

# Inhibition of Copper Electrodeposition by Polyethylene Glycol and Chlorine Ion

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The superfilling of copper electrodeposition is achieved by the presence of additives in the acid copper sulfate electroplating bath. In order to understand the superfilling mechanism, it is important to understand the role of each elements. In this study, the inhibiting effect of PEG and  $\text{Cl}^-$  is investigated by measuring overpotential of an electrode being electroplated in constant current mode.

## EXPERIMENTS AND RESULTS

The cell for electroplating experiments is a 500mL beaker submerged in a water bath at  $298 \pm 0.5\text{K}$  as shown in figure 1. The working electrode (WE) is a polished platinum disk in an epoxy resin. In order to assume 1-dimensional flow of current, ions and additives, the WE is covered by a resin plate which has a cylindrical hole ( $\phi=3\text{mm}$ ). The WE is preplated with copper in the electrolyte of interest before each experiments. In order to avoid the contamination of  $\text{Cl}^-$ , a copper plate in the cover resin is used as a reference electrode which is expected to work as a stable  $\text{Cu}/\text{CuSO}_4$  electrode. The composition of the standard electrolyte is  $225\text{ g/L CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $55\text{ g/L H}_2\text{SO}_4$ .

Figure 2 shows time variation of overpotential when only PEG (average molecular weight 3000) is added to a standard electrolyte bath.  $50\text{A/m}^2$  is applied current for 30 sec. No obvious differences for the PEG concentration is observed. Figure 3-4 shows time variation of overpotential when HCl is added to a PEG (300mg/L) containing electroplating bath. Figure 5 shows time variation of overpotential when only HCl is added to a standard electrolyte bath.

## DISCUSSION

It is reconfirmed that PEG alone does not have strong inhibiting effect. It is supposed that  $\text{Cl}^-$  adsorbs on copper surface and PEG adsorbs to this adsorbed  $\text{Cl}^-$  on the copper surface, then the strong inhibiting effect appears. Let us pay attention to figures 3-4. Line (A) and (C) show gradual decreases of inhibiting effect along time and they are reasonable for the diffusion-adsorption theory. However, when enough amount of  $\text{Cl}^-$  is supplied, the inhibiting effect keeps constant along time as shown by line (B) and (D) and it is found that larger amount of  $\text{Cl}^-$  is needed for the inhibition at higher current density.

Assuming that some fraction of adsorbed  $\text{Cl}^-$  on the copper surface is buried in reduced copper, it is reasonable to suppose that the decrease of  $\text{Cl}^-$  in the trench is larger than the decrease on the top surface and it weakens the inhibition

of copper electrodeposition on the trench bottom. Then the electrodepositing rate on the bottom is accelerated. This effect may be the dominant mechanism of the superfilling.

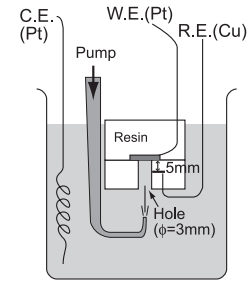


Fig.1 Schematic view of the experimental cell.

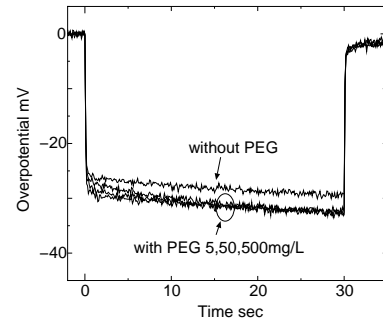


Fig.2 Time variation of overpotential at  $40\text{A/m}^2$ . PEG is added to a standard electrolyte bath.

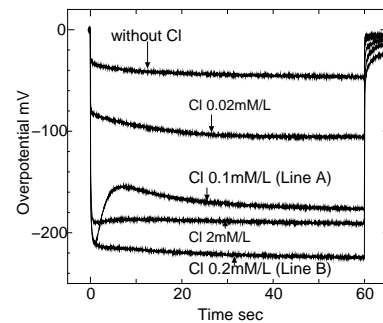


Fig.3 Time variation of overpotential at  $50\text{A/m}^2$ . PEG is added to a standard electrolyte bath.

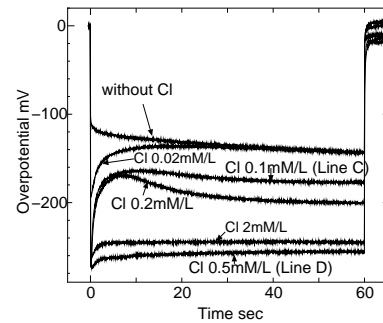


Fig.4 Same experiment as Fig.3 at  $200\text{A/m}^2$ .

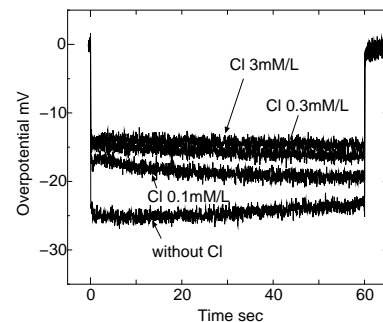


Fig.5 Time variation of overpotential at  $50\text{A/m}^2$ . HCl is added to a standard electrolyte bath.