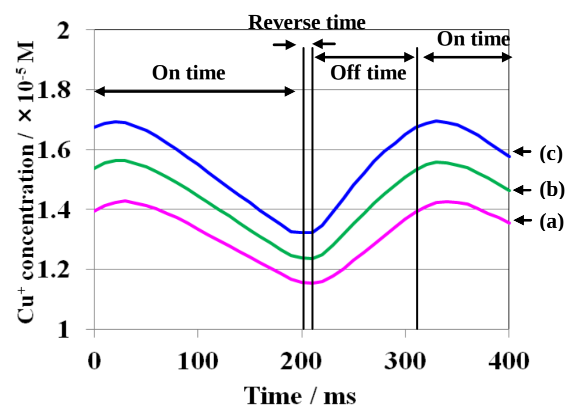

Figure 3. Simulated cuprous ion concentration at the via bottom. (a) $i_{rev}/|i_{on}|=2.0$, (b) $i_{rev}/|i_{on}|=4.0$, (c) $i_{rev}/|i_{on}|=6.0$.

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