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Copper Bottom-up Deposition by Breakdown of PEG-Cl Inhibition

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Copper bottom-up deposition in 200 nm trenches by an acid-copper sulfate with only two additives [poly(ethylene glycol) (PEG) and Cl^-] is achieved. The inhibiting effect of electrodeposition by PEG is strongly related to Cl^- concentration. Secondary-ion mass spectroscopy measurements show that Cl^- is consumed in the electroplating process. The explanation of bottom-up deposition realized in copper superfilling, in which the decrease of Cl^- concentration causes rapid electrodeposition on trench bottoms, is verified experimentally.
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Copper on-chip interconnection is a current topic in the semiconductor industry. It became possible by copper superfilling[1] of trenches and vias in the damascene process. The superfilling is achieved by the presence of additives in the acid-copper sulfate electroplating bath. Many studies based on the diffusion-adsorption theory[2-11] have been carried out to understand the superfilling process. In those studies, it is assumed that additives inhibit the electrodeposition and are consumed on the plating surface. Due to the diffusional limitation, concentration of additives is decreased in the trench bottom and rapid deposition from the bottom occurs. However, the mole fraction of additive-derived impurities (C, O, S, Cl) measured by secondary-ion mass spectroscopy (SIMS) is smaller than the expected value from the diffusion-adsorption based theories.[12-14] So far, poly(ethylene glycol) (PEG, Mw about 3000) is considered a main inhibitor. The expected diffusion coefficient of the inhibitor is the same order of Cu^{2+} [8] and it is large for the size of the additives. Then, recent studies showed interest in catalytic additives like bis(3-sulfopropyl)disulfide (SPS) or 3-mercapto-1-propanesulfonate (MPSA).[15-17] In this study, to understand the superfilling mechanism, the inhibition by PEG and Cl^- is carefully investigated by measuring overpotential of an electrode being electroplated.

Overpotential Measurement

The cell for the electroplating experiments is a 500 mL beaker submerged in a water bath at 298 ± 0.5 K. The working electrode (WE) is a polished platinum disk in an epoxy resin. To assume a one-dimensional flow of current, ions, and additives, the WE is covered by a resin plate which has a cylindrical hole ($\phi = 3$ mm). The WE is preplated with copper at 200 A/m^2 for 20 s in the electrolyte of interest before each experiment. After preplating, the electrolyte of the bath is spit out from a thin tube connected to a pump for supplying fresh electrolyte in the hole. To avoid contamination of Cl^-, a copper plate in the cover resin is used as a reference electrode which is expected to work as a stable $Cu/CuSO_4$ electrode. The composition of the standard electrolyte is 225 g/L $CuSO_4 \cdot 5H_2O$ and 55 g/L H_2SO_4. All electrodes are connected to a potentiostat (Hokuto Denko, HABF501) and constant current is applied for copper electrodeposition on the WE.

Figure 1 shows the time variation of overpotential when Cl^- is added to a 3000 Mw PEG containing electroplating bath. The concentration of PEG is constant at 300 mg/L. Applied current density is 50 A/m^2. Figure 2 shows the same result as Fig. 1 at a different current density of 200 A/m^2. Healy and Pletcher showed that the inhibition weakens with time using 10,000 Mw PEG in potentiostatic experiments.[18] Significant decreases of overpotential, which means that the inhibition weakens with time, are also observed with 3000 Mw PEG and the overpotential is sensitive to Cl^- concentration.

Lines A and C in Fig. 1 and 2 show gradual decreases of inhibition with time and they are reasonable for the diffusion-adsorption theory. Experiments are performed in approximately one-dimensional flow and the diffusional supply of PEG is limited. Therefore, it is expected that the decrease of inhibition along time can be observed at a larger current density from the diffusion-adsorption based theories. However, when enough Cl^- is supplied, the inhibition effect keeps constant with time as shown by lines B and D and a larger amount of Cl^- is needed for inhibition at higher current density. It is reasonable to suppose that the decrease of Cl^- concentration causes these decreases of overpotential shown by lines A and C.

Decrease of Chloride Ion

As a cause of Cl^- decrease, migration and consumption are considered in this section. Let us roughly estimate the concentration distribution by migration. Although the plating bath is a highly concentrated solution, the following one-dimensional Nernst-Planck

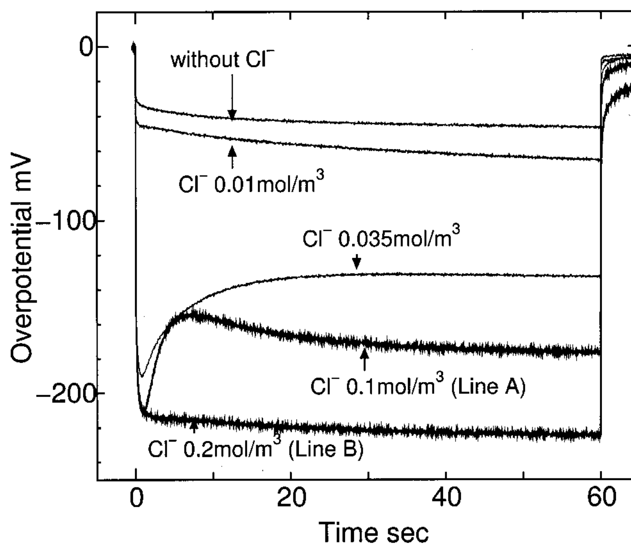

Figure 1. Time variation of overpotential at 50 A/m^2. Cl^- is added to a PEG (300 mg/L) containing electrolyte bath.

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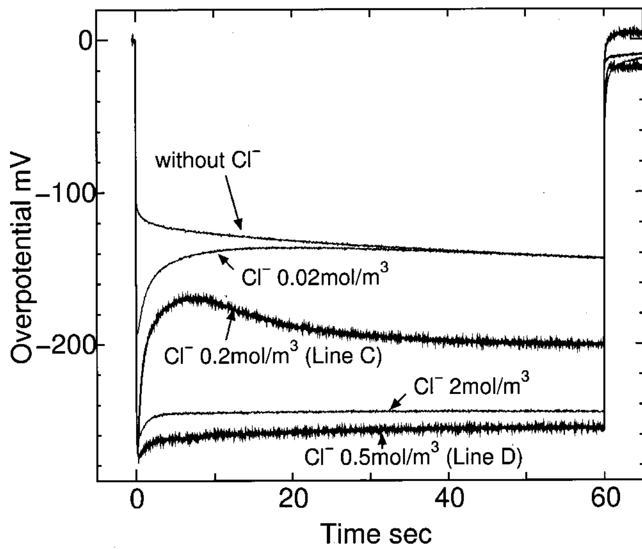

Figure 2. Same experiment as Fig. 1. Current density is 200 A/m^2.

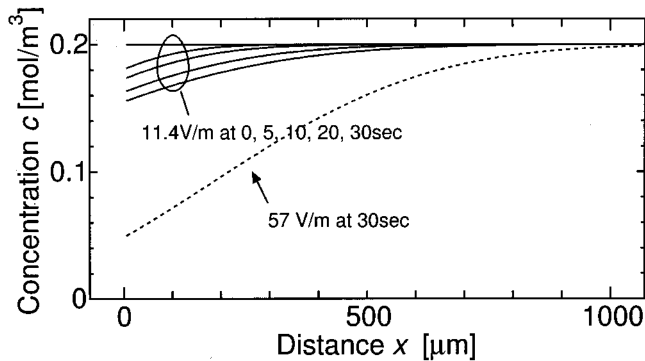

Figure 3. Estimation of Cl^- concentration distribution by migration. Supposing a current density of 200 A/m^2, $\partial\phi/\partial x = 11.4$ V/m is calculated. Cl^- migrates from cathode and the concentration decreases near the cathode surface.

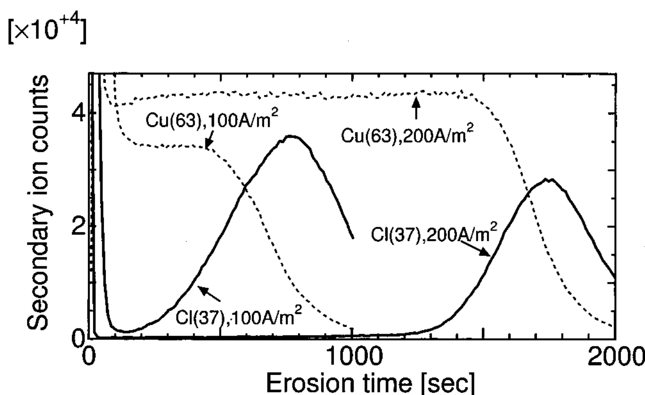

Figure 4. Cl depth profile by SIMS. Cl (mass no. 37) is traced. Copper is electroplated for 30 s on platinum substrate in a standard bath with Cl^- of 0.2 mol/m^3. The Cl counts are large at initial period of electroplating.

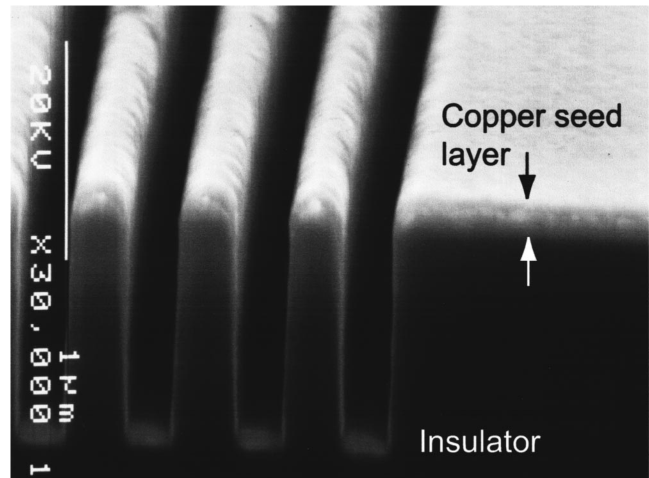

Figure 5. SEM micrograph of the trench cross section before electroplating. Copper seed layer on the top surface is about 100 nm thick. The specimen is inclined 10°.

equation and equation of material balance are used for simplicity. The potential gradient is assumed to be constant over time and space

$$f = -D\frac{\partial c}{\partial x} - \frac{zFDc}{RT}\frac{\partial \phi}{\partial x} \quad [1]$$

$$\frac{\partial c}{\partial t} = -\frac{\partial f}{\partial x} \quad [2]$$

where f is flux of ion, D is diffusion coefficient, c is concentration, z is charge number, F is the Faraday constant, R is the gas constant, T is temperature, ϕ is electric potential, and x is the distance from the electrode. Finite difference method is used for calculating spatial derivatives and Runge-Kutta method is used for time progress.

Figure 3 shows the numerical results. As the diffusion coefficient of Cl^-, 2.03×10^{-9} m^2/s is used. Conductivity of the plating bath is 5.7×10^{-2} Ω m and 11.4 V/m is chosen for the potential gradient, $\partial\phi/\partial x$, supposing 200 A/m^2. The potential gradient may be raised due to nonuniform ion distribution, a result from large potential gradient of 57 V/m is shown, for example. The migration causes

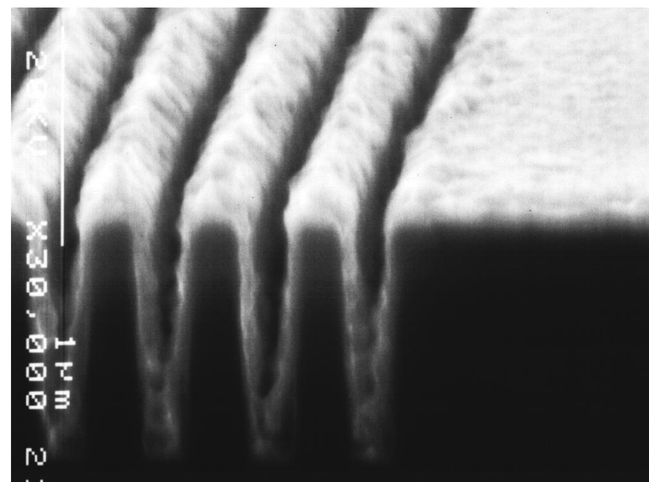

Figure 6. SEM micrograph of the trench cross section. Copper is electrodeposited by applying 50 A/m^2 for 15 s in a standard electrolyte bath with PEG 300 mg/L and Cl^- 0.2 mol/m^3. Slight bottom-up deposition can be seen. The specimen is inclined 10°.

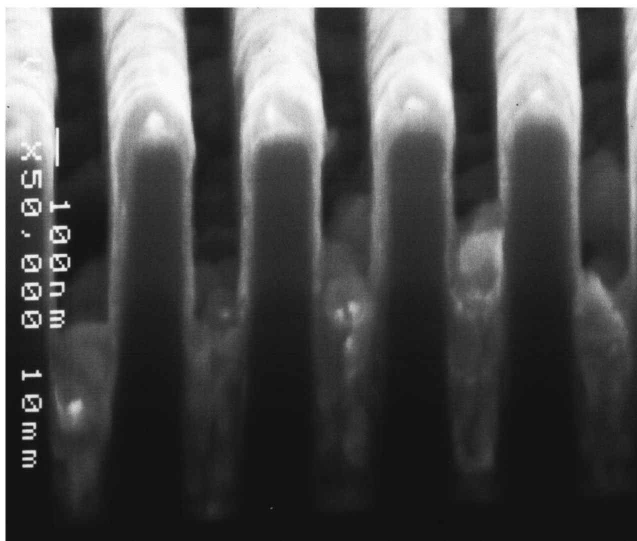

Figure 7. SEM micrograph of the trench cross section. Copper is electrodeposited by applying 100 A/m^2 for 10 s in a standard electrolyte bath with PEG 300 mg/L and Cl^- 0.2 mol/m^3. Obvious bottom-up deposition can be seen. The specimen is inclined 10° and the bottom-up deposition is realized along the trench direction.

the Cl^- decrease on the electrode surface to some extent, however, the effect is not enough to explain the data shown in Fig. 1 and 2.

To verify the consumption of Cl^-, depth profiles of Cl concentration in electroplated copper on a platinum electrode are measured by SIMS (Cameca, IMS 4f). Cl (mass no. 37) and Cu (mass no. 63) are traced as shown in Fig. 4. Irradiation area of Cs^+ beam is a 250×250 μm square.

Electroplating is carried out in a standard electrolyte bath with Cl^- of 0.2 mol/m^3 for 30 s. Disturbances at initial period (until 100 s) in erosion time may be due to the contamination after the plating. The dull curve is caused by the averaging of the large irradiation area. Cl background level observed with the copper which is electroplated in non-Cl bath is 100. The interfaces between the platinum substrate and the plated copper appear around 700 s (100 A/m^2) and 1600 s (200 A/m^2) in erosion time.

Although the absolute amount of Cl concentration cannot be obtained by the SIMS measurements, it is obvious that Cl is absorbed into the electroplated copper and Cl^- is consumed during the electroplating. The Cl profile, in which the detection counts are high around the copper interface with substrate and the counts decrease toward the surface, shows the possibility of the significant decrease of Cl^- near the WE surface during electroplating. This assumption matches the overpotential measurements shown in Fig. 1 and 2.

Fill Experiment

If the Cl^- is consumed on the plating surface, it is reasonable to suppose that the decrease of Cl^- in the trench bottom is larger than the decrease on the top surface because of the diffusional limitation. The inhibition weakens at the trench bottoms, then rapid electrodeposition at the trench bottom can occur. This effect may be a dominant mechanism of the superfilling. Also, this mechanism can be interpreted as a "Cl^- consumption model."

To verify this assumption, filling experiments were carried out. The additive concentrations (PEG 300 mg/L, Cl^- 0.2 mol/m^3) and current density (50-100 A/m^2, based on the superficial area) are used. Figures 5-8 show the scanning electron micrographs (SEM) of trench cross sections before and after electroplating. Slight bottom-up deposition can be seen in Fig. 6, while obvious bottom-up deposition can be seen in Fig. 7. It is supposed that the larger current density and narrower trench width produce the larger concentration difference of Cl^- between the top surface and trench bottoms, then obvious bottom-up deposition is realized.

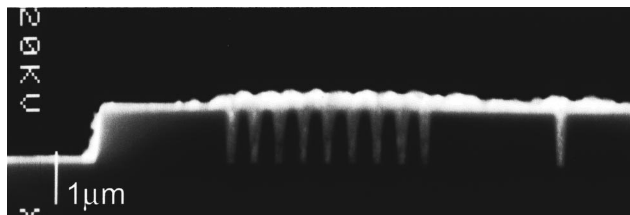

Figure 8. SEM micrograph of the wide area cross section. Copper is electrodeposited by applying 100 A/m^2 for 20 s in a standard electrolyte bath with PEG 300 mg/L and Cl^- 0.2 mol/m^3. Slight hump can be seen above the tight trench formation.

The breakdowns occur mainly from the trench bottom areas, however, there are some trenches where no deposition can be seen. It can be assumed that the inhibition effect is not uniform over space because the seed layer is not perfectly uniform as shown in Fig. 5 and the size of PEG also varies in some extent. It is reasonable to suppose that the breakdown occurs in some trenches and in some trenches the breakdown does not occur. Once the inhibition breaks, the following rapid copper deposition produces a significant decrease of Cl^- and this decrease of Cl^- weakens the neighboring inhibition. Therefore, the unstable localized deposition growth happens, while no deposition can be seen in some areas where the inhibition breakdown does not occur at initial period of electroplating. Figure 8 shows this unstable deposition growth. A slight hump can be seen above the tight trench formation. The large amount of deposition can be seen on the flat surface on the right side of the tight trench formation, although no obvious deposition can be seen on the flat surface on the left side of the tight trench formation.

Conclusion

Inhibition of copper electrodeposition by PEG and Cl^- was carefully investigated and it was found that Cl^- concentration strongly affects the inhibition in the PEG-containing electrolyte bath. An explanation of bottom-up deposition realized in the copper superfilling, in which the decrease of Cl^- in the trenches by consumption causes rapid deposition on trench bottoms, was proposed and was verified by SIMS measurements and filling experiments. Further quantitative studies are needed to understand superfilling with other additives.

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