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Effect of Post-CMP Cleaning On Electrochemical Characteristics of Cu and Ti in Patterned Wafer

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Abstract The effects of post-CMP cleaning on the chemical and galvanic corrosion of copper (Cu) and titanium (Ti) were studied in patterned silicon (Si) wafers. First, variation of the corrosion rate was investigated as a function of the concentration of citric acid that was included in both the CMP slurry and the post-CMP solution. The open circuit potential (OCP) of Cu decreased as the citric acid concentration increased. In contrast with Cu, the OCP of titanium (Ti) increased as this concentration increased. The gap in the OCP between Cu and Ti increased as citric acid concentration increased, which increased the galvanic corrosion rate between Cu and Ti. The corrosion rates of Cu showed a linear relationship with the concentrations of citric acid. Second, the effect of Triton X-100®, a nonionic surfactant, in a post-CMP solution on the electrochemical characteristics of the specimens was also investigated. The OCP of Cu decreased as the surfactant concentration increased. In contrast with Cu, the OCP of Ti increased greatly as this concentration increased. Given that Triton X-100® changes its micelle structure according to its concentration in the solution, the corrosion rate of each concentration was tested.

Key words post-CMP cleaning, organic acid surfactant chemical corrosion galvanic corrosion.

1. Introduction

Chemical mechanical polishing (CMP) has received great interests since it can induce the local and global planarization of copper (Cu) patterns in the integrated circuits (IC).[1-3] Cu as an interconnecting metal can replace aluminum (Al) in IC fabrication since Cu has low electrical resistivity, showing high immunity to electromigration compared to Al.[1-3] However, pure Cu can not sustain its structure during the conventional etching process. CMP is the planarization method using abrasive particles instead of conventional acid solution. Therefore, the Cu side walls are safe from the chemical attack during CMP. On the other hand, CMP slurry contains some chemically active slurries and abrasive particles, and thus there exist leftover particles on the wafer after CMP. Therefore, the post-CMP cleaning has to be introduced in order to remove residues derived from the slurry. Extensive studies have been carried out to enhance post-CMP cleaning ability.[4-6] However, there have been few studies on corrosion occurring during post-CMP cleaning. Since the corrosion can deteriorate device yields, the protection of Cu against the corrosion is a critical issue in post-CMP cleaning.

In general, chemical and galvanic corrosion is reported in post-CMP cleaning. Chemical corrosion occurs due to an organic acid included in cleaning solution, while galvanic corrosion occurs due to the electrochemical potential difference building between Cu used as an interconnecting metal and Tantalum (Ta) or Ti used as a barrier metal in IC.[7] The objective of this study is to understand the effect of two major constituents in post-CMP cleaning solution on the corrosion reactions of wafer. In order to investigate the effect of the organic acid contained in cleaning solution on the wafer, the respective corrosion rate of Cu, Ti and the patterned wafer in the citric acid solution with various concentrations was measured using an electrochemical analyzer. The effect of Triton X-100® well known as an excellent surfactant for the post-CMP cleaning solution[8] on the corrosion rates was also investigated. Based on the experimental results, the Cu corrosion mechanism of wafer during post-CMP cleaning process was discussed in detail.

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2. Experimental procedure

Cu layer (15,000 Å) was deposited on the Ti (250 Å)/Si wafer using RF-sputtering. Ti layer (2000 Å) was deposited on bare Si wafer. Both wafers were sliced into the size of 10 × 15 mm using a low-speed diamond saw. They were covered with room temperature vulcanizing (RTV) silicone rubber except areas in contact with an electrode (3 × 7 mm) and reacted with post CMP solution (7 × 7 mm). A pattern mask was designed and fabricated for making Cu lines with the dimension of 10 × 15,000 μm on SiO_2-deposited (1 μm) wafer and the space between the lines was identical to thickness of Cu lines. After oxide etching to the depth of 0.4 μm, a Ti barrier layer (500 Å) and a sequent Cu seed layer (1000 Å) were deposited in the trenches. The trenches were filled with Cu via electrodeposition and the excess of Cu was removed by CMP process. The patterned wafer was also sliced and covered with RTV silicone rubber which was the same as above Cu- and Ti-deposited wafers. A silver electrode was covered on each slice of the patterned wafer for the full contact of Cu lines.

Citric acid (99.5%, Aldrich) and Triton X-100® (Aldrich) were purchased for corrosion experiments. The concentration of citric acid was varied at 0.15, 0.3, 0.6, 1.5 and 3.0 wt%. Triton X-100® was used as a surfactant whose critical micelle concentration (CMC) is 0.22 mM[9] and the concentration of Triton X-100® in 0.15 wt% citric acid solution was varied at 1, 2, 5, 10 and 20 CMC.

The electrochemical analyzer (CompactStat, Ivium, Netherlands) with three electrode cells was used for the corrosion experiment. The Ag/AgCl electrode was used as a reference electrode to which all potentials were referred and platinum (Pt) mesh was used as a counter electrode. The working electrodes were the samples of Cu, Ti and patterned wafer which were immersed in post-CMP cleaning solution with exposed area of 49 mm^2.

3. Results and Discussion

Open circuit potentials (OCPs) were measured to determine the redox limit. Each OCP of samples in the citric acid with different concentration varied slowly due to the removal of the oxide film naturally produced in the air. They became nearly constant after 300 seconds, and then these values were adopted as the OCP of each sample. The OCP of Cu decreased as the concentration of the citric acid increased. In contrast, the OCP of Ti increased with the concentration of the citric acid. Fig. 1(a) shows the variation in OCPs of Cu and Ti as the function of the citric acid concentration. The difference between the two data was also plotted. The OCP difference between two metals increases with the concentration of the citric acid, which may lead to the increase of galvanic corrosion rate.

The corrosion parameters were measured by potentiodynamic polarization experiments, and the Tafel calculation[10] was used to determine the rate of corrosion occurring at the surface of each sample. Fig. 1(b) shows the relationship between the corrosion rate and the concentration of citric acid and, and the overall corrosion reaction can be described as following.

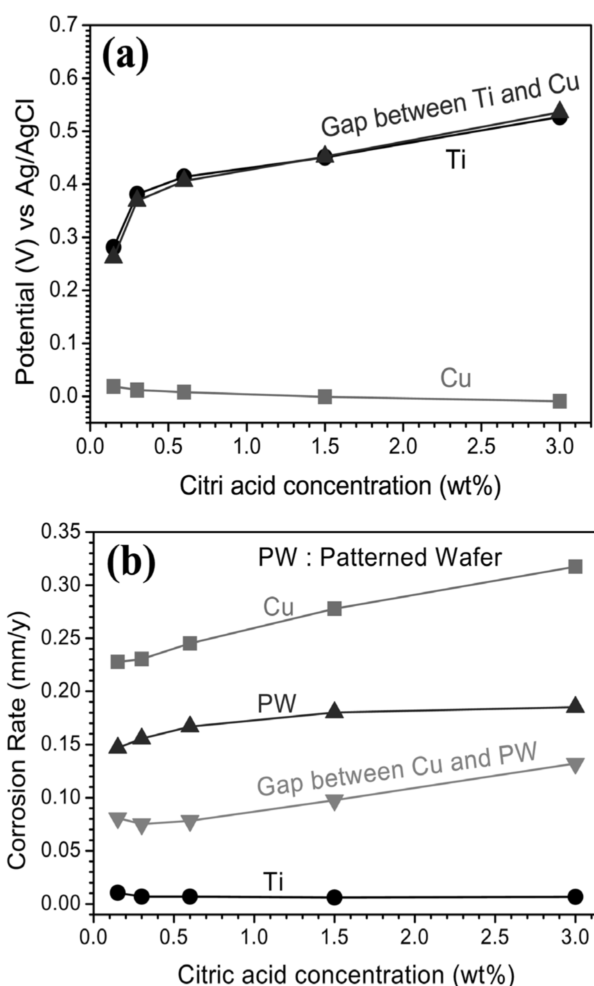

Fig. 1. (a) Open circuit potential (OCP) of Cu and Ti as a function of citric acid concentration. The difference in OCPs is also plotted. (b) Corrosion rate of Cu, Ti and patterned wafer as the function of citric acid concentration.

$$Cu \rightarrow Cu^{2+} + 2e^- \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

Below pH 3, Cu can be dissolved to Cu^{2+} ions owing to the high oxidizing ability of acid and these ions do not form a complex with the citric acid.[11] Then, the corrosion of metal is mainly related to the reduction of hydrogen ions in acid solution. As the citric acid concentration increases, hydrogen ions can diffuse into the surface of wafer more easily. Therefore, the increase in acid concentration leads to the increase in corrosion rate of a metal. As shown in Fig. 1(b), the corrosion rate of Cu shows the linear relationship with the concentration of the citric acid. In contrast to Cu, Ti is hardly affected by the citric acid and it maintains its very low corrosion rate due to the extremely passive and compact native TiO_2 layer.

On the other hand, if only the chemical corrosion occurs in the patterned wafer having the reaction area consisting of 99.4% Cu and 0.6% Ti except the SiO_2 area, the corrosion behavior is expected to be identical to the Cu plot shown in Fig. 1(b). However, the patterned wafers show the different results with Cu samples, and this can be explained by the galvanic effect. The electrons in Ti transfer to Cu due to its lower electrochemical potential compared to Cu, and then the oxidation rate of Cu decreases by the electron transfer. Since the potential difference between Cu and Ti increases with citric acid concentration as shown in Fig. 1(a) and the galvanic effect is proportional to the potential difference, the galvanic effect increases with the citric acid concentration. This could be the reason that the corrosion rate of Cu and that of patterned wafer was different from each other.

The effect of Triton X-100® on the OCPs of Cu and Ti is presented in Fig. 2(a). The OCP of Cu decreases as the concentration of Triton X-100® increases. In contrast, the OCP of Ti increases with Triton X-100®. The OCP of Cu shows extremely small change compared to Ti, and the OCP difference between Cu and Ti increases with Triton X-100® concentration. This could lead to the increment of galvanic corrosion. The corrosion rate of the samples is presented in Fig. 2(b). Since Triton X-100® changes its micellar structure with responding to concentrations,[12,13] the effect of surfactants can be considered from a molecular structure point of view. At a concentration of Triton X-100® below 1.0 CMC, there exist only monomers in the solution, and the monomers attach to the surface of wafer by their hydrophilic heads. As a result, these monomers act as a protection layer to prevent corrosion of Cu in each wafer. At a concentration ranging from 1.0 to 2.0 CMC of Triton X-100®, monomers combine with each other to make anisotropic structures. They also prevent corrosion of Cu in the wafer. On the other hand, corrosion rate of Ti is extremely low, and it seems not to be seriously affected by the concentration of surfactants. It has been proposed that Triton X-100® starts to form spherical micellar structures at a concentration beyond 2.0 CMC. These structures have hydrophilic outer layers, and thus they cannot combine with the anisotropic micellar structures previously attached to wafer. Some of dimmers combined with the wafer participate in the formulation of spherical micellar structures, and then the surface passivation effect decreases. Therefore, the corrosion rate of Cu ceases to

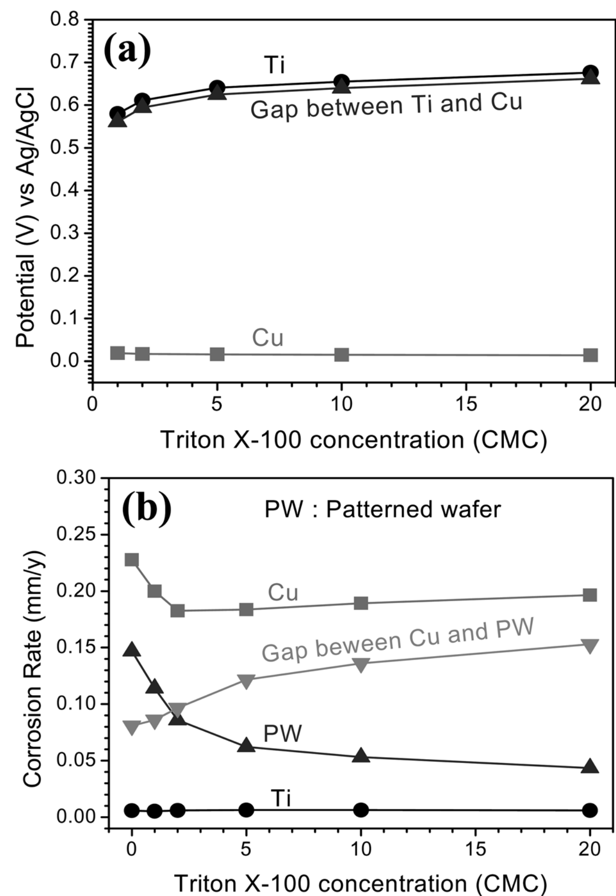

Fig. 2. (a) Open circuit potential (OCP) of Cu, Ti as a function of Triton X-100® concentration. The difference was also plotted. (b) Corrosion rate of Cu, Ti and patterned wafer as a function of Triton X-100® concentration.

decrease and starts to increase slowly beyond 2.0 CMC of Triton X-100®. The corrosion rate of the patterned wafer also decreases as the surfactant layer forms below 2.0 CMC of Triton X-100®. Since the difference in OCPs between Ti and Cu increases with Triton X-100® concentration, the galvanic effect could also increase with it. Accordingly, the corrosion rate of the patterned wafer decreases slowly in spite of the reduction of the passivation effect above 2.0 CMC of Triton X-100®.

Fig. 3 shows optical microscopy images of the patterned wafer corroded without (a) and with (b) Triton X-100®. Fig. 3 (a) shows that yellow Cu lines on the wafer were corroded randomly, and this indicates that the chemical corrosion is dominant by citric acid. Fig. 3 (b) shows the image of the wafer corroded in a solution containing 20.0 CMC Triton X-100®. Since surfactants form the passivation layer and Ti tends to be corroded instead of Cu by galvanic effect, yellow Cu lines were partially left in the patterned wafer.

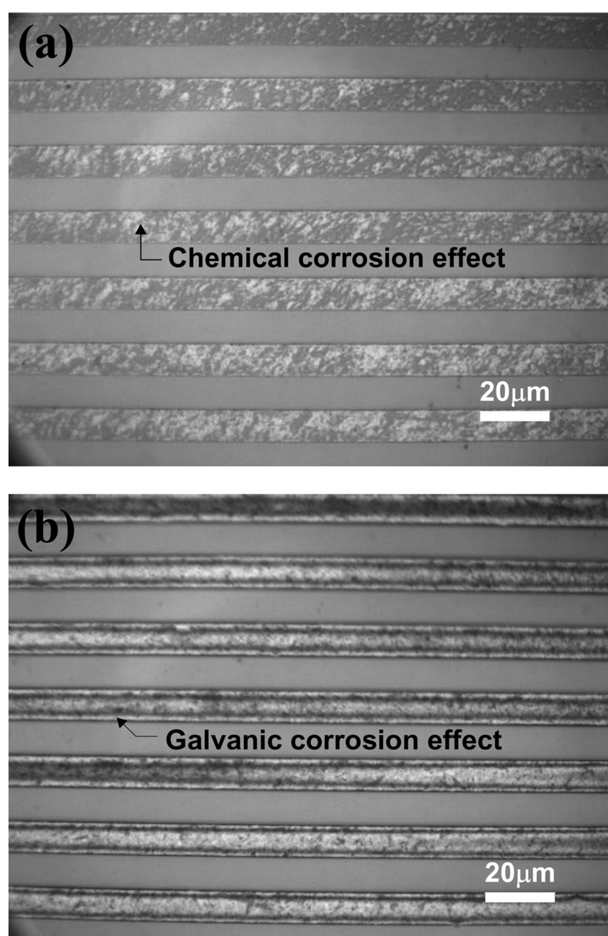

Fig. 3. Optical microscopy images of the patterned wafer corroded by citric acid (a) without and (b) with Triton X-100®.

4. Conclusion

In this study, the effect of post-CMP cleaning on electrochemical characteristics of Cu and Ti in the patterned wafer was investigated. The OCP of Cu decreased as citric acid concentration increased, while the OCP of Ti increased with it. The chemical corrosion rate of Cu showed a linear relationship with the concentration of citric acid and the corrosion mechanism was discussed in detail. Since the difference in the OCPs between Cu and Ti increased with citric acid, the galvanic corrosion rate increased. On the other hand, the OCP of Cu decreased as Triton X-100® concentration increased and the OCP of Ti increased with it. The corrosion rate of each specimen varied with the concentration of Triton X-100® and the mechanism was discussed from its molecular structure point of views. The suggested mechanism would contribute to in-depth understanding of Cu corrosion occurring during post-CMP cleaning and this understanding would help semiconductor industries control the corrosion and increase device yields

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