1. Introduction

For fabricating compact and high-quality electronic devices, high-density multi-layer printed wiring boards (PWBs) are required. Accordingly, multi-layer PWBs including through-holes with high aspect ratio and high-frequency boards designed to match impedance requirements have been developed.

Electroless copper plating is becoming an increasingly important technology for fabricating such PWBs. One of the processes for forming the wiring of the PWB is the “subtractive process,” by which wirings are formed by electroplating followed by etching. An alternative process is the “full-additive process,” by which wirings are directly and selectively formed on the surface of boards by electroless plating. Because it produces a wiring pattern whose cross-sectional shape is more rectangular, the full-additive process would be superior to the subtractive process in regard to fabricating high-frequency PWBs.[1] Moreover, another advantage of electroless plating is uniformity in the thickness of the deposited film, especially on the inner surface of through-holes with high aspect ratio.

However, electroless-plating technology has the following two issues that need to be addressed: first, improving productivity by increasing plating rate and, second, reducing frequency of making up of the plating solution to reduce environmental loads. Recently, improving productivity and reducing environmental loads of electroless plating have been extensively studied. One of the approaches to achieve these goals is to extend the lifetime of the electroless plating solution, leading to reduction in environmental loads.

Abstract

Under the goal of prolonging lifetime of an electroless-copper-plating solution, a new method for supplying Cu\(^{2+}\) ions to the solution, copper-ball dissolution method was developed. The effect of the developed method was examined by comparing with conventional methods: CuO-particle dissolution method and CuSO\(_4\)-supply method. Studies on copper-ball dissolution reactions clarified that Cu\(^{2+}\) ion could be supplied to the plating solution by dissolving copper ball in the oxygen-supplied solution. Compared with CuSO\(_4\)-supply method, copper-ball dissolution method prevents salts from being accumulated in the solution, which can potentially double the lifetime of the solution, similar to CuO-particle dissolution method. The films obtained by copper-ball dissolution method contain fewer impurities than those deposited by CuO-particle dissolution. As a result, the mechanical properties of the deposited film and the reliability of through-hole connection are improved. It is concluded that copper-ball dissolution method is an effective method for prolonging the lifetime of an electroless copper-plating solution, leading to reduction in environmental loads.
Therefore, suppressing accumulation of SO$_4^{2-}$ and HCOO$^-$ ions is effective in prolonging the solution lifetime.

Various methods for prolonging the solution lifetime have been reported. Electrodialysis and reverse osmosis, for removing SO$_4^{2-}$ and HCOO$^-$ ions from electroless-copper-plating solutions, have already been developed.[2, 3] A method called CuO particle dissolution, for supplying Cu$^{2+}$ ions to the solution without adding excess counter ions, has also been developed.[4] As for this method, to compensate Cu$^{2+}$ ions consumed by the plating reaction, CuO particles are added to the solution and dissolved by the following reaction:

$$\text{CuO} + \text{EDTA}^{4-} + \text{H}_2\text{O} \rightarrow \text{CuEDTA}^{2-} + 2\text{OH}^- \quad (1)$$

However, the plated film was found to exhibit insufficient mechanical properties, which may be mainly due to impurities contained in commercially available CuO particles.

In this study, an alternative method for supplying Cu$^{2+}$ ions—to prolong the plating-solution lifetime while maintaining mechanical properties of the deposited film—is proposed and evaluated. Aiming to overcome the above-mentioned issues concerning the method applying CuO particles, copper balls, which have been widely applied as anode materials for electro-plating and have fewer impurities compared to CuO particles, were focused on.

2. Concept of Copper-ball Dissolution

Copper-ball dissolution is based on the following concept. Partial-polarization curves for HCHO and copper on a copper electrode in an electroless-plating solution are shown in Fig. 1. The electroless-plating reaction proceeds at about $-750$ mV vs. Ag|AgCl, where the anodic current with HCHO oxidation on the copper surface is equivalent to the cathodic current with reduction of copper ions.[5–7] Electroless plating can proceed continuously because plated copper exhibits a catalytic effect for HCHO oxidation.

On the other hand, in cases that the potential applied to the copper electrode is more positive than $-400$ mV vs. Ag|AgCl and/or excess oxygen gas is supplied to the solution, the plating reaction fails to proceed due to formation of oxide films on the copper surface.[8, 9] Therefore, on the basis of reaction (2), which is followed by reaction (1) mentioned above, Cu$^{2+}$ ions could be supplied to the plating solution under the condition that copper was in contact with the solution containing excess dissolved oxygen gas.[10, 11]

$$2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO} \quad (2)$$

A schematic of a copper-ball-dissolution reactor developed in this study is shown in Fig. 2. Copper balls widely used as anode materials for electro-plating were used as sources of Cu$^{2+}$ ions. The balls were arranged in the 180-mm-inner-diameter copper-dissolution reactor. The solid and dashed lines show flows of solution and oxygen gas, respectively. The solution in the plating-solution storage tank, partially extracted from the plating tank, was pumped from the bottom to the top of the reactor. At the same time, oxygen gas was supplied at the bottom of the reactor under a controlled flow rate.

3. Experimental Details

3.1 Preliminary study on copper-dissolution reaction

The constituents of electroless-copper-plating solutions used are listed in Table 1. Only CuSO$_4$ was used as the source of Cu$^{2+}$ ions during the initial preparation of the plating solution. The relationship between copper-dissolution rate and related factors, such as supplied gaseous spe-
cies, solution temperature, concentration of ingredients in the solution (Cu, pH, HCHO, and HCOO\(^-\)), was experimentally clarified first. In the experiment, electrolytic copper foils (width: 100 mm; length: 100 mm; thickness: 0.036 mm) or copper balls (diameter: 27 mm) were used. Prior to the experiments, they were immersed in 5 wt% H\(_2\)SO\(_4\) aq., rinsed in water, and dried. In the case copper foils were used, copper-dissolution rate was calculated from the variation in weight of the foils an hour after copper dissolution was started. In the case copper balls were used, copper-dissolution rate was calculated from the variation in copper-ion concentration in the solution an hour after copper dissolution was started. Potential of the copper foils was measured by potentiostat during the experiments. A platinum wire and a Ag|AgCl electrode were used as counter and reference electrodes, respectively. Cathodic current accompanying the oxygen-reduction reaction, which is attributed to the amount of oxygen dissolved in the solution, was measured by a standard electrochemical method. Oxygen-saturated solutions without Cu\(^{2+}\) ions and HCHO were used to isolate the current accompanying oxygen reduction from the currents accompanying reduction of Cu\(^{2+}\) ions and oxidation of HCHO. A platinum microdisk electrode (diameter: 0.015 mm), a platinum wire, and a Ag|AgCl electrode were used as a working, counter, and reference electrodes, respectively. Potential of the working electrode was swept from rest potential to \(-0.8\) V at 20 mV/s. The diffusion-limited current was observed between \(-0.8\) to \(-0.6\) V.[12] The current does not represent the absolute amount of oxygen dissolved in the solution; instead, it represents the relative amount of oxygen supplied to a surface under various conditions, so it can reveals the influence of oxygen on copper-dissolution rate.

### 3.2 Plating method

#### 3.2.1 Electroless copper plating and supplementation methods

The constituents of the electroless-copper-plating solution used are listed in Table 1. As mentioned above, only CuSO\(_4\) was used in the preparation of the plating solution. The plating rate of the solution was about 3 \(\mu\)m/h. HCHO and NaOH consumed by the plating reaction were periodically supplied by using 14 mol/dm\(^3\) of HCHO(aq) and 5 mol/dm\(^3\) of NaOH(aq), respectively. Cu\(^{2+}\) ions were supplied by the copper-ball-dissolution method described in the following section. To demonstrate the advantages of the method, two conventional methods, namely, CuO-particle dissolution and CuSO\(_4\) supply, were used as references.

#### 3.2.2 Method for supplying copper ions

(i) Copper-ball dissolution

The copper balls used were 27 mm in diameter. Volume of the copper-dissolution reactor and plating-solution storage tank were 22 and 13 dm\(^3\), respectively. Total volume of plating-solution-flow pipes was 7 dm\(^3\). The flow rate of oxygen gas supplied to the reactor was 2.2 dm\(^3\)/min per unit volume of plating solution. By operating the reactor prior to plating treatment, a solution with 0.11 mol/dm\(^3\) of Cu\(^{2+}\) ions was prepared as a concentrated solution for supplementation of Cu\(^{2+}\) ions during repeated plating test.

(ii) CuO-particle dissolution

The CuO particles were dissolved in the plating solution to supply Cu\(^{2+}\) ions by reacting with the EDTA complex in accord with reaction (1). By applying this method, Cu\(^{2+}\) ions can also be supplied to the solution without adding excess counter ions (such as SO\(_4^{2-}\)). The diameter of the CuO particles used was approx. 0.030 to 0.060 mm on average. A schematic of the setup used for supplying Cu\(^{2+}\) ions during plating treatment is shown in Fig. 3. About one-twentieth of the solution was first extracted from the plating tank and moved to the CuO-dissolution reactor. CuO particles, stoichiometrically equivalent to the consumed Cu\(^{2+}\) ions, were then added to the reactor, stirred, and dissolved. Finally, the solution was returned to the plating tank via the filter (with a pore size of 0.5 \(\mu\)m in diameter).

(iii) CuSO\(_4\) supply

1 mol/dm\(^3\) of CuSO\(_4\)(aq) was used as a concentrated solution for supplementation of Cu\(^{2+}\) ions during repeated plating treatment.

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**Table 1 Constituents of electroless-copper-plating solution.**

| Constituent | Concentration |
|-------------|---------------|
| CuSO\(_4\)  | 0.040 mol/dm\(^3\) |
| HCHO        | 0.034 mol/dm\(^3\) |
| EDTA        | 0.11 mol/dm\(^3\) |
| NaOH        | pH 12.5       |
| Additive    | Adequate amount |
3.2.3 Substrates and plating treatment procedure for repeated plating test

(i) Substrates

Five kinds of substrates (details listed in Table 2) were employed for plating treatment. Titanium boards were employed for evaluating the mechanical properties of the deposited film. Printed wiring board A (with through holes of 0.9-mm diameter) and printed wiring board B (with through holes of 0.3-mm diameter) were used for tests on the reliability of through-hole connection. A glass-epoxy-resin board was used for evaluating the lifetime of the plating solution. Copper-clad laminates were used as dummy boards for adjusting bath load, defined as plated-board area per volume of solution. A glass-epoxy-resin board was prepared by fully etching copper from the copper-clad laminates. Roughness of the matte surface of the board ($R_z$) was 6 to 8 $\mu$m.

(ii) Plating procedure

Plating and its pre-treatments were conducted according to a conventional procedure as following. The substrates were immersed in an aqueous alkaline conditioning solution to remove impurities on the surface of substrates and modify the surface of the glass-epoxy-resin board. They were then immersed in aqueous acid solutions to etch an oxide film on the copper. Next, palladium catalysts were formed on the surface of the substrates by pre-dipping, catalyst, and sensitizing processes. The substrates pre-treated by the above processes were then immersed in the plating solution. Note that the glass-epoxy-resin boards for evaluating the lifetime of the solution were directly immersed in the plating solution without palladium catalysts process. A plating system with plating-solution capacity of 36 dm$^3$ as well as circulation and filtration apparatuses were used in the plating process. Bath load was 1.5 dm$^2$/dm$^3$. The plating thickness was 25 $\mu$m. Concentrations of Cu$^{2+}$ ions and HCHO were controlled within 0.036 to 0.044 mol/dm$^3$ and 0.031 to 0.037 mol/dm$^3$, respectively. pH was maintained from 12.5 to 12.6, and temperature was maintained within 73 to 75°C.

3.3 Evaluation of lifetime of electroless-plating solution

The lifetime of the solution was determined by observing whether or not extraneous copper deposited on the matte surface of the non-catalyzed glass-epoxy-resin board immersed in the solution. New boards were immersed in the solution every plating time. The plating time when deposition of extraneous copper was detected was defined as the lifetime of the solution. Specific gravity of the solution was measured at 25°C to monitor the status of the solution.

3.4 Evaluation of mechanical properties of deposited films

The deposited films (12.7 mm wide, 100 mm long, and 25 $\mu$m thick) were delaminated from the titanium board and used as specimens for the mechanical tests. As-deposited films and films annealed at 180°C for an hour were tested. Tensile strength and elongation of the films were measured by using an Autogrph AGS-100G (Simadzu Corp.). Chuck distance and tensile rate were set to 50 mm and 2 mm/min, respectively. Six areas of the deposited films were measured in each experiment, and the mean values were calculated.

3.5 Reliability tests on through-hole connection

Soldering-heat-resistance and thermal-cycling tests were performed on the deposited printed wiring boards. For the former test, the boards were immersed in a solder bath at 288°C for 10 s, and then this immersion procedure was repeated five times. In the latter test, the boards were exposed to the heat cycling 120 times. Each cycle was composed of four stages: heating to $-65°C$ for 120 mins, 25°C for 5 mins, 125°C for 120 mins, and 25°C for 5 mins. In both tests, reliabilities were evaluated by examining whether cracks appear in the walls of 36 through holes in the deposited test.

### Table 2  List of substrates for repeated-plating test.

| Substrate                  | Purpose                              | Specification                                      |
|----------------------------|--------------------------------------|---------------------------------------------------|
| Ti board                   | Mechanical-properties evaluation     | width: 110 mm; length: 150 mm; thickness: 1 mm     |
| Printed wiring board (A)   | Through-hole-connection reliability tests | FR-4; width: 50 mm; length: 50 mm; thickness: 5 mm; through-hole diameter: 0.9 mm |
| Printed wiring board (B)   | Through-hole-connection reliability tests | FR-4; width: 50 mm; length: 100 mm; thickness: 1.6 mm; through-hole diameter: 0.3 mm |
| Glass-epoxy-resin board    | Solution-lifetime evaluation         | width: 30 mm; length: 40 mm; thickness: 0.3 mm     |
| Copper-clad laminates      | Adjusting bath load                  | thickness: 0.3 mm                                  |
the tested boards.

3.6 Analysis of impurities in deposited films

Calcium, iron, chromium, zinc, and nickel were typically analyzed as impurities in the deposited copper films. Inductively-coupled-plasma atomic-emission spectroscopy (ICP-AES), flameless atomic-absorption spectroscopy, and inductively-coupled-plasma mass spectroscopy (ICP-MS) were used for the calcium, iron, and the other impurities, respectively.

4. Results and Discussion

4.1 Copper-ball-dissolution reaction

The relationship between copper-dissolution rate and related factors (such as supplied gaseous species, solution temperature, and concentration of ingredients in the solution) were clarified first. The relationship between copper-dissolution rate and temperature of the plating solution without HCHO (under the condition of supplied air or pure oxygen, under which no plating reaction proceeds) is shown in Fig. 4. Gas supply rate was 0.55 L/min per unit volume of solution. Regardless of supplied air or oxygen, copper-dissolution rate increases with increasing solution temperature and peaks at 74°C. Above 74°C, dissolution rate decreases with increasing solution temperature. Generally, it is known that concentration of oxygen dissolved in a solution decreases with increasing solution temperature.[13] Accordingly, decrease in oxygen concentration with increasing temperature may bring about decrease in copper-dissolution rate, which is not able to explain the phenomena observed in Fig. 4. Besides, it was presumed that increasing dissolution rate might be caused by increasing amount of oxygen supplied to the copper surface because of increasing diffusion rate of oxygen with increasing temperature. On the basis of such an assumption, the amount of oxygen supplied to the surface (depending on temperature) was investigated by the electrochemical method described in 3.1. The amount of oxygen supplied to the platinum microdisk electrode in oxygen-saturated pure water under different temperatures was determined by measuring diffusion-limited current involved in oxygen reduction. Dependence of diffusion-limited current on temperature is plotted in Fig. 5. As clear from the figure, diffusion-limited current increases with increasing temperature and peaks at about 70°C. This result is consistent with the relationship between copper-dissolution rate and temperature shown in Fig. 4. As shown in Fig. 4, copper-dissolution rate in the oxygen-supplied solution became 3.6 to 3.9 times higher than that in the air-supplied solution within the measured temperatures. On the other hand, concentration of oxygen dissolved in the solution under the constant temperature may be proportional to oxygen partial pressure, so copper dissolution rate in the oxygen-supplied solution become approximately five times higher than that in the air-supplied solution. The disagreement between the results in Fig. 4 and the copper dissolution rate estimated on the basis of the consideration mentioned above may be due to insufficient supply of oxygen to the copper surface: In the oxygen-supplied solution, copper dissolution rate increased and consumption rate of oxygen became higher concurrently. Thus, the copper-dissolution reaction could be rate-determined by the supply of oxygen to the copper surface under the condition that oxygen supply rate is 0.55 L/min per unit volume of solution.

The potentials of copper in the air-supplied solution and

Fig. 4 Relationship between copper-dissolution rate and temperature of plating solution under the condition of supplied air or pure oxygen; [HCHO] = 0 mol/dm³; flow rate of gas: 0.55 (dm³/min)/dm³; substrate: copper foil.

Fig. 5 Temperature dependence of diffusion-limited current involved in oxygen-reduction reaction on the platinum microdisk electrode in the oxygen-saturated pure water. Potential of electrode was swept from rest potential to −0.8 V at 20 mV/s. Diffusion-limited current was observed −0.8 to −0.6 V.
the oxygen-supplied solution were –370 to –430 mV and –270 to –300 mV, respectively. This implies that the copper-dissolution reaction proceeds preferentially under the oxygen-supplied condition.

The influence of Cu$^{2+}$-ion concentration on copper-dissolution rate was investigated by using the solution without HCHO. The influence of Cu$^{2+}$-ion concentration on copper-dissolution rate in the plating solution is shown in Fig. 6. Clearly, copper-dissolution rate decreases with increasing Cu$^{2+}$-ion concentration. This trend might be due to reduction in concentration of free EDTA$^{4-}$ necessary for the dissolution reaction and decrease in dissolved oxygen with increasing Cu$^{2+}$ concentration.

The influence of pH of solution on copper-dissolution rate was investigated by using the oxygen-saturated solution at 74°C. Dissolution rates at pH 12.2 and 12.6 are 1.21 and 1.25 μm/h, respectively. It is therefore concluded that pH has no significant influence on dissolution rate within the pH range investigated in this study.

The influence of HCHO on copper-dissolution rate was investigated by using the oxygen-saturated solution. The influence of HCHO concentration on copper-dissolution rate in the plating solution is shown in Fig. 7. Regardless of the existence of HCHO in the plating solution, the copper-dissolution reaction occurs. Potential of copper in the solution was approximately –280 mV, at which no copper-deposition reaction proceeded. This result implies that CuO is formed on the copper surface immediately when excess oxygen is supplied to the solution, by which copper-dissolution reaction proceeds preferentially. Copper-dissolution rate decreases with increasing HCHO concentration. The oxidation reaction of HCHO proceeds according to the partial anodic polarized curve of HCHO reported in a previous study.[14] Because copper-dissolution reaction and HCHO oxidation reaction might proceed competitively, copper-dissolution rate decreases with increasing HCHO concentration.

The behavior of the copper-dissolution reaction in the solution including HCHO and HCOO$^-$ was investigated. HCOO$^-$ is a product accumulated in the solution on repeating the plating reaction. The influence of HCOO$^-$ concentration on copper-dissolution rate is shown in Fig. 8. The copper-dissolution rate decreases with increasing HCOO$^-$ concentration, which may be due to decrease in dissolved oxygen concentration in the solution. By the electrochemical method mentioned above, the amount of oxygen supplied to the platinum microdisk electrode in the oxygen-saturated solution without HCHO measured under different HCOO$^-$ concentrations. The result shows that diffusion-limited current decreases with increasing HCOO$^-$ concentration, implying that dissolved oxygen concentration decreases with increasing HCOO$^-$ concentration. In Fig. 8, current data was normalized on the basis of diffusion-limited current and copper-dissolution rate measured at 0.3 mol/dm$^3$. The normalized data show a linear relationship, which is overwritten as the dotted line on Fig. 8. The tendency of the obtained line is consistent with the behavior of copper-dissolution rate, implying that an increase in HCOO$^-$ concentration brought about a decrease in dissolved oxygen concentration, thereby determining copper dissolution rate.

The effect of oxygen flow rate on copper-dissolution rate was investigated by using the copper-ball-dissolution reactor. As shown in Fig. 9, dissolution rate increases with increasing flow rate, suggesting that the dissolution rate can be controlled by oxygen flow rate.
Note that the dissolution rate was almost equivalent to the plating rate. This result implies that Cu$^{2+}$ ions consumed by the plating reaction can be compensated by dissolving copper balls under the condition that the balls are set in the reactor so as to make the total surface area of the balls equivalent to that of all plated boards. It is thus concluded that copper-ball dissolution can be applied as a method for supplying Cu$^{2+}$ ions to the plating solution.

### 4.2 Evaluation of plating-solution lifetime

To evaluate the lifetime of the plating solutions applied in the copper-ball dissolution and other conventional methods, repeated plating test was carried out. Increase in specific gravity of the plating solutions with plating time (by applying the copper-ball dissolution and other methods) is shown in Fig. 10. Clearly, the slope of the increase in specific gravity of the solutions with plating time is smaller in the cases of the copper-ball and CuO-particle dissolution methods compared with the CuSO$_4$ supply method. This result can be attributed to the fact that SO$_4^{2-}$ and HCOO$^-$ (product of HCHO) are accumulated in the solution in case of CuSO$_4$ supply method, while SO$_4^{2-}$ is not accumulated in case of the copper-ball and CuO-particle dissolution methods.

The lifetime of plating solutions was evaluated by observing extraneous copper deposited on the surfaces of non-catalyzed epoxy-resin boards. Extraneous copper deposition was observed in the eighth, sixteenth, and sixteenth cycles of plating in the case of the CuSO$_4$-supply, CuO-particle, and copper-ball dissolution methods, respectively. Consequently, it is concluded that the copper-ball dissolution can potentially double the solution lifetime in comparison with that in the case of the CuSO$_4$-supply method.

### 4.3 Mechanical properties of deposited films

The mechanical properties of the films obtained by both dissolution methods and the CuSO$_4$-supply method were evaluated. The tensile strengths of the as-deposited and annealed films versus plating time are plotted in Fig. 11. Regardless of whether the films were annealed or not, the films obtained by copper-ball dissolution exhibit slightly lower tensile strength than the films obtained by the other methods (i.e., CuO-particle dissolution and CuSO$_4$-supply).

Elongation of the deposited films with plating time is plotted in Fig. 12. Elongations of the films deposited by copper-ball dissolution and those deposited by CuSO$_4$ sup-
ply differ very little regardless of whether the films were as-deposited or annealed. Annealing increased the elongation of the deposited films by approximately 2%. On the other hand, the annealed films obtained by CuO-particle dissolution method and those obtained by the other methods significantly differ. That is, the films obtained by CuO-dissolution remained unchanged even after they were annealed. This result could mainly be due to impurities contained in the deposited films (as discussed later).

4.4 Reliability of through-hole connection

The reliability of through-hole connection was evaluated by employing the boards obtained by copper-ball dissolution method. Table 3 shows results of the reliability tests. Figure 13 (a) and (b) show a typical cross-sectional image of a through-hole deposited at the fifteenth plating cycle and tested in soldering-heat-resistance and thermal-cycling test, respectively. Reliability tests show that cracks are not observed in the cross sections of through-holes deposited, even after the fifteenth plating cycle. It is thus concluded.

Table 3 Result of reliability of through-hole connection tests (value: the number of crack).

| Substrate               | Soldering-heat-resistance test | Thermal-cycling test |
|-------------------------|-------------------------------|----------------------|
| Printed wiring board (A)| 0/36                          | 0/36                 |
| Printed wiring board (B)| 0/36                          | 0/36                 |

Fig. 13 Typical cross-sectional images of through-holes deposited at the fifteenth plating cycle and tested in the reliability tests; (a) after soldering-heat-resistance test and (b) after thermal-cycling test; through-hole diameter: 0.3 mm, board thickness: 1.6 mm.
that reliable films can be obtained by applying copper-ball dissolution.

4.5 Analysis of impurities contained in deposited films

Impurities contained in the films deposited after the first, seventh, and fifteenth plating cycles of copper-ball and CuO-particle dissolutions are compared in Table 4. The films obtained by applying copper-ball dissolution contain fewer impurities than those deposited by applying CuO-particle dissolution. In addition, impurities in the copper balls and CuO particles themselves were analyzed. As for the results of the analysis, more impurities exist in a CuO particle than in a copper ball. Thus, more impurities were observed in the films obtained by CuO dissolution, because impurities as well as CuO were dissolved in the solution and then incorporated into the deposited films. Especially, chromium tended to be incorporated into the deposited films.

As discussed above, the superior elongation properties of the films obtained by copper-ball dissolution could be attributed to the lower impurity level contained in the deposited films. Accordingly, chromium (with highest concentration among the impurities in the deposited films) was focused on. To confirm the influence of chromium on elongation of the deposited film, the elongation of a film deposited by a solution containing 2 mg/dm² of CrO₃ as an additive was evaluated. CrO₃ would change into Cr(OH)₃, CrO₂⁻ in an alkaline and reducing electroless-plating solution. Some chromium constituents would react with EDTA to form Cr(III)-EDTA complexes.[15] The same would be true of chromium constituents dissolved from CuO in the CuO dissolution method. The evaluation results confirm that the deposited film contains approximately 250 ppm of chromium, and the film only elongated approximately 5%. As the copper deposits, CrO₃ would be incorporated in the copper film or Cr metals would be co-deposited by reduction reaction.[16] These precipitates would suppress the crystal growth of copper in the annealing process, resulting in reduction in elongation of the deposited film.

4.6 Estimation of the scale of copper-ball dissolution reactor

The scale of the copper-ball dissolution reactor in an electroless-plating system was estimated. Because the copper-dissolution reaction occurs on the surface of the copper balls, the entire amount of dissolved copper depends on the entire surface area of the copper balls when excess oxygen gas is supplied to the plating solution. In this study, copper balls with diameter of 27 mm were applied as the source of Cu²⁺ ions, but those with diameter of 11 mm are also currently available. An example of estimated scale of a copper-dissolution reactor corresponding to a plating tank of 2,000 dm³ is detailed in Table 5. By using smaller balls, the volume of the copper-dissolution reactor could be reduced to approximately one-eighth of that of the plating tank, thereby extending the lifetime of the electroless-plating solution. Note that it is necessary to carefully control concentration of HCHO, pH, temperature as well as Cu²⁺ in the plating solution, in order to obtain the copper film with reliable mechanical properties.

5. Conclusions

Copper-ball dissolution was proposed as a method for prolonging the lifetime of an electroless copper-plating
solution. Compared with a conventional method such as CuSO₄ supply, this method can potentially double the solution lifetime. In addition, the films obtained by copper-ball dissolution contain fewer impurities than those deposited by CuO-particle dissolution. As a result, the mechanical properties of the deposited film and the reliability of through-hole connection are improved. It is concluded that copper-ball dissolution method is an effective method for prolonging the lifetime of an electroless copper-plating solution.

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