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# Analysis of Cu(I) Complexes in Copper Sulfate Electroplating Solution by Using Reaction Kinetics with a Chelate Reagent

Hiroaki Noma, Toshiaki Koga, Chieko Hirakawa, Kazuhiro Nonaka, Kazuhisa Shobu
Measurement Solution Research Center, National Institute of Advanced Industrial Science and Technology (AIST)
807-1, Shuku-machi, Tosu-shi, Saga 841-0052, Japan

## 1. Introduction

In the manufacturing of metal interconnections for electric printed circuits and semiconductor devices, electroplating process of copper is a key technology. The electroplating process depends on the additives in copper sulfate plating solutions. The role of the additives is classified as an inhibition effect and an acceleration effect. The additives form Cu(I) complexes in the solutions, such as Cu(I)-PEG [1], $Cu(I)Cl_2^-$, Cu(I)-thiolate, Cu(I)-SPS[2]. The correlation between the effects of additives and Cu(I) complexes has been investigated.[2] But the analysis of Cu(I) complexes has not been established.

In the previous study[3], we have succeeded in analyzing a total amount of Cu(I) ions in copper sulfate plating solutions by absorption of Cu(I) with a chelate reagent. In this study we tried to analyze the Cu(I) complexes by using reaction kinetics between Cu(I) complexes and a chelate reagent.

## 2. Experimental

### 2.1. Measurement of Cu(I) with a chelate reagent

We used bathocuproinedisulfonic acid, disodium salt (BCS). BCS is soluble in water, so we were able to observe the color reaction process of Cu(I) ions and BCS. BCS reagent shows stable coloring at pH 4 – 5.5, so we kept pH in this range by using a buffer of acetic acid and NaOH.

Samples of copper sulfate electroplating solutions, A solution and B solution, were obtained from two production lines with different types of copper sulfate electroplating solutions. A new solution (A-1, B-1) and an operating solution (A-2, B-2) for each solution were prepared.

The color reaction buffer solution, 2.5 ml, was added to a sample cell and a reference cell for a spectrometer. A copper sulfate electroplating solution, 50 μl, was added into the sample cell and the solution was mixed quickly. Absorbance change at 485 nm of the sample cell was measured in 20 min.

## 3. Results and Discussion

### 3.1 Color reaction of Cu(I) in electroplating solutions

The absorbances of the color reaction of Cu(I) of the operating plating solutions (A-2, B-2) increased quickly in a few minutes after mixing with the chelate reagent and subsequently continued to increase slowly as shown in Fig. 1, while the absorbances of the new solutions (A-1, B-1) were less than 0.009.

### 3.2. Analysis of Cu(I) states in electroplating solutions

Measuring $^1$H-NMR of organic compounds of the plating solutions, new one B-1 and operating one B-2, we observed a large amount of PEG in the plating solutions. Furthermore, we detected Cu(I)+PEG complexes: $[Cu(I)+H(OCH_2CH_2)_nOH]^+$, n=4–43, in B-2, using MALDI-MS for the dried sample of B-2. The results strongly suggest the existence of Cu(I)+PEG complexes in the copper sulfate electroplating solutions, which was proposed by Yokoi [1].

### 3.3. Reaction kinetics of Cu(I) complexes with BCS reagent

To analyze the reaction kinetics of the color reaction of BCS with Cu(I) complexes, we divide Cu(I) complexes in the copper plating solutions into two groups, "Small Complex" and "Large Complex", and assume each "Complex" has a specific reaction rate constant, $k$, and a time constant $T=1/k$ of the reaction with BCS reagent. Small Complex represents the small Cu(I) complexes such as $Cu(I)Cl_2^-$, Cu(I) thiolate, and Cu(I)-SPS according to Kondo et al.[2], and Large Complex represents Cu(I)-PEG with different chain lengths.

Assuming the color reaction is a first order reaction on Cu(I) complex concentration, we obtained the following reaction kinetics of absorbance $A$.

$$A = A_S\,[1 - \exp(-t/T_S)] + A_L\,[1 - \exp(-t/T_L)]$$

$A_S$: absorbance caused by initial Small Complex,
$A_L$: absorbance caused by initial Large Complex.
$T_S$, $T_L$ : time constant for Small and Large Complexes.

We applied this equation to simulate absorbance curves with a curve-fitting software, the Microcal Origin Ver.6. The variations of the absorbances of the color reaction of operating electroplating solution A-2 and B-2 were simulated and are shown in the Fig. 1. Both of the curves are fitted very well with $r^2$ value of 0.999. The parameters of the absorbance, $A_S$, and time constant, $T_S$, of Small Complex, the absorbance, $A_L$, and time constant, $T_L$, of Large Complex, and the total absorbance, $A_T$, were obtained.

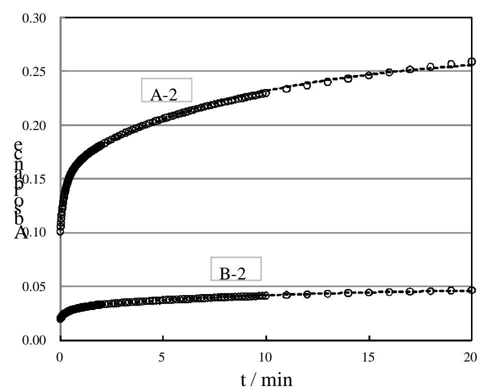


Fig. 1 Measured points and simulation of absorbances of plating solutions A-2 and B-2 with time.
○ : measured point, dotted line : simulation.

## 4. Conclusions

To analyze the reaction kinetics of the color reaction of Cu(I) and a chelate reagent, we divided Cu(I) complexes into two groups, small complexes and large Cu(I)-PEG complexes, and simulated the absorption curve with a good correlation and obtained the concentrations and the time constants, inverse of rate constants, of small Cu(I) complexes and large Cu(I)-PEG complexes. These concentrations and time constants are important parameters to control plating solutions.

## References

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