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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 with a ratio of 7.5 is perfectly filled within 25 minutes by changing electrodeposition in high-aspect-ratio via is one of the key technologies for 3D packaging. Voids or seams formed in the via may cause 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 periodic reverse current. Additionally, we have reported the advantage of via filling performance by purging oxygen gas in the bulk electrolyte.

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.

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0
\]

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

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

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

\[
\begin{align*}
\frac{1}{R_T} & = F k_1 (c_{Cu^2+} (1 - \theta_{Cu^2+}) - \theta_{Cu^2+}) \\
& + F k_{-1} \theta_{Cu^+} \exp \left( \frac{-\beta_{Cu^{2+}} F}{RT} \right) \phi_{Cu^2+}(t) \\
& - F k_2 \theta_{Cu^+} \exp \left( \frac{-\beta_{Cu^{2+}} F}{RT} \right) \phi_{Cu^2+}(t) \\
& + F k_{-2} \theta_{Cu^+} \exp \left( \frac{-\beta_{Cu^{2+}} F}{RT} \right) \phi_{Cu^2+}(t)
\end{align*}
\]

The reaction equations of cuprous ion is

\[
Cu^{2+} + e^- \xrightarrow{k_1} Cu^+ \quad (6)
\]

\[
Cu^+ + e^- \xrightarrow{k_2} Cu \quad (7)
\]

Kinetic parameters \( k_1, k_2, k_3, k_4 \) are \( 2 \times 10^4 \) m/s, \( 8 \times 10^{-7} \) mol/(m²s), \( 130 \) mol/(m²s), \( 3.9 \times 10^{-7} \) mol/(m²s), 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 \( i_{on}/i_{off} \) ratios (Fig. 2). Cuprous ion is the accelerators which are accumulated and accelerates the via bottom.

2. We simulated produced cuprous ion concentration at the via bottom with changing \( i_{on}/i_{off} \) ratios. From the simulation results, produced cuprous ion concentration was increasing with the increasing \( i_{on}/i_{off} \) ratios.

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

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

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