Video Article

Accumulation and Analysis of Cuprous Ions in a Copper Sulfate Plating Solution

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URL: https://www.jove.com/video/59376
DOI: doi:10.3791/59376

Keywords: Chemistry, Issue 145, copper plate, solution, cuprous ion, monovalent copper ion, BCS, absorbance, concentration, plating film, surface structure, quality, evaluation, on-site

Date Published: 3/20/2019

Citation: Koga, T., Sakata, Y., Terasaki, N. Accumulation and Analysis of Cuprous Ions in a Copper Sulfate Plating Solution. *J. Vis. Exp.* (145), e59376, doi:10.3791/59376 (2019).

Abstract

Knowledge of the behavior of cuprous ions (monovalent copper ion: Cu(I)) in a copper sulfate plating bath is important for improving the plating process. We successfully developed a method to quantitatively and easily measure Cu(I) in a plating solution and used it for evaluation of the solution. In this paper, a quantitative absorption spectrum measurement and a time-resolved injection measurement of Cu(I) concentrations by a color reaction are described. This procedure is effective as a method to reproduce and elucidate the phenomenon occurring in the plating bath in the laboratory. First, the formation and accumulation process of Cu(I) in solution by electrolysis of a plating solution is shown. The amount of Cu(I) in the solution is increased by electrolysis at higher current values than the usual plating process. For the determination of Cu(I), BCS (bathocuproinedisulfonic acid, disodium salt), a reagent that selectively reacts with Cu(I), is used. The concentration of Cu(I) can be calculated from the absorbance of the Cu(I)-BCS complex. Next, the time measurement of the color reaction is described. The color reaction curve of Cu(I) and BCS measured by the injection method can be decomposed into an instantaneous component and a delay component. By analysis of these components, the holding structure of Cu(I) can be clarified, and this information is important when predicting the quality of the plating film to be produced. This method is used to facilitate the evaluation of the plating bath in the production line.

Video Link

The video component of this article can be found at https://www.jove.com/video/59376/

Introduction

As printed circuit boards become denser and multilayered, management of plating solutions during the manufacturing process becomes more important to maintain product quality. In copper sulfate electroplating, the monovalent copper ion (cuprous ion: Cu(I)) has been determined to be one of the main causes of the large roughness and dull finish of the copper plating surface. The behavior and role of Cu(I) in the plating process[1,2,3,4,5], the effect of each additive, and the holding structure[6,7,8] have been investigated. It is necessary to analyze Cu(I) in the plating solution, but it was difficult to quantify its concentration because of the instability of Cu(I) in an aqueous solution. Therefore, the on-site analysis of Cu(I) in the plating bath is an effective tool for controlling the plating solution.

We performed colorimetric analysis using an aqueous chelating reagent, BCS (bathocuproinedisulfonic acid, disodium salt), to establish on-site quantitative analysis of Cu(I) in a copper sulfate plating solution. The BCS can be used to quantify the Cu(I) concentration in the aqueous solutions[9,10,11]. The cuproine type color reaction reagent, which has been conventionally used for the determination of Cu(I), is hydrophobic and extraction with alcohol is necessary. It was shown that BCS is hydrophilic and can directly measure Cu(I) in an aqueous solution. Two molecules of BCS coordinate to one Cu(I) to form 1:2 complexes that absorb visible light at wavelengths between 400 and 550 nm (See **Figure 1**). We established a method to determine the concentration of Cu(I) in the plating solution from the measurement of the absorbance of the Cu(I)-BCS complex[12,13]. In the first part of this protocol, a method of accelerating the Cu(I) formation in a copper sulfate plating solution in a model experimental system and the quantitative measurement of the Cu(I) concentration in a plating solution are described. This is fundamental to clarify the process of formation and accumulation of Cu(I) in the plating bath.

Further, it was shown that the color reaction of Cu(I) and BCS can be divided into rapid reaction components and relatively slow reaction components. This increases the uncertainty in the absorbance measurement. To overcome this problem, we developed a method of measuring reaction curves by an injection method[14,15]. The second part shows the measurement of Cu(I) based on the injection method. By analyzing the components obtained by the injection method, it is possible to approximate the understanding of the Cu(I) formation mechanism and holding structure in solution.

Conventionally, it has been claimed that Cu(I) in a plating solution is instantly oxidized to cupric ions (Cu(II)). We have confirmed that there are several millimoles (mmol/L) of Cu(I) in the plating bath of the production line[12]. According to this experiment method, the accumulation of Cu(I) similar to the plating bath can be reproduced even in the beaker of the laboratory. This is a fundamental technology to elucidate the Cu(I) production and accumulation process in a copper sulfate electroplating solution, which was unknown[14]. Furthermore, by controlling Cu(I) in the plating solution, it is also possible to predict the effect of Cu(I) on the quality of the plating film[15].

Protocol

NOTE: Please check all related material safety data sheets (MSDS). Please wear protective equipment when experimenting with the copper sulfate plating.

1. Preparation of the copper sulfate plating solution

NOTE: The copper sulfate plating aqueous solution is prepared by combining sulfuric acid (0.5 mol/L), copper sulfate (0.4 mol/L), chlorine (Cl, 1.41 mmol/L), polyethylene glycol (PEG; MW 4000: 0.025 mmol/L), bis(3-sulfopropyl) disulfide (SPS, 0.003 mmol/L), and Janus Green B (JGB, 0.004 mmol/L) in pure water.

1. Place a stir bar in a 1 L beaker and pour in 600 mL of pure water. Add sulfuric acid (95.0%: 49.04 g) in small portions while stirring. Leave it until the solution cools down.
2. Add copper sulfate (99.5%: 99.876 g) to the solution little by little. Stir for 30 min.
3. Add 23.7 mL of hydrochloric acid (0.02 mol/L), 0.1 g of polyethylene glycol, 1 mL of 1 mg/L SPS solution, and 1 mL of 2 mg/L JGB solution.
4. Transfer the solution to a volumetric flask (1 L). Add pure water and adjust to 1 L. Transfer the copper sulfate plating solution to a polyethylene container and store it at room temperature in the dark.

2. Formation of the Cu(I) in the plating solution

1. Pour 150 mL of the copper sulfate plating solution into a 200 mL beaker. Put the stir bar in the beaker and stir at 500 rpm. Leave the plating solution in advance at room temperature (23 °C ± 1 °C) for 1 hour.
2. Insert a tube into a beaker and let nitrogen flow (about 85 mL/min). Deoxygenate the plating solution with nitrogen gas for over 30 min.
3. Cut the 0.3 mm thick copper plate with metal shears to 9.5 cm x 2 cm dimensions. Cut the platinum plate with a thickness of 0.1 mm in the same way.
4. Wash the copper plate and the platinum plate with ethanol and rinse with pure water. Dry with nitrogen gas.
5. Attach the copper plate and platinum plate to the fixing jig, insert it inside the beaker and fix it. The immersed area of each plate to the plating solution is 4 x 2 cm^2 (See **Figure 2**).
   NOTE: The jig consists of an acrylic beaker fixing part (**Figure 3** (1)) and metal electrode parts (**Figure 3** (2)). The electrode part consists of the parts to fix the plate, and the part connects to the cord from the power supply.
6. Connect the electrode (anode) of the copper plate to the positive end of the power supply (**Figure 3** (3)), and the electrode of the platinum plate (cathode) to the negative end of the power supply (**Figure 3** (4)).
7. Turn on the power supply at a constant current of 1.0 A (current density: 62.5 mA/cm^2). Cu(I) is formed in the plating solution according to the electrolysis time, and Cu(I) concentration (accumulated amount) is maximized in about 10 min.
   NOTE: If the plate is inserted while the stirrer rotates, the plating solution may scatter and the beaker may fall over. Please install the jig before turning on the power to avoid danger.
8. Turn off the power after 10 min and stop the stirrer. Leave it for about 10 min until the particles settle.

3. Quantitative measurement of the Cu(I)

1. Prepare the BCS solution (10^{-2} mol/L) by dissolving 0.36 g of the molecule in 100 mL of pure water. Stir the solution and dissolve the BCS in an excess amount relative to the monovalent copper. Store the BCS solution in a light-proof container and store the container in the dark.
   NOTE: In the measurement, the BCS concentration in the sample solution is adjusted to 1,000 times or more the Cu(I) concentration.
2. Add 60 mL of acetic acid (1 mol/L) and 25.2 mL of NaOH solution (1 mol/L) to 120 mL of pure water to prepare a neutralizing solution (buffer solution).
3. Put a stir bar in the absorption measurement cell (optical path length: 1 cm) and pour in 2.5 mL of neutralization solution and 219 µL of BCS solution.
4. Mix in 22 µL of plating solution sample (step 2.9). Stir for 20 min.
   NOTE: In order to ensure that the function of BCS is normal, the pH of the sample solution to be measured should not fall below 4. BCS selectively forms a complex with Cu(I). The Cu(I)-BCS complex absorbs in the visible region (400 to 550 nm), and the neutralizing solution develops an orange color (**Figure 4**).
5. Measure the absorption spectra of the sample solution (3.4) with an UV/vis spectrophotometer (wavelength range: 400–600 nm) (**Figure 5e**).
   NOTE: There are no constrained measurement apparatus and conditions, and it is desirable to make them identical in one experiment series.
6. Calculate the concentration of Cu(I) using the Lambert-Beer law:
   $A = \varepsilon l c$
   where A is absorbance, L is the optical path length, ε is the molar absorption coefficient (BCS: 1.2×10^4 at 485 nm), and c is the molar concentration (mol/L) of the solute.
   NOTE: Because the optical path length is 1 cm, the Cu(I) concentration in the cell is simply the absorbance divided by the molar extinction coefficient. The value obtained by multiplying the ratio 125 (the fold dilution with the neutralizing solution) is the Cu(I) concentration of the plating solution.

4. Injection measurement of Cu(I) and BCS color reaction curves

1. Use a UV/vis spectrophotometer with time measurement function of more than 20 min for injection measurement. The spectrometer should have a sample chamber cover with a syringe port (**Figure 6** left) and a thermostat cell holder with a stirrer.
2. Use a square cell of 1 cm x 1 cm for the absorbance measurement. Put s stir bar in the absorption cell.
3. Pour 2.5 mL of the neutralized solution prepared in 3.2 and 219 µL of the BCS solution prepared in 3.1 into the cell. Maximize stirrer rotation speed.
4. Set the measurement time to 1,270 s in the time measurement mode at 485 nm and start. One min after starting, inject 22 µL of the plating solution sample (2.9) with a pipette from the syringe port of the chamber cover. Reaction curves of Cu(I) and BCS will be acquired (**Figure 6** right).

Representative Results

The concentration of Cu(I) in the plating solution can be determined from the absorbance at 485 nm of Cu(I)-2BCS chelate. **Figure 5** shows the absorption spectra of the plating solutions that were electrolyzed for 0, 4, 6, 8 and 10 min. The Cu(I) concentration tends to increase from 0 to 10 min depending on the electrolysis time. However, as a result of the time-resolved measurement, a delay component appeared in addition to the instantaneous component in the reaction between BCS and Cu(I). This reduces the signal-to-noise ratio (S/N ratio) of the absorbance value and prevents accurate determination of Cu(I) concentration. It is preferable to use the injection method to determine the Cu(I) concentration, because the change in absorbance caused by the injection of plating solution is measured by time decomposition (**Figure 6**).

Information on the Cu(I) holding structure in the plating solution is obtained by numerical analysis of the reaction curve. In general, Cu(I) is quickly oxidized to Cu(II) in an aqueous solution; but in the plating solution it is considered to be stabilized by forming a complex with an additive (especially PEG)[14]. The reaction curve reflects the chelation process of Cu(I) and BCS. The reaction curve is composed of a component that increases immediately after the plating solution injection and a component that slowly increases over several tens of min. These components suggest that there are multiple holding structures of Cu(I) in the plating solution. Characteristics of the plating solution involved in Cu(I) can be evaluated by analyzing the reaction curve. Assuming that the reaction of Cu(I) with BCS is a first order reaction with respect to the Cu(I) concentration, we obtained the following reaction kinetics of the absorbance, At:

At = A0 + AL [1 – exp (−t/TL)]

t is the time from the start of measurement, A0 corresponds to a component that reacts instantaneously (absorbance at t = 0) and AL corresponds to a component that reacts slowly (At - A0). TL is the time constant of the AL component. To simulate the color reaction curve, we applied the formula to the original analysis software (software may be commercially available)[13,15]. A curve simulating the change in the absorbance of the color reaction of the electroplating solution is shown in **Figure 7**. From the simulation, the parameters (A0, AL, TL) related to Cu(I) accumulation are quantified. The simulation results in this figure were A0 = 0.053, AL = 0.098, TL = 13.6 min, and r^2 = 0.998. **Figure 8** (graph) plots the simulation value A0 in the plating solution that was electrolyzed for different times. Although the value of A0 did not change greatly until 4 min of electrolysis, an increase corresponding to electrolysis time was seen from 6 min to 10 min.

Plating was carried out on a copper substrate for 10 min with the electrolysis solutions to investigate the effect of Cu(I) on the quality of the copper plating such as roughness and morphology. **Figure 8** shows the SEM (Scanning Electron Microscope) images of the film surface structure deposited with electrolysis solutions. The film structure at 0 min and at 4 min of electrolysis plating are nearly indistinguishable. There are fine particles adsorbed densely with a size of several tens of nanometers and a smooth surface morphology. After 6 min of electrolysis plating, there is some swelling on the surface. After 10 min of electrolysis plating, there is a large chunky roughness.

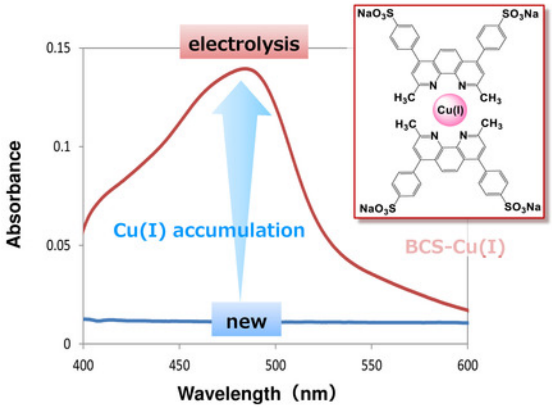

Figure 1: Structure and absorption spectrum of Cu (I)-BCS complex. Fresh copper sulfate plating solution and electrolysis solution. Since Cu(I) is accumulated in the plating solution by electrolysis, the absorption spectrum of Cu(I)-BCS complex is observed in the electrolysis plating solution sample. Please click here to view a larger version of this figure.

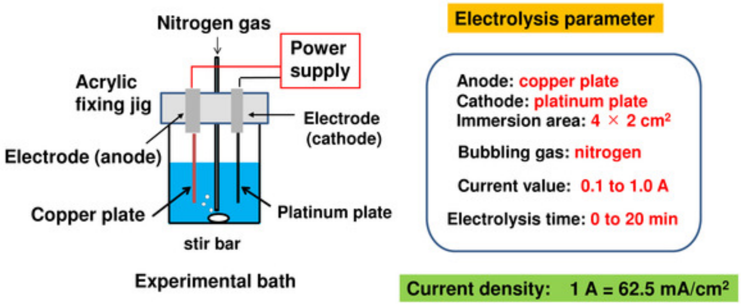

Figure 2: Schematic diagram of the equipment for electrification experiment (left) and representative conditions of the electrolysis experiment (right). Please click here to view a larger version of this figure.

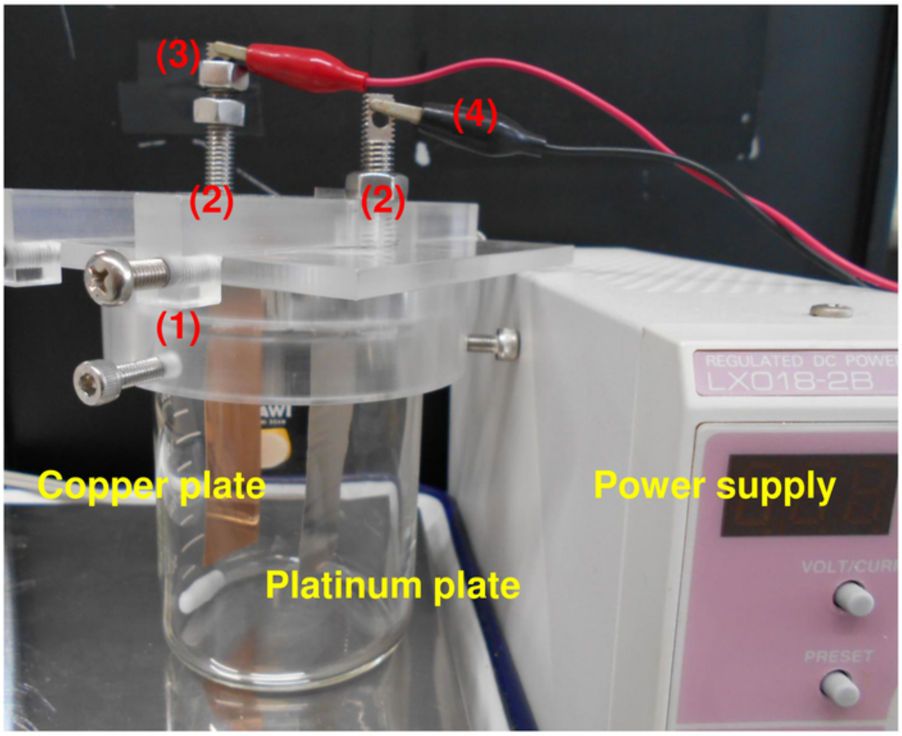

Figure 3: Picture of a combinations of parts to be energized in the experiment. Attach the jig with the electrode plate to the glass beaker and connect it to the power supply. (1) Acrylic beaker fixing part, (2) metal electrode parts, (3) copper plate electrode (anode), and (4) platinum plate electrode (cathode). Please click here to view a larger version of this figure.

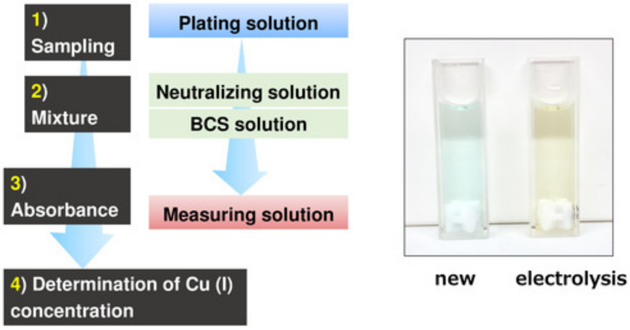

Figure 4: Absorption measurement of Cu(I). Absorption measurement procedure (left) and photos of sample solution (right). Fresh copper sulfate plating solution (blue) and electrolysis solution (orange). Since Cu(I) is accumulated in the plating solution by electrolysis, it is colored orange in the electrolysis plating solution sample. Please click here to view a larger version of this figure.

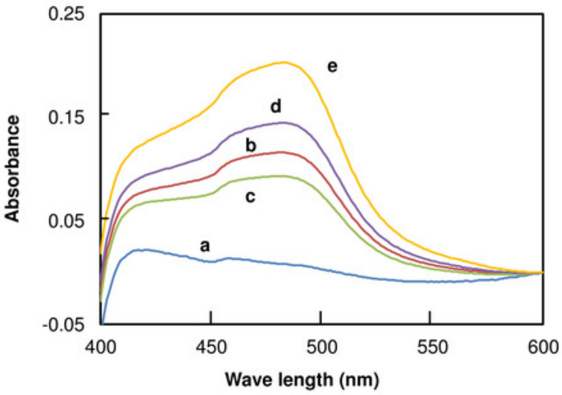

Figure 5: Absorption spectra of Cu(I)-BCS in electrolysis solutions. Electrolysis time: (**a**) 0, (**b**) 4, (**c**) 6, (**d**) 8, and (**e**) 10 min. Since the absorbance of Cu(I)-BCS generally increases as the electrolysis time becomes longer, it is considered that the amount of Cu(I) accumulated in the plating solution is increased. This figure is a modification of Figure 2 of Koga et al. 2018[15]. Please click here to view a larger version of this figure.

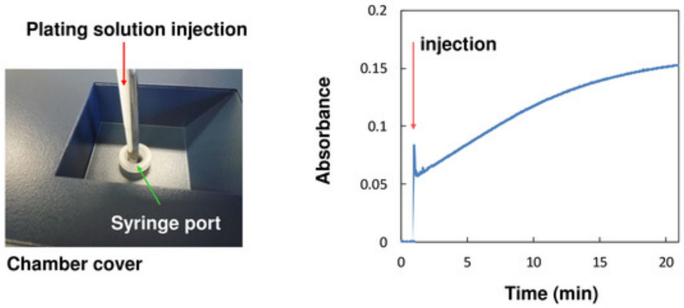

Figure 6: Injection measurement. Left: Picture of chamber cover. There is a syringe port at the top of the cell; insert a pipette there and inject sample solution. Right: Reaction curve of plating solution which was electrolyzed at 1.0 A for 10 min. A sharp increase in absorbance immediately after injection and a gentle increase are clearly observed. Please click here to view a larger version of this figure.

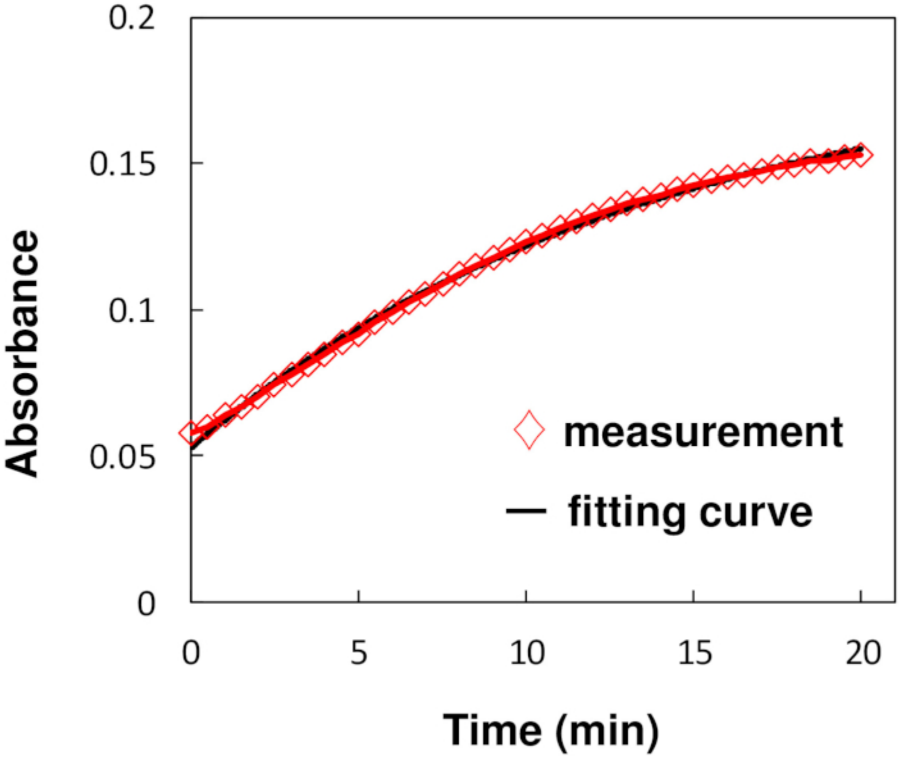

Figure 7: Simulation of absorbance of plating solution (1.0 A, 10 min). ◇: measured point, solid line: fitting curve. This figure is a modification of Figure 4 of Koga et al. 2018[15]. Please click here to view a larger version of this figure.

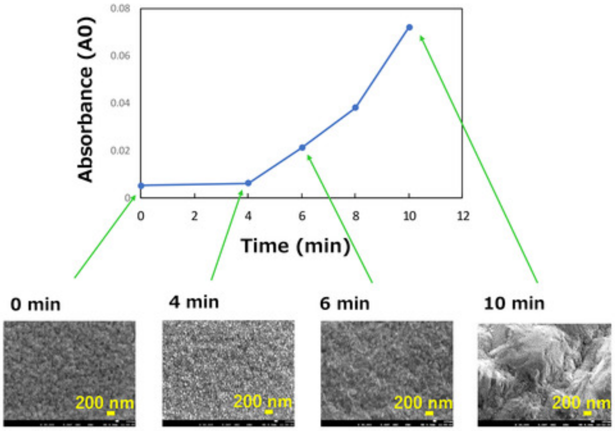

Figure 8: Deposition versus electrolysis time. (Graph) Normalized absorbance fitting parameters are plotted against electrolysis time, A0. (Pictures) SEM images of the plating film surface that were deposited in each electrolysis solution (times above pictures are electrolysis times). Please click here to view a larger version of this figure.

Discussion

Figure 2 schematically shows a system for electrolysis experiment. The jig is an ordered item, which consists of an acrylic part to be fixed to beakers and metal parts for attaching plates and for connecting with the power supply. By this mechanism, the immersion area of the plates becomes constant, and the relationship between the current value and the current density is kept constant. In our conditions, immersion is 4 cm x 2 cm, and the current density will be 62.5 mA/cm^2 with a current of 1 A. In the accumulation procedure of Cu(I), a copper plate is attached to the anode and a platinum plate is attached to the cathode. In order to increase the accumulation efficiency of Cu(I), it is preferable to deoxidize the plating solution with nitrogen gas beforehand.

Quantitative measurement of Cu(I) consists of a simple procedure. Pour the neutralization solution and BCS solution into the cell and mix the plating solution (**Figure 4**). It is necessary to stir for more than 20 min until Cu(I) and BCS react sufficiently. This is to ensure the accuracy of the measurement by sufficiently advancing the reaction. If Cu(I) is contained in the plating solution, the sample solution appears orange and an absorption spectrum having a peak at 485 nm is obtained. Changes in solution color due to the complex formation were dramatic and surprised many copper plating technicians.

It is confirmed that Cu(I) accumulates in the solution when a current is passed through the copper sulfate plating solution (**Figure 5**). The absorption spectrum shows the shape of the Cu(I)-BCS complex, which is suitable for calculating the Cu(I) concentration from the absorbance at 485 nm. Although the current value is arbitrary, Cu(I) is hardly accumulated at a current value of 0.2 A, and a higher current value is required. Although the accumulation amount of Cu(I) tends to increase with electrolysis time, it is saturated by excessive current (for example, electrolysis for more than 10 min at 1.0 A). The accumulation amount of Cu(I) increased by electrolysis for 10 min when the current value was 0.5 to 1.0 A[14]. When an excessive current flowed (for example, at 1.0 A for 20 min), the Cu(I) concentration decreased. This is thought to be related to the formation of copper particles due to the progress of the disproportionate reaction.

The reaction of Cu(I) and BCS in the plating solution has multiple time components, which often make the accurate determination of the concentration difficult. In order to solve this problem, an injection measurement is desirable (**Figure 6**). In this measurement, the absorption intensity of the Cu(I)-BCS complex is acquired as a changed amount from the baseline before injection of the plating solution, so it can be determined more accurately. In addition, since the reaction curve can be simply numerically analyzed, the concentration can be known with high accuracy even if the reaction is not completed. The components of the reaction curve are thought to reflect the retention structure of Cu(I) in the plating solution[14].

It is important to model the holding structure of Cu(I) in the plating solution against the assertion that Cu(I) in the plating bath instantaneously oxidizes Cu(II). We propose the following model from analysis of characteristics of the current amount, formation, and accumulation of Cu(I). A portion of the Cu(I) eluted from the copper plate is retained in solution in the form of a Cu(I)-PEG complex. In early stages of the complex formation, chloride ions are thought to play a role as a temporary stabilizer for Cu(I)[6,8]. Cu(I) coordinated to PEG is incorporated inside the three-dimensional structure, and it is in a hydrophobic environment. When the formation of Cu(I) is promoted, excess Cu(I) is coordinated to the surface of the PEG and may be in the vicinity of the liquid. Since Cu(I) on the surface reacts promptly with BCS, it will reflect the A0 component of the reaction curve. Since the Cu(I) inside the PEG is protected from BCS attack, it has a slow AL component. It has been pointed out that the A0 component mainly influences the quality of the plating film[15]. This information is important for management of the plating solution.

By accelerating the denaturation of the plating solution and verifying the accumulated Cu(I) concentration and the holding structure, it is possible to clearly characterize the plating solution. This is important not only for understanding the plating process but also for predicting the quality of the plating film to be produced. From the verification of the SEM image, it was shown that the Cu(I) concentration, especially the A0 component, is strongly involved in the generation of the roughness of the plating film (**Figure 8**). On-site measurement of Cu(I) gives new indications for the management of plating baths.

This research can contribute to the management of the plating bath based on optical measurement. We aim to develop a system that can evaluate the state of the plating bath on the production line on-time and in situ.

Disclosures

We have nothing to disclose.

Acknowledgments

We thank Miss. Hirakawa for her great contribution to this research.

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