

## Role of Additives in the Bright Copper Plating from Acid Copper Sulfate Bath and the History

-Invited Talk

M.Yokoi<sup>1</sup>, T.Hayashi<sup>2</sup>

<sup>1</sup>Department of Evaluation Technology,  
Technology Research Institute of Osaka Prefecture  
2-7-1 Ayumino, Izumi, Osaka 594-1157 Japan

<sup>2</sup>Department of Applied Chemistry,  
Osaka Prefecture University

1-1 Gakuen-cyo, Sakai, Osaka, 599-8531 Japan

### Introduction

The excellent additives were developed successfully in 1960s to obtain the bright copper deposits with smooth surface and high ductility. Since then, many applications of copper plating were found in the electronic device and through-hole plating for PCB as well as the conventional decorative plating for steel, electroforming, and etc.. And systematic investigation on the addition agents, which play an important role in practical copper plating, were needed in order to overcome ceaseless troubles occurring in both the bath control and deposits quality control. However, no fundamental studies of the practical copper plating were carried out until 1980s due to the complication of additive composition and lack of appropriate experimental techniques. In spite of the abundance of studies on the copper deposition mechanism by many researchers, the bath composition investigated seemed to be too simple to elaborate the practical plating process.

In those situations, the behavior of the reaction intermediate  $\text{Cu}^+$  in the copper deposition and dissolution, which might have correlate with additives to affect the deposit quality and bath control, and also effects of  $\text{Cl}^-$  on them were investigated using rotating ring-disc electrode system. About the same time, role of addition agents in copper deposition from acid copper sulfate baths were studied through observing the changes in Hull cell patterns and cathodic polarization curves with additive component concentrations. In these studies, adsorption of polyoxyethylene-type surfactant, one of the additive components, was found to be the key phenomena to fabricate excellent bright copper deposits from an acid copper sulfate bath.

### The behavior of intermediate, $\text{Cu}^+$

By using a rotating ring-disc electrode system, the behavior of intermediate  $\text{Cu}^+$  in the copper deposition and dissolution was examined in a wide potential range<sup>1)</sup>. The  $\text{Cu}^+$  concentration on copper surface was found to change obeying the Nernst's equation in low polarization region and reach the minimum values in the high cathodic overpotential. These phenomena confirmed two-step consecutive discharge reactions of copper deposition and dissolution, in which the second discharge reaction ( $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$ ) is in quasi equilibrium state, that is, much faster than the other consecutive reactions. By the addition of  $\text{Cl}^-$  in acid copper sulfate bath, intermediate ions ( $\text{Cu}^+$ ,  $\text{Cu}^+ \cdot \text{Cl}^-$ ) increased with  $\text{Cl}^-$  concentration and the step-wise mechanism of copper deposition and dissolution reactions were believed to remain essentially unchanged.

### Interactions of $\text{Cl}^-$ and additive components in copper plating

The roles of  $\text{Cl}^-$  ions and additive components in the bright copper plating were studied by observing the changes in Hull Cell patterns and cathodic polarization

curves with the concentration of additive components in the presence or absence of  $\text{Cl}^-$  ions<sup>2)</sup>. The additive components were a polyoxyethylene-polyoxypropylene glycole (P), 2-Mercaptobenzothiazole-S-propanesulfonic acid (S) and a derivative of safronic dyes (Janus Green B, J). (P) was found to adsorb on the copper surface to give an adhesive film causing remarkable suppression of the reaction current only in the presence of  $\text{Cl}^-$ , and bright copper plating was obtained under the addition of the three components in appropriate amounts.(Fig.1) The component P and  $\text{Cl}^-$  ions were confirmed to be the main components to obtain the bright copper plating, and the others, (S) and (J), contributed to the brightening and softening of copper deposits only in the presence of the main additive components. In these studies, we proposed an adsorption mechanism of polyoxyethylene type surfactant<sup>3)</sup>. In which (P) with the polymerization degree of more than 7 to 10 grasps the  $\text{Cu}^+$  ions inside the molecule, and adsorbs as a cationic film on the copper surface where  $\text{Cl}^-$  ions are specifically adsorbed.

In 1990s, copper plating was found in applications as an improved interconnect material for fabrication of PCB and IC. With this as a turning point, roles of addition agents including sulfur containing component (S) and safronic dyes (J) have been studied further in detail using advanced analytical techniques such as Enhanced Raman Spectrometry, QCM, TEM, Electrochemical Impedance spectroscopy<sup>4)5)6)</sup>.

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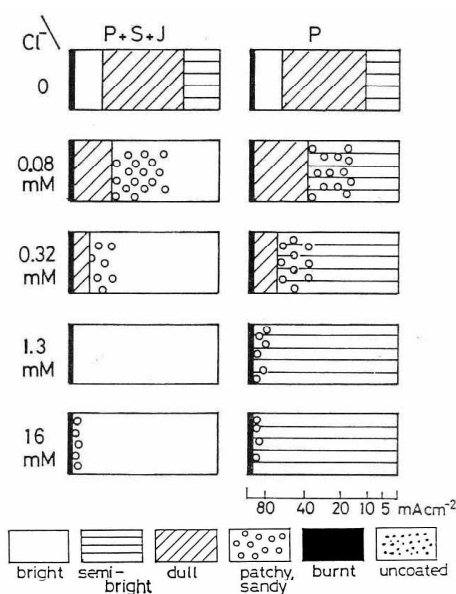


Fig.1 Changes in Hull Cell patterns with the concentration of  $\text{Cl}^-$  in the acid copper sulfate baths containing all three components or only one component P :