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Bottom-Up Filling Using Electrochemical Oxidation on Patterned Wafers

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Cu electroplating has been researched to form the interconnect in integrated circuits. A suppressor and an accelerator are required to accomplish superconformal deposition by electroplating on patterned wafers. Under these conditions, however, it is complicated to control the process and the incorporation of additives in the Cu film increases its overall resistivity. Hence, it is necessary to reduce the amount of additive in the electrolyte. In this paper, gap filling using electrochemical oxidation instead of an accelerator was investigated. This approach resulted in the realization of genuine bottom-up filling.
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In conventional electroplating, it is known that both a suppressor and an accelerator must be used to carry out gap filling.[1] In this paper we describe gap filling using electrochemical oxidation. This process resulted in good bottom-up filling.

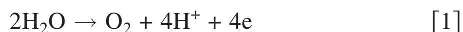
The structure of the trench used in this study was TiN (10 nm)/Ti (15 nm)/Si. The TiN layer was used as the diffusion barrier against Cu. Ti and TiN layers were deposited by ionized metal plasma physical vapor deposition (PVD) and metallorganic chemical vapor deposition, respectively. The width of the trench was 0.6 μm and aspect ratio was 1.5:1. A seed layer is necessary for depositing Cu by electroplating. In this experiment, a seed layer with a thickness of 100 nm was prepared by PVD. The area of the cathode was controlled to be 1 cm^2. The electrolyte for electroplating was composed of 1 M H_2SO_4, 0.25 M $CuSO_4 \cdot 5H_2O$, and deionized water. 88 μM polyethylene glycol (PEG)-1 mM Cl [2] and 1.4 mM benzotriazole (BTA)[3] were used as suppressors. The current density was applied at 2 mA/cm^2. Au wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

A seam or void is generated in Cu film electroplated with only a suppressor. In order to etch defects in Cu film, a constant oxidation potential was applied to the substrate in 85% H_3PO_4 solution. Finally, to achieve bottom-up filling electroplating was carried out on the etched substrate at a constant current of 2 mA/cm^2.

When only a suppressor such as PEG-Cl or BTA is used as an additive for Cu electroplating, a Cu layer with a void or seam is generated. Since BTA plays the role of a brightener as well as a suppressor in Cu electroplating,[4] a seam is generated. In the absence of voids, the etching profile of the Cu film could be controlled with ease, which is the reason for choosing BTA as a suppressor in these experiments.

In order to eliminate a seam or void formed in the trench and retain the Cu layer at the bottom part of trench, Cu was oxidized by various methods. As a result of oxidation in the electrolyte for Cu electroplating, Cu was oxidized nonuniformly.

85% H_3PO_4, which was effective in electrically polishing Cu film,[5] was used as the electrolyte for Cu oxidation. As the oxidation voltage increased to 0.5 V vs SCE, the current increased to −200 mA. In this potential range, Cu was oxidized nonuniformly due to variations in the etch rate of crystallographic faces. However, it was remarkable that Cu was evenly oxidized due to the generation of a passivation layer at the oxidation voltage above 0.5 V vs SCE. Since a higher voltage led to a decrease in the current efficiency owing to the generation of O_2 gas by Reaction 1,[6] the optimum potential was determined to be 1.25 V vs SCE



$$2H_2O \rightarrow O_2 + 4H^+ + 4e \quad [1]$$

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According to West et al.,[6] the electrochemical oxidation of Cu, utilizing the H_3PO_4 solution as the electrolyte, is generated by an acceptor mechanism as follows

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

$$6H_2O + Cu^{2+}_{ads} \rightarrow [Cu(H_2O)_6]^{2+} \quad [3]$$

In the H_3PO_4 solution, H_2O plays the role of an acceptor for the Cu ion. Since the 85% H_3PO_4 solution is viscous, the mobility of the Cu ion is decreased. Therefore, this reaction is under diffusion control of H_2O, showing that the Cottrell equation can be applied in this system. In the Cottrell equation, current i is inversely proportional to reaction time $t^{0.5}$ (Ref. 7). In other words, $i\sqrt{t}$ remains constant in this system.

Figure 1a depicts chronoamperometry at 1.25 V vs SCE. When $i\sqrt{t}$ is plotted according to polishing time, it is apparent from Fig. 1b that the polishing trend can be separated into two parts. This value is reduced owing to the decrease in the electrode area when Cu at the upper part of trench is removed and Cu etching inside the trench is started. The etching trend was confirmed by field emission scanning electron microscopy (FESEM) images (Fig. 1c-e). When the Cu layer was etched for 15 s, the seam portion was completely removed (Fig. 1e). Hence, the polishing time was determined to be 15 s.

If the TiN barrier is etched by the Cu electrochemical oxidation process, Cu can diffuse into devices. Therefore, it is important that the TiN barrier is not etched during electrochemical oxidation. As a result of cyclic voltammetry of the TiN barrier in 85% H_3PO_4, it was found that the TiN barrier was not oxidized at the electrochemical oxidation condition for Cu.

Figure 2 describes chronopotentiometry at a constant current density of 2 mA/cm^2 on the Cu layer that was polished for 15 s and FESEM images at specific time. It was remarkable that the Cu layer was deposited vertically. Therefore, genuine bottom-up filling can be realized by this method.

Theoretically, chronopotentiogram for a Nernstian electrode process is described as follows[7]

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad [4]$$

where E is the potential of an electrode, $E_{\tau/4}$ the quarter wave potential, R molar gas constant, T temperature, n the stoichiometric number of electrons consumed in the electrode reaction, F the Faraday constant, τ the transition time, and t time.

According to Eq. 4, the potential can approach infinity after the transition time. However, in this system, the potential decreased after 800 s of deposition time (Fig. 2a). This was attributed to an increase of the electrode area by deposition at the upper part of trench. This assumption was confirmed by FESEM images as shown in Fig. 2b-e.

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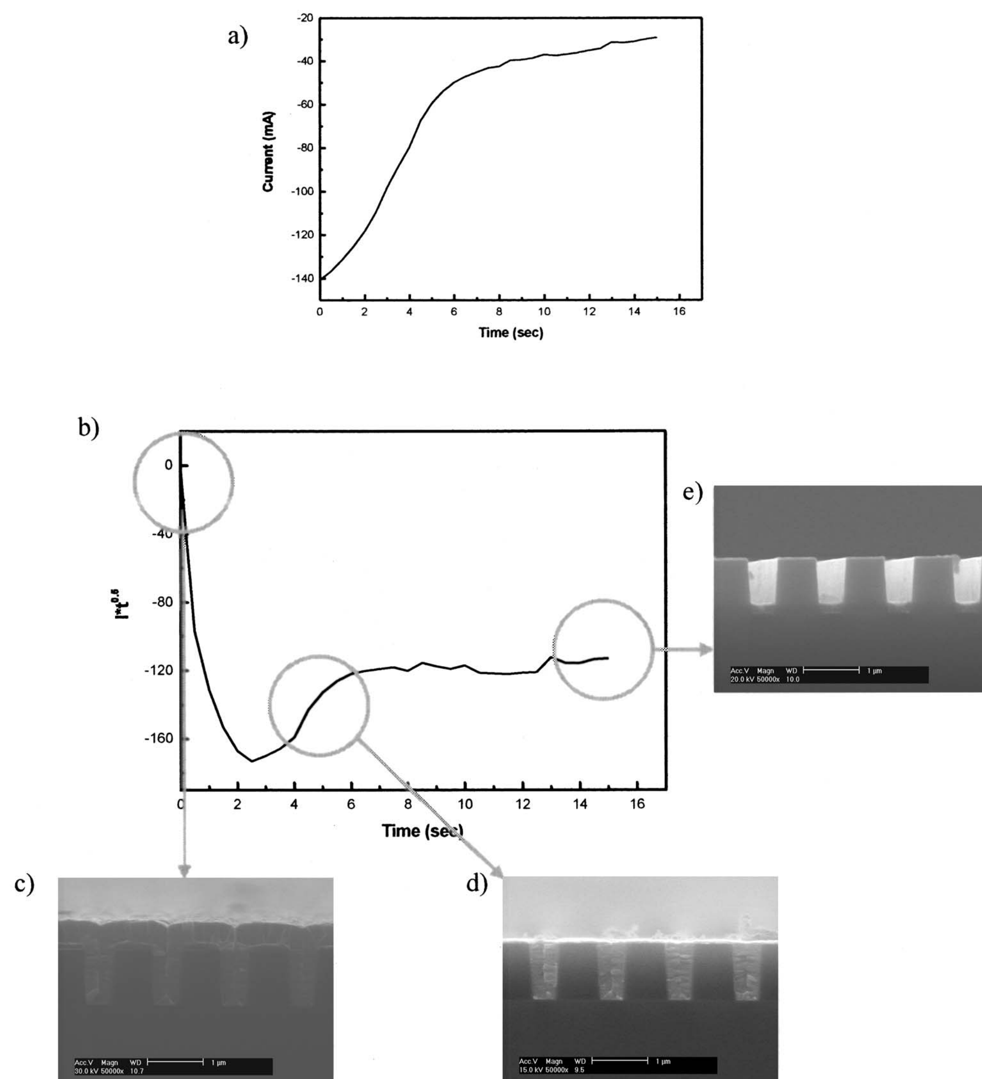

Figure 1. (a) Chronoamperometry of electrochemical oxidation at 1.25 V vs SCE and (b) value of $i\sqrt{t}$ as a function of time and FESEM images of Cu film etched for (c) 0, (d) 5, and (e) 15 s.

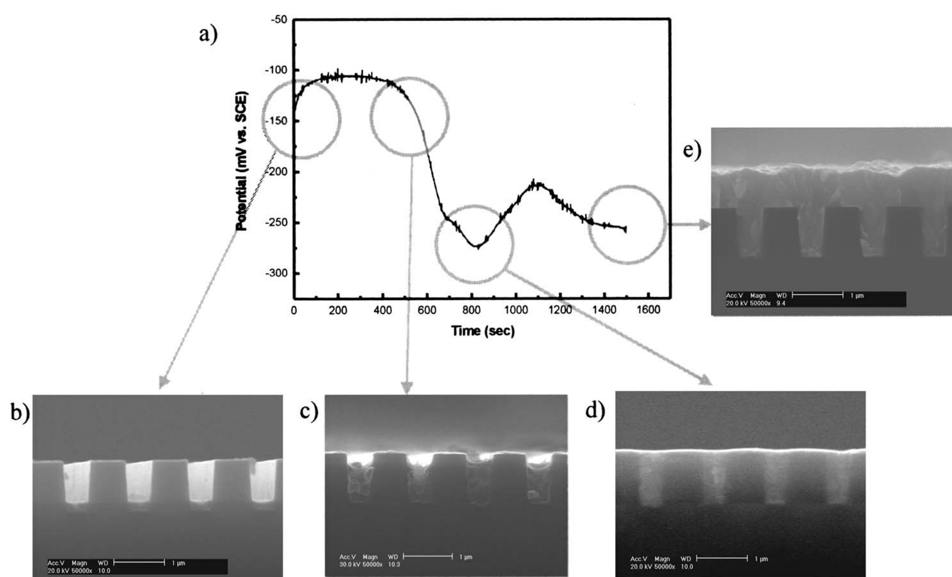

Figure 2. (a) Chronopotentiometry at 2 mA/cm^2 of current density on Cu layer polished for 15 and FESEM images of Cu film deposited for (b) 0, (c) 500, (d) 900, and (e) 1500 s.

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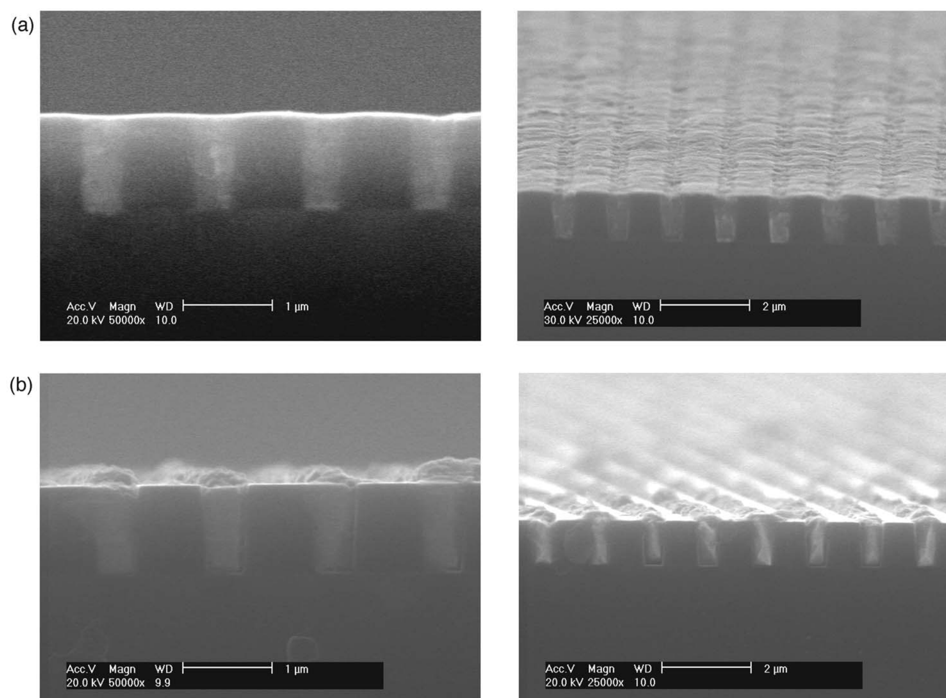

Figure 3. Cu electroplating using (a) BTA and (b) PEG-Cl on etched Cu layer.

From a result of chronopotentiometry (Fig. 2a), the end point of electroplating can be determined. Subsequent chemical mechanical polishing (CMP) process can be minimized if electroplating is halted at the time when the electrode potential begins to decrease (Fig. 2d).

Finally, when BTA was used in this system, a brightening effect as well as bottom-up filling was accomplished (Fig. 3a), indicating that the CMP process could be minimized. In addition, when electroplating was performed using PEG-Cl on an etched Cu layer, the trench was filled with Cu by bottom-up filling but the surface was rough (Fig. 3b). However, the resistivity of Cu film deposited using PEG-Cl, 2.2 $\mu\Omega$ cm, was lower than that of Cu film done using BTA, 6.0 $\mu\Omega$ cm.

In these experiments, electrochemical oxidation was used in place of an accelerator in order to achieve gap-filling by electroplating. Defects made by using only a suppressor can be removed vertically by electrochemical oxidation using 85% H_3PO_4. At this time, Cu film exists at the bottom part of trench. The trench can then be filled with defect-free Cu when electroplating is performed on the etched substrate. Furthermore, the need for a subsequent CMP process can be minimized by the brightening effect that results from the use of BTA as an additive.

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