Electroless Copper Deposition Using Fe(II) Complex as a Reducing Agent

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1. Introduction

A wet process like electroplating and electroless plating is generally used in the formation of Cu wiring¹⁾. Although the conventional electroless Cu plating method using formaldehyde is known to be an effective method to obtain fine wiring²⁾, 1 mol of hydrogen gas is generated for 1 mol of Cu deposition and subsequently sometimes voids are generated in the wiring.

To avoid hydrogen gas evolution, a Cu plating method using Co(II) complex as a reducing agent is proposed³⁾. Since Co is an expensive metal, this research examined the possibility of performing electroless Cu plating using an inexpensive Fe(II) compound as the reducing agent.

2. Experimental

Potential-pH diagrams of Fe(III)/Fe(II) and Cu (II)/Cu were measured using Pt and Cu electrodes, respectively in the presence of some sorts of organic acids under N₂ atmosphere. When conducting electroless plating, Cu substrate (1.0 cm²) was immersed in several plating baths for up to 3 hours and deposition speed was calculated from its weight

change. The optimal bath composition and plating bath conditions are listed in Table 1. The surface morphology of the deposit was observed by scanning electron microscopy(SEM).

3. Results and Discussion

First, a potential pH diagram was prepared in order to investigate the possibility of copper plating. In the potential-pH diagram, the rest potential of Fe(III)/Fe (II) appeared to be less positive than that of Cu(II)/Cu system in the pH range of 4-8.5, when citric acid was used as a ligand. It is expected that citrate complexes of Fe(II), Fe(III) and Cu(II) were formed respectively. The anodic and cathodic polarization curves were measured as shown in Fig. 1 using the conventional potential sweep method. Cu electrode (1.0 cm²), Ag/AgCl electrode (3.3 M KCl) and Pt electrode (2.0 cm²) were used as working, reference, and

Fig. 1 Fe²⁺ anodic (a), and Cu²⁺ cathodic (b) polarization curves in the presence of 1.2 mol/dm³ ethylenediamine and 0.1 mol/dm³ trisodium citrate dihydrate at 60°C. Scan rate : 10 mV/s.

Table 1 Basic bath composition and plating conditions.

Trisodium Citrate Dihydrate	0.1 mol/dm ³
Ethylenediamine	1.2 mol/dm ³
CuSO ₄ ·5 H ₂ O	0.1 mol/dm ³
FeSO ₄ ·7 H ₂ O	0.03 mol/dm ³
2'2-Bipyridyl	100 ppm
Cl-(NaCl)	1.2 mol/dm ³
pH(Adjusted by H ₂ SO ₄)	6.0
Bath Temp	60°C
Atmosphere	N ₂

Fig. 2 Effect of plating conditions on deposition rate.

counter electrodes, respectively. At potentials less negative than -0.25 V, the anodic current of Fe(II) ion oxidation was observed, while the cathodic current of Cu(II) ion reduction was observed at potentials less positive than $+0.23$ V. The mixed potential obtained from both polarization curves was about $+0.12$ V. This value was approximately equal to the rest potential of Cu electrode in the plating bath, suggesting the possibility of the electroless plating of Cu using Fe(II) complex as a reducing agent.

At first, the plating bath composed of metal ions and complexing agent was unstable and fine Cu particles were precipitated in the bath. Chloride ion concentration was found to be an important factor that controls the Cu particle formation. Deposition rates by changing pH and bath temperature were measured. These results are shown in Fig. 2. Although

deposition rate increased with an increase in pH, Cu fine particles were generated and the stability of the bath decreased at pH greater than 6.5. As the bath temperature increased, the deposition rate increased up to 50°C , but particles were formed in the bath. The optimal bath conditions were pH 6.0 and 60°C . Comparing the surface of samples obtained by the conventional method using formaldehyde and that using Co(II) complex as a reducing agent³⁾, the surface of the sample obtained from this study showed polycrystalline structure and had many block-like particles. By adding 100 ppm of polyethylene glycol to the bath, this block-like structure was reduced and the surface became smooth. Deposition thickness of about 1.7 micrometers was obtained after 3 hours of plating under optimal conditions.

4. Conclusion

It is confirmed that the electroless Cu plating using Fe(II) complex as a reducing agent is possible. Particle formation in the bath could be avoided by adding chloride ion. Under optimal conditions, over 1 micrometer of deposit with smooth surface was obtained after 3 hours of plating. The lifetime of this bath was not very long. Although further improvement is required in order to put this method into practical use, it is expected that electroless Cu plating using Fe(II) complex as a reducing agent is promising process.

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