Two-Step Filling in Cu Electroless Deposition Using a Concentration-Dependent Effect of 3, N, N-dimethylaminodithiocarbamoyl-1-propanesulfonic Acid

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This paper describes electroless Cu filling of trenches with different widths ranging from 130 to 300 nm, using a concentration-dependent effect of 3-N,N-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS). With a fixed DPS concentration, it is shown that these trenches with different dimensions cannot be superfilled simultaneously. This is presumably caused by different surface concentrations of the adsorbed additive, which depends on the feature size and surface area. A two-step filling method is employed to superfill those trenches, which is also effective in control of the deposited Cu amounts to obtain uniform growth fronts regardless of the trench dimensions.

Superconformal electrodeposition of Cu using organic additives such as bis(3-sulfopropyl)-disulfide (SPS)-polyethylene glycol (PEG)-chloride (CI−) has been successfully implemented for the metallization of ultra-large-scale integrated circuits.1,2 Such void-free filling of trenches and vias is quantitatively predicted by the curvature-enhanced adsorbate coverage model, which involves the competitive adsorption between accelerating species (SPS-CI) and suppressing species (PEG-CI) coupled with the effect of local area change.3-6

However, Cu electroless deposition, for which reducing agents (such as formaldehyde or glyoxylic acid) are used to reduce Cu ions instead of an externally supplied current, has been applied only to the seed repair process for physical vapor deposition (PVD) seeds or to the seed layer itself for Cu superconformal electrodeposition, because of its conformal deposition characteristics.7,8 Recently, however, Cu electroless deposition has been explored as a possibility for direct void-free filling of features covered with barrier layers because it is one approach to solving the pinch-off caused by poor step coverage of PVD seeds, as the feature size shrinks down and the aspect ratio increases. To date, Cu electroless gap filling has been achieved either in the presence of S and/or N bearing sulfonic acid series additives.1-15 some of which are well known in Cu electrodeposition, or in the absence of deposition-rate-controlling additives.16-19

When SPS, a well-known accelerator for superfilling in Cu electroless deposition, was applied to Cu electroless deposition, it was evident that the deposition rate depended on the SPS concentration, namely, accelerating at low concentration and suppressing at higher concentration. The difference of surface concentration between the top and the bottom of 500 nm wide trenches led to bottom-up filling of Cu without seams or voids in electroless deposition, showing the typical overfill bumps.20,21 Similarly, the use of 3-N,N-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS), which has a molecular structure similar to 3-mercapto-1-propanesulfonic acid (MPS), also showed the concentration-dependent effect on the deposition rate for the planar substrate and bottom-up filling profiles with smoother surface characteristics than SPS.22

Although Cu electroless bottom-up filling was achieved in 500 nm wide trenches using the concentration-dependent bifunctional additives, different kinetics would be anticipated for electroless Cu filling of differently sized features because the variation in the surface concentration of additives would be more strongly affected by the dimension of the trenches.

Therefore, in this article, we investigate how the effect of the concentration-dependent bifunctional additive in Cu electroless filling depends on the trench dimension, especially the widths being <320 nm, through the electron microscopic observation of Cu gap filling using a representative bifunctional additive, DPS. Furthermore, we suggest an effective way to superfill the patterns of various dimensions with uniform growth fronts by modifying the conventional Cu electroless deposition.

Experimental

The substrates used in the experiments comprised barrier layers of TaN (7.5 nm) and Ta (7.5 nm) deposited on SiO2/Si wafers with lithographically patterned trenches. The trenches covered with the barrier layers had widths ranging from 130 to 300 nm at the bottom and depths ranging from 290 to 300 nm. Their aspect ratios ranged from 1.0 to 2.3 after the barrier layer deposition. Prior to electroless deposition, the substrates were immersed in a mixture of 1% dilute HF solution and 1.4% HNO3 for 10 min to remove Ta native oxide from the surface. Surfaces were catalyzed by wet Pd activation processes comprising Sn sensitization step and Pd activation step.20

Cu electroless deposition was carried out in a base electrolyte composed of 0.025 M CuSO4·5H2O, 2.9 g/L paraformaldehyde [(HCHO)10], 0.054 M ethylenediaminetetraacetic acid (EDTA), and 0.49 M KOH at a temperature of 70°C. In addition, 0.1 g/L 2,2’-dipyridyl as a stabilizer, and DPS as an accelerating/suppressing agent, were utilized for the Cu electroless bottom-up process.

Cu electroless gap filling was performed with two sequential depositions using electrolytes containing different concentrations of DPS. Between the two depositions, there was a surface cleaning process to eliminate the strongly adsorbed DPS and/or byproducts from the Cu surface deposited during the first filling step. It was introduced to prevent them affecting the second filling step. The process was done by lightly etching the Cu surface with a dilute NH4OH solution (1:100) for 1 min. To verify indirectly that adsorbed species were removed, the amount of carbon adsorbed and incorporated in the deposited Cu film was measured by total organic carbon (TOC) method, using 20 mL of a 1/20 diluted solution in which Cu film was dissolved in 10 mL of a 70% HNO3. The TOC measurement was done three times for each step and the average value was calculated. Deposition profiles for various trench widths were examined using field emission scanning electron microscopy (FESEM, JEOL 6330F). The cross section of the trench was ob-

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is disturbed by the additive, and the reoriented molecular structure
higher concentrations, it is significant that the reduction of Cu ions
affected by the surface area per unit volume.28 In Cu electroless deposition, the accelerating
transfer mechanism through the formation of dimer.21 Conversely, at
trench caused by diffusion of the additive,12-14 which is significantly
difference of additive between the bottom and top surfaces of the
fill appearing in Cu electroless deposition is due to the concentration
SPS or DPS in Cu electroless deposition is required.

Results and Discussion

There have been several studies on the concentration-dependent
effect of the additive in electroless deposition21-24 as well as in Cu
electrodeposition.25-27 In Cu electroless deposition, the accelerating
effect at low additive concentrations is known to be caused by the
delocalized \( \pi \)-electron bond in its molecular structure which en-
hances the reduction of Cu ions,23 making the breakage of the
Cu\( ^{2+} \)-ligand easier by adsorbing at the surface,22 or by the electron
transfer mechanism through the formation of dimer.21 Conversely, at
higher concentrations, it is significant that the reduction of Cu ions
is disturbed by the additive, and the reoriented molecular structure
(including dimer or its byproducts) is strongly adsorbed on the ac-
tive site, where the oxidation of the reducing agent occurs. However,
further investigation of the concentration-dependent mechanism for
SPS or DPS in Cu electroless deposition is required.

In previous experiments, we have concluded that the bottom-up
copper filling was carried out by electroless deposition in the pres-
ence of two different concentrations of DPS of 0.5 and 2 mg/L, on
trenches with bottom widths of 300 and 130 nm, as shown in Fig. 1.
Interestingly, the 300 nm trenches were filled with bottom-up shape at 0.5 mg/L DPS, in a manner similar to the previous experiment14 where successful bottom-up filling was achieved with
trenches of 400 nm width and 1000 nm depth, conformal deposition with bottom voids was observed at the 130 nm wide trenches, which have greater surface areas per unit volume than those of the 300 nm wide trenches. However, the 130 nm wide trenches showed V-notches at their centers when 2.0 mg/L DPS was added, which is regarded as proof of bottom-up filling, while a robust suppressing effect appeared on the 300 nm wide trenches. As schematically depicted in Fig. 2, this implies that bottom-up filling does not occur at low DPS concentrations on smaller trenches, due to significant depletion of DPS concentration at the bottom, caused by the increased surface area or by the difficulty of diffusion into the trench.

Although we verified that bottom-up fill could be achieved for
smaller feature sizes using Cu electroless deposition, it does depend
on the surface area and pattern density. This factor chiefly makes bottom-up fill difficult for trenches of different sizes, when a con-
tant additive concentration is used.28

In order to achieve electroless superfilling on different-sized
trenches, a two-step filling method was applied. Similarly to the
concept proposed for superfilling27 and leveling29 in Cu electrodepo-
sition, the process is divided into two filling steps using two differ-
cent DPS concentration, as outlined in Fig. 3. The first deposition
step is to superfill the smaller sized patterns, and the second step is
to fill up the highly suppressed regions of the wider trenches, includ-
ing the remaining parts of smaller trenches. To minimize the impact
of accumulated additive on the surface during the two filling steps,
two alternatives for removing the adsorbed DPS and its thiolate
compounds between the two deposition steps were tried, namely
deionized (DI) water rinsing and slight etching of the surface with
NH\( _4 \)OH.

To compare feature filling by the two-step method with conven-
tional one-step filling method, one-step deposition was conducted
using 0.5 mg/L DPS for 12 min, which was the same as the total
deposition time for two-step filling (5 min for the first step and
7 min for the second step), and presented in Fig. 4a. Despite the
deposition time of 12 min, comparison to Fig. 1a and b shows that
there was no major difference in the deposited amount, except for a
slight increase for smaller-width trenches, which indicates a continu-
ous accumulation of additive on the active site of the Cu surface
with time and its resulting suppression effect, even at 0.5 mg/L
DPS. The bottom voids generated at the early stage of deposition

1st filling at high DPS concentration

Removal of adsorbed DPS

2nd filling at low DPS concentration

Figure 3. (Color online) The concept of the two-step filling method in Cu
electroless deposition.
were evident for most trench sizes, resulting in further disparity in deposited Cu at the centers of the 300 wide and 130 nm wide trenches.

By contrast, for the case of two-step filling using the DI water-rinsing method to eliminate the adsorbed additive, the bottom voids seen in one-step filling did not appear at all, as shown in Fig. 4b because of the preferential deposition at the bottom of smaller features by control of the DPS concentration. However, the wider trenches, of 300 and 220 nm widths, on which a relatively large amount of the additive would be expected to adsorb, were not completely filled because of the inefficient removal by DI water rinsing. The sulfur-containing additives are attached to metal surfaces with a strong coordinative bond via the deprotonation of the S-H group of thiol molecules. The thiolate compounds are incorporated with the forms of Cu sulfides into Cu deposits, which has been observed in the previous result. In the final experiment, a diluted NH₄OH solution was used to remove the adsorbed DPS and its byproducts from the first filling.

As shown in Fig. 5, in a magnified SEM image of 150 nm wide trench, no voids or seams were observed, even though the surface was slightly rough.

### Conclusion

We have found that conventional one-step Cu electroless deposition using the concentration-dependent bifunctional effect of DPS is hard to apply directly to the simultaneous filling of patterns with various dimensions, as the bifunctional effect depends on the effective surface concentration, thus surface area at a given DPS bulk concentration. For void-free electroless gap filling regardless of the pattern size, low concentrations of DPS for wider trenches and high concentrations of DPS for narrower trenches are required. By using a two-step filling process that involves an initial filling for relatively small trenches at high DPS concentration, followed by a second filling for the wide trenches at low DPS concentration, bottom-up filling can be achieved for trenches <300 nm wide simultaneously, without voids. This shows the feasibility of Cu electroless deposition for subquarter-micrometer feature technology.

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