**Wet etching rate in the cavity of printed circuit board**

Katsutoshi Matsumoto*, Daiki Takahashi**, Kazutoshi Matsumura***, Takaharu Suzuki***, and Shoji Taniguchi*

*Tohoku University
**Graduate student, Tohoku University
***Former graduate student, Tohoku University
Aoba-yama6-6-02, Sendai, JAPAN

**ABSTRACT**

The mechanism of wet etching of copper in a ferric chloride solution is studied using an agitated vessel and a spray nozzle. First, the etching rate of a plate-shaped copper specimen is measured to confirm the rate-limiting step. The effects of flow rate and solution temperature on the etching rate are investigated. From the results of the dissolution of the copper plate, it is found that the liquid-phase mass-transfer process is the main rate-limiting step in wet etching. Second, line-patterned copper specimens are etched to study the cavity formation. A mass-transfer model of wet etching for printed circuit boards is developed by using the observed diffusivity of Fe$^{3+}$. In conclusion, it is found that this model is fairly reliable in evaluating the cavity formation for fine pattern etching. However, the calculated cavity shape appears to be inconsistent with the observed one in the case of wide line spacing. It is considered that this deviation is caused by the effect of bulk convection.

**Introduction**

Recently, the techniques of large-scale integration (LSI) for integrated circuits (IC) have been advanced dramatically. Therefore, the necessity of studying the fabrication of fine circuit boards has been noticed. In order to produce finer circuits in an efficient manner, the kinetics of the etching rate of a copper foil in aqueous solutions must be clarified. In this regard, some studies on wet etching in small cavities have been carried out [1 - 5]. These studies have been performed under the condition that the flow of the etching solution is laminar. However, almost all industrial operation systems use turbulent flows for wet etching; the rate-limiting step for this system has not been determined. Therefore, it is very important to study the mechanism of wet etching in turbulent flows.

In our previous studies [6 - 8], a mechanism of wet etching of copper was studied using an agitated vessel. It is known that by using ferric chloride solution, a faster etching rate can be achieved than that with cupric chloride solution. In the present work, in addition to this, a spray nozzle was used to determine the mechanism of wet etching of copper. Etching experiments for copper by using ferric chloride solution were carried out. Investigations for the rate-limiting step were conducted by considering the dependency of the etching rate on several parameters. Subsequently, line-patterned copper specimens were etched to study the cavity formation. Furthermore, a mass-transfer model for the wet etching of printed circuit boards was developed, and the reliability of this model was verified.

**Experimental**

In this study, two kinds of experiments were conducted: using an agitated vessel that is the same as that in our previous studies, and others using a spray nozzle, as shown in Fig.1.

Furthermore, two kinds of specimens were used.

First, the etching rate of plate-shaped copper was measured to confirm the rate-limiting species. The etching rate was obtained by measuring the weight loss of the specimen after the reaction. The effects of agitation speed, and temperature on the etching rate were investigated.

Second, line-patterned copper specimens were etched in an agitated vessel to study the cavity formation. The specimen was prepared from a TAB segment that had line openings of various widths (20 to 100μm) on the photoresist film. This is called the line spacing. After the experiment, the specimen was mounted on a resin and polished. The cross-section was observed under a microscope to measure the quantity of dissolved copper.
The experimental conditions were as follows:

Concentration of $\text{FeCl}_3$: 2.89 kmol/m$^3$
Liquid temperature: 303~323 K

Results

1. Experiment in an agitated vessel

Figure 2 shows the etching rate of copper against the agitation speed for various solution temperatures. It is seen from the figure that the dissolution rate has almost a 0.7-order dependence on the agitation speed. This relationship is the same as that of the liquid-phase mass-transfer characteristics for this apparatus, which was investigated by an experiment on the dissolution of benzoic acid in water, and is expressed as follows:

$$ k_L = 0.0629 D^{0.7} \nu^{-0.4} n^{0.7} $$

where

- $k_L$ = liquid-phase mass-transfer coefficient
- $D$ = diffusivity
- $\nu$ = kinematic viscosity
- $n$ = agitation speed

Furthermore, it is evident that the etching rate increases with temperature, and the apparent activation energy is approximately 25kJ/mol. From these results, the rate-limiting step for this etching process can be considered to be the liquid-phase mass-transfer.

In the agitated vessel, perfect mixing was achieved by using a stirrer. Consequently, film theory was used to estimate the evolution of the cavity shape during wet etching. In our previous study [8], it was determined that the etching reaction of copper by ferric chloride solution is expressed by the following reaction:

$$ \text{Cu(s)} + 2\text{FeCl}_3(l) \rightarrow \text{CuCl}_2(l) + 2\text{FeCl}_2(l) $$

In this study, it was assumed that the ferric ion ($\text{Fe}^{3+}$) is the mass-transfer species in the etching reaction of copper.
2. Experiment using a spray nozzle

First, the etching rate for a plate-shaped copper specimen was measured to confirm the rate-limiting step. The etching rate was obtained by measuring the weight loss of the specimen after the experiment. The effects of flow rate and solution temperature on the etching rate were investigated. From these results, it was found that the liquid-phase mass-transfer process is the main rate-limiting step in wet etching.

Second, line-patterned copper specimens were etched by using a spray to study the cavity formation. Figure 3 shows a schematic of a cavity formed on the surface of a copper foil. In the case of line-patterned copper specimens, the mean etching rate of copper during the period $t = 0 - t$ was calculated using the following equation:

$$-r = \frac{\rho \cdot S}{(L_0 - L)/2 \cdot M \cdot t}$$

(3)

where

$r$ = mean etching rate

$\rho$ = density of copper

$S$ = cross-sectional area of cavity

$L_0$ = line spacing

$L$ = peripheral length of the cavity

$M$ = atomic weight of copper

$t$ = time
Figure 3 Schematic of an etching cavity.

Figure 4 Change in the etching rate with time.

<table>
<thead>
<tr>
<th>t(s)</th>
<th>r (mol m(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>30</td>
<td>0.05</td>
</tr>
<tr>
<td>40</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Figure 4 shows the change in the etching rate with time for various line spacing. From this figure, it is clear that the etching rate decreases with increasing time and decreasing line spacing.

3. Mass-transfer model

In this study, perfect mixing was achieved; consequently, film theory was used to estimate the evolution of the cavity shape during wet etching.

In this model, it was assumed that the etching rate is controlled by the diffusion rate of Fe\(^{3+}\) as mentioned earlier. A schematic diagram of the mass-transfer system is shown in Fig. 5.

Figure 5 Schematics of the computational domain.
A copper foil was partially protected by a photoresist. The line spacing was varied from 20 to 100 μm. As the line pattern was sufficiently long the z direction, a two-dimensional system was considered. In addition, Fick’s second law of diffusion in two dimensions was applied as follows;

\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) \tag{4}
\]

where

\[c = \text{concentration of Fe}^{3+}\]

In this study, the computational domain was divided into small elements and fractions of the solid-phase (f) were introduced to evaluate the solid-liquid interface.

Liquid phase: \( f = 0 \)

Solid phase: \( f = 1 \)

Intermediate phase: \( 0 < f < 1 \)

At the interfacial element, f decreases from one to zero with dissolution. This phenomenon can be expressed as follows:

\[
\frac{\partial f}{\partial t} = -\frac{MD}{2\rho} \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) \tag{5}
\]

The initial conditions were as follows (t=0):

\[
c = 0 \quad \text{at} \quad y \geq 0, \quad x > 0
\]
\[
c = C_{Fe^{3+}} \quad \text{at} \quad y < 0, \quad x > 0
\]

The boundary conditions are described as follows:

\[
c = 0 \quad \text{at the surface of the copper foil}
\]
\[
c = C_{Fe^{3+}} \quad \text{at} \quad y = -\delta
\]
\[
\frac{\partial c}{\partial x} = 0 \quad \text{at the surface of the photoresist}
\]
\[
\frac{\partial c}{\partial y} = 0 \quad \text{at the surface of the photoresist}
\]
\[
\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = 0
\]
\[
\frac{\partial c}{\partial x} = 0 \quad \text{at the right-hand side of the computational domain}
\]

By solving these equations numerically, the shapes of the reacted cavity for a given period of time were obtained.

Figure 6 shows a comparison between the calculated and observed cavity shapes. For narrow line spacing (a), the calculated shape of the cavity is in good agreement with the observed shape; however, the calculated cavity shape appears to be inconsistent with the observed one in the case of wide line spacing (b). It is considered that this deviation is caused by the effect of bulk convection.
Conclusions

The mechanism of wet etching of copper was studied using an agitated vessel. In addition, a spray nozzle was used to determine the mechanism of wet etching of copper in ferric chloride solution. It was found that the liquid-phase mass-transfer process, that is, the diffusion rate of Fe$^{3+}$, is the main rate-limiting step in wet etching. A mass-transfer model was proposed to estimate the cavity formation during the wet etching of copper. However, it was considered that the liquid flow can go through into a liquid film in the case of wide line spacing, it was found that this model is fairly reliable in evaluating pattern etching with cavity formation.

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References


Figure 6 Comparison between the observed and calculated cross-sections of two cavities. 
(q = 1.67x10$^{-5}$m$^3$s$^{-1}$, t=5s)