Effects of DC Biases and Post-CMP Cleaning Solution Concentrations on the Cu Film Corrosion

Yong K. Lee and Kangsoo Lee[1],[†]

Graduate School of NID Fusion Technology, Seoul National University of Science and Technology,
172 Gongreung-2 Dong, Nowon-Gu, Seoul 139-743 Korea
[1]Xerochem Inc., #101 993-14 Yeongdeok-dong Giheung-gu, Yongin-si Gyeonggi-do (Seoul 446-908 Korea)

Copper(Cu) as an interconnecting metal layer can replace aluminum (Al) in IC fabrication since Cu has low electrical resistivity, showing high immunity to electromigration compared to Al. However, it is very difficult for copper to be patterned by the dry etching processes. The chemical mechanical polishing (CMP) process has been introduced and widely used as the mainstream patterning technique for Cu in the fabrication of deep submicron integrated circuits in light of its capability to reduce surface roughness. But this process leaves a large amount of residues on the wafer surface, which must be removed by the post-CMP cleaning processes. Copper corrosion is one of the critical issues for the copper metallization process. Thus, in order to understand the copper corrosion problems in post-CMP cleaning solutions and study the effects of DC biases and post-CMP cleaning solution concentrations on the Cu film, a constant voltage was supplied at various concentrations, and then the output currents were measured and recorded with time. Most of the cases, the current was steadily decreased (i.e. resistance was increased by the oxidation). In the lowest concentration case only, the current was steadily increased with the scarce fluctuations. The higher the constant supplied DC voltage values, the higher the initial output current and the saturated current values. However the time to be taken for it to be saturated was almost the same for all the DC supplied voltage values. It was indicated that the oxide formation was not dependent on the supplied voltage values and 1 V was more than enough to form the oxide. With applied voltages lower than 3 V combined with any concentration, the perforation through the oxide film rarely took place due to the insufficient driving force (voltage) and the copper oxidation ceased. However, with the voltage higher than 3 V, the copper ions were started to diffuse out through the oxide film and thus made pores to be formed on the oxide surface, causing the current to increase and a part of the exposed copper film inside the pores gets back to be oxidized and the rest of it was remained without any further oxidation, causing the current back to decrease a little bit. With increasing the applied DC bias value, the shorter time to be taken for copper ions to be diffused out through the copper oxide film. From the discussions above, it could be concluded that the oxide film was formed and grown by the copper ion diffusion first and then the reaction with any oxidant in the post-CMP cleaning solution.

Keywords : *CMP, cleaning, Cu film, DC bias, concentration*

1. Introduction

Copper(Cu) as an interconnecting metal layer can replace aluminum (Al) in IC fabrication since Cu has low electrical resistivity, showing high immunity to electromigration compared to Al.[1)-3)] The electrical conductivity of Cu is 35% higher than that of Al and electromigration resistance is 2-4 orders higher than that of Al.[4)] Because of its higher electrical conductivity and electromigration resistance copper metallization can significantly decrease RC delay and increase device speed and reliability. In addition, its excellent thermal conductivity and low electrical resistivity can also help to reduce the power consumption of semiconductor devices. However, it is very difficult for copper to be patterned by the dry etching processes. The chemical mechanical polishing (CMP) process has been introduced and widely used as the mainstream patterning technique for Cu in the fabrication of deep submicron integrated circuits in light of its capability to reduce surface roughness.[5)-6)] CMP is a process of smoothing surfaces with the combination of chemical and mechanical forces, it can be thought of as a hybrid of chemical etching and

---

[†] Corresponding author: kslee@xerochem.com

free abrasive polishing.[1)-3)]

But this process leaves a large amount of residues on the wafer surface, which must be removed by the post-CMP cleaning processes. The major residues include abrasives from the slurry, undesired metallic ions and other chemical components.[7)] 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.[8)-10)] However, there have been few studies on corrosion occurring during Furthermore, the copper corrosion phenomenon during the post-CMP cleaning process must be prevented.[11)] Copper is very easily corroded in a wet environment and its oxidation is not self-limiting like aluminum. Thus copper corrosion is one of the critical issues for copper metallization processes. Severe corrosion can directly cause wafer low yield and any minor corrosion can lead to a potential reliability issues.[12)] Any minor corrosion will result in copper voids at the copper surface, either interfaced with barrier metal or nitride. So, understanding and controlling copper corrosion are very important to improve the device reliability.

Thus, in order to understand the copper corrosion problems in post-CMP cleaning solutions and study the effects of DC biases and post-CMP cleaning solution concentrations on the Cu film, a constant voltage was supplied at various concentrations, and then the output currents were measured and recorded with time.

2. Experimental procedure

The 304 stainless steel plate ($10 \times 20 \times 1.5$ mm^3) was used as a cathode material. The 1,500 nm PVD Cu / Ta 25 nm 150 mm Prime p-type(1-0-0) wafer (SKW Associates, Inc. 2920 Scott Blvd. Santa Clara, CA 95054, USA) was used as an anode material. The wafer was cut into pieces (15×10 mm^2) using a low-speed diamond saw. The current measurements were done using the 34401A digital multimeter (Agilent Technologies, Inc. 5301 Stevens Creek Blvd. Santa Clara CA 95051). Prior to the measurement, the stainless steel plates ($10 \times 20 \times 1.5$ mm^3) were polished with silicon carbide abrasive paper (#600 grit) and cleaned in the ultrasonic cleaner for 10 minutes using acetone, ethanol, de-ionized water sequentially, and followed by blow-drying with the compressed air gun.

To start the measurements, 60 ml of deionized water was poured into the 100 ml size beaker and 0.15 mL, 0.3 ml, 0.6 ml, 1.2 ml of the most widely used Wako Clean-100(Wako Pure Chemical Industries, Ltd. 1-2, Doshomachi 3-Chome, Chuo-Ku, Osaka 540-8605, Japan) post-CMP cleaning solution was injected into the beaker

using a syringe to make 50:1, 100:1, 200:1, 400:1 diluted solutions. The anode and cathode electrodes were installed in the diluted solution and the distance between the anode and cathode electrodes was maintained to 2.5 cm. The anode area size immersed inside the diluted solution was controlled to 5×10 mm^2. The potential voltages were measured and recorded with time by the 34401A digital multimeter.

Constant voltage measurements were performed with the E3634A DC power supply (Agilent Technologies, Inc. 5301 Stevens Creek Blvd. Santa Clara CA 95051). Constant voltage values were set at 1 V, 2 V, 3 V, 4 V, and 5 V, respectively, and the output currents were measured and recorded with time. The surface microstructures were examined at the magnification of 2,000 using the optical microscope (PSM1000SH, Motic Inc. Hong Kong) with the digital camera.

3. Results and discussion

In order to study the effect of DC biases and post-CMP cleaning solution concentrations on the Cu film, a constant voltage was supplied at 1 V, 2 V, 3 V, 4 V, and 5 V, respectively at various concentrations (50:1, 100:1, 200:1, 400:1), and then the output currents were measured and recorded with time as shown in Fig. 1. The current was decreased sharply and then stabilized. It could be explained by the oxide film formation on the copper film and the oxide film was not growing any further. The higher the constant supplied DC voltage values, the higher the initial output current and the saturated current values. However the time to be taken for it to be saturated was almost the same for all the DC supplied voltage values. It was indicated that the oxide formation was not dependent on the supplied voltage values and 1 V was more than enough to form the oxide. However, with the applied voltage higher than 3 V and the concentration higher than 1:200, the current was not stabilized, but increased initially and then decreased a little. It could be explained that copper ions underneath the copper oxide film perforated the copper oxide film, making pores to be formed on the surface of copper oxide film and thus the copper film was exposed directly to the electrolyte and oxidized. With applied voltages lower than 3 V combined with any concentration, the perforation through the oxide film rarely took place due to the insufficient driving force (voltage) and the copper oxidation ceased. However, with the voltage higher than 3 V, the copper ions were started to diffuse out through the oxide film and thus made pores to be formed on the oxide surface, causing the current to increase and a part of the exposed copper film inside the
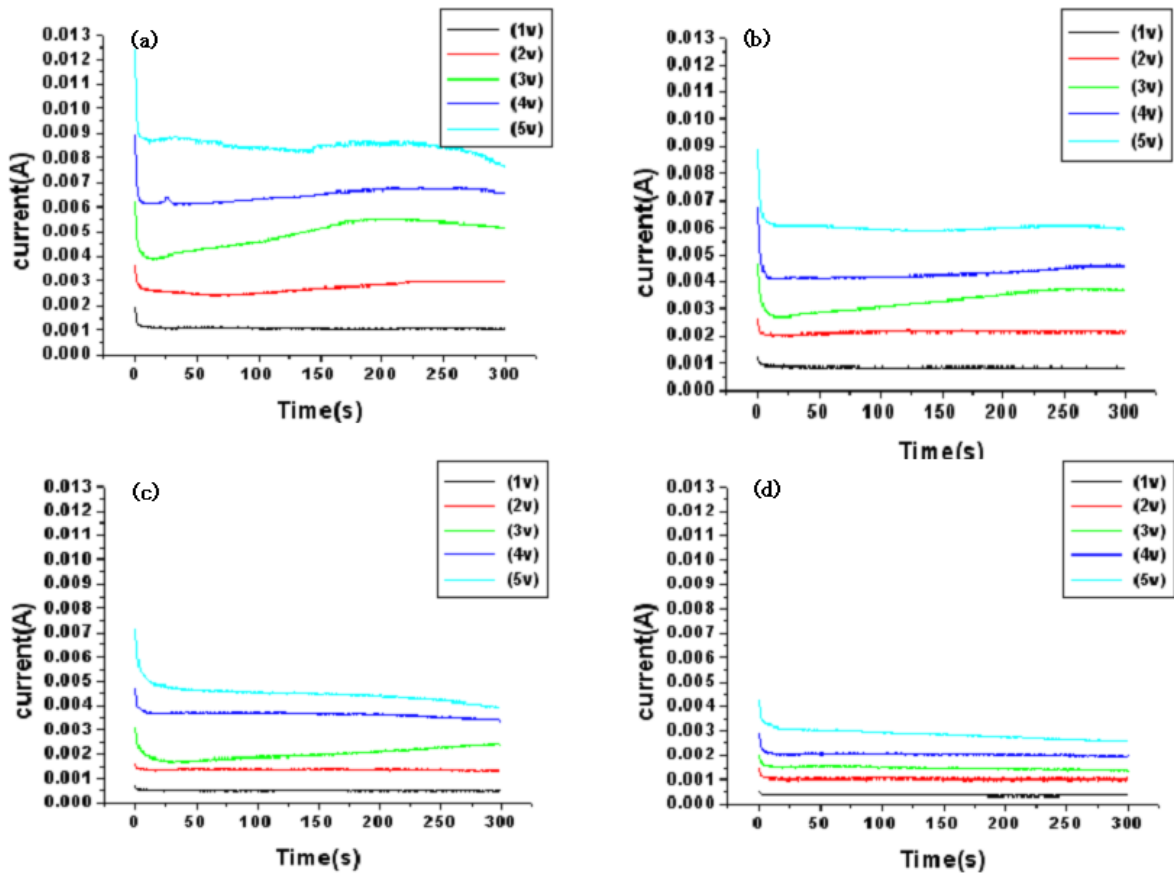
Fig. 1. Measured currents with time at various concentrations (a)1:50, (b)1:100, (c)1:200, (d)1:400.
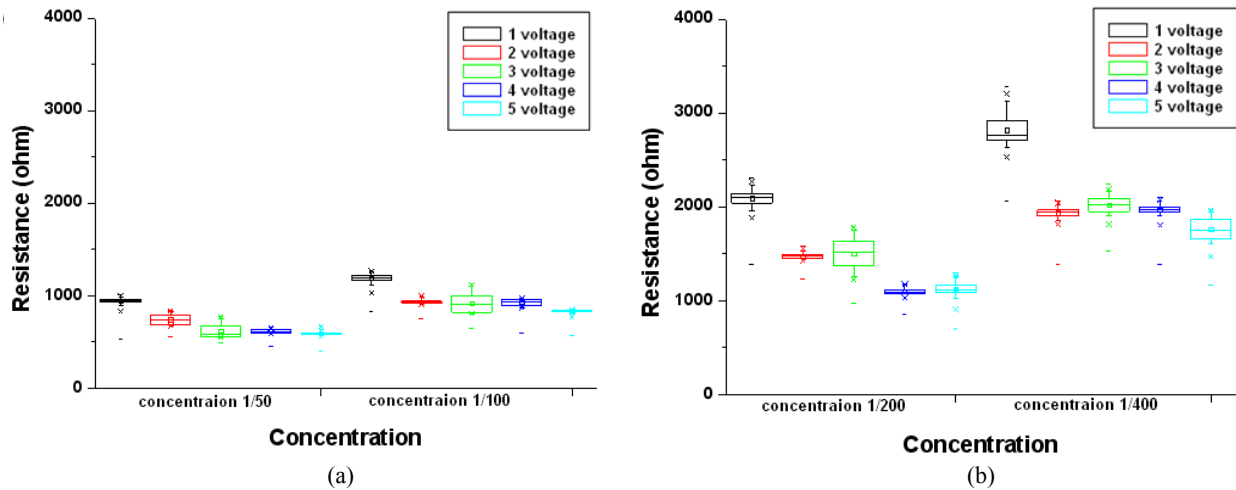

Fig. 2. Resistances at various concentrations (a) 1:50, 1:100 (b) 1:200, 1:400.

pores gets back to be oxidized and the rest of it was re-mained without any further oxidation, causing the current back to decrease a little bit. With increasing the applied DC bias value, the shorter time to be taken for copper ions to be diffused out through the copper oxide film.

From the discussions above, it could be concluded that the oxide film was formed and grown by the copper ion diffusion first and then the reaction with any oxidant in the post-CMP cleaning solution. The higher applied DC bias values, the shorter time to be taken for copper ion's
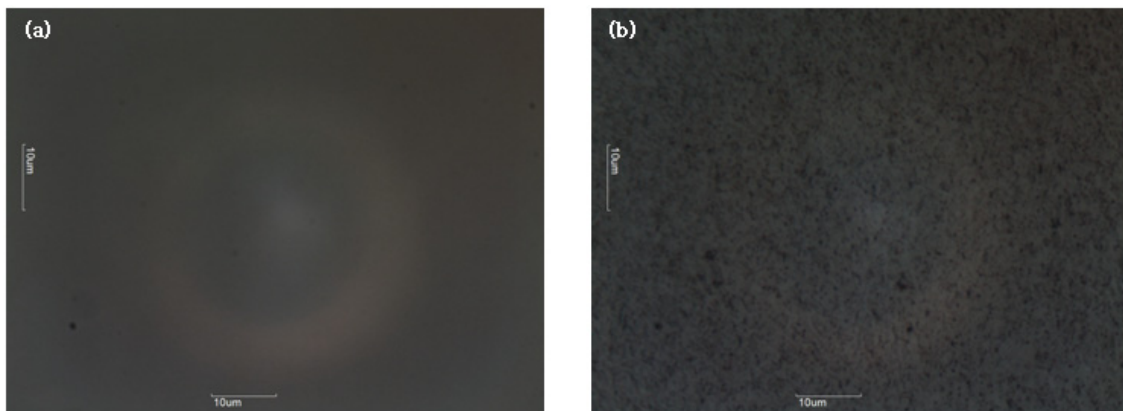
Fig. 3. Copper wafer surface morphologies examined by the optical microscope (a) before the oxidation, (b) after the oxidation.

perforation and creating pores on the oxide surface such as 66, 16, 11 seconds for the applied 2 V, 3 V, and 4 V DC bias values, respectively.

As shown in Fig. 2, the resistances decreased with increasing concentrations, which could be explained that the resistance due to the electrolyte (the post-CMP cleaning solution) was getting smaller, thus total resistance decreased. As for 1:100 and 1:50, their resistances showed a minimum compared to those for 1:200 and 1:400. With concentrations higher than 1:100 combined with the applied DC bias, it was observed that the copper film was ripped off completely and the copper ions were deposited on the surface of the cathode. It could be justified that there were not enough oxidants in the electrolyte to react with copper ions as quickly as coppers ions knocked off from the anode and the copper film removal is only due to the applied external bias. Thus, without the applied external bias, it would be difficult for copper film to be etched out only due to the chemical reaction with the post-CMP cleaning solution.

Fig. 3 shows the surface morphologies that were examined at the magnification of 2,000 using the optical microscope before and after the oxidation. Copper film was very smooth before the oxidation. However, as shown in Fig. 3, with the applied voltage, the surface roughness was increased after the oxidation.

4. Conclusions

Copper corrosion is one of the critical issues for various semiconductor manufacturing processes. So in order to understand the characteristics of copper corrosion by the electrical test, the correlations of the different magnitude of applied voltages and concentrations were investigated with time. Most of the cases, the current was steadily decreased (i.e. resistance was increased by the oxidation).

In the lowest concentration case only, the current was steadily increased with the scarce fluctuations. The higher the constant supplied DC voltage values, the higher the initial output current and the saturated current values. However the time to be taken for it to be saturated was almost the same for all the DC supplied voltage values. It was indicated that the oxide formation was not dependent on the supplied voltage values and 1 V was more than enough to form the oxide. With applied voltages lower than 3 V combined with any concentration, the perforation through the oxide film rarely took place due to the insufficient driving force (voltage) and the copper oxidation ceased. However, with the voltage higher than 3 V, the copper ions were started to diffuse out through the oxide film and thus made pores to be formed on the oxide surface, causing the current to increase and a part of the exposed copper film inside the pores gets back to be oxidized and the rest of it was remained without any further oxidation, causing the current back to decrease a little bit. With increasing the applied DC bias value, the shorter time to be taken for copper ions to be diffused out through the copper oxide film. From the discussions above, it could be concluded that the oxide film was formed and grown by the copper ion diffusion first and then the reaction with any oxidant in the post-CMP cleaning solution.

References

1. R. Rosenberg, D. C. Edelstein, C. K. Hu, and K. P. Rodbell, *Annu. Rev. Mater. Sci.*, **30**, 229 (2000).
2. J. M. Steigerwald, S. P. Murarka, R. J. Gutmann, and D.J. Duquette, *Mater. Chem. Phys.*, **41**, 217 (1995).
3. P. B. Zantye, A. Kumar, and A. K. Sikder, *Mater. Sci. Eng. R.*, **45**, 89 (2004).
4. L. Arnaud, G. Tartavel, T. Berger, D. Mariolle, Y. Gobil, and I. Touet, *Microelectron. Rel.*, **40**, 77 (2000).
5. M. Kodera, Y. Nishioka, S. Shima, A. Fukunaga, and

M. Tsujimura, *J. Appl. Phys*., **10**, 677 (2008).

6. A. Nishi, M. Sado, T. Miki, and Y. Fukui, *Appl. Surf. Sci*., **470**, 203 (2003).

7. L. Zhang, S. Raghavan, and M. Weling, *J. Vac. Sci. Technol. B*, **17**, 2248 (1999).

8. F. Zhang, A. A. Busnaina, and G. Ahmadi, *J. Electrochem. Soc*., **146**, 2665 (1999).

9. Y. K. Hong, D. H. Eom, S. H. Lee, T. G. Kim, J. G. Park, and A. A. Busnaina, *J. Electrochem. Soc*., **151**, G756 (2004).

10. D. Ng, S. Kundu, M. Kulkarni, and H. Liang, *J. Electrochem. Soc*., **155**, H64 (2008).

11. Tung Ming Pan, Tan Fu Lei, Fu Hsiang Ko, Tien Sheng Chao, Ming Chi Liaw, Ying Hao Lee, and Chih Peng Lu, *J. Electrochem. Soc*., **49**, G336 (2002).

12. D. Ernur, S. Kondo, D. Shamiryan, and K. Maex, *Microelectron. Eng*., **64**, 117 (2002).