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Electroless Cu Bottom-Up Filling Using 3-*N*,*N*-Dimethylaminodithiocarbamoyl-1-propanesulfonic acid

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Cu bottom-up filling in Cu electroless deposition was attempted using 3-*N*,*N*-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS). An accelerating effect on the planar surface was observed at low DPS concentrations, while a suppressing effect was found at higher concentrations. Co-addition of 2,2′-dipyridyl enhanced the surface morphology. Filling profiles were dependent on the concentration of DPS added, and Cu bottom-up filling was achieved due to a concentration gradient by diffusion of DPS between the top and bottom of the trench.
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Copper (Cu) is an attractive substitute for aluminum interconnects due to its low resistivity and superior resistance to electromigration in ultralarge scale integrated circuits (ULSIs).[1] Among Cu deposition methods, electrodeposition (ED) combined with the damascene process is the most commonly used for on-chip metallization because of its bottom-up filling capability by organic additives.[2-4] However, it is becoming increasingly recognized that shrinking the devices to smaller feature sizes leads to higher performance, and efforts are being made to reduce or exclude the seed layer of electrodeposition through the use of electroless seed layer or direct electroplating.[5,6] Electroless deposition is applicable to the repairing process for physical vapor deposition (PVD) or chemical vapor deposition (CVD), seeds and the formation of a thin and uniform seed layer for electrodeposition due to its excellent step-coverage.[7-9] Recently, studies have been performed using only electroless deposition on Cu gap-filling in vias or trenches because it does not need additional seed layers.[10-12] Although electroless deposition has a conformal deposition property, a bottom-up filling or superfilling was achieved in Cu electroless deposition by controlling the partial deposition rate with additives such as bis-(3-sulfopropyl)-disulfide (SPS) or SPS combined with surfactants.[13,14] In a previous study on Cu electroless deposition, we confirmed that SPS, an accelerator in Cu electrodeposition, played the role of either an accelerator at low concentrations or a suppressor at high concentrations.[14] Combining SPS with 2,2′-dipyridyl, defect-free bottom-up filling by Cu electroless deposition was accomplished using a two-step method, which consisted of the formation of a seed layer and a filling step.[15]

In this study, we attempted bottom-up filling in Cu electroless deposition using a new additive, 3-*N*,*N*-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS). Superfilling in Cu electrodeposition using DPS, which is known to be a suppressing-accelerating agent[16,17] instead of SPS, has been achieved through a two-step electrodeposition process or derivitization method.[18] In this paper, the effect of DPS in Cu electroless deposition is described, and its bottom-up filling capability is discussed.

Experimental

To investigate the effect of DPS according to its concentration, blanket wafers covered with 140 nm of PVD Cu seed layers on the barrier layer were used after removing the native oxide on the surface with 1:200 NH_4OH for 30 s.[19] The removal of the native oxide was carried out to make the same surface conditions as the autocatalytic reaction which occurs in electroless deposition.

For Cu electroless gap-filling, (100)-oriented p-type Si patterned wafers with an aspect ratio of 2.5 and a bottom width of 400 nm were used, and they were deposited with TiN (10 nm)/Ti (15 nm) as a diffusion barrier layer. Prior to Cu electroless deposition, the native oxide of the TiN substrate surface was removed in a 1:100 diluted hydrofluoric acid (HF) solution for 10 min. Pd catalysts were then formed on the surface in an activation solution composed of 0.1 g/L palladium dichloride ($PdCl_2$), 5 mL/L HF (50%), and 3 mL/L hydrochloric acid (HCl, 35%), for 20 s.

Cu electroless deposition on the pretreated substrates was carried out in the electrolyte consisting of 0.025 M copper sulfate ($CuSO_4 \cdot 5H_2O$), 0.054 M ethylenediaminetetraacetic acid (EDTA), and 0.078 M paraformaldehyde $(HCHO)_n$. The pH of the electrolyte was adjusted to approximately 12.6 using KOH and the deposition temperature was 70°C. Various concentrations of DPS and 0.1 g/L of 2,2′-dipyridyl were added to the electrolytes. After Cu filling, a heat-treatment was performed at 400°C for 30 min under N_2 atmosphere.

Field emission scanning electron microscopy (FESEM, JEOL 6330F) was used to measure the film thicknesses and investigate the filling profiles in accordance with the concentrations of additives. The resistivities were calculated from sheet resistances measured by a four-point probe (Chang Min CMT-SR 1000N).

Results and Discussion

Figure 1 shows the cross-sectional SEM images according to DPS and 2,2′-dipyridyl concentrations in Cu electroless deposition. The DPS concentration was varied from 0 to 5.0 mg/L in the absence of and presence of 0.1 g/L 2,2′-dipyridyl. The relative thickness of the samples (including PVD Cu) was analyzed after 3 min of deposition, as shown in Fig. 2a. When 0.1 mg/L of DPS was added, the Cu thickness increased as compared to that without additives. As the DPS concentration increased, the deposition rates gradually decreased and the surface roughness increased. Electroless Cu deposition was strongly inhibited at 5.0 mg/L DPS, which demonstrated that DPS, as with SPS,[14] showed an accelerating effect at lower concentrations and a suppressing effect at higher concentrations. In Cu electroless deposition, the effect of SPS is similar to that in Cu electrodeposition, yet there seems to be a different mechanism involved due to the complexity of the electrolyte. In preliminary experiments, it was found that SPS made complexes with Cu ions by decomposing to MPSA. Cu-MPSA complexes accelerate Cu reduction, affecting the rate-determining step. Likewise, DPS, which has a similar structure to MPSA, is expected to combine with uncomplexed cupric ions or parts of cupric ions complexed with EDTA and aid in Cu reduction with the dimerization of DPS. Whereas it is considered that at higher concentrations of DPS, dimerized DPS adsorbs and obstructs Cu deposition. Even in Cu electroplating, the critical point exists at the center of which concentration-dependent behaviors occur.[18]

When 0.1 g/L of 2,2′-dipyridyl was contained, the tendency of acceleration and suppression was in agreement with the result in the absence of 2,2′-dipyridyl. However, as a whole, the thickness and

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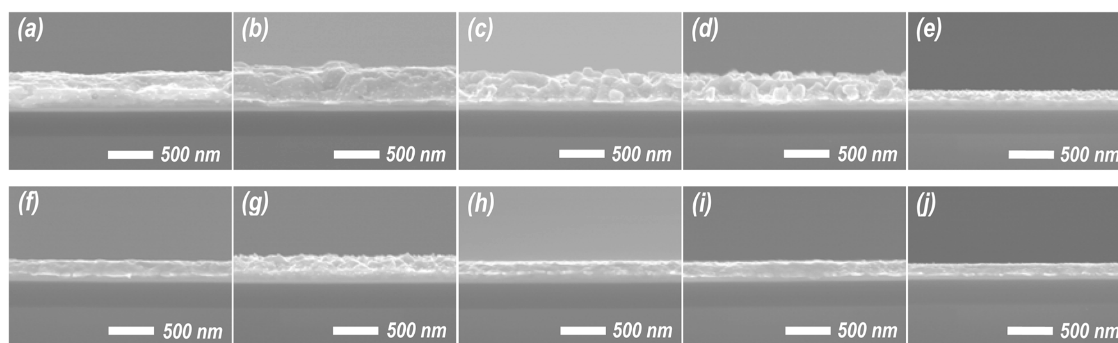

Figure 1. Cross-sectional FESEM images of electroless Cu films deposited for 3 min as a function of DPS and 2,2′-dipyridyl concentrations: (a) 0, (b) 0.1, (c) 0.5, (d) 1.0, and (e) 5.0 mg/L of DPS in the absence of 2,2′-dipyridyl, and (f) 0, (g) 0.1, (h) 0.5, (i) 1.0, and (j) 5.0 mg/L DPS at 0.1 g/L 2,2′-dipyridyl. Substrates covered with 140 nm of PVD Cu were used for examining the effect of DPS.

roughness of Cu films remarkably decreased, and the standard deviation of the thickness decreased. In particular, Cu deposition was completely inhibited at 5.0 mg/L DPS in the presence of 0.1 g/L of 2,2′-dipyridyl. In Cu electroless deposition, 2,2′-dipyridyl, which has been used as a stabilizer and a brightener, plays a role in preventing oxygen incorporation into the film at high deposition temperatures by stabilizing Cu(I) intermediates.[20] Although 2,2′-dipyridyl induced a slight increase in the resistivity at low DPS concentration, the film resistivity was highly reduced with an increase in the DPS concentration by decreasing the surface roughness (Fig. 2b). It has been concluded that there is an optimum condition of additive concentrations which shows an accelerating effect with low surface roughness.

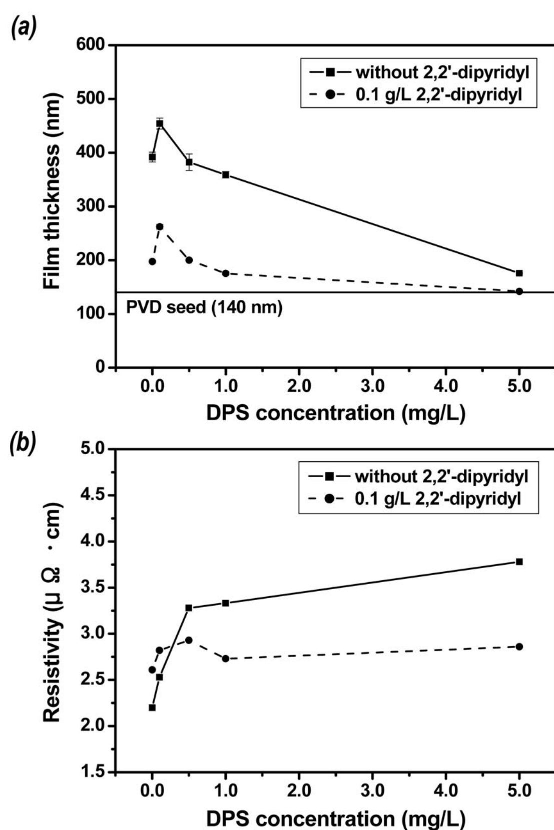

Figure 2. Changes in (a) the film thickness and (b) resistivity according to DPS and 2,2′-dipyridyl concentrations.

To investigate the effect of DPS on the trench patterns, electroless Cu filling was carried out for the same deposition time at different concentrations of DPS with 0.1 g/L of 2,2′-dipyridyl, as presented in Fig. 3a-e. Although conformal filling occurred in the absence of DPS, as the DPS concentration increased, the deposition rate at the bottom increased and deposition at the top was suppressed up to 0.5 mg/L DPS. As shown in Fig. 3a and c, it is clear that DPS has not only a suppressing effect in Cu electroless deposition but also has an accelerating effect. However, as the DPS concentration went beyond 1.0 mg/L, Cu deposition was gradually inhibited from the top through the bottom of the trenches. The deposition rate difference between the top and the bottom of the trench in terms of DPS concentration is thought to be due to the concentration gradient between the top and bottom by diffusion of DPS. When DPS was added at the concentration that showed a suppressing effect on the planar surface, even if Cu deposition was inhibited on the top of the trench, a concentration gradient was generated by the diffusion of DPS during the deposition. Thus, the acceleration of Cu deposition appeared at the bottom, which had a relatively low DPS concentration. However, with a higher concentration on the surface, as shown in Fig. 3e, even at the bottom, DPS showed a suppressing effect.

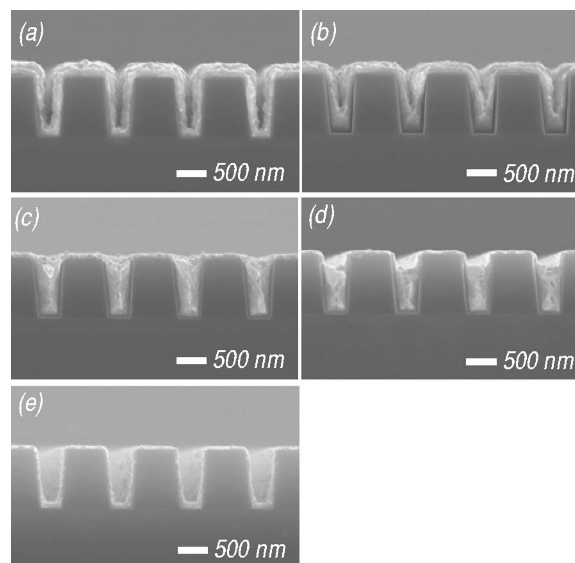

Figure 3. Electroless Cu filling profiles with varying DPS concentrations with 0.1 g/L 2,2′-dipyridyl: (a) 0, (b) 0.1, (c) 0.5, (d) 1.0, and (e) 5.0 mg/L DPS.

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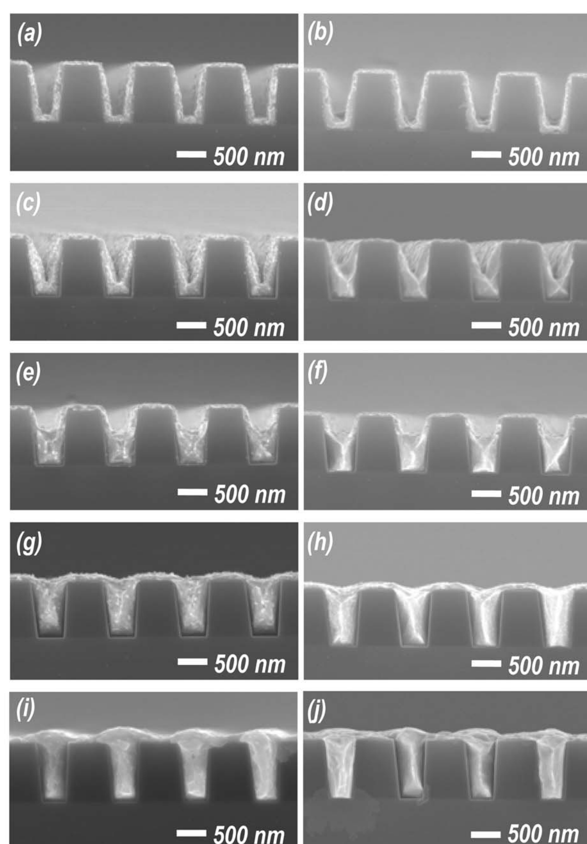

Figure 4. Time evolution profiles of electroless gap-filled Cu at 0.5 mg/L DPS and 0.1 g/L 2,2′-dipyridyl: (a) 2, (c) 5, (e) 8, (g) 16, and (i) 25 min, and (b), (d), (f), (h), and (j) after annealing at 400°C for 30 min under N_2 atmosphere.

Figures 4a, c, e, g, and i show the result of Cu filling with elapsed deposition time performed with the electrolytes containing 0.5 mg/L DPS and 0.1 g/L 2,2′-dipyridyl, which provided the best profiles in the experiment. Bottom-up filling of Cu was observed over time in Cu electroless deposition, and the evidence of superfilling was confirmed from the formation of bumps on the top surface without any voids or seams after 25 min of deposition. After deposition, thermal annealing was carried out at 400°C under N_2 atmosphere for 30 min, as displayed in Fig. 4b, d, f, h, and j. The surface morphologies were improved after thermal annealing because of the stabilization of microstructure by surface diffusion.

The acceleration of the deposition rate at the bottom is possible when the gradient of DPS concentration inside the trench is maintained. We can estimate that the incorporation of DPS into the film produced the concentration gradient, as seen from the increase in the resistivity by the addition of DPS. Therefore, the formation of bumps can be controlled with DPS concentration. Despite the one-step method omitting a seed layer formation step, the low surface roughness and improved filling profiles compared with the use of SPS[15] makes it possible to perform a subsequent chemical mechanical polishing (CMP) step and thereby enhance the reliability of Cu interconnection.

Conclusions

DPS, which has a similar molecular structure to MPSA, showed an accelerating effect at lower concentrations and a suppressing effect at higher concentrations. The rough surface from the acceleration was improved by the addition of 2,2′-dipyridyl.

On trench patterns, Cu bottom-up filling was successfully achieved with a considerably smoother surface using DPS in Cu electroless deposition, resulting in void-free and seam-free filling of Cu. The formation of bumps, which is evidence of bottom-up filling, was observed after 25 min of deposition, and it can be controlled by additive concentrations. Consequently, DPS is expected to be an effective accelerating-suppressing additive for Cu superfilling by the electroless deposition.

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