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Copper Bottom-Up Filling by Electroplating Without any Additives on Patterned Wafer

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In conventional Cu electroplating, various additives are used to fill pattern without defects in patterned wafers. Pulse plating and electrochemical oxidation were used to deposit Cu without any additives. Defects such as voids and seams were generated if only pulse plating was carried out. Electrochemical oxidation was performed to remove Cu metal containing defects and to remain Cu species only at the bottom part of the trenches. Then, defect free Cu films could be obtained when Cu electroplating without additives was performed on the etched substrate.
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Electroplating has been recently developed to form Cu interconnects in ultralarge scale integrated chips.[1] It is known that additives such as suppressors and accelerators are required in the electrolyte to perform gap filling in patterned wafers.[2] In this case, however, it is difficult to control the electroplating process and the incorporation of additives in Cu films increases their overall resistivity. Hence, it is desirable to plate Cu layers using an electrolyte without additives.

In our previous paper,[3] Cu gap filling using electrochemical oxidation instead of accelerators was accomplished. In those experiments, defect free Cu films were electroplated after Cu films which were conformally deposited using suppressor were etched by phosphoric acid. Cu can be conformally plated by two methods: Cu electrodeposition using suppressors and Cu pulse plating. Polyethylene glycol–Cl and benzotriazole have been used as suppressors in order to plate Cu layers conformally.[3] According to Seah, Cu can be conformally deposited by pulse plating as well.[4] Therefore, in this experiments, a pulse plating technique was attempted to produce defect free Cu films in trenches by electroplating without additives.

The structure of trenches used in this study were TiN (10 nm)/Ti (15 nm)/Si. The TiN layer was used as a Cu diffusion barrier. The Ti and TiN layers were deposited by ionized metal plasma physical vapor deposition (PVD) and metallorganic chemical vapor deposition, respectively. The width of the trenches were 0.6 um and the aspect ratio was 1.5:1. A seed layer is necessary to deposit Cu by electroplating. In this experiment, a 100 nm thick seed layer was prepared by Cu PVD. During electroplating, the area of the cathode was set at 1 cm^2. The electrolyte used for electroplating was composed of 1 M H_2SO_4, 0.25 M $CuSO_4 \cdot 5H_2O$, and deionized water. No additives were present in the electrolyte. An Au wire and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively.

To deposit the Cu layer conformally, pulse plating was performed for 5 min. The current density during on time was controlled at 10 mA/cm^2. When the current density was above 15 mA/cm^2, Cu was deposited mainly at the upper part of the trench; deposit was controlled by a mass transfer limited reaction. The on/off frequencies used in these experiments were 50 Hz, 250 Hz, 1 kHz, and 5 kHz, and the duty cycle was 50%.

As a result of pulse plating, seams and voids were generated in the deposited Cu layer. To etch the defects in the Cu film and to remain Cu metal only at the bottom part of trench, a constant potential of 1.25 V vs SCE was applied for 15 s to the substrate in a 85% H_3PO_4 solution, as optimized in our previous paper.[3] Finally, electroplating was performed on the etched substrate at a constant current of 2 mA/cm^2 to achieve bottom up filling.

First, Cu was electrodeposited on a Cu seed layer under a constant current of 10 mA/cm^2 in electrolyte without any additives. Cu was conformally deposited while Cu ions existed in a diffusion layer in the initial stage of electroplating. Cu ions were supplied by diffusion from the bulk phase after all of the Cu ions in the diffusion layer were deposited, indicating that the deposition rate of Cu ions is determined by mass transfer. Diffused Cu ions were reduced at the upper part of trench before the ions were uniformly distributed in the diffusion layer. As a result, voids were generated in the trench, as shown in Fig. 1, because Cu was mainly deposited at the upper part of the trench without filling the trench with Cu metal.

Pulse plating on the Cu seed layer was performed without additives. In pulse plating, uniform Cu reduction throughout the substrate surface can be generated by Cu ion diffusion during the off time.[5] At the frequencies of 50 Hz, 250 Hz, 1 kHz, and 5 kHz, a considerable amount of Cu was deposited in the trench (Fig. 2). The amount of Cu reduced in the trench increased with an increase in frequency. This was attributed to the increase in mass transfer limited Cu reduction time during the longer on time at shorter frequencies. However, defects such as voids still existed in

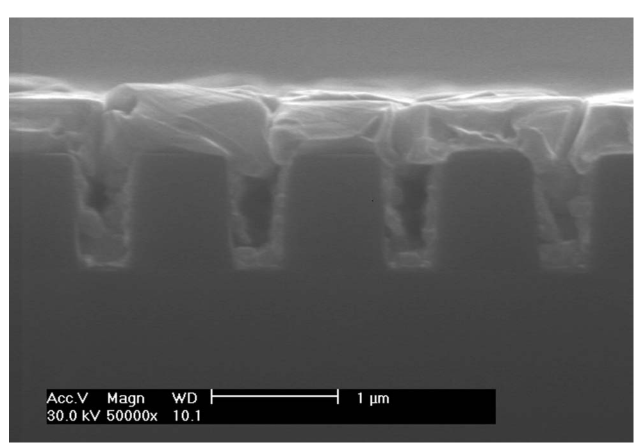

Figure 1. FESEM of electroplated Cu species without any additives.

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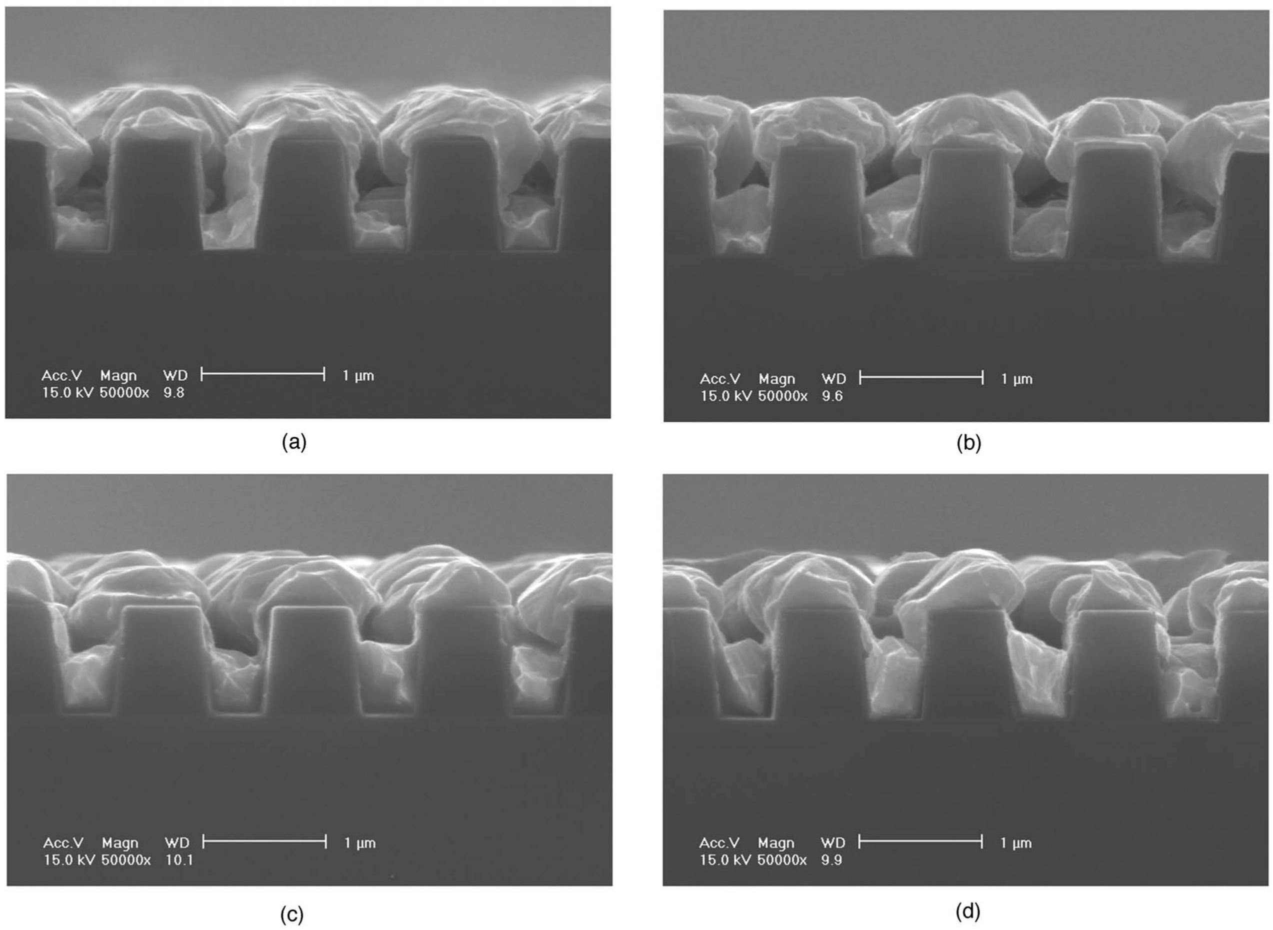

Figure 2. FESEM of Cu film which was pulse plated at the frequency of (a) 50 Hz, (b) 250 Hz, (c) 1 kHz, and (d) 5 kHz.

the trench at allfrequencies. It has been reported that it is impossible to perform Cu gap filling without defects by using only pulse plating.[4,6]

The subsequent Cu etching process was carried out to remove Cu metal at the upper part of the trench and Cu species containing defects in the trench. Because Cu was etched vertically

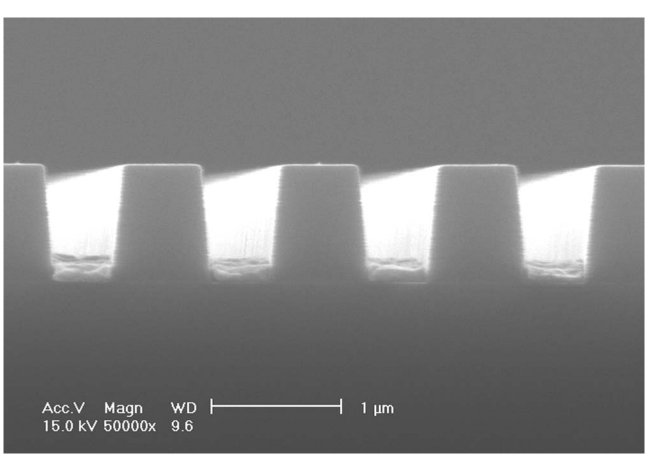

Figure 3. Cu electrochemical oxidation of Cu film which was pulse plated at the frequency of 1 kHz.

in a H_3PO_4 solution,[3] the Cu film could remain only at the bottom part of the trench after Cu electrochemical oxidation, as shown in Fig. 3.

In this experiment, Cu is electrochemically etched by[7]

$$Cu \rightarrow Cu^{2+}_{ads} + 2e^- \quad [1]$$

$$6H_2O + Cu^{2+}_{ads} \rightarrow [Cu(H_2O)_6]^{2+} \quad [2]$$

If Cu was electrically isolated after the complete Cu etching at the upper part of trench, Cu would not be etched any more in H_3PO_4 solution. However, Cu etching kept going so that the proper etching time led to Cu remaining only at the bottom part of trench since a TiN diffusion barrier played a role of the current path to etch. The TiN diffusion barrier remained even after Cu electrochemical oxidation and was also used as the current path for the subsequent electroplating process.

Finally, Cu was electroplated without any additives on the etched substrate. Because Cu was deposited vertically,[3] defect free Cu films could be generated by dc plating at all frequencies (Fig. 4).

Conclusion

In this study, Cu electroplating on patterned wafers was performed. To obtain defect free Cu films, pulse plating and electrochemical oxidation were used in place of additives. By using pulse plating, the amount of Cu metal reduced in the trench could increase. As a result, the margin of subsequent electrochemical oxida-

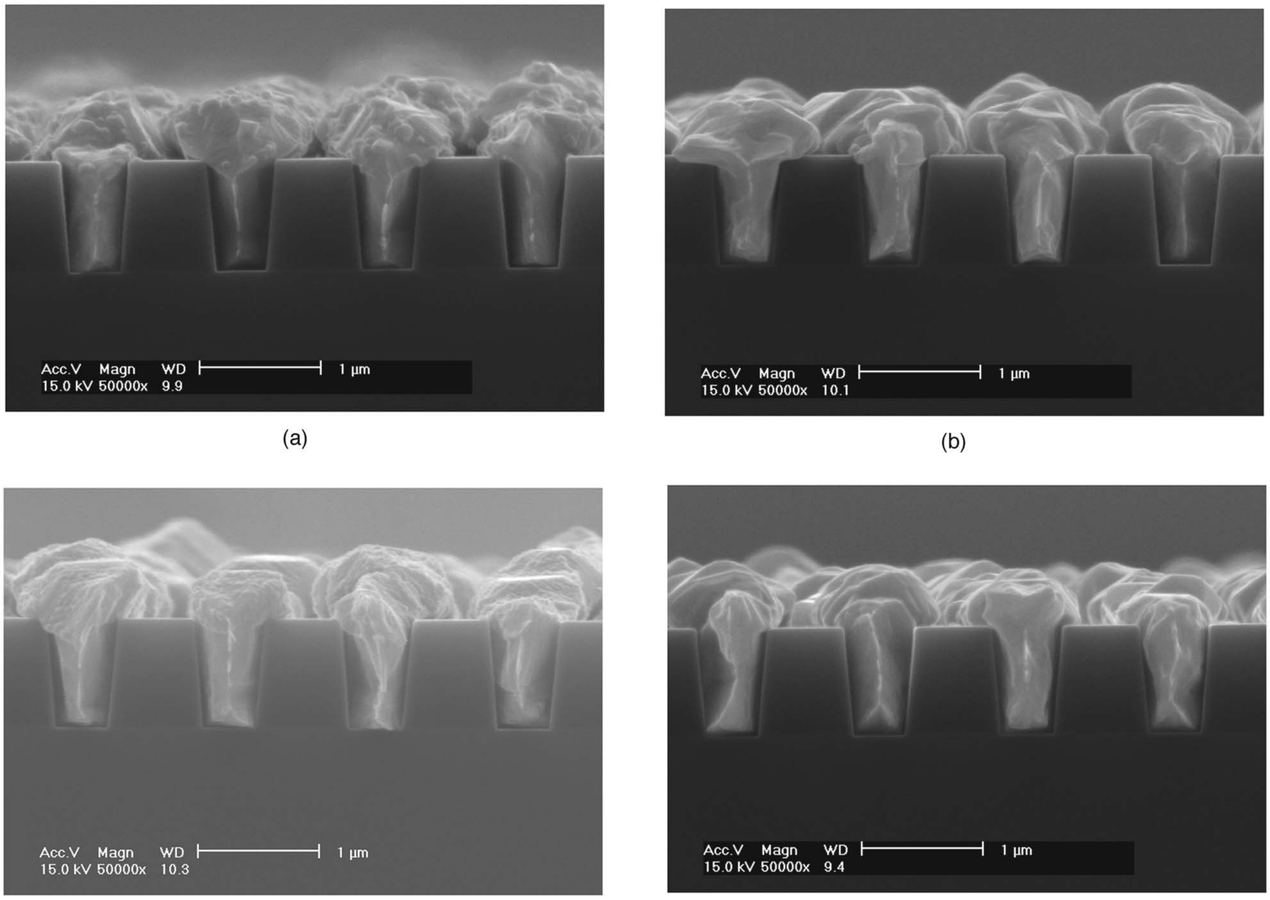

Figure 4. Cu dc electroplating after etching substrate which was pulse plated at the frequency of (a) 50 Hz, (b) 250 Hz, (c) 1 kHz, and (d) 5 kHz.

tion of Cu species in the trench increased. After electrochemical oxidation, defect free Cu gap filling was achieved by electroplating without any additives.

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