

## Detection of Cu(I) in Copper Sulfate Plating Solution Using BCS Fluorescence

Toshiaki Koga<sup>1</sup>, Chieko Hirakawa<sup>1</sup>, Michinori Takeshita<sup>2</sup>  
and Nao Terasaki<sup>1</sup>

<sup>1</sup>Advanced Manufacturing Research Institute, Department of Electronics and Manufacturing, National Institute of Advanced Industrial Science (AIST)

807-1, Shuku-machi, Tosu-shi, Saga 841-0052, Japan

<sup>2</sup>Saga University

1, Honjo-machi, Saga, 840-8502, Japan

### Abstract

We successfully detected unstable Cu (I) in copper sulfate plating solution using BCS fluorescence. Quantitative measurement at  $10^{-6}$  mol/L or less, out of range with the conventional absorption method, was possible by the fluorescence method. The fluorescent method is promising for Cu (I) analysis in Cu electroplating solution to assure the quality of Cu plating film in higher sensitivity.

### 1. Introduction

With density growth of printed circuit board and the development of through-silicon via (TSV) plating technology, it becomes more important to fine management of the plating solution during the manufacturing process in order to keep high quality of product. In copper sulfate electroplating, monovalent copper ions (cuprous ion: Cu(I)) has been implicitly pointed out as one of the main cause of low quality such as high roughness and dull metallic on the Cu plated surface. There are a number of studies about the behavior and roles of Cu(I) in the plating process (1,2), however its analysis in aqueous solutions is not sufficient.

Bathocuproinedisulfonic acid, disodium salt (BCS: Fig. 1) is used to quantify the Cu(I) concentration in the aqueous solutions (3,4). We have succeeded in optical analyzing the Cu(I) containing in the plating solutions conducted by absorption of a chelate of Cu(I) with BCS (5). Furthermore, it showed that the concentration and the holding structures of Cu (I) in the solution are closely related to the roughness of the plating film surface (6). However, in the absorption method, the quantification of Cu (I) is about sub-millimolar, and a method with higher sensitivity is expected. Here, as a new attempt, we report high sensitivity detection of Cu (I) using BCS fluorescence

### 2. Experimental

BCS was purchased from Dojindo. Pure water was manufactured with Milli-Q Advantage.

Copper sulfate plating aqueous solution was prepared by resolving sulfuric acid (0.5 M), copper sulfate (0.4 M), chlorine (Cl), polyethylene glycol (PEG : M.W. 4000), bis (3-sulfopropyl) disulfide (denoted as SPS: 0.003 mmol), and janus green B (denoted as JGB: 0.004 mmol) in ultrapure water. For Cu plating experiment, the copper plate and a platinum plate were immersed into a beaker containing sulfuric acid

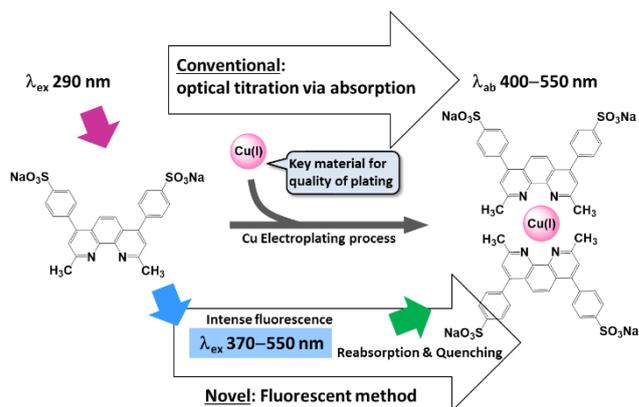


Fig. 1 Concept of Cu(I) detection, molecular structures of BCS and BCS-Cu(I) complex

copper plating solution (150 mL) with each electrochemically active area as  $40 \times 20$  mm, and used as an anode and a cathode respectively. Electrolysis was carried out under the current density of 15.6 through 62.5 mA/cm<sup>2</sup>.

Absorbance was measured with JASCO V-630, and fluorescence measurement was performed with JASCO FR-8500.

### 3. Results and Discussion

BCS dye has been used to form a 2:1 complex with Cu (I) for stabilizing in aqueous solution and to appear absorption peak for detection, but the ability of detection has never been discussed using the fluorescence so far. When BCS was dissolved in water, bright fluorescence was observed from 370

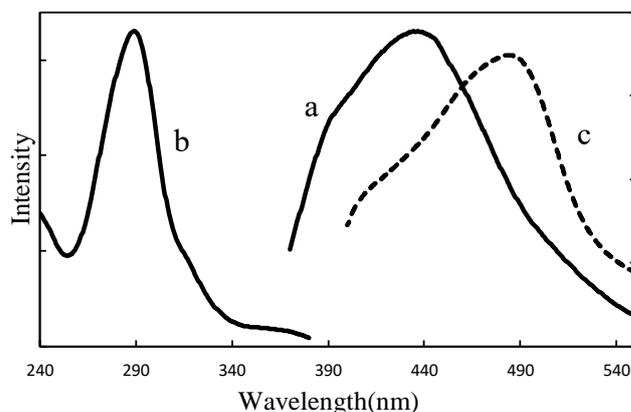


Fig. 2 (a) Fluorescence and (b) Excitation spectrum of BCS, (c) absorbance of BCS-Cu(I) complex.

to 550 nm (Fig. 2a). The fluorescence quantum yield is very high, comparable to pyrene, a typical fluorescent dye, at  $10^{-6}$  mol/L solution. An absorption band appears at 400 to 550 nm due to the complex of BCS and Cu (I), which overlaps a broad range with the fluorescence band of BCS (Fig. 2c). This indicates that in the aqueous solution containing Cu (I), the fluorescence of BCS could be reabsorbed by the BCS-Cu (I) complex and quench. Using the fluorescent phenomena, it can be considered that Cu (I) in the plating solution can be detected through the difference of the fluorescence intensity of the plating sample from the fresh plating solution.

Furthermore, fluorescence method is more sensitive than absorption because it measures emitted light. The detection limit of the molecular concentration due to the color reaction is approximately  $10^{-6}$  mol/L, but for fluorescence it is possible to detect as much as  $10^{-9}$  mol/L without any special operation. Quenching of fluorescence is a phenomenon in which fluorescence intensity decreases due to some factor, and the number and state of quenchers can be inferred from intensity change. Our aim is to detect BCS-Cu (I) which is a quencher from the change of fluorescence intensity of BCS. Compared with fluorescence analysis, fluorescent quenching method are inferior in resolution, but they will have sufficient advantages over color reactions.

Fluorescence characteristics of BCS in aqueous solution

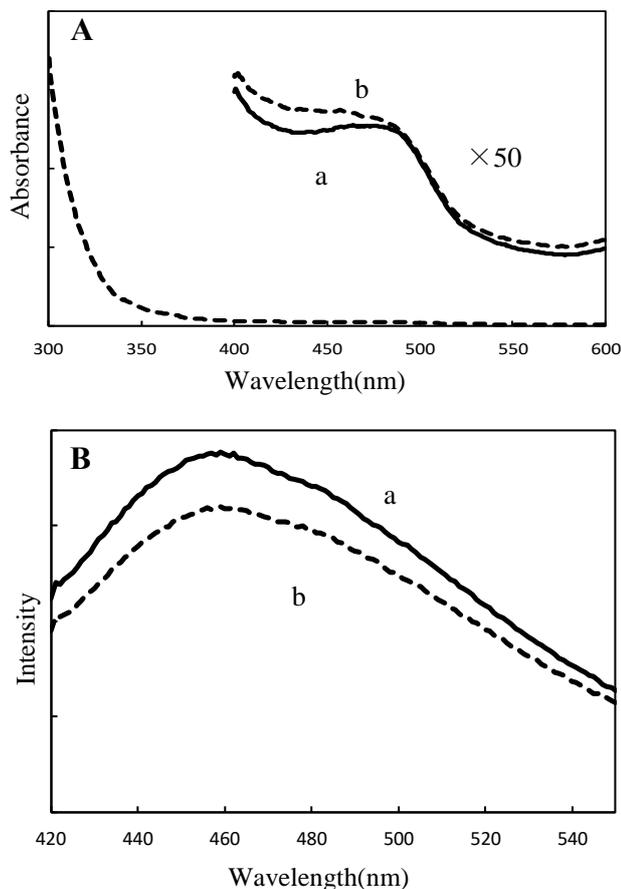


Fig.3 (A) Absorption spectra of (a) fresh solution (b) electrolysis solution, (B) Fluorescence spectra

were confirmed. BCS forms an aggregate at  $10^{-4}$  mol/L, but it was free at  $10^{-5}$  mol/L or less. For detection of BCS-Cu (I), the pH had to be 4 or higher, and the fluorescence of BCS was observed in the range of pH 4 to 7.

A sample was prepared by electrolysis the copper sulfate plating solution. The Cu (I) concentration of the sample solution was about  $10^{-4}$  mol/L. The plating solution (22  $\mu$ L) was added to BCS buffer solution (2.7 mL) and the absorption (Fig. 3 (A)) and fluorescence spectra (Fig. 3 (B)) were measured. The Cu (I) concentration of the plating fresh solution (a) was almost 0, and the value of the sample to which the electrolysis solution was added (b) was about  $10^{-6}$  mol/L. The absorption of BCS-Cu(I) could not be identified due to the large absorption of copper sulfate in the ultraviolet region. (A). On the other hand, the fluorescent peak intensity decreased by about 15% in the electrolysis solution compared to the fresh solution, and clear distinction was possible (B). This indicates that Cu (I) detection in the plating solution is possible by fluorescence quenching measurement. Since the fluorescence yield of BCS is high, quantitative measurement at  $10^{-6}$  mol/L or less, which was impossible in the color reaction, is considered to be sufficiently possible.

#### 4. Conclusions

Bright fluorescence was observed in the blue region with BCS aqueous solution. Fluorescence of BCS is reabsorbed and quenched by BCS-Cu(I) complexes. It was possible to detect Cu (I) at  $10^{-6}$  mol/L by quenching measurement of BCS fluorescence, in spite that it was impossible to detect it by the optical titration via absorption. Detection of Cu (I) in a plating solution using fluorescence is a new measurement method which has never been before, and it is also expected to greatly improve detection sensitivity. This method is effective not only for the evaluation of plating solution but also for the analysis of Cu ion in various aqueous solutions such as natural water, drinking water, industrial wastewater and medical blood.

#### Acknowledgements

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#### References

- [1] M. Yokoi, in *Copper Electrodeposition for Nanofabrication of Electronics Devices* (2014) 3.
- [2] K. Kondo, T. Nakamura and N. Okamoto, *J. Appl. Electrochem.* **39** (2009) 1789.
- [3] Y. Kikuchi, K. Satoh, K. Sawada and T. Suzuki, *BUNSEKI KAGAKU* **39** (1990) 301.
- [4] J. Palmer, *The Plymouth Student Scientist*, **7**(2) (2014) 151.
- [5] H. Noma, T. Koga, C. Hirakawa, K. Nonaka and K. Shobu, *ECS Trans.* **58**(17) (2014) 77.
- [6] T. Koga, C. Hirakawa, Y. Sakata, H. Noma, K. Nonaka and N. Terasaki, *ECS Trans.* **75**(35) (2017) 21.