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Improvement of Electrolessly Gap-Filled Cu Using 2,2′-Dipyridyl and Bis-(3-sulfopropyl)-disulfide (SPS)

Chang Hwa Lee, Sang Chul Lee, and Jae Jeong Kim[z]

Research Center for Energy Conversion and Storage, School of Chemical Engineering, College of Engineering, Seoul National University, Seoul, 151-742, Korea

The use of bis(3-sulfopropyl) disulfide (SPS) in Cu electroless deposition resulted in Cu bottom-up filling. However, the high accelerating effect of SPS led to a poor electrical property of the film and generated many voids in the film by increasing the surface roughness and causing unstable deposition behavior. The addition of 2,2′-dipyridyl together with SPS substantially improved the film quality of the gap-filled Cu maintaining the bottom-up filling behavior. It lowered the film resistivity by approximately 23% and enhanced the crystallinity. No voids were detected in the as-deposited Cu even after annealing.
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Recently, as feature sizes in ultralarge scale integrated circuits (ULSIs) shrink faster, electroless deposition for Cu interconnect processes has been vigorously researched.[1-4] Compared to physical vapor deposition (PVD) and chemical vapor deposition (CVD), the Cu electroless deposition has the advantage of superior step coverage, thin, and uniform deposition on large and insulating substrates, which is applicable to the repairing process for PVD[5,6] or CVD Cu seeds[7] and formation of a seed layer for electrodeposition.[8,9] Currently, defect-free Cu filling using only electroless deposition in vias or trenches without sequential electrodeposition is being studied.[10,11] We achieved electroless Cu filling in submicrometer-patterned TiN wafers without additives by controlling the variables.[12] Shingubara *et al.* observed Cu electroless bottom-up filling using bis(3-sulfopropyl) disulfide (SPS), a well-known accelerator in electrodeposition, with polyethylene glycol (PEG) in submicrometer via holes where the ionized cluster beam (ICB)-Pd layer was formed.[13,14]

In a previous study, addition of only SPS resulted in bottom-up filling following Pd catalysts activation by wet processes. Depending on the concentration, SPS has been found to act either as an accelerator or an inhibitor in Cu electroless deposition.[15] However, in Cu electroless deposition, the incorporation of oxygen causes an increase in the resistivity, and unstable deposition behavior by the use of the accelerator causes a rough surface and declining film properties. To improve the film properties when SPS was added, stabilizers or surfactants that are well-known in Cu electroless deposition, such as RE610,[1] polyethylene glycol (PEG),[11] 2, 2′-dipyridyl,[16-18] and Triton-X,[19] can be applied. 2,2′-Dipyridyl is one of the effective additives for restraint of oxygen incorporation in the film and electrolyte stabilization in Cu electroless deposition.

This paper discusses the Cu bottom-up filling carried out by the two-step method consisting first of the seed layer formation and gap-filling through electroless deposition and the effect of 2, 2′-dipyridyl combined with SPS on the quality of the filled Cu in the second step of gap-filling.

Experimental

The substrates used in the experiments for analyzing the filling profiles were (100)-oriented p-type Si trench-type patterned wafers (aspect ratio, 2.5; width of the bottom, 400 nm) covered with TiN (10 nm)/Ti (15 nm) as a diffusion barrier layer. To investigate the characteristics of the film, blanket wafers deposited with 120 nm of PVD Cu seed layers on the barrier layer were used.

The blanket wafer was prepared after removing the native Cu oxide on the PVD Cu seed layer with 1:200 NH_4OH for 30 s.[20] In the seed layer formation on a patterned wafer, the surface was first activated by Pd activation solution containing palladium dichloride ($PdCl_2$, 0.1 g/L), 50% HF (5 mL/L), and 35% hydrochloric acid (HCl, 3 mL/L), for 20 s. The electrolyte for fabricating the seed layer was a sevenfold diluted solution of the standard solution. The standard solution for electroless gap-filling was composed of 0.025 M copper sulfate ($CuSO_4 \cdot 5H_2O$), 0.054 M ethylenediaminetetraacetic acid (EDTA), 0.078 M paraformaldehyde $(HCHO)_n$, and 0.49 M KOH.[12] The thickness of the electroless seed layer was approximately 50 nm. In the filling step, Cu electroless deposition was carried out in the standard solution adding various concentrations of SPS and 2,2′-dipyridyl. The pH of the electrolyte was adjusted to approximately 12.6, and all experiments were performed at 70°C. After Cu filling, a heat-treatment was performed at 400°C for 30 min under N_2 atmosphere.

Field emission scanning electron microscopy (FE-SEM, Philips XL30FEG), four-point probe (Chang Min CMT-SR 1000N), atomic force microscopy (AFM, Digital Instruments Dimension™ 3100), X-ray diffractometry (XRD, Bruker D8 Advance), and Auger electron spectroscopy (AES, Perkin-Elmer model 660) were applied to compare the film properties. We observed the grain structure of the filled Cu on the patterned wafers through transmission electron microscopy (TEM, JEOL JEM-100CX).

Results and Discussion

Figure 1 shows the cross-sectional images of electroless gap-filled Cu according to the SPS concentration at the filling step after plating seed layers in the diluted electrolyte. The deposition time was fixed at 5 min. As shown in Fig. 1a, a conformal filling profile appeared when 0.5 mg/L of SPS was added without 2,2′-dipyridyl, and bottom-up-like filling profiles which have thicker deposits at the bottom than at the top were observed at 2-10 mg/L SPS. Particularly in Fig. 1c and d, the deposition was strongly inhibited and Cu was barely deposited on the top surface. However, Cu was not plated on both the top and the bottom of the trenches at SPS concentrations higher than 25 mg/L since SPS acts as an accelerator at lower concentrations and a suppressor at higher concentrations.[15] The amount of adsorbed SPS affected by the diffusion of SPS in the mass-transfer region caused deposition rate differences between the bottom and the top of the trenches.

To verify the bottom-up filling with elapsed deposition time, filling profiles at 5 mg/L SPS were constructed (Fig. 2a-e). The deposition rate between 1 and 3 min rapidly increased and was obviously reduced after 5 min. The SPS concentration at the bottom gradually increased during bottom-up filling and the deposition rate was severely diminished above certain values of SPS concentration.

Although the bottom-up filling took place by the addition of SPS, a rough surface and fine voids were observed. These were detected after annealing as displayed in Fig. 2f, where large voids were found on the inside of the trenches due to the densification of the Cu deposits. The accelerating effect of SPS resulted in high surface roughness with voids causing degradation of the electrical and mechanical properties. The incorporation of oxygen into the film when HCHO is utilized as a reducing agent is an intrinsic problem result-

[z] E-mail: jjkimm@snu.ac.kr

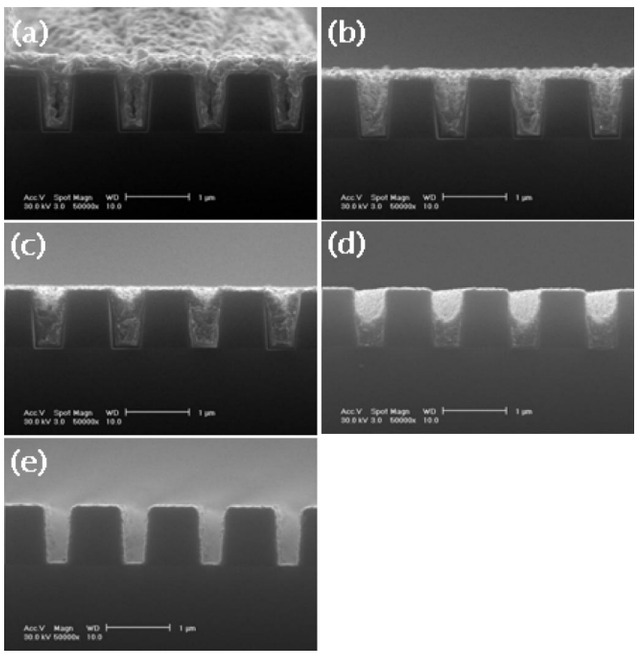

Figure 1. FE-SEM images of electroless gap-filling Cu on trenches deposited for 5 min at 70°C. Only SPS was added. SPS concentrations in the electrolyte were: (a) 0.5, (b) 2.0, (c) 5.0, (d) 10, and (e) 25 mg/L.

ing in the increase of film resistivity in Cu electroless deposition.[21] In this respect, 2,2′-dipyridyl effectively improves the ductility by inhibiting Cu reduction and keeps the Cu film from depositing as Cu_2O by producing stable complexes with Cu^+ ions.[10,16]

Figure 3 shows the electroless Cu gap-filled trenches plated for 10 min, varying the SPS concentration at 0.1 g/L 2,2-dipyridyl. In order to improve the film properties, 2,2-dipyridyl was added. As

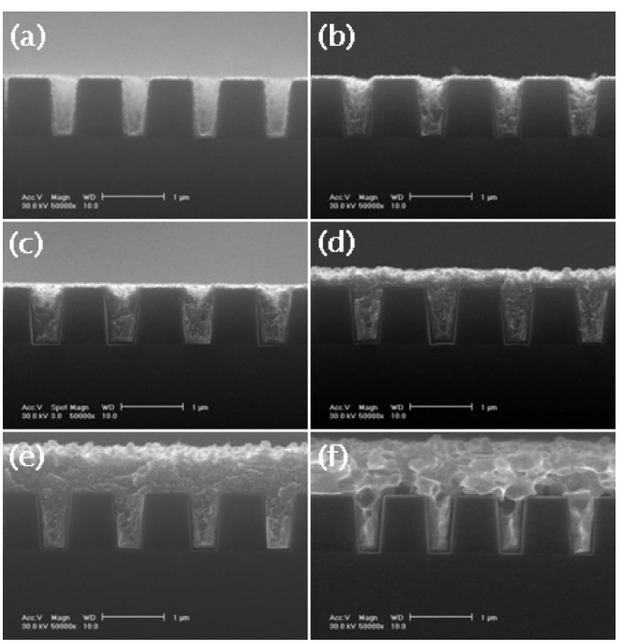

Figure 2. Cross-sectional images of trenches showing the time evolution of electroless gap-filled Cu at 5 mg/L SPS: (a) 1, (b) 3, (c) 5, (d) 8, (e) 10 min, and (f) (e) after annealing at 400°C for 30 min under N_2 atmosphere.

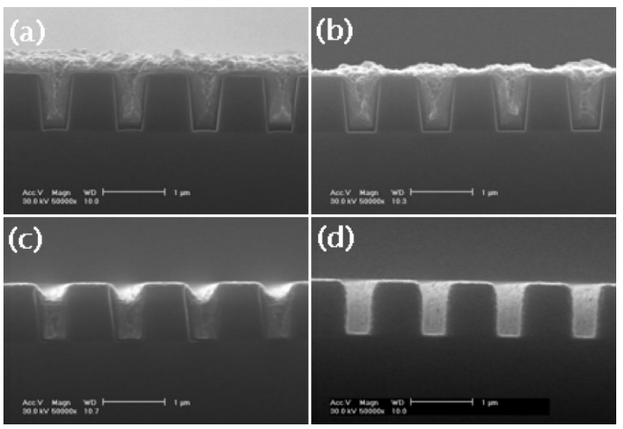

Figure 3. Electroless Cu filling profiles with varying SPS concentrations with 0.1 g/L 2,2′-dipyridyl: (a) 0.3, (b) 0.5, (c) 1.0, and (d) 5 mg/L SPS.

indicated in the figure, Cu electroless filling occurred at a lower SPS concentration region as compared to when SPS was used alone. Cu was barely deposited except for a small amount on the sidewall of the pattern at 5 mg/L SPS, where the bottom-up filling was achieved with SPS alone. At the higher concentrations of SPS and 2, 2′-dipyridyl, reduction of Cu did not take place regardless of the deposition time because they both acted as suppressors. In the range of 0.3 to 5 mg/L of SPS, the deposition rate was lowered with increased SPS concentration. The addition of 2,2′-dipyridyl with SPS improved the surface roughness and adhesion property and decreased the voids inside the trenches. Bumps, evidence of bottom-up filling, were observed when 0.1 g/L 2,2′-dipyridyl was added with 0.5 mg/L of SPS. The formation of bumps signifies that SPS did not simply inhibit the plating on the surface but played the role of an accelerator at the bottom of the pattern.

The effect of 2,2′-dipyridyl on improving the film was evident from the gap-filling profiles as a function of time (Fig. 4a-f). As shown in Fig. 4a, the bottom and sidewall of the pattern were thicker than the top and Cu was rapidly filled up from the bottom to the top surface with time. The deposition rate was slightly decreased by the addition of 2,2′-dipyridyl, but the surface roughness and void formation were notably reduced. Even after Cu filling for 13 min and subsequent heat-treatment, voids were not observed in the film.

Figure 5 shows the cross-sectional TEM images of electroless gap-filled Cu at specific deposition times using the same conditions as in Fig. 4. The results confirmed the absence of voids or seams and predicted an improved electrical property due to the relatively large grains of Cu.

To compare the film properties for the additives, Cu electroless deposition was carried out on blanket wafers and the results are listed in Table I. Comparison of the root-mean-square (rms) roughness and the area-intensity ratio of Cu(111) to (200), at the same thickness of 700 nm, showed an extreme improvement in the surface roughness and structural stability of the film with the combination of the two additives. The resistivity of the film deposited with 0.1 mg/L SPS and 0.01 g/L 2,2′-dipyridyl was 2.52 $\mu\Omega$ cm without the annealing process, lower than when SPS was used alone. We hypothesized that 2,2′-dipyridyl reduced the oxygen content in the Cu film and lowered the surface roughness simultaneously. This was confirmed through AES depth profiles as presented in Fig. 6a and b. While there was a slight increase in the amount of carbon on the top surface, the amount of oxygen decreased with the addition of 2, 2′-dipyridyl. Different sputtering times at the same thickness between two films are considered to result in densification of the Cu deposits. The oxygen on the surface and inside of the film was considerably reduced. However sulfur was barely detected in both films due to the adsorption and desorption mechanisms of SPS.

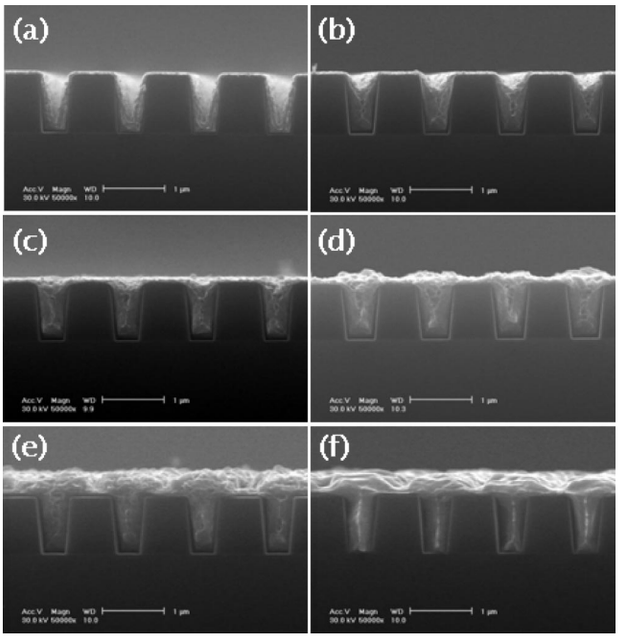

Figure 4. Bottom-up filling in Cu electroless deposition with the addition of 0.5 mg/L SPS and 0.1 g/L 2,2′-dipyridyl, as a function of time: (a) 3, (b) 5, (c) 8, (d) 10, (e) 13 min, and (f) (e) after annealing at 400°C for 30 min under N_2 atmosphere.

Table I. Film properties of electrolessly deposited Cu as prepared with additives.

Characteristics	No additives	0.1 mg/L SPS	0.1 mg/L SPS +0.01 g/L 2,2′-dipyridyl
RMS roughness (nm)	32.9	52.1	22.8
Cu(111)/(200) ratios	-	57.7	94.1
Resistivity ($\mu\Omega$ cm)	2.47	3.27	2.52

Therefore, the improvement of the film properties by the addition of 2,2′-dipyridyl with SPS shows the possibility of Cu electroless gap-filling applicable to Cu interconnection in ULSI processes.

Conclusions

Cu bottom-up filling was achieved using SPS in electroless deposition, and it was observed with a time sequence of the deposition through SEM. However, after annealing at 400°C, voids were generated in the sidewalls of filled Cu by densification due to SPS accelerating the unstable growth of Cu.

The addition of 2,2′-dipyridyl, a well-known stabilizer and brightener in Cu electroless deposition, improved the quality of gap-filled Cu by lowering surface roughness, preventing oxygen incorporation and enhancing the crystallinity. TEM analysis confirmed that no voids and seams existed in the filled Cu.

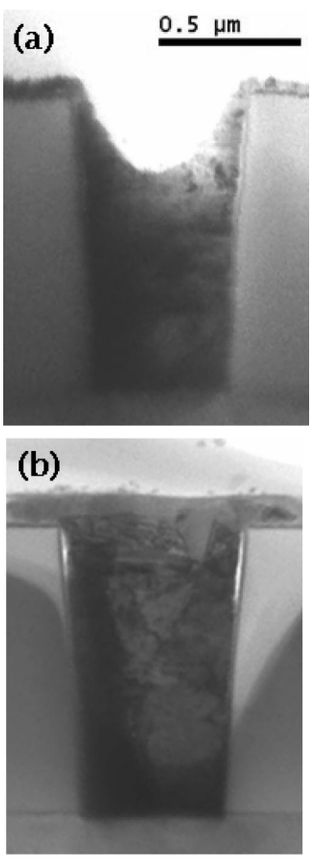

Figure 5. TEM images of bottom-up filled Cu deposited at 0.5 mg/L SPS and 0.1 g/L 2,2′-dipyridyl for (a) 5 and (b) 9.5 min.

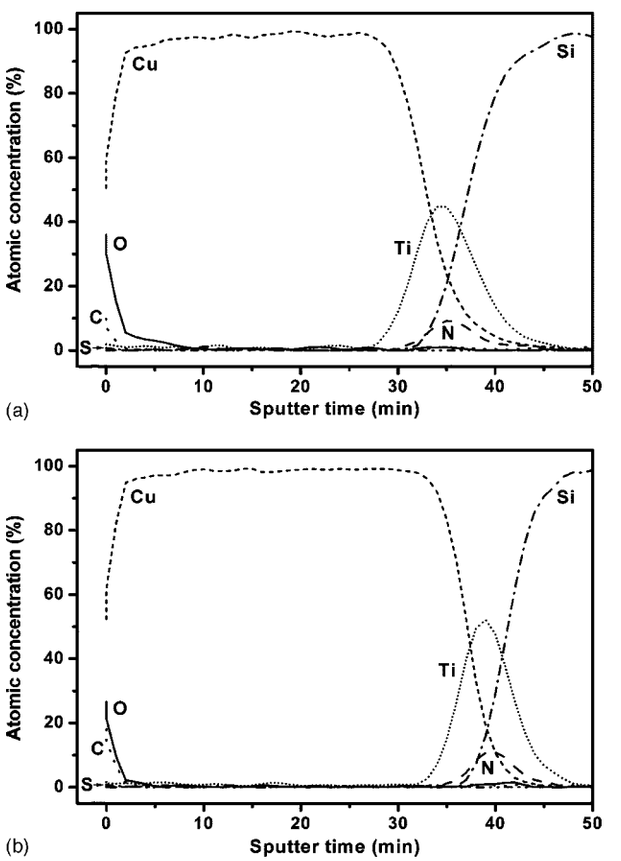

Figure 6. AES depth profiles of electrolessly deposited Cu films with addition of (a) 0.5 mg/L SPS and (b) 0.5 mg/L SPS+0.01 g/L 2,2′-dipyridyl.

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