

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

Michinari Sone, Koichi Kobayakawa, and Yuichi Sato
 Department of Applied Chemistry, Faculty of Engineering,
 Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku,
 Yokohama 221-8686, Japan

Introduction : Cu dual damascene in semiconductor devices is currently formed by dry processes such as PVD and CVD. Wet process like electroplating and electroless plating are, in contrast, used in the formation of Cu wiring. Although the electroless plating method is known to be an effective method to obtain fine wiring in particular, 1 mol hydrogen gas is generated during 1 mol Cu deposition and voids are generated in wiring when electroless Cu plating is now applied to fine wiring. Therefore, a Cu plating method using Co (II)/Co (III) as a reducing agent to avoid the generation of performing gas is proposed¹⁾. 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.

Experimental : Polarization curves for Fe²⁺ oxidation and Cu²⁺ reduction were measured to ascertain the possibility of performing copper electroless plating using Fe²⁺ ions. Copper substrate (1 cm²), an Ag/AgCl electrode (3.3 M KCl) and a Pt electrode (2 cm²) were used as the working, reference and counter electrode, respectively. The Cu substrate (10 x 10 x 0.3 mm) was immersed in a plating bath for a predetermined time and deposition speed was calculated from the weight gain. The surface of the deposited film was observed with SEM.

Results and Discussion : Anodic and cathodic polarization curves are shown in Fig.1. In the potential 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 in the potential less positive than + 0.23 V. The mixed potential obtained from both polarization curves was about + 0.12 V. This value is approximately equal to the rest potential in the plating bath solution, which suggests the possibility of performing Cu electroless plating using Fe²⁺ as a reducing agent. Cu plating proved possible. The plating speed and stability of plating bath were examined by changing the complexing agent and chloride concentration. Chloride ion concentration was found to be an important factor that controls the formation of fine Cu particles. Fig.2 shows the influence of pH and bath temperature on the Cu deposition speed. The amount of Cu deposition increased with plating time and depended on the pH and temperature of the bath. The deposits contained about 0.1 wt% Fe. Numerous experimental results produced the bath composition and plating conditions shown in Table 1.

References : 1) A. Vaskelis, E. Norkus, *Electrochimica Acta*, **44**, 3667-3677 (1999).

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

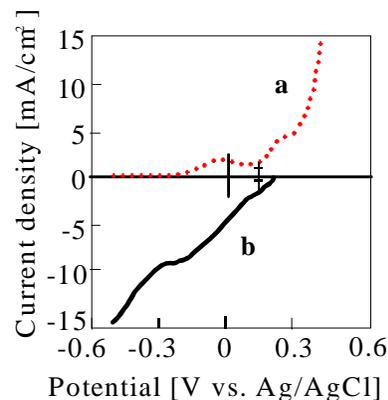


Fig. 1 Fe²⁺anodic (a) and Cu²⁺cathodic (b) polarization curves of Cu electrode at 60 °C . Scan rate: 10 mV/sec.

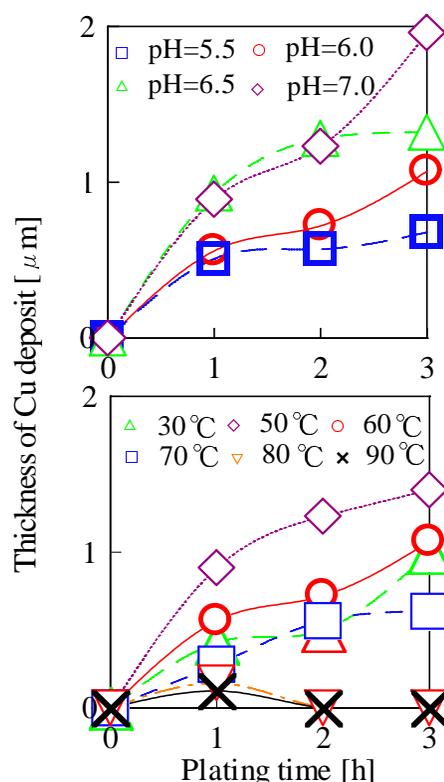


Fig. 2 Effect of plating conditions on Cu deposition rate.