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Perfect Conformal Deposition of Electroless Cu for High Aspect Ratio Through-Si Vias

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In three-dimensional integration technology, through-silicon vias (TSVs) with a high aspect ratio in excess of 10 are required, due to a strong demand for a higher packing density. We achieved perfect conformal electroless plating of Cu by the addition of Cl^- and bis(3-sulfopropyl) disulfide to a standard plating bath. With this technology, the Cu thickness of the TSV sidewalls remained constant with depth, even for the TSV with an aspect ratio of 20. Perfect conformal plating is a promising technology that could lower the resistance of high aspect ratio TSVs.

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The formation of through-silicon vias (TSVs) to enable the stacking of multiple layers of thin Si substrates is a key technology for three-dimensional integration. It is expected that the minimum pitch of TSVs is smaller than 10 μm, which will require the diameter of the TSVs to decrease below a few micrometers in the near future.[1,2] In such a structure, the TSV will take the place of a large-scale integration circuit global interconnection. Cu filling of the TSV is an important technology because it enables a lower resistance TSV than chemical vapor deposition of tungsten (CVD-W) filling by an order of magnitude; however, there have been many technical problems in Cu filling of a high aspect ratio TSV. Cu electroplating technology has been studied extensively,[3] and a so-called superconformal deposition that enables a bottom-up fill of submicrometer vias has been proposed.[4-13] In Cu electroplating, the formation of a sputtered Cu seed layer is very difficult for a high aspect ratio via because the film thickness at the sidewall is much lower than on the flat surface. Therefore, conformal deposition using chemical vapor deposition of titanium nitride (CVD-TiN) or CVD-W was studied before Cu electroplating.[14-16] However, it is not easy to fill a high aspect ratio via by superconformal Cu electroplating.

Cu electroless plating can result in good conformal deposition and is rather insensitive to the electrical conductivity of the seed layer. We found that a bottom-up fill was possible for a submicrometer ultra-large scale integration via using Cu electroless plating with the addition of a sulfuric organic compound with polyethylene glycol (PEG). We found that a sulfuric organic compound such as bis(3-sulfopropyl) disulfide (SPS) acted as a strong inhibitor.[17,18] The diffusion of inhibitor molecules into the bottom of fine holes is limited, resulting in faster growth of Cu within the via. Furthermore, Cu can be deposited on TaN, WN, and W barrier layers without a Pd catalyst through displacement plating mechanisms.[19,20] In the preliminary stages of this study, we attempted to use an SPS-contained plating bath to fill TSVs. However, these additives were unable to achieve a bottom-up fill of high aspect ratio TSVs with diameters of a few micrometers. In this study, we investigated Cu-filling characteristics when adding Cl^- as a third additive to a PEG and a sulfuric organic compound plating bath.

Experimental

We prepared the TSV samples with a depth of 37 μm on a Si substrate using the Bosch process of reactive ion etching (RIE).[21,22] The size of the TSV openings was 2 × 8 μm and the aspect ratio was 18.5. After RIE, a silicon oxide (350 nm) layer was formed by thermal oxidation, then poly-Si (210 nm) and CVD-W (120 nm) layers were successively deposited in the TSVs. We studied Cu electroless plating with the addition of Cl^- to the SPS-added plating bath to fill the TSV. The Cl^- concentration was varied between 5 and 25 mg/L. The composition of the Cu electroless plating bath was 6.4 g/L copper sulfate as a Cu source, 18 g/L glyoxylic acid as a reducing agent, 70 g/L ethylenediaminetetraacetic acid (EDTA) as a complexing agent, and 500 mg/L PEG (with molecular weight of 4000) as a surfactant. The temperature was 70°C and pH was adjusted to 12.5. After the Cu electroless plating, we observed the cross-sectional view of the TSVs with focused ion beam (FIB, JEOL JFIB-2300) cutting and scanning ion microscopy (SIM) using Seiko-9000. The deposition rate was measured by an electrochemical quartz crystal microbalance (QCM, Hokuto Denko HQ-101B). The Cu atomic composition was measured with energy-dispersive X-ray (EDX, JEOL JSF-7500F) analysis. After electroless plating, annealing was carried out at 400°C for 30 min in vacuum (1×10^{-4} Pa). The sheet resistance of the deposited films was measured using a four-point-probe method.

Results and Discussion

TSV filling characteristics with the addition of SPS and Cl ions.— At first, we investigated Cu electroless plating in a high aspect ratio TSV with the addition of SPS, which was very effective for the bottom-up fill of submicrometer vias. A cross-sectional FIB-SIM image of a Cu-filled TSV with the addition of SPS to the plating bath is shown in Fig. 1a. Near-conformal Cu deposition was observed in the TSV using an SPS concentration of 0.1 mg/L and a plating time of 90 min. However, the Cu thickness of the TSV sidewall gradually decreased toward the bottom. A pinch-off occurred at the entrance of the TSV, and a large void formed on the central axis of the TSV. An image of a Cu-filled TSV with the addition of 5 mg/L Cl^- into the electroless plating bath is shown in Fig. 1b. The Cu thickness of the surface was more suppressed than in the case of SPS addition. Several Cu grains showed abnormal growth, especially at the top corner of the TSV, and the surface of the Cu films was very rough. Images of a Cu-filled TSV with the addition of both SPS and Cl^- to the plating bath are shown in Fig. 2. The Cu thickness on the flat surface was significantly suppressed, and the Cu surface was very smooth, indicating that there was no abnormal grain growth. As a consequence, the pinch-off at the TSV entrance did not occur. A full cross section of the Cu-filled TSV with the addition of both SPS and Cl^- to the plating bath is shown in Fig. 2a. As shown in the figure, the Cu thickness of the TSV sidewall did not change from the bottom to the top. Images of the top, the middle, and the bottom of the TSV are shown in Fig. 2a-c, respectively.

Cu was uniformly deposited on the TSV sidewall, even at the

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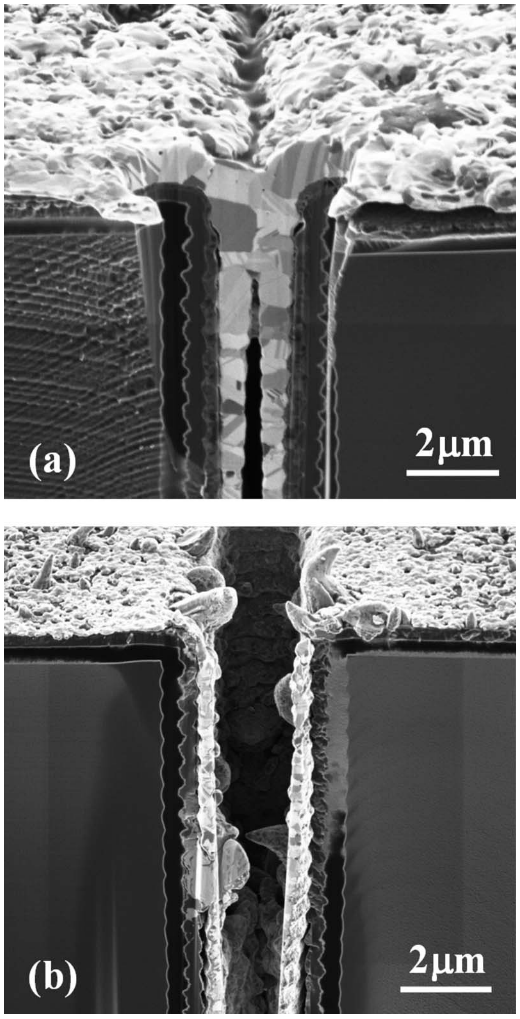

Figure 1. Cross-sectional FIB-SIM images of electroless Cu deposited in TSVs with various additives: (a) SPS 0.1 mg/L and (b) Cl^- 5 mg/L. pH 12.5, temperature of 70°C, and plating time of 90 min.

bottom, and there was no apparent bottom-up deposition tendency. It is remarkable that the Cu thickness remained so uniform from the bottom to the top of such a high aspect ratio TSV; the Cu thickness was approximately 700 nm at the top of the TSV and was 650 nm at the bottom.

Measurement of film thickness by QCM for various electroless plating additives.— The Cu thickness during electroless plating was measured by QCM, with Au as an electrode. The temperature was 60°C, which was lower than the actual plating conditions for the TSV filling, because the Cu deposition rate at 70°C was too high for measurement by QCM. The time dependence of the Cu thickness during electroless plating for various additives is shown in Fig. 3. After adding SPS only, the Cu deposition rate was slightly suppressed. When adding Cl^- only, the Cu deposition rate was even more suppressed. The suppressive effect was so strong that the Cu film thickness was saturated at 10 nm. In adding both SPS and Cl^-, the suppressive effect was as weak as when adding SPS only. Under superfill conditions in Cu electroplating, it was reported that both SPS and Cl^- were included in the Cu film.[22] These additives accelerated of Cu deposition, and the curvature-enhanced adsorption coverage (CEAC) model was proposed, which suggested an enhanced adsorption of deposition accelerators at corners with small curvatures.[23] The CEAC model explained the superfill property, in which the deposition rate was higher at the bottom of a submicrometer via than that at the top. However, in the present study of electroless plating, the Cu deposition rate was reduced by the addition of SPS and Cl^-. There is a substantial difference in the effect of adding SPS and Cl^- between the electroplating and the electroless plating methods. Also, in both cases, SPS and Cl^- are included in the Cu film. It is believed that the differences are caused by the variation of the electropotential distribution with or without the bias.

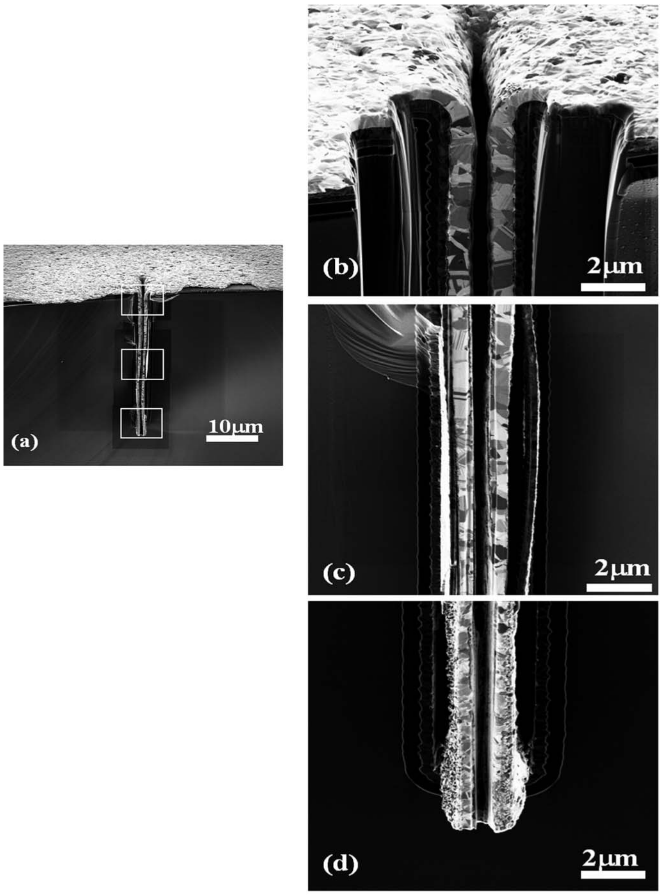

Figure 2. Cross-sectional FIB-SIM images of a TSV after Cu electroless plating with the addition of SPS and Cl^-. SPS concentration is 0.1 mg/L and Cl^- concentration is 5 mg/L; pH 12.5, temperature of 70°C, and plating time of 90 min. (a) Cu-filled TSV, (b) top, (c) middle, and (d) bottom.

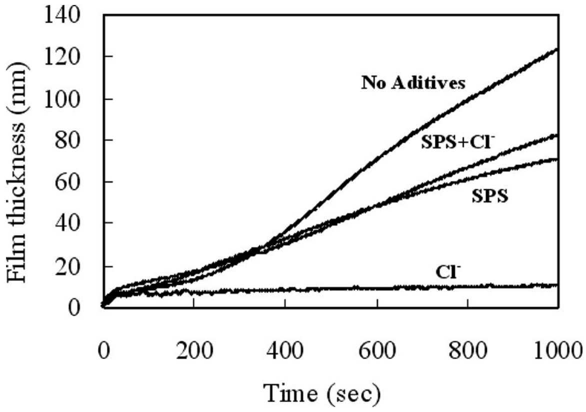

Figure 3. Cu film thickness measured by QCM as a function of time. Cu plating with PEG (500 mg/L), no additives, SPS, Cl^-, and SPS + Cl^-.

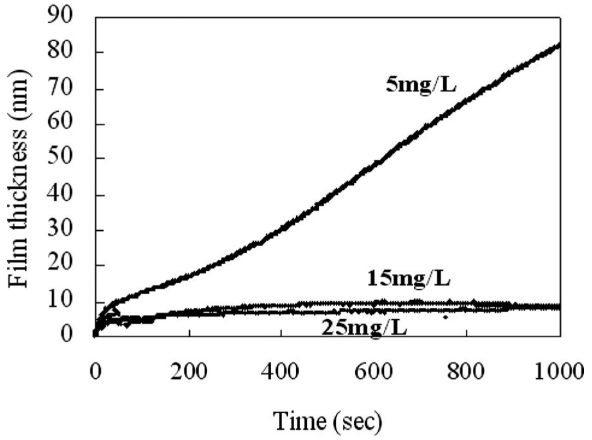

Figure 4. Cu film thickness measured by QCM as a function of time with the addition of both SPS (0.1 mg/L) and Cl^-. Concentration of Cl^- was 5, 15, or 25 mg/L.

The properties of grain growth are enhanced by the addition of SPS and Cl^-, as in the case of superfill electroplating, in which grain growth was observed at room temperature. It is not yet clear why grains grow more easily with these additives.

The time dependence of the surface Cu thickness during electroless plating with the addition of SPS and Cl^- is shown in Fig. 4. When the Cl^- concentration was more than 15 mg/L, the suppressive effect was too strong for deposition to continue, and the Cu thickness was limited to 10 nm. It seems that a strong suppressive effect occurred due to the coupling of Cl^- and PEG molecules.

There was a difference in the deposition rate between adding SPS and adding both SPS and Cl^-, and pinch-off did not occur in the latter case. To clarify the effect of adding both SPS and Cl^-, we evaluated the atomic composition of the Cu film using EDX analysis, as shown in Table I. The Cu contained a small concentration of S and Cl at the top of the TSV; however, the Cu contained no S and a small amount of Cl in the middle of the TSV. Thus, the diffusion of SPS molecules into the TSV was more suppressed than that of Cl^-.

When adding both SPS and Cl^-, the Cu growth rate was drastically suppressed at the upper edge of the TSV, resulting in the absence of the pinch-off at the top of the TSV during Cu deposition. The amounts of sulfur and Cl included in the Cu film gradually decreased from top to bottom, as measured by EDX analysis. This suggests that the inhibition of Cu growth in the presence of SPS and Cl gradually became weaker from top to bottom. The diffusion flux of the Cu–EDTA complex and the reducing agent (glyoxylic acid) became smaller from top to bottom, resulting in a lower deposition rate of Cu at the bottom. With these two effects in balance throughout the TSV, conformal deposition was achieved and the Cu growth rate was nearly constant from the top to the bottom of the via.

SPS and Cl^- adsorb on the Cu surface, thus it has an influence on the deposition properties.[24] Stangl et al. reported that the amounts of adsorption are a few monolayers for SPS and Cl^- in the case of electroplating.[25] Strehle et al. reported that the electroplated Cu film contained about 0.1–0.01 atom % S atoms.[26] In our experiments, the additive contents in the plating solution are similar to those of the electroplating solution, hence our EDX results are reasonable.

Table I. Composition of as-plated electroless Cu in the TSV measured by EDX analysis.

Location at TSV	Concentration (wt %) S	Concentration (wt %) Cl
Top	0.05	0.07
Middle	0	0.03
Bottom	0	0

Table II. Sheet resistivity of electroplated Cu films with added Cl^-, SPS, and both SPS and Cl^-.

	Sheet resistance ($\mu\Omega$ cm)		
	Cl^-	SPS	SPS + Cl^-
Before annealing	3.57	3.68	3.65
After annealing	3.03	2.95	2.52

Measurements of Cu film electrical conductivity with various additives.— We evaluated the electrical resistance of Cu films with various additives, as shown in Table II, and in most cases, the resistances were reduced after annealing at 400°C in vacuum. There was little difference in the resistivities before annealing; however, the sheet resistivity, when adding both SPS and Cl^-, decreased remarkably compared to the other cases after annealing. This significant decrease in sheet resistivity is attributed to the large grain growth during annealing.

Conclusion

We studied the filling of Cu into a high aspect ratio TSV with displacement electroless Cu plating, which occurred directly upon a CVD-W layer. We found that the addition of SPS and Cl^- to the plating bath was highly effective in suppressing pinch-off of the TSV. As a result, complete conformal deposition of Cu was obtained for a deep TSV, with an aspect ratio of approximately 20. This technology is a candidate for practical application of Cu filling of TSVs. The resistance of the TSV can be reduced by 1 order of magnitude from that of a tungsten-filled via, and perfect conformal deposition of Cu would be one of the most promising technologies for lowering the resistance of the high aspect ratio TSV in the near future.

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