Electrochemical and Simulative Studies of Trench Filling Mechanisms in the Copper Damascene Electroplating Process

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The role of additives in copper electroplating baths in the damascene process has been investigated. We proposed a bottom-up filling model and confirmed it by comparing the experimental and simulation results. Janus Green B and Basic Blue 3 which absorb on the copper surface and suppress copper deposition were examined for additive use to improve filling capability. Damascene copper grow uniformly in the bath that contained Basic Blue 3. But it grew preferentially from the bottom of the trench for Janus Green B. Addition of Janus Green B produced a continuous concentration gradient in the sub-micron trench when the additive’s diffusion rate and consumption rate on the copper surface were well balanced. We estimated filling profiles from numerical simulation using parameters that were determined by an electrochemical method. These profiles agreed well with the experimental results.

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1. Introduction

Electroplating is a mainstream method to make copper (Cu) interconnections for ULSI (ultra-large scale integration). Techniques for filling damascene trenches include physical vapor deposition (PVD), chemical vapor deposition (CVD), and plating. The PVD method provides poor coverage on the sides of trenches with a high aspect ratio. This may lead to voids or seams forming in the trenches. The CVD method, on the other hand, provides good coverage. But it has disadvantages of high costs of source materials and high impurities concentrations in the deposited copper. Electroplating offers an excellent filling capability and is the most attractive process for copper wiring.

Typically, copper electroplating baths which were sulfuric acid-based contain some additives to facilitate filling of sub-micrometer trenches and to improve deposit properties. There are various classes of additives, brighteners (or accelerators), carriers (or suppressors or polymers), and levelers. The concentration of some additives and proper plating conditions results in a higher deposition rate is higher at the bottom of the trench. That phenomenon is called “bottom-up filling”. In the future, improved ULSI performance will continue to be in demand, meaning that the wiring minimum pitch will be scaled down and the aspect ratio of the trenches will become high. With a high aspect ratio, it is more difficult to fill trenches without voids or seams. Therefore, it is important to understand a bottom-up filling mechanism to improve filling capability.

In this study, we propose the bottom-up filling model which we confirm using experimental and numerical simulation results.

2. Filling Model

Some models for bottom-up filling have been reported.\textsuperscript{1–6)} They can be divided into two types. In one type, the additive has a promotional effect on copper deposition and it is concentrated in the bottom of the trench. In the other, the additive has an inhibition effect on copper deposition and the reaction of the additive is diffusion-controlled. We previously proposed a filling model for the latter type.\textsuperscript{6)} If additives react electrochemically on the copper surface, we can evaluate the diffusion coefficient and the reaction rate constant of the additives by using electrochemical measurements. When the additive is consumed on the copper surface, a concentration gradient of the additive due to its diffusion is formed. If this concentration gradient is maintained steadily, the concentration of additives at the bottom of the trench drops. This leads to a decrease in the inhibition effect on copper deposition at the bottom of the trench. Therefore, the deposition rate at the bottom of the trench becomes higher than that at the top and bottom-up filling is realized.

3. Experimental

3.1 Electrochemical measurements

The electrochemical measurement system (Model 100 W type, BAS Inc.) and rotating disk electrode equipment (AFMSR type, PINE INSTRUMENT) shown in Fig. 1 were used. The working electrode was a platinum rotating disk electrode (φ5 mm) for polarization curve measurements. It was plated with copper at 1.0 A/dm\textsuperscript{2} for 2 min (about 400 nm thick) in the electrolyte before each measurement. A glassy carbon disk electrode (φ3 mm) was used for cyclic-voltammetry of additive reactions. A platinum micro-electrode (φ15 μm) was used to determine the diffusion rate and the reaction rate of additives. The reference electrode was Ag/AgCl (saturated KCl) and the counter electrode was a platinum wire. The basic electrolyte composition included 0.30 mol/L CuSO\textsubscript{4} (Wako Chemical) and 1.8 mol/L H\textsubscript{2}SO\textsubscript{4} (Wako Chemical) and 1.7 × 10\textsuperscript{-3} mol/L HCl (Wako Chemical). Janus Green B (Aldrich) and Basic Blue 3 (Aldrich) were used for additives. The electrolyte and experimental
Table 1 Electrodes and composition of electrolytes.

<table>
<thead>
<tr>
<th></th>
<th>Cu (φ5.0 mm)</th>
<th>Glassy carbon (φ3.0 mm)</th>
<th>Platinum (φ15 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference electrode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Counter electrode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration, C/mol L⁻¹</td>
<td>0.30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Copper sulfate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Chloride ion</td>
<td>1.7 × 10⁻³</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Additive</td>
<td>10 mg/L</td>
<td>2 × 10⁻³</td>
<td>2 × 10⁻³</td>
</tr>
<tr>
<td>Temperature, T/°C</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scan rate, v/mVs⁻¹</td>
<td>0.5 or 2</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

3.2 Filling experiment

A φ200 mm Si wafer with 1 µm thick SiO₂ on which the trenches were formed was used for the substrate. A tantalum barrier layer was first deposited on the substrate to 50 nm thickness and then 150 nm thick copper seed layer was deposited by sputtering. It was plated at a constant current density 1.0 A/dm² for 20 s during which time the growth process of copper in the trench was observed. A commercial additive for printed circuit boards (CC-1220, Japan Energy) is added to improve the copper surface morphology. Copper which contained phosphorous was used for the anode. Cross-sectioned copper images were taken with a scanning electron microscope (S-900, Hitachi).

3.3 Simulation method

The Laplace equation for potential in the copper electroplating bath was coupled with the diffusion equation for both the concentration of cupric ion (= C) and the concentration of an additive (= G) as shown in Fig. 2. These were solved by the boundary element method. Then the current density distribution on the copper surface was calculated and the form of the copper film was predicted. The boundary moves according to the current distribution given by a string model. The boundary condition of G in the diffusion equation of the additive on the copper surface is

\[ DdG/dn = k\Theta G \]  \hspace{1cm} (1)

where D, n, k, and Θ are the diffusion coefficient of the additive, position vector normal to the surface, the consumption rate constant of additive on the copper surface, and the surface coverage of the additive, respectively. This equation is balanced between the incident flux of an additive and the consumption rate over the unit area. The D/k value determines the distribution of an additive concentration in the trench. Therefore, the D/k value influences the bottom-up filling profile. All the parameters used in the present method were determined by electrochemical measurements.

4. Results and Discussion

4.1 Characteristics of additives

Based on our model, additives must have some characteristics to realize bottom-up filling. 1) It must have an inhibition effect on the plating reaction. It must be adsorbed on a copper surface and include atoms, such as sulfur, nitrogen and so on. 2) It must be consumed in the plating reaction which means the inhibition effect is lost. We selected two candidate additives, Janus Green B which was to have an effect on bottom-up filling and Basic Blue 3. It has some functional groups that are the same as Janus Green B (Fig. 3) and we felt it might be applicable.
4.1 Inhibition effect on the plating reaction

Figure 4 shows the current-potential curves for the electroplating bath with and without additives. When potential was scanned from the rest potential in the negative direction, reduction current due to the copper deposition began to flow. In the positive potential region from $-100 \text{ mV}$, reduction current in the plating bath that contained Basic Blue 3 or Janus Green B was small compared to the value when the bath contained no additive. These compounds inhibited a deposition of copper in this potential region. There was a difference in the inhibition effect between Basic Blue 3 and Janus Green B. We thought that the inhibition effect reflected the adsorption condition and the amount of adsorption of each additive.

4.1.2 Consumption on the Cu surface

Consumption of the additive on the copper surface was evaluated by an electrochemical method. We assumed that additives lost their inhibition effect on the plating reaction when they were electrochemically reduced. Figure 5 shows cyclic voltammograms measured in sulfuric acid that contained Basic Blue 3 or Janus Green B. A one-step reduction peak was observed for the Basic Blue 3 containing solution and a two-step peak was observed for the Janus Green B one. This meant that Basic Blue 3 and Janus Green B were reduced electrochemically in acidic solution.

Basic Blue 3 and Janus Green B both had an inhibition effect on the plating reaction and they were consumed on the copper surface. Therefore, both Basic Blue 3 and Janus Green B were thought to possibly have the characteristics required for bottom-up filling.

4.2 Filling capability

Figure 6 shows cross-sectional SEM images of partially filled 0.25 $\mu\text{m}$ wide trenches prepared in baths containing no additive, Basic Blue 3 and Janus Green B. Copper grew uniformly using the baths with no additive and Basic Blue 3. On the other hand, copper grew preferentially from the bottom of the trench using the bath containing Janus Green B. Janus Green B resulted in bottom-up filling. Bottom-up filling was expected for both additives from characteristics discussed above. However, conformal growth was observed for addition of Basic Blue 3 under the present plating conditions. We thought this might be explained as follows. Each additive had the required characteristics qualitatively. The difference in filling capability depended on whether the concentration gradient of the additive was maintained properly in the trench. The balance between the supply of the additive by diffusion and the consumption of the additive by the reaction on the copper surface was inappropriate in the bath which contained Basic Blue 3.

We investigated the diffusion of additives in plating baths using a rotating disk electrode. Figure 7 shows the current-potential curves of the copper deposition while changing the rotation speed of the electrode from 0 to 2000 rpm. The deposition current increased with the increase in the rotation speed of the electrode in the bath that contained no additive. When the diffusion layer on the surface of the electrode became
thin, the supply rate of cupric ion to the copper surface increased. The deposition current in the bath containing Basic Blue 3 also increased with the increase of rotation speed. On the other hand, in the plating bath containing Janus Green B, the deposition current decreased with the increase of rotation speed in the potential range from 100 mV to −120 mV. This was because the decrease in the current due to the inhibition effect of additives became larger than the increase in the current due to the increase in the supply rate of cupric ion. The inhibition effect of each additive was different though they had the same functional groups and similar characteristics would be expected.

4.3 Simulations

The model was confirmed by the comparison with results from experiments and numerical simulations and the difference between Basic Blue 3 and Janus Green B was explained quantitatively. The concentration distribution of the additive in the trench was influenced by a balance between the diffusion coefficient, $D$, and the reaction rate constant, $k$. As mentioned above, $D$ and $k$ are important parameters for bottom-up filling. These parameters were determined by electrochemical methods.

4.3.1 Experimental determinations of the parameters which are necessary for simulations

(a) Reaction rate constant of additives, $k$

The current-potential curves of additives in sulfuric acid were measured using the microelectrode. The reaction rate constant of additives on the copper surface $k$ was calculated from the slope of the current-potential curves. If the charge transfer reaction is the rate determining step, the current against the overpotential $\phi$ is given by

$$i = nFGA_k = nFGA_k_0 \exp(\phi/b) \quad (2)$$

where $i$, current; $F$, Faraday constant; $A$, electrode area; $k_0$, standard rate constant of additive on the copper surface.

Figure 8(a) shows the current-potential curve of Basic Blue 3 in the sulfuric acid solution. The slope of the straight part of the curve gave, $i = 8.8 \times 10^{-1} \exp(-59\phi)$. When $G = 2 \text{ mol·m}^{-3}$ and $A = 1.8 \times 10^{-10} \text{ m}^2$ was substituted in eq. (2) and $n = 1$ was assumed; $k_0$ for Basic Blue 3 was $2.6 \times 10^4 \text{ m/s}$. The overpotential $\phi$ was $−8.1 \times 10^{-2} \text{ V}$ from Fig. 4 when the plating current density was 1.0 A/dm². The reaction rate constant of Basic Blue 3 $k$ was $3.1 \times 10^6 \text{ m/s}$.

Figure 8(b) shows the current-potential curve of Janus Green B. Janus Green B reacted in two steps. The second step was considered the rate determining step from the slope of the curve. The $k$ value was calculated for the second step.
and at 1.0 A/dm², kₘ was 1.8 × 10⁻⁴ m/s.

**b) Diffusion coefficient of additives: D**

The diffusion coefficient of additives was calculated from the diffusion limiting current of current-potential curves. The diffusion coefficient \( D \) is given by

\[
D = \frac{i_{\text{lim}}}{(4 \cdot n \cdot F \cdot G \cdot a)}
\]

where \( i_{\text{lim}} \), the diffusion limiting current, \( a \), electrode radius.

The diffusion limiting currents are also shown in Fig. 8. The diffusion limiting current in the Basic Blue 3 containing solution was 1.0 × 10⁻⁸ A. The diffusion limiting current in the Janus Green B containing solution was 1.7 × 10⁻⁹ A for the second-step reaction. Therefore, the diffusion coefficient of Basic Blue 3 and Janus Green B were 1.7 × 10⁻⁹ m²/s and 2.9 × 10⁻¹⁰ m²/s respectively.

### 4.3.2 Comparison of experimental and simulation results

Figure 9 shows trench filling profiles obtained by simulations and experiments. The experimental profiles were in good agreement with calculated profiles. For Basic Blue 3, copper thickness was equal at all points of the trench for both experiment and simulation. For Janus Green B, copper grew preferentially at the bottom of the trench. This suggested our model was reasonable.

Figure 10 shows the predicted filling profiles and the distribution of the additives in a trench against \( D/k \) value. Filling profiles changed with \( D/k \) value.

**Case (a)** The \( D/k \) value was too small for bottom-up filling. The distribution of the additive concentration was uniform. This was because the reaction rate of additive was so fast relative to the diffusion rate of additive that almost all additives were consumed around the top of a trench. The filling profile of the bath without additive was the same as that with additive.

**Case (b)** \( D/k \) value was suitable for bottom-up filling. The diffusion rate and the reaction rate of the additive were in the appropriate range. In this case, the reaction of additives was diffusion-controlled and the concentration gradient of additives along the trench was formed. The concentration of the additive decreased toward the bottom of the trench, and because of this decreases, the inhibition effect on the copper deposition at the bottom dropped. Therefore, preferential growth from the bottom of the trench was realized.

**Case (c)** \( D/k \) value was too large for bottom-up filling. A large \( D/k \) value meant that the reaction rate of additives was slow and the diffusion rate was fast. In this situation, the concentration of additives in the trench was high and had less concentration gradient. Therefore, the filling profile was conformal.

The \( D/k \) values for Basic Blue 3 and Janus Green B was 1.8 × 10⁻¹⁶ and 1.8 × 10⁻⁶, respectively. Thus, Janus Green B fit case (b) and had a suitable \( D/k \) value for bottom-up filling. Basic Blue 3 fit case (a) and its \( D/k \) value was too small. We concluded for bottom-up filling to occur, the diffusion rate and the reaction rate of the additive must be in appropriate ranges. The filling profiles of the trench would be predicted by calculating the \( D/k \) value.

### 5. Conclusions

The role of additives in the copper electroplating bath in the damascene process has been investigated. We proposed a bottom-up filling model. Filling profiles change with characteristics of additives. The continuous concentration gradient of the additive in the sub-micron trench was necessary to achieve bottom-up filling. There was a suitable balance between the diffusion rate and the reaction rate of the additive.
on the copper surface. We estimated the filling profile by numerical simulation using parameters that were electrochemically determined. The predicted filling profiles agreed very well with the experimental results. This suggested that the diffusion coefficient and reaction rate constant of an additive played important roles in bottom-up filling and that our model was reasonable.

List of Symbols

\begin{align*}
D & \quad \text{diffusion coefficient of the additive, m}^2/\text{s} \\
n & \quad \text{position vector normal to the surface} \\
k & \quad \text{reaction rate of additive on the copper surface} \\
k_0 & \quad \text{reaction rate of additive on the copper surface at standard condition} \\
\Theta & \quad \text{additive coverage on the copper surface} \\
G & \quad \text{additive concentration, mol/m}^3 \\
C & \quad \text{copper concentration, mol/m}^3 \\
i & \quad \text{current, A} \\
F & \quad \text{Faraday’s constant, C/mol} \\
A & \quad \text{electrode area, m}^2 \\
\phi & \quad \text{overpotential, V} \\
b & \quad \text{constant} \\
n & \quad \text{electrons transferred} \\
i_{\text{lim}} & \quad \text{diffusion limiting current, A} \\
a & \quad \text{electrode radius of microelectrode, m}
\end{align*}

REFERENCES