



Bottom-Up Fill for Submicrometer Copper Via Holes of ULSIs by Electroless Plating

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The bottom-up fill of copper in fine via holes is reported in electroless copper plating with the addition of bis(3-sulfopropyl) disulfide (SPS). When the concentration of SPS in the plating bath was varied from 0.05 to 0.5 mg/L with a plating time of 10 min, the ratio of the Cu thickness at the bottom of the hole (T_b) to that at the surface (T_s), called the bottom-up ratio, increased from 1.05 to 2.8 for a \varnothing 1.0 μm hole. The bottom-up ratio increases with SPS concentration and decreases with an increase in hole diameter. X-ray diffraction structure analyses and cross-sectional transmission electron microscopy observations indicated that the grain size of Cu film was reduced by the SPS addition, but Cu(111) texture was enhanced by the SPS addition. Bottom-up fill may be attributed to a higher SPS concentration at the surface than at the bottom of the holes due to SPS incorporation in the Cu film and diffusion-limited flux of SPS molecules into fine holes.

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Copper (Cu) is used widely as an interconnection metal in ultralarge-scale integration (ULSI) circuits due to its lower resistivity and superior resistance against electromigration compared to conventional aluminum alloys. The present damascene copper interconnections are fabricated by electroplating on a sputtered Cu seed layer. To produce void-free and seamless fill for high-aspect-ratio trenches and via holes, superfill or bottom-up fill, in which the deposition rate at the bottom of the hole is higher than at the surface, is necessary. Cu electroplating baths containing additives, such as chloride ion, polyethylene glycol (PEG), bis(3-sulfopropyl) disulfide (SPS), 3-mercaptopropanesulfonate (MPSA), or Janus Green B (JGB), have yielded desirable plating characteristics.¹⁻⁸ Inhibition to Cu deposition in the Cl-PEG-SPS system is due primarily to the combination of PEG and chloride ions,²⁻⁵ with acceleration attributed to SPS. However, a major premise of the superfill deposition of electroplating is a continuous sputtered Cu seed layer. Because a shrinkage in dimensions occurs for next generation interconnections, forming a continuous sputtered Cu film on the sidewalls of fine via holes becomes more difficult as sputtering suffers from poor step coverage. Consequently, copper electroless plating and chemical vapor deposition (CVD) are the most promising processes for the formation of a seed layer for electroplating.⁹⁻¹⁵ Bottom-up filling of submicrometer features by iodine-catalyzed CVD was reported by Shim *et al.*,⁹ Hwang and Lee,¹⁰ and Josell *et al.*,¹¹ but adhesion between the copper film and the barrier metal layer was poor and the deposition rate was slow. Copper electroless plating, which does not require a sputtered Cu seed layer, is an efficient means of filling high aspect ratio holes and has become increasingly important.¹²⁻¹⁵ However, when the hole diameter is less than 70 nm, filling the high-aspect-ratio hole with normal electroless plating is difficult.

Many studies report bottom-up fill of Cu in electroplating baths using additives, but few reports about bottom-up fill of Cu in electroless plating solutions have been published. Lopatin *et al.* reported the deposition of a thicker Cu film at the bottom corner of submicrometer trenches than at the top opening when surfactant Triton and RE 610 were added to an electroless Cu plating bath.¹⁶ We investigated Pd catalysis layer formation by the ionized cluster beam (ICB) method, which can provide highly directional deposition suitable for high aspect holes, and found that the adhesion between electroless plated Cu film and a TaN barrier layer was able to endure chemical mechanical polishing (CMP) when the thickness of the ICB-Pd was 1 nm.¹⁷⁻²⁰ Further, we have found a bottom-up fill of Cu in fine holes by the addition of SPS to electroless plating bath with the use of ICB-Pd.^{21,22}

In this report, the hole-filling characteristics upon addition of SPS were evaluated in detail by cross-sectional scanning electron microscopy (SEM), and the effects of SPS concentration on bottom-up fill ability, and fundamental film properties such as contaminant level, crystal texture, and surface morphology were investigated.

Experimental

ICB-Pd layers with a thickness of 1 or 2 nm were deposited on the surface of three types of TaN/SiO₂/Si substrates, hole patterns (diameter, 0.31-1.0 μm ; depth, 1.5 μm) for investigating filling via-hole; trench patterns (length, 100 μm ; width, 0.21-100 μm ; depth, 0.3 μm) for electrical resistivity measurement; and blankets for measurement of the deposition rate of electroless plating with SPS concentration. The thickness of the Pd layer was determined by a quartz microbalance placed on the substrate surface. Prior to electroless copper plating, all substrates were cleaned by ultrasonication in acetone at room temperature for 10 min.

The composition of the electroless copper plating solution was CuSO₄ · 5H₂O (6.6 g/L), C₁₀H₁₆N₂O₈ (EDTA; 70.0 g/L), glyoxylic acid (18.0 g/L) as a reducing agent, 2,2'-dipyridine (0.04 g/L) as stabilizer, polyethylene glycol (4000 M_w, 0.5 g/L) as the surface activator. The pH of the plating bath was adjusted to approximately 12.5 using tetramethylammonium hydroxide (TMAH) and the bath temperature was maintained at 70°C.

The interfacial structure and morphology of samples were characterized by field-emission scanning electron microscopy (FE-SEM) and field-emission transmission electron microscopy (FE-TEM). All SEM and TEM samples were prepared by focused ion beam (FIB). To protect the surface of the Cu film for etching during FIB cutting, a fine film of epoxy resin was coated on the surface of Cu by spin

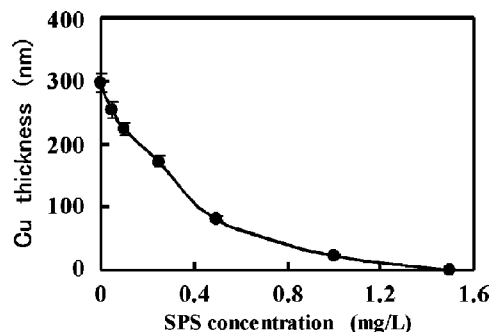


Figure 1. Dependence of SPS concentration on Cu deposition rate. Plating time, 15 min; SPS concentration, 0.5 mg/L.

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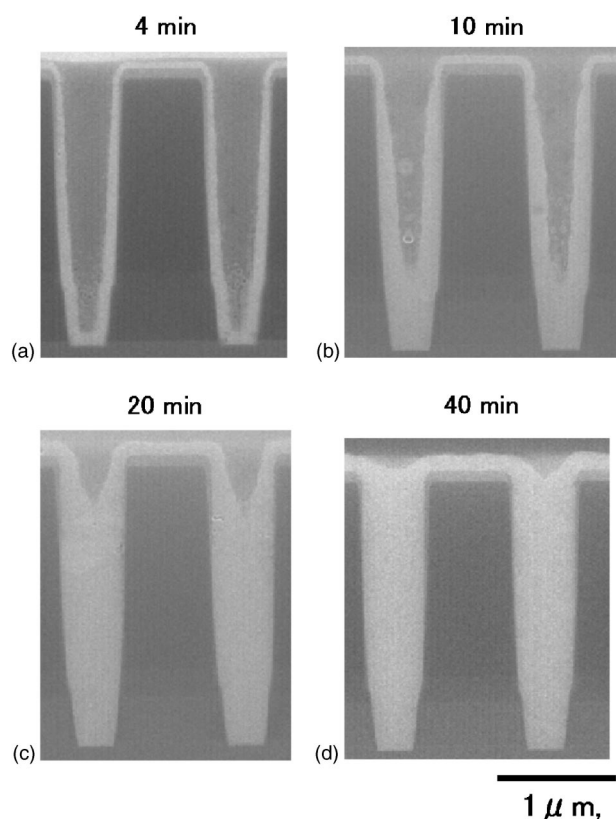


Figure 2. Cross-sectional SEM images of holes with plating time. Hole diameter, 0.5 μm ; hole depth, 2.3 μm ; SPS concentration, 0.5 mg/L.

coating. The crystalline structures of electroless plated Cu film were measured by an X-ray diffractometer (XRD, M03XHF22 MacScience Company Ltd) using θ - 2θ scan with a Cu $K\alpha$ source working at 45 kV and 35 mA.

Results and Discussion

The effects of additives, such as chloride (Cl^-), thiourea, benzotriazol, and SPS, on the deposition rate of electroless Cu plating were examined. The deposition rate decreased on addition of SPS or thiourea, but bottom-up filling capability appeared only on addition of SPS. A plating temperature of 70°C and plating time of 15 min were used to investigate the deposited Cu thickness as a function of SPS concentration; results are shown in Fig. 1. Cu thickness decreased with an increase in SPS concentration, and electroless plated Cu was not deposited when the SPS concentration in the plating bath was greater than 1.5 mg/L. although SPS in the electroplating bath acted as an accelerator for bottom-up fill Cu, it was added into the electroless plating bath as an inhibitor.

The dependence of plating time on hole-filling characteristics was investigated in the plating bath containing 0.5 mg/L SPS; cross-sectional SEM images of holes for different plating times are shown in Fig. 2. Although Cu deposition rates at the surface and bottom of the holes were inhibited by addition of SPS, the level of inhibition of SPS on the surface and bottom of the hole was different. Inhibition on the surface was greater than that on the bottom of the holes. At a plating time of 4 min, Cu thickness at the surface (T_s) and at the bottom of hole (T_b) were approximately 32 and 129 nm, respectively; when the plating time was 10 min, T_s and T_b became 87 and 709 nm, respectively (see Fig. 2a and b). These results indicate that the Cu deposition rate at the bottom of the holes was higher than the rate on the surface. The holes were almost filled with Cu at a plating time of 20 min (Fig. 2c), which suggests that bottom-up filling with electroless plated Cu could be obtained by addition of SPS into the electroless Cu plating solution.

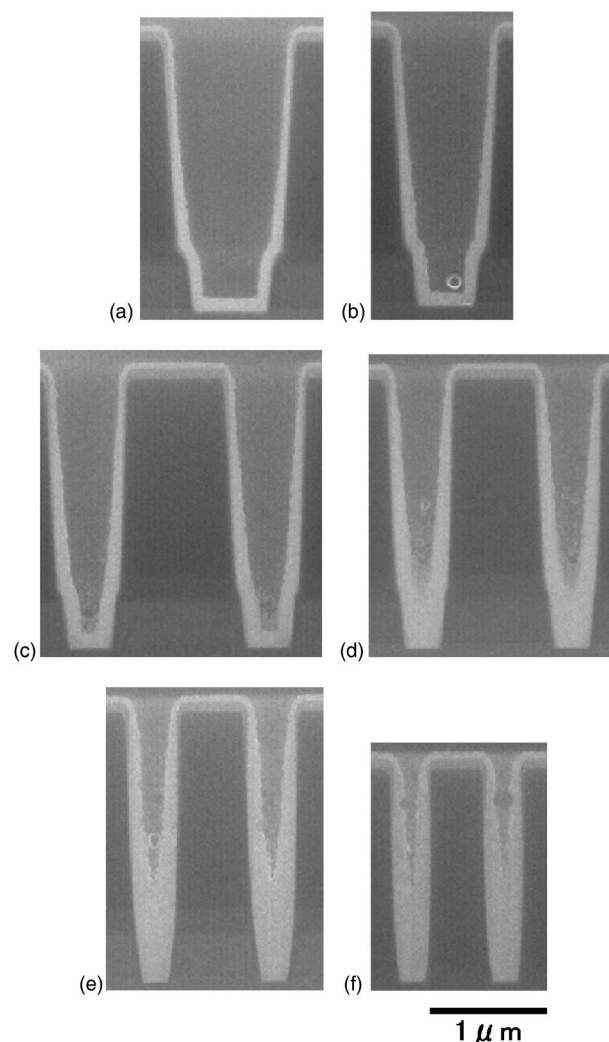


Figure 3. Cross-sectional SEM images of holes with various diameters deposited by electroless plated Cu. SPS concentration, 0.5 mg/L; plating time, 10 min. Hole diameter: (a) 1.0, (b) 0.8, (c) 0.60, (d) 0.5, (e) 0.40, and (f) 0.31 μm .

Experiments were conducted with holes having a diameter from 0.31 to 1.0 μm and a depth of 2.3 μm . The cross-sectional SEM images of holes with different diameters are shown in Fig. 3 for conditions of 0.5 mg/L SPS in the plating bath and a plating time of 10 min. For a 1.0 μm hole, T_b and T_s were 110 and 31 nm, respectively. For a 0.30 μm hole, T_b and T_s became 902 and 32.5 nm,

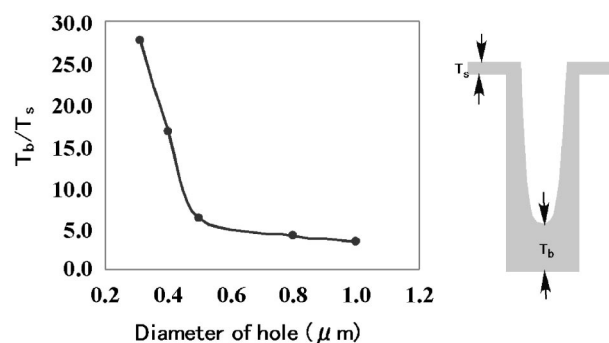


Figure 4. Dependence of bottom-up ratio: T_b/T_s , of electroless plated Cu on hole diameter. SPS concentration, 0.5 mg/L; plating time, 10 min.

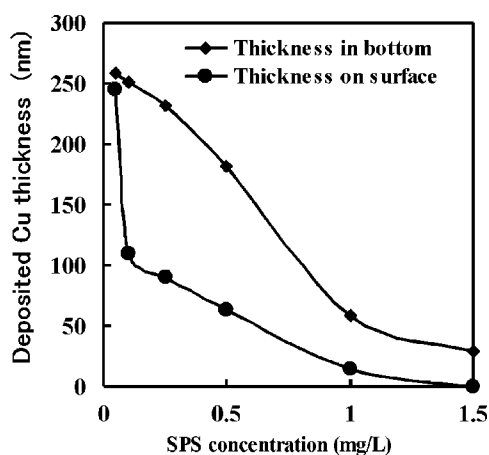


Figure 5. Dependence of Cu deposition thickness on SPS concentration at the surface (T_s) and bottom of the hole (T_b). Hole diameter, 1.0 μm ; hole depth, 2.3 μm ; plating time, 10 min.

respectively, indicating that the Cu deposition rate increased with a reduction in hole diameter. The dependence of bottom-up ratio on hole diameter is shown in Fig. 4. The bottom-up ratio increased slowly with a decrease in hole diameter from 1.0 to 0.5 μm . However, the bottom-up ratio increased rapidly with a decrease in hole diameter from 0.5 to 0.31 μm .

The effect of SPS concentration on bottom-up ratio was examined. Figure 5 shows the SPS concentration dependence on Cu thickness at the surface (T_s) and bottom of \varnothing 1.0 μm holes (T_b). With SPS concentration of 0.05 mg/L and plating time of 10 min, T_b and T_s were 259 and 245 nm, respectively, indicating that SPS concentration was too low to inhibit Cu deposition, resulting in conformal Cu deposition. With a SPS concentration of 0.1 mg/L and plating time of 10 min, T_b and T_s became 251 and 110 nm, respectively, indicating that the suppressive effect on the surface increased, but changed less than that at the bottom of the hole. At SPS concentrations greater than 1.0 mg/L, although the bottom-up ratio was high, Cu deposition rates both at the surface and bottom of the hole decreased beyond practical application. The dependence of the SPS concentration on the bottom-up ratio is shown in Fig. 6. When the SPS concentration increased from 0.05 to 0.1 mg/L, the bottom-up ratio increased from 1.04 to 2.30 and the via-hole-filling capability of electroless Cu changed from conformal de-

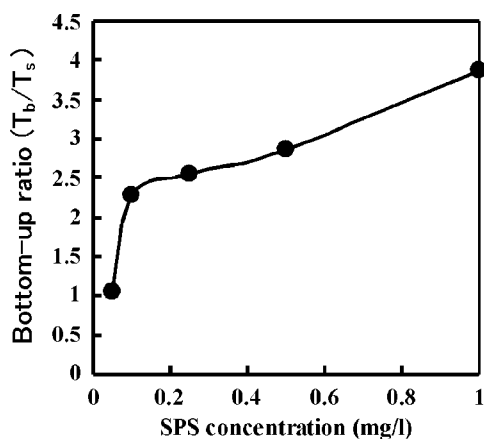


Figure 6. SPS concentration dependence of bottom-up ratio of electroless plated Cu deposition. Hole diameter, 1.0 μm ; hole depth, 2.3 μm ; plating time, 10 min.

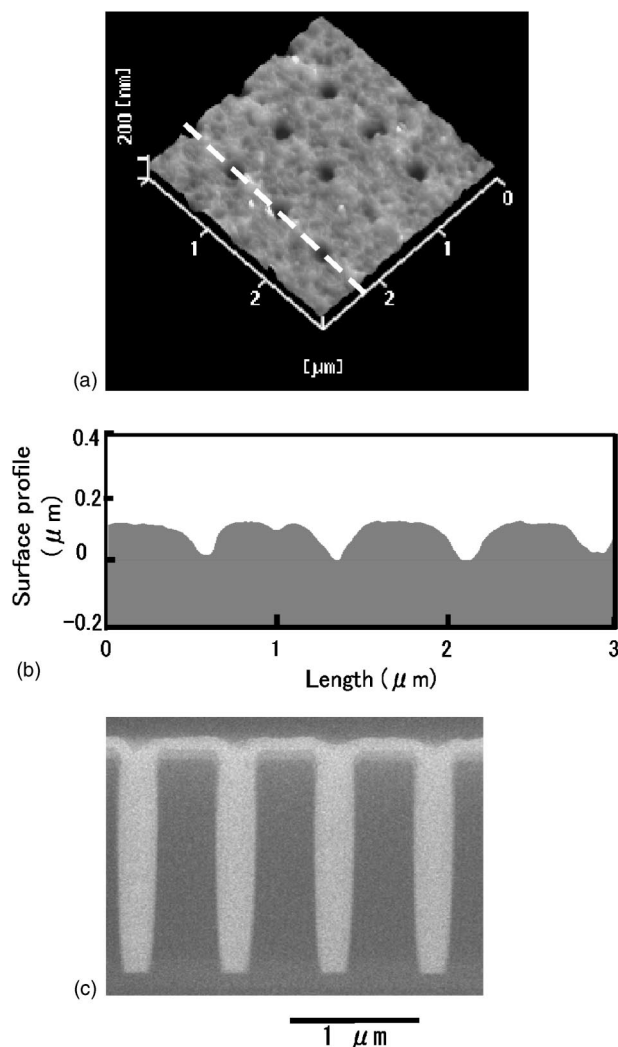


Figure 7. Surface roughness of electroless plated Cu filling in 0.31 μm holes. SPS concentration, 0.5 mg/L; plating time, 40 min. (a, top) AFM image, (b, middle) line profile of surface roughness, and (c, bottom) cross-sectional SEM image.

position to bottom-up filling. When the SPS concentration was greater than 0.10 mg/L, the bottom-up ratio increased with SPS concentration.

After bottom-up filling of Cu in fine holes during electroplating, Cu deposition at the hole was higher than at other areas, called an overgrowth phenomenon, which results in problems in the CMP process and increases fabrication cost. The overgrowth phenomenon was not found for bottom-up filling of Cu in holes during electroless plating. Cross-sectional scanning electron microscopy (SEM) and atomic force microscopy (AFM) images for 0.31 and 0.50 μm holes at an SPS concentration of 0.5 mg/L and plating time of 40 min are shown in Figs. 7 and 8, respectively. AFM images indicated a smooth surface of the Cu film except near the hole, with an average surface roughness (R_a) of 15.2 nm, which is comparable to electroless-plated Cu films without additives. Holes with a diameter of 310 or 500 nm were not filled completely by electroless plated Cu, and hollows were observed in the AFM images (see Figs. 7a and 8a). The depth of the hollows measured by a line profile of surface roughness at the center of the holes were 125 and 200 nm for 0.31 and 0.50 μm holes, respectively (see Figs. 7b and 8b). However, cross-sectional SEM images indicated that both 0.31 and 0.50 μm holes were filled by electroless plated Cu when T_b was greater than the depth of the hole (see Figs. 7c and

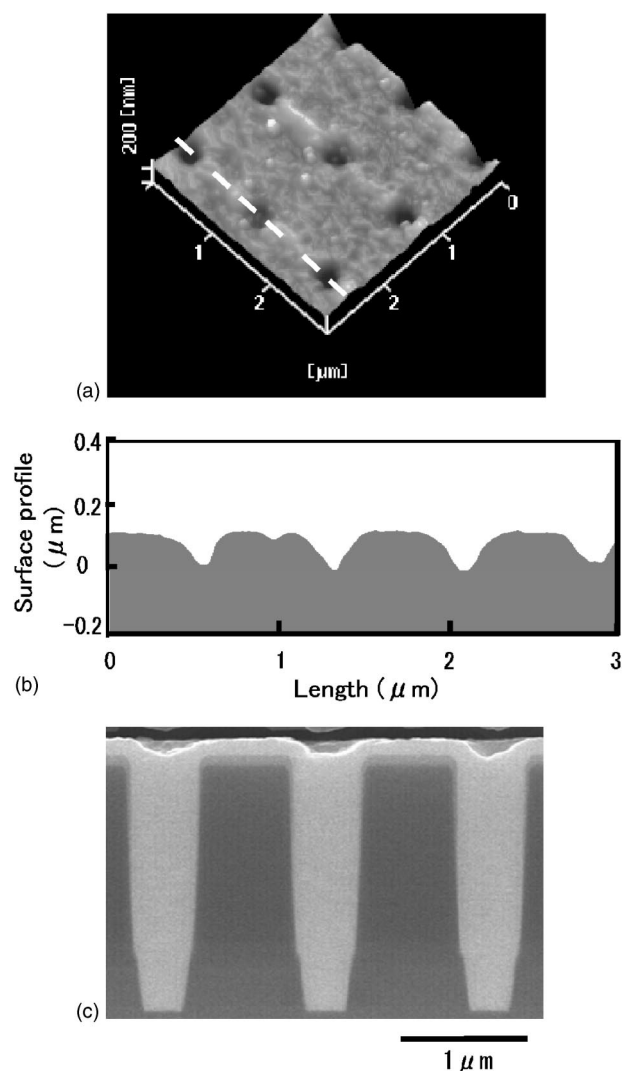


Figure 8. Surface roughness of electroless plated Cu filling in $0.50\ \mu\text{m}$ holes. SPS concentration, $0.5\ \text{mg/L}$; plating time, 40 min. (a, top) AFM image; (b, middle) line profile of surface roughness; (c, bottom) cross-sectional SEM image.

8c). Consequently, the overgrowth phenomenon did not occur during electroless plating with bottom-up fill Cu, which simplified the CMP process and reduced the cost. In contrast, fine holes could be filled completely by electroless Cu during bottom-up plating, but was difficult for holes with a diameter at the micrometer level, requiring two-step plating, one step involving SPS and another SPS-free.

The crystallography of electroless-plated Cu film deposited from the SPS plating solution was characterized by XRD and cross-sectional transmission electron microscopy (TEM). When the SPS concentration was $0.1\ \text{mg/L}$, the peak intensity ratio $I(111)/I(200)$ was 5.6, and the full-width at half-maximum (fwhm) of (111) for $0.8\ \mu\text{m}$ thick Cu film was 0.26° (see Fig. 9a). After annealing at 400°C under an N_2 atmosphere at $1.0\ \text{mTorr}$, the peak intensity ratio $I(111)/I(200)$ increased from 5.6 to 6.3, and the fwhm of (111) decreased from 0.26° to 0.24° . For electroless-plated Cu film without an SPS addition, the peak intensity ratio $I(111)/I(200)$ was 2.82 and fwhm of (111) for $1.5\ \mu\text{m}$ thick Cu film was 0.23° before annealing (see Fig. 9b). Plane TEM images (see Fig. 10) indicated that the average grain size was about $40\ \text{nm}$ for Cu film deposited from a $0.1\ \text{mg/L}$ SPS plating bath and was smaller than that deposited from an SPS-free plating bath (average grain size of $60\ \text{nm}$).

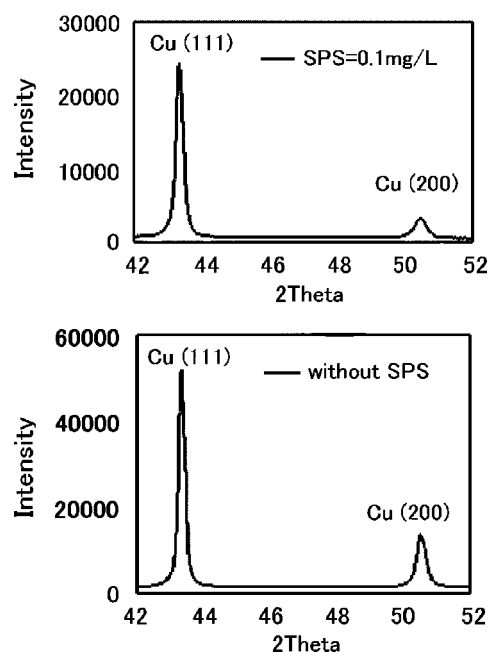


Figure 9. XRD patterns of electroless plated Cu films before annealing. (top) SPS concentration, $0.1\ \text{mg/L}$; (bottom) SPS-free bath.

Consequently, the crystallinity of electroless plated Cu film was reduced by addition of SPS, but peak intensity ratio $I(111)/I(200)$ was increased upon addition of SPS.

We propose a mechanism of bottom-up fill of Cu in an electroless Cu plating bath as follows (see Fig. 11). SPS acted as an inhibitor, which is attributed to SPS adsorption on the copper film surface, and reduced the active area of self-catalytic deposition of Cu. Although deposition rates at the bottom of the hole and at the substrate surface were the same initially, the deposition rate at the bottom of the hole increased faster than that at the substrate surface. Secondary ion mass spectroscopy (SIMS) analysis demonstrated that the SPS adsorbed on the Cu film became incorporated into the Cu film during plating, reducing the SPS concentration on the Cu surface.²³ The concentration of SPS in the plating bath was small (on the order of parts per million) compared to CuSO_4 and glyoxylic acid, and the Cu deposition rate was controlled by the SPS concentration at the Cu surface. Because diffusion of SPS from the plating bath to the bottom of the hole was slower than that to the substrate surface, the SPS concentration at the bottom of the hole was lower than that at the substrate surface, resulting in a higher Cu deposition than at the substrate surface. Experimental results indicated that the bottom-up ratio of Cu deposition increased with an increase in SPS concentration and with a decrease in hole diameter, suggesting that the difference in SPS concentration at the surface of the substrate and at the bottom of the hole increased with a reduction in hole diameter, which is in agreement with the proposed mechanism. Thiourea also inhibited electroless-plated Cu deposition, but did not exhibit bottom-up deposition behavior. The molecular weight of thiourea is smaller than that of SPS, thus, the diffusion rate of thiourea in the plating bath is faster than that of SPS and the concentration of thiourea on the surface of substrate is not as high as that at the bottom of the hole.

Conclusions

Bottom-up Cu fill in via holes succeeds in electroless copper plating bath with the addition of SPS. When the concentration of SPS in the plating bath was varied from 0.05 to $0.5\ \text{mg/L}$ with a plating time of 10 min, the bottom-up ratio of Cu deposition increased from 1.05 to 2.8 for a $\varnothing 1.0\ \mu\text{m}$ hole. Also the bottom-up ratio of Cu deposition increased with SPS concentration and a re-

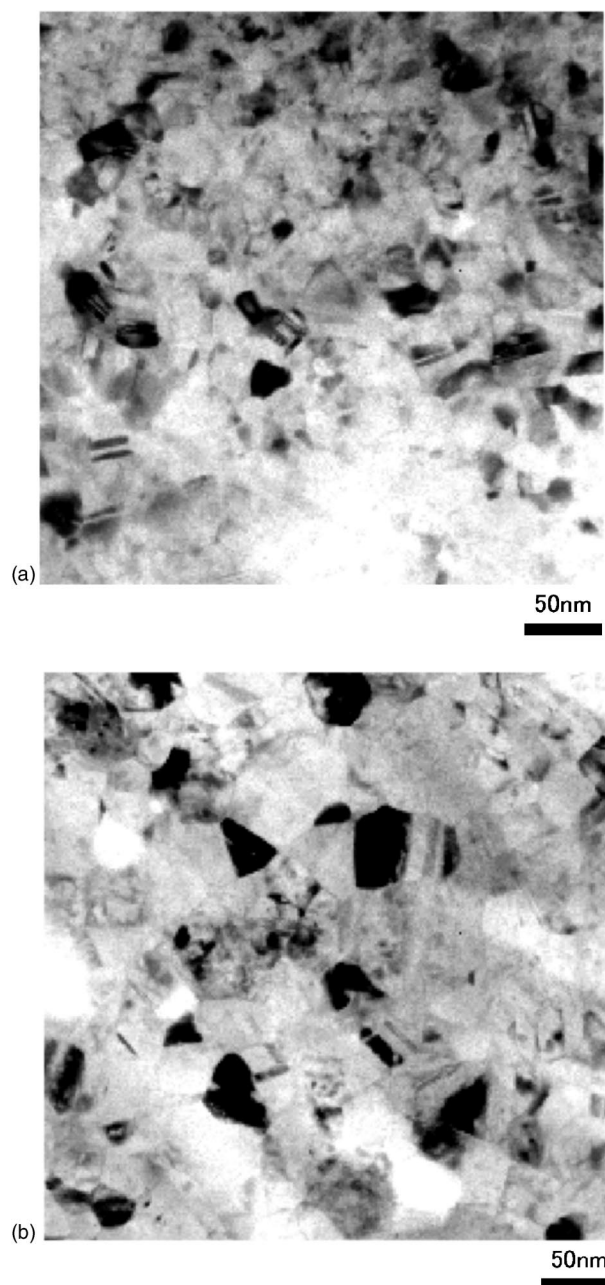


Figure 10. TEM images for copper film deposited by electroless plating. (a) SPS concentration, 0.1 mg/L; (b) SPS-free bath. No anneal.

duction in hole diameter, by which the high-aspect via-hole was able to be filled easily. After electroless plating with bottom-up fill Cu, the overgrowth phenomenon did not occur on the surface of the Cu film, which simplified the CMP process and reduced the cost. Consequently, this technology is an important candidate to replace the electroplating technology for filling Cu into via holes of ULSIs. However, for micrometer level diameter holes, it was difficult to fill with Cu completely. Two-step plating, one step involving SPS and another SPS-free, are being investigated. On another hand, the effect of SPS concentration on electrical resistivity of damascene Cu interconnections is also being studied.

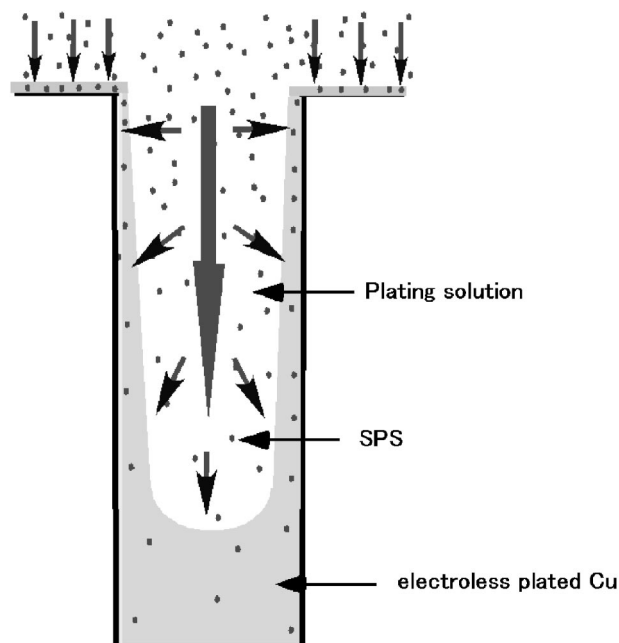


Figure 11. Model of SPS diffusion in electroless Cu plating for bottom-up fill of holes.

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