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Dissolution of Copper by a Dilute Anodically Electrolyzed NaCl Solution

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The dissolution, or etching, of copper by an anodically electrolyzed sodium chloride solution (AES) and the surface morphology of the copper after dissolution were investigated. Hydrochloric acid, which is usually used as an acid cleaning solution for copper, was used as a reference by adjusting it to the same pH as the AES. As a result, the dissolution rate of the electroplated copper immersed in the AES was 30 × 10^{-9} g/cm^2•min, while it was 5 × 10^{-9} g/cm^2•min when using the hydrochloric acid solution. When the etched surface was observed by SEM, etching was only slightly visible for the sample immersed in the hydrochloric acid solution. By contrast, significant dissolution was observed at the grain boundary of the plated copper immersed in the AES. When heated AES was sprayed, a higher etching rate was obtained as compared to mere immersion. Furthermore, the surface roughness was increased. Based on these results, it is suggested that the AES is capable of functioning as an etchant and roughening agent for copper. This etching effect is considered to be attributable to the hypochlorous acid formed in the AES solution.

Key words: *Anodically electrolyzed sodium chloride solution, copper, dissolution, etching, hypochlorous acid*

Introduction

The solution produced in the anolyte compartment by the electrolysis of a dilute NaCl solution, *i.e.*, anodically electrolyzed sodium chloride solution (hereafter, expressed as AES), exhibits a high positive redox potential, as well as acidity. One of the features of AES is that an acidic water of about pH 2 to 3 can be obtained without using an acid such as hydrochloric acid. Previously, the authors have shown that AES had the ability to remove the natural oxide layer formed on copper.[1] Moreover, AES also has the ability to dissolve the oxide layer on the surface of a metal produced during etching, which lightly dissolves the metal surface, (*e.g.*, a plating pretreatment cycle), without using hydrochloric acid. As such, there is the possibility of using it as a substitute for hydrochloric acid. Furthermore, if AES can dissolve copper, it may be possible to use AES to etch and/or roughen the surface of electroplated copper. In this study, the differences in the dissolution characteristics and surface morphology of copper etched in AES and in an aqueous solution of hydrochloric acid at the same pH value as that of the AES, were examined. The possibility of etching and roughening copper was studied as an application for AES.

Experimental

Reagents, samples and equipment

Extra-pure reagent grade sodium chloride was used to prepare the electrolyzed salt water, as a 0.05 wt% aqueous solution. Samples were prepared by electroplating a 10-μm thick copper deposit on a copper-clad laminated board,** which consisted of a glass cloth epoxy resin substrate sandwiched with 18-μm copper foil layers (hereafter called an "electroplated copper substrate").

An acid copper sulfate plating bath was used for copper plating. The bath composition was 220 g/L copper sulfate, 60 g/L sulfuric acid and 50 mg/L chloride ion. The plating current density was 4.0 A/dm^2 and the solution temperature was 25°C.

A diaphragm-type electrolytic cell was used to prepare the AES. The apparatus consisted of a cathode compartment and an anode compartment, separated by a diaphragm. Platinum-coated 74 × 113-mm titanium electrodes were used for both electrodes. Electrolysis was carried at 0.72 A/dm^2 (0.6 A, 100 V) for 15 min. The pH, redox potential and dissolved oxygen concentration of the aqueous solution were measured using a pH meter, an ORP meter and a dissolved oxygen meter, respectively. Quantitative measurement of the copper dissolved in the AES used inductively-coupled plasma emission spectrometry. Surface analysis of the sample was done using Auger electron spectrophotometry. The surface roughness of the sample was measured using a color laser microscope and scanning electron microscopy was used to observe the surface morphology.

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Copper dissolution rate

Each of the AES and the hydrochloric acid solutions at 20°C and pH 2.2 was prepared in a volume of 200 cm^3, and the electroplated copper substrates were then immersed in them. The weight change of the samples after a 100-minute immersion was measured, and the dissolution rates were obtained. The concentration of copper dissolved in each aqueous solution was measured by ICP.

Copper surface characteristics

The electroplated substrate was immersed either in the AES or in the hydrochloric acid solution at 20°C for 10 min, and the changes in the plated surface after immersion were observed by SEM. The surface roughness, R_y, in an area 139 × 105 μm, was measured for each sample.

Application to etching and roughening

In order to examine the possibility of etching or roughening the electroplated copper using AES, the AES was heated to 40°C and sprayed on the electroplated copper substrate for five minutes. The sample was then neutralized by immersing it in a *cathodically* electrolyzed sodium chloride solution, which was formed at the same time as the AES in the cathode compartment. The efficacy of etching and roughening was confirmed by observing the surface of the sample by SEM and measuring the surface roughness. They were also analyzed by Auger electron spectroscopy, and the spectrum and the depth profile were examined. The analysis area was about 120 × 120 μm, and the sputtering rate on the surface of the sample was 4.81 nm/min (SiO_2 layer thickness equivalent).

Results and discussion

Characteristics of electrolyzed water

The characteristics of the hydrochloric acid solution and the AES obtained are shown in Table 1. The redox potential and dissolved oxygen of the AES were high compared to the hydrochloric acid solution, and AES exhibited strong oxidizability.

Dissolution rate

The changes in the mass of the electroplated copper substrates after immersion in AES or hydrochloric acid solution at pH 2.2 are shown in Fig. 1. For AES, the dissolution rate was 30×10^{-9} g/cm^2·min (3.6 equivalent nm/min). For hydrochloric acid solution, the rate was 5×10^{-9} g/cm^2·min (0.6 equivalent nm/min). The dissolution rate of the electroplated copper in the AES was as much as six times that in the hydrochloric acid solution at the same pH. The electroplated copper very readily dissolved in the AES. In addition, it was confirmed by ICP analysis that the copper ion concentration in the solution after the substrate had been immersed for 100 min was nearly equal to the substrate weight loss. The copper dissolution behavior can be related to the observation that the pH value of 2.2 and the redox potential of 1300 mV_{SHE} corresponded to the dissolution region indicated by the Pourbaix diagram.[2]

Copper surface characteristics

The surface morphology of the electroplated copper observed by SEM is shown in Fig. 2, at 10,000X. In the sample immersed in AES, significant dissolution along the grain boundary of the plated copper was observed. On the other hand, for the sample soaked in hydrochloric acid, a faint dissolution along the grain boundary of the plated copper was observed, but the surface became smooth at the same time. The surface roughness, R_y, was 0.60 μm before immersion (Fig. 2a), 1.28 μm after immersion in AES for 10 min (Fig. 2b) and 0.57 μm after immersion in hydrochloric acid solution for 10 min (Fig. 2c). Although the plated copper was generally dissolved at the grain boundaries by hydrochloric acid, AES is seen to further promote further intergranular dissolution of the plated copper. Significantly, it promoted the formation of pits on the copper surface.

Application to etching and roughening

The SEM image of the sample is shown in Fig. 3. The surface roughness increased remarkably when it was sprayed with AES. The surface roughness, R_y, was 1.0 μm. The weight loss was 150×10^{-9} g/cm^2·min and the dissolution rate was 17 nm/min equivalent when the AES was heated to 40°C and sprayed. The dissolution rate was five times the rate when simply immersed in AES at 20°C.

Table 1

Characteristics of AES and hydrochloric acid solutions

	AES	HCl Solution
pH	2.2	2.2
Redox potential, mV_{SHE}	1300*	620
Sodium ion, mM	0.09	0.10
Chloride ion, mM	0.11	0.10
Dissolved oxygen, mg/L	16.0*	7.2

*measured within 10 min after electrolysis

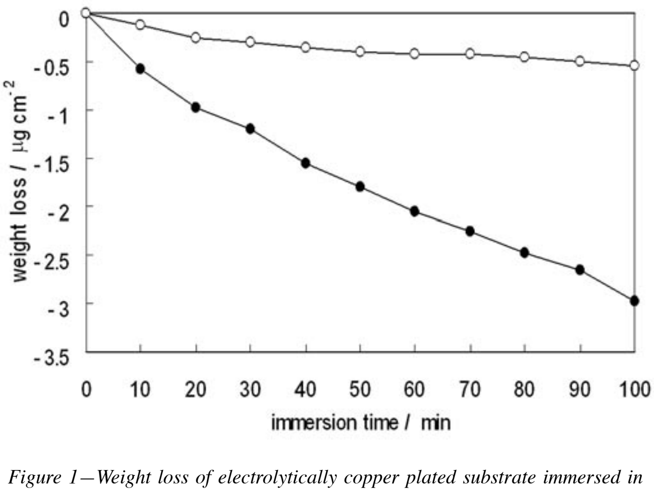

Figure 1—Weight loss of electrolytically copper plated substrate immersed in AES and HCl solution: • - AES, pH 2.2; ○ - HCl solution, pH 2.2.

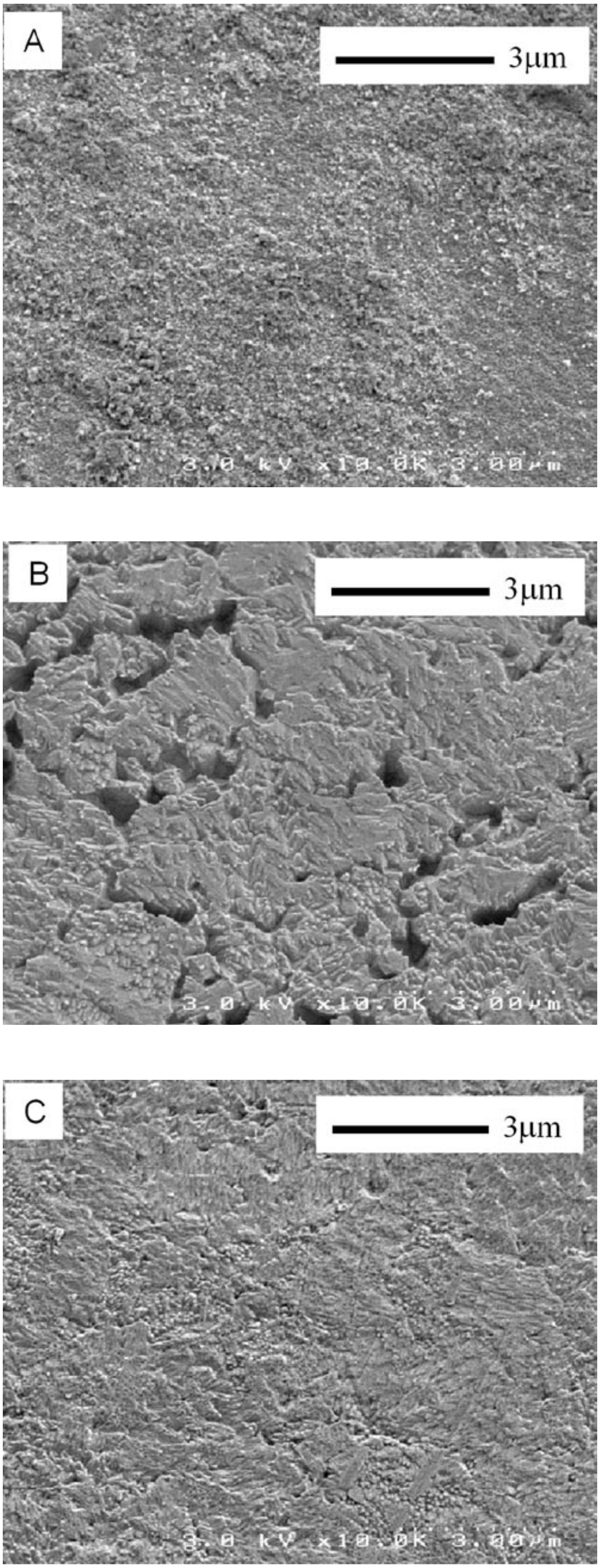

Figure 2—Surface morphology of electrolytically plated copper: (a) as plated; (b) immersed in AES for 10 min; (c) immersed in hydrochloric acid solution for 10 min.

The Auger electron spectroscopy results for the etched copper surface is shown in Fig. 4. For the sample sprayed with AES at 40°C for five minutes, the spectral intensity of the oxygen decreased, and the spectrum of copper increased. The depth profile also indicated that the thickness of the oxide layer decreased to 14 nm (SiO_2 layer thickness equivalent). Therefore, the majority of the natural oxide layer was removed by the AES. Based on these results, the copper oxide layer was removed by spraying the heated AES, and the dissolution of the copper was promoted. Based on these results, it is possible to use this solution for etching copper. At the same time, because the copper surface was roughened, the solution may be applicable to surface roughening as well. Such a treatment would be useful in improving adhesion to solder resists or in etching the outermost surface of the electroplated copper in the manufacture of printed circuit boards. If these features are viable, AES is a potential candidate for use as an environmentally-friendly substitute process in PCB manufacture.

Dissolution effect of AES

The nature of the copper dissolution generated by AES is attributed to the hypochlorous acid present. In anodically electrolyzed salt solutions other than those based on chloride, *e.g.*, sodium sulfate, no copper pitting was observed. The following reactions take place at the anode during electrolysis of the sodium chloride solution[3]:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (1)$$

$$2Cl^- \rightarrow Cl_2\uparrow + 2e^- \qquad (2)$$

$$Cl_2(aq) + H_2O \Leftrightarrow HClO + H^+ + Cl \qquad (3)$$

The standard electrode potentials, E_o, in the $HClO/Cl_2$, Cl_2/Cl^- and O_2/H_2O systems are 1.63 V, 1.36 V and 1.21 V, respectively, and they are remarkably high positive values compared to the standard electrode potential of copper, $E_o = 0.337$ V. Therefore, the dissolution will proceed. The concentration of the hypochlorous acid in the AES was obtained by the titration method which conformed to JIS (Japanese Industrial Standard) K0102.*** Potassium iodide and acetic acid were added to the sample solution, and it was adjusted to about pH 5.0. The solution was then titrated with sodium thiosulfate solution using starch solution as an indicator. The hypochlorous acid concentration in sodium chloride-based AES was 110 mg/dm^3. On the other hand, it was below the minimum limit of detection for the anodically electrolyzed sodium sulfate solution.

The oxidizing power of the dissolved oxygen[4] included in the AES is also considered be a cause of increased dissolution. Generally, the concentration of dissolved oxygen in an aqueous solution is 7 to 8 mg/dm^3, while in the AES, it was 16 mg/dm^3 as shown in Table 1. Further, the formation of hydroxyl radical in the AES has been confirmed by electron spin resonance (ESR) analysis.[5] The hydroxyl radical may also enhance copper dissolution.

*** *JIS K0102:1998, "Testing Methods for Industrial Wastewater."*

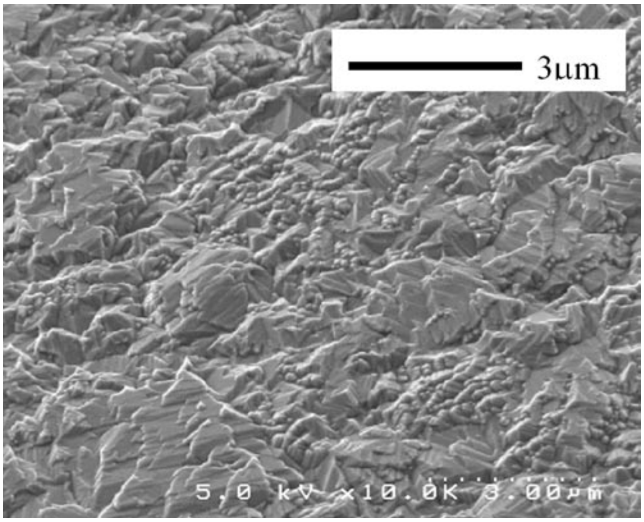

Figure 3—Surface morphology of electroplated copper etched with AES at 40°C by spraying for 5 min.

Conclusions

1. The dissolution rate of the plated copper was 5×10^{-9} g/cm^2·min in hydrochloric acid solution, while it was 30×10^{-9} g/cm^2·min in AES. When the plated copper was immersed in hydrochloric acid, a slight dissolution at the grain boundary was observed, and the surface roughness slightly decreased. On the other hand, when it was immersed in AES, a significant dissolution along the grain boundaries of the plated copper was observed, and the surface roughness increased by more than twice.
2. When AES was heated to 40°C and sprayed, the dissolution rate of the plated copper layer increased fivefold when compared with immersion at room temperature. The natural oxide layer was removed and the surface roughness, R_y, increased from 0.6 to 1.0 μm. Based on these results, the possibility of etching and roughening the copper by AES in PCB manufacture is feasible.
3. A high concentration hypochlorous acid was measured in sodium chloride-based AES. The higher dissolution rate of AES as compared to the results for hydrochloric acid solution having the same pH seems to be mainly attributable to the presence of this hypochlorous acid.

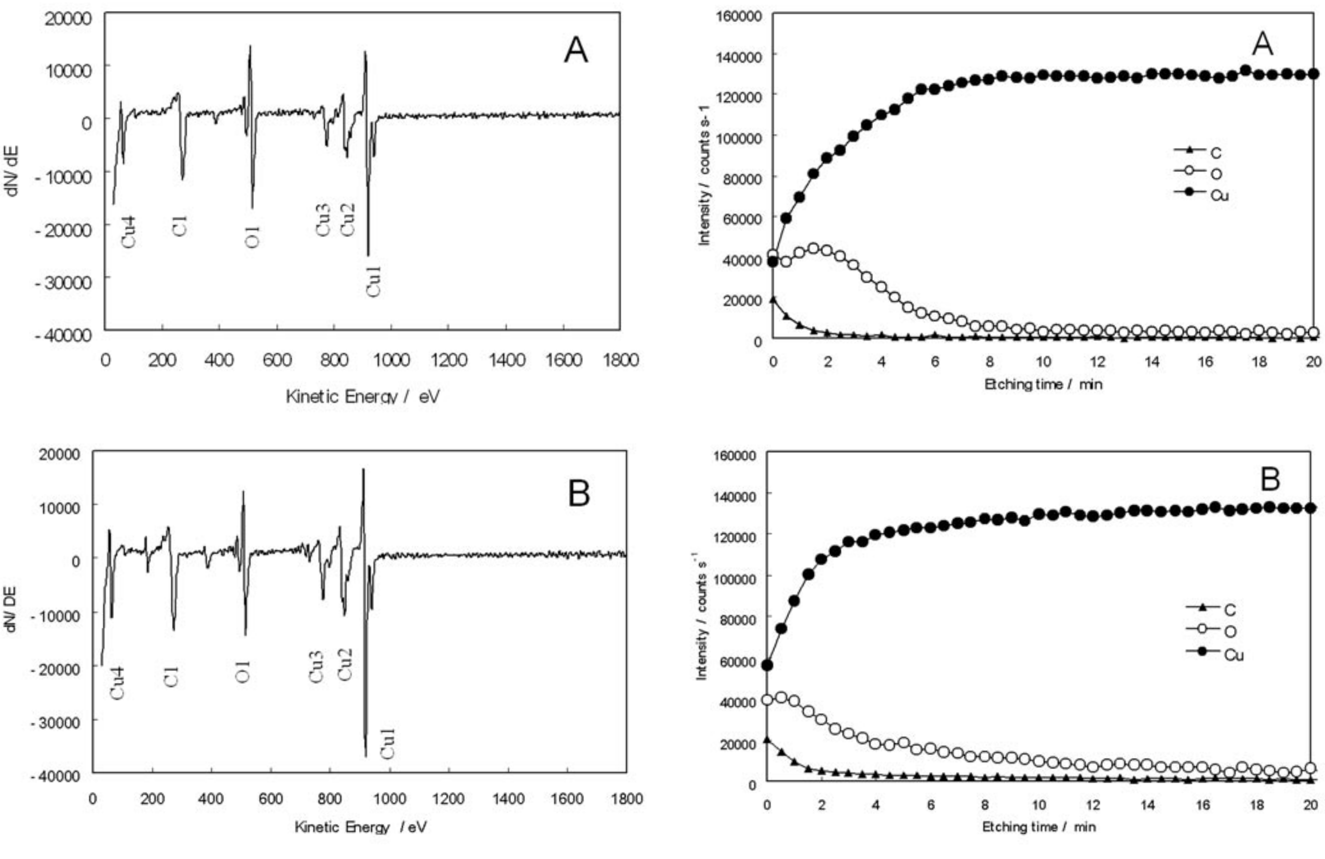

Figure 4—Surface analysis by Auger electron spectrometry: (a) as plated; (b) immersed in AES for 10 min.

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