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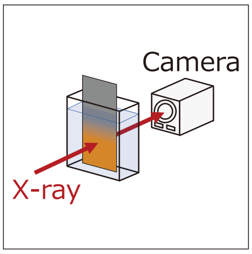

In Situ Analysis of Electroless Copper Plating Using Synchrotron Radiation

Misato TAKAHASHI*, Junji IIHARA, and Kazuhiro GOTO

In recent years, manufacturing of high-performance electronic devices requires more and more precise control over the thickness and uniformity of fine circuits. Though electroless copper plating is indispensable to form circuits on insulating substrates, the plating involves such complicated chemical reactions that the process conditions can be optimized only empirically. In this study, we developed *in situ* measurement techniques utilizing synchrotron radiation to quantitatively and spatially visualize the copper plating behaviors. X-ray absorption fine structure (XAFS) technique enabled us to monitor real-time the copper valence changes in the reduction of Cu^{2+} ions in the solution to metallic copper. We also developed X-ray imaging techniques to visualize in-plane deposition thickness, which clarified that bubble adhesion locally inhibits the deposition. These techniques are expected to be very useful to understand the plating process more deeply and to advance the manufacturing technology in the future.

Keywords: electroless plating, *in situ* measurement, synchrotron radiation, X-ray imaging, X-ray absorption fine structure (XAFS)

1. Introduction

The everyday electronic devices that make our lives more convenient continue to evolve in diverse ways year after year. For example, as the functionality of mobile devices increases, the number of components grows, making it crucial to minimize the weight and volume of electrical wiring. Copper, the most commonly used material for wiring, is the second most conductive metal. By forming copper circuits as thin films on insulating resin, space savings can be achieved in wiring. Copper thin films can be grown in the gas phase or liquid phase, with the latter commonly employing electroplating processes industrially.(1)-(4) Among these processes, electroless copper plating is indispensable for reducing wiring weight, as it enables the formation of a thin copper film regardless of the conductivity of the insulating resin substrate (hereinafter referred to as the substrate). In recent years, as electronic devices have become increasingly sophisticated, there is a growing demand for both thinness and uniformity, making precise optimization of manufacturing conditions essential. However, due to the complexity of the copper deposition process in the plating solution, it is currently difficult to accurately predict deposition behavior based on fundamental principles, and optimization is often achieved through trial and error. To further enhance device performance, it is crucial to understand the timescale over which copper deposition progresses and to determine its spatial distribution—where it occurs and at what thickness. Obtaining this information is difficult using conventional analytical methods. However, by utilizing synchrotron radiation*1 analysis, which our company has focused on for many years, it is possible to reliably reproduce and measure the copper precipitation phenomenon "*in situ*." In this paper, we report on real-time analysis of the deposition process of electroless copper plating using synchrotron radiation, visualizing the chemical state of the deposited material and the distribution of the thickness of the copper layer.

2. Characteristics of Electroless Copper Plating and Development Motivation

Electroless copper plating is a process that deposits metallic copper through the reduction reaction of copper ions mediated by a catalyst. As shown in Fig. 1, the reduction reactions where copper ions in the plating solution receive electrons from the reducing agent and transform into metallic copper, and the oxidation reaction where the reducing agent releases electrons, proceed simultaneously. The deposition characteristics of the plating are also significantly affected by the state of the substrate. Guidelines for adjusting the precipitation state are essential for stable manufacturing. However, due to the complexity of the reactions involved in precipitation, it is sometimes necessary to rely on the experience and knowledge of the manager overseeing production. From a materials analysis perspective, we developed an *in situ* measurement technique to visualize plating deposition behavior as a tool for identifying factors necessary for stabilizing copper deposition rates. Our goal is to enable feedback into the design of substrates and other components. In this study, we aimed to investigate the precipitation of copper alongside changes in its valence state, quantify the thickness of the copper layer, and visualize its spatial distribution.

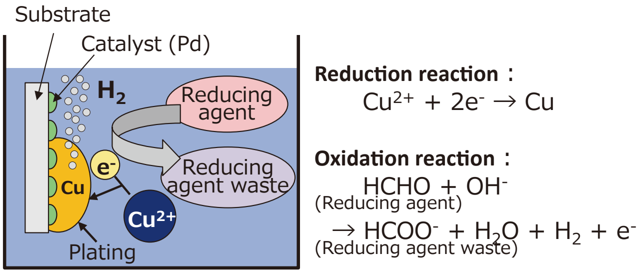

Fig. 1. Schematic diagram of electroless copper plating

3. Synchrotron Radiation Analysis and *In Situ* Measurement

A key point in analyzing plating reactions is that even if the plated film is removed after the end of the reaction and the chemical state of the copper is observed, the copper surface reacts with atmospheric oxygen and changes, resulting in a state different from that in the solution. As a countermeasure to this problem, we turned our attention to *in situ* measurement. *In situ* measurement has the advantage of enabling the observation of the product in its true state under conditions simulating its actual environment like liquid concentration and temperature. However, this requires repeated measurements at short time intervals, which is extremely difficult to achieve using commercially available instrumentation. This study utilized high-intensity synchrotron radiation to shorten measurement times to overcome the aforementioned issues. Specifically, the technological development was conducted using the SPring-8*[2] and Sumitomo Electric beamlines*[3](5) operated at the SAGA Light Source.*[4]

Table 1 is a list comparing synchrotron radiation analyses: X-ray diffraction, X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS), and X-ray imaging. One key focus of this study is the chemical reaction where copper ions are reduced to metallic copper at the interface between the plating solution and the plated material. Therefore, *in situ* XAFS measurements are the most promising approach, as they do not require maintaining the sample under vacuum and allow simultaneous evaluation of both solid and liquid phases.(6) Additionally, we attempted to quantify the thickness distribution of copper, which is another point of interest. As shown in Fig. 2 (a), XAFS requires extracting monochromatic X-rays (schematically shown in red in Fig. 2) from synchrotron radiation using a spectroscopic crystal, then focusing them onto a single point on the sample for measurement. Consequently, an area only approximately 0.1 mm tall by 1 mm wide can be measured. This results in a discrepancy with the millimeter-to-centimeter dimensions of industrially mass-produced plated products, making it impossible to visualize the spatial distribution. Therefore, as shown in Fig. 2 (b), we employed X-ray imaging, where monochromatic X-rays are directed onto the sample without focusing and captured by a camera, to secure a wide analytical field of view. Since X-ray imaging cannot perform chemical state analysis as shown in Table 1, XAFS was used to capture changes in chemical state and copper film thickness at the "point" level, while X-ray imaging was employed to capture changes in copper film thickness at the "surface" level, allowing for a differentiated approach.(7)

Table 1. Comparison of synchrotron radiation analysis methods and their advantages and disadvantages

Method	Time resolution	Liquid measurement	Copper thickness	Chemical condition
X-ray diffraction	Available (< 1 min)	Not available	Available	Not available
XAFS	Available (< 1 min)	Available	Available	Available
XPS	Not available (> 10 min)	Not available (Vacuum)	Not available	Available
X-ray Imaging	Available (< 1 min)	Available	Available	Not available

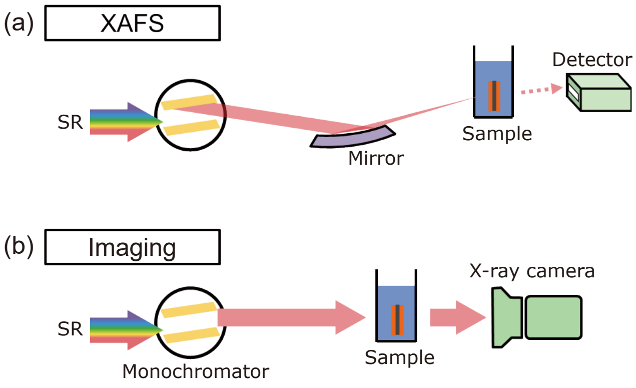

Fig. 2. Schematic diagram of synchrotron radiation analysis
(a) XAFS (b) X-ray imaging

4. Experiments and Results

4-1 Construction of an *in situ* measurement system

To perform *in situ* measurements of electroless plating within synchrotron radiation analysis equipment, it is necessary to advance the plating reaction within a limited space (approximately 1 m in height, width, and depth) where the sample can be installed, while precisely directing X-rays at the area of interest. Since large-scale equipment like that used in mass production plants would not fit, we fabricated a compact analytical cell capable of reproducing the plating reaction and conducted experiments by bringing it to the synchrotron radiation facility. Figure 3 shows an overview of the *in situ* measurement system developed in this study. The analysis cell in which the substrate is placed was set to a thickness of 4 mm, taking into account liquid flow characteristics and X-ray absorption by the plating solution. The cell containers were made of polypropylene material with excellent chemical resistance and X-ray transmittance, with a thickness of 1 mm. The substrates were fixed within the containers to allow X-rays to pass through them vertically. As the reaction progresses and metallic copper precipitates, the copper ion concentration in the plating solution gradually decreases. Therefore, a system was also constructed to circulate the plating solu-

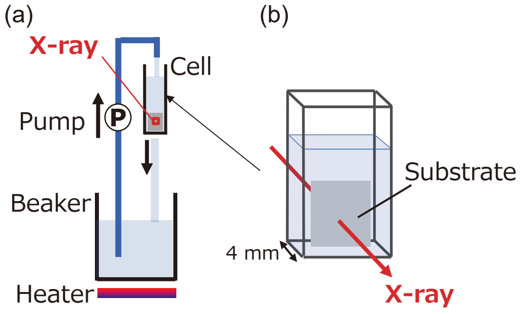

Fig. 3. Schematic diagram of the *in situ* measurement system
(a) Overall view (b) Close-up near the substrate within the cell

tion at a rate of 30 mL/min using a tubing pump to replenish the consumed copper ions. The liquid temperature was maintained at 35°C using a Peltier element. A polypropylene film coated with palladium (Pd), the catalyst required for the reduction reaction, was used as the substrate. A tartaric acid bath[8] was used as the plating solution. After preparing the plating solution by mixing the necessary reagents during preparation of the plating bath, the plating reaction begins immediately upon immersing the substrate into the solution. To prevent the reaction from starting before measurement, we began filling the plating solution into the cell container at precisely the moment the synchrotron radiation was directed onto the sample, ensuring the substrate was immersed simultaneously.

Note that during the initial stages of this project, it was discovered that transporting plating solutions prepared in our in-house laboratory to the synchrotron radiation facility caused the solutions to deteriorate over time, making it impossible to reproduce the *in situ* measurements. Therefore, we brought the pre-bathing reagents to the facility, prepared the bath immediately before measurement, and conducted the experiment within 10 hours. This confirmed that the newly developed analysis cell enables reproducible *in situ* measurements. Regarding the temporal changes after bath formation, prior to conducting *in situ* measurements at the synchrotron radiation facility, electrochemical verification was performed using the same experimental equipment in our in-house laboratory for this study. This confirmed in advance that reproducible plating was possible from bath formation until the completion of the *in situ* measurements.

4-2 Chemical state analysis during electroplating reaction

XAFS measurements were conducted at the BL16B2 of SPring-8, with incident and transmitted X-ray intensities measured using an ionization chamber.

We confirmed that metallic copper was deposited on both surfaces of the substrate within the cell fabricated for this study. The Cu-K edge XAFS spectrum shown in Fig. 4 was observed with a shape corresponding to the sum of copper ions in solution (Cu^{2+} in the fig.) and precipitated metallic copper (Cu in the fig.). As the electroless plating reaction progressed, a time-dependent change in the spectrum was observed (Fig. 4 (a)). The rise of the absorption edge shifted toward lower energies over time, confirming a decrease in the valence state of copper. Each spectrum was fitted using a linear combination of the spectra for Cu^{2+} in the plating solution and metallic copper to convert into the abundance ratio of Cu^{2+} to metallic copper (Fig. 4 (b)). Figure 5 shows the equivalent copper thickness and Cu^{2+} concentration converted from transmittance with respect to reaction time. From these results, it was determined that copper deposition begins within 2 minutes of immersing the substrate in the plating solution, and the subsequent deposition rate remains nearly constant at 0.035 µm/min. This rate is equivalent to the value obtained by *ex situ* experiments[6], suggesting that the *in situ* measurement system developed in this study successfully reproduces the actual plating reaction. Thus, it became possible to quantify the rate at which divalent copper ions in solution transform into metallic copper, the primary reaction in electroless copper plating, at approximately 40-second intervals.

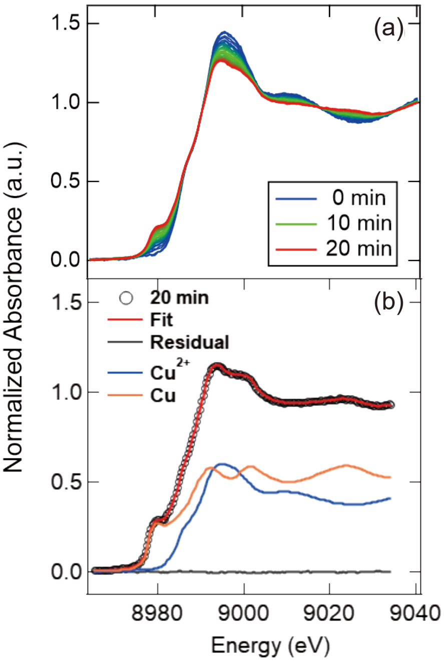

Fig. 4. (a) Time-dependent changes in the XAFS spectrum
(b) XAFS spectrum 20 minutes after reaction initiation and fitting results

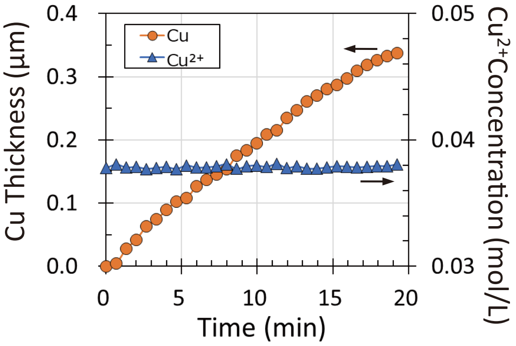

Fig. 5. Time-dependent changes in copper film thickness and copper ion concentration in solution

4-3 Visualization of in-plane distribution during electroplating reactions

X-ray imaging observations were conducted at SPring-8 BL16B2. The sample was irradiated with 20 keV monochromatic synchrotron radiation, and the transmitted image was observed using the XSight MicronLC two-dimensional X-ray detector (manufactured by Rigaku Innovative Technologies Europe). The effective pixel size in X-ray fluoroscopy images is 1.3 × 1.3 µm, with a field of view of 2.66 × 2.66 mm. The exposure time was 1 second per image, and 900 images were captured consecutively.

Figure 6 shows an example of X-ray images of a substrate during plating. The center part is the substrate. When the substrate comes into contact with the plating solution, a reaction begins, causing copper to precipitate and hydrogen gas to be generated. Over time, areas where the copper had thickened exhibited reduced X-ray transmission and appeared darker. Since the monochromatic X-rays shown in Fig. 2 are used for observation, the copper thickness can be determined from the transmission rate. The average transmittance of a 50×50 pixel area, which can be quantified with an accuracy of ±0.05 µm per second, was calculated for each X-ray image. The change in transmittance was then converted into the thickness of copper. Figure 7 shows side-by-side graphs of the locations where copper thickness was converted and the changes over time. The increased thickness of the copper was also confirmed by visual inspection after plating.

In the X-ray images shown in Figs. 6 and 7, the bubbles generated during the reaction were also visible as round outlines. Bubbles were observed locally adhering to the substrate edge, growing, and then detaching. The bubbles gradually grew larger in the same location from their formation until their detachment, and are thought to be hydrogen gas generated simultaneously with copper precipitation. It was found that locations prone to bubble retention could be identified from the X-ray images, and results suggesting that bubbles inhibit copper precipitation were also obtained, as shown in Fig. 8. At present, it is difficult to clearly distinguish whether the light and dark areas in the X-ray image are caused by bubbles or variations in copper thickness, making it challenging to quantify the impact of localized bubble formation on plating thickness. In order to resolve this issue, we plan to investigate synchrotron radiation analysis techniques that combine XAFS and imaging to simultaneously measure the in-plane distribution of the chemical state and thickness.

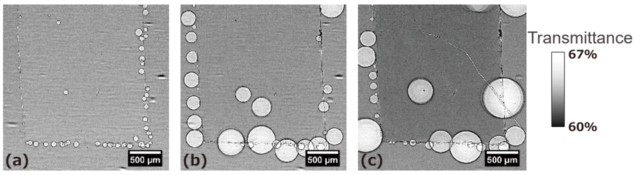

Fig. 6. X-ray image of the substrate during plating
(a) Before reaction (b) After 5 minutes of plating (c) After 15 minutes of plating

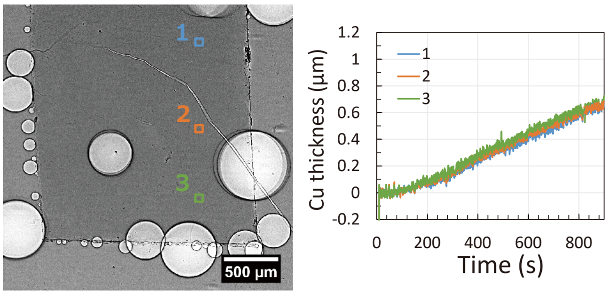

Fig. 7. Time-dependent changes in equivalent precipitation thickness

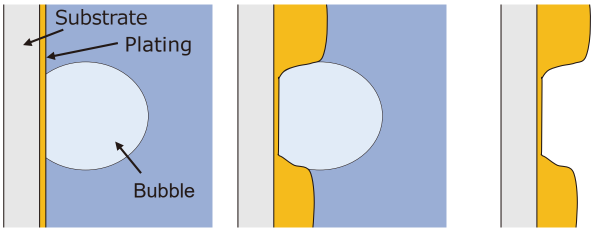

Fig. 8. Effect of bubbles on plating growth

5. Conclusion

In this study, we developed an *in situ* measurement method for copper valence changes during electroless copper plating, enabling the calculation of copper deposition rates. This method is expected to provide guidance for process design aimed at achieving thin and uniform copper control, while also advancing the understanding of detailed mechanisms.(9) Moreover, imaging observations now enable the quantification of copper thickness and the analysis of the spatial distribution of the precipitation rate. It was also found that bubbles accompanying the reaction could be observed on X-ray fluoroscopy images. While it was difficult to directly observe copper reduction reactions and copper film thickness while reliably performing electroless copper plating reactions using commercially available equipment, this became possible for the first time through the use of synchrotron radiation. Furthermore, this result visually confirmed the previously known phenomenon that bubbles inhibit metal precipitation(10)-(13), thereby reaffirming the effectiveness of measures to prevent bubble retention. This technology can also be used as a tool to understand how changes in manufacturing conditions affect the product, and we will continue to utilize it for manufacturing process optimization.

6. Acknowledgements

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Technical Terms

∗1 Synchrotron radiation: High-intensity white electromagnetic radiation generated tangentially when the trajectory of electrons accelerated to nearly the speed of light is bent by an electromagnet.

∗2 SPring-8: Abbreviation for Super Photon Ring-8 GeV, one of the world's largest synchrotron radiation facility located in Sayo District, Hyogo Prefecture. Stored energy of 8 GeV, put into service in operation since October 1997.

∗3 Sumitomo Electric Beamline: The beamline installed by Sumitomo Electric within the SAGA Light Source. In operation since November 2016. Approximately 3,000 hours a year of synchrotron radiation analysis are conducted annually using two beamlines: soft X-rays and hard X-rays.

∗4 SAGA Light Source: The synchrotron radiation facility established by Saga Prefecture in Tosu City is operated by the Saga Prefecture Industrial Promotion Organization (Public Interest Incorporated Foundation). Stored electron energy is 1.4 GeV, in operation since February 2006.

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Contributors

The lead author is indicated by an asterisk (∗).

M. TAKAHASHI*

- Doctor of Science
  Analysis Technology Research Center

J. IIHARA

- Doctor of Science
  Analysis Technology Research Center

K. GOTO

- Doctor of Engneering
  Group Manager, Analysis Technology Research Center