

In-situ Characterization of Electrochemical and Frictional Behaviors During Copper CMP

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Abstract

As the organic acids were added in the slurry, zeta potential of alumina was changed to negative value and IEP value was shifted from alkaline to acidic pH. In citric acid based slurry, Cu surface continuously dissolved and etching depth linearly increased. On the contrary, passivation layer was grown on Cu surface in oxalic acid based slurry. As the platen rotation speed increased, Preston coefficient decreased in both slurries. With oxalic acid based slurry, at low velocity, removal rate is high value because of high friction force compared to citric acid based slurry. As platen velocity increased, removal of Cu in citric acid based slurry became higher value than oxalic acid based slurry. Typical lubrication behaviors were observed in both slurries. As Sommerfeld number increased, COF values gradually decreased and then re-increased. It indicated that lubrication was changed to direct contact or semi-direct contact mode to hydro-lubrication mode.

Key Words : Cu CMP, Organic acids, corrosion potential and current, Preston equation, friction force, Stribeck curve

1. Introduction

Copper CMP process is widely researched for the next generation of interconnection because of lower electrical resistivity of copper compared with aluminum and higher resistance to electro-migration [1]. During CMP process, Cu surface is chemically passivated by the oxidants and complexing agents in slurry and then passivation layer is simultaneously mechanically removed by abrasive particles and CMP pads [2]. Generally, the removal rates of Cu surface are significantly influenced by the electrochemical and frictional behaviors during CMP process. During Cu CMP, mechanical abrasion is strongly dependent on the applied pressure and linear velocity. The chemical and mechanical removal mechanisms of Cu are very important to obtain the suitable removal rate of Cu. In this study, the removal rates of Cu surfaces were evaluated in terms of frictional and electrochemical aspects. Also, the surface properties of Cu were characterized in Cu CMP slurries containing various additives.

2. Experimental Materials and Procedures

In this study, hydrogen peroxide based slurries were used to investigate the electrochemical and frictional characteristics of Cu. Gamma-alumina (primary particle size : 16 nm, Degussa) and colloidal silica particles were used as abrasives in slurries. Two types of organic acids such as citric acid ($C_6H_8O_7$) and oxalic acid ($C_2H_2O_4$) were used as the complexing agent. NH_4OH and BTA were chosen to add to slurry solutions as pH adjustor and corrosion inhibitor, respectively.

Electroplated Cu wafers (1~1.5 m thickness on Ta) and Cu disk (4-inch, 99 %) were polished on IC 1400 pads (K-Groove, Rodel) using frictional polisher (POLI_LP500, GNP Technology, Korea). Etch and removal rates of Cu were evaluated as a function of slurry composition using a four-point probe method. For the polishing experiments, the slurry for CMP was prepared by changing the ratio of abrasives, oxidizer (H_2O_2) and organic acids. The removal rate of Cu was measured as a function of process

parameters such as applied pressure and rotation speed of head and platen.

Figure 1 shows the schematic diagram of friction measurement method. During CMP process, in-situ normal force and shear force can be measured by the friction polisher with two piezoelectric sensors.

Pressure can be controlled from 1.4 psi to 7 psi in 4 wafer polishing and head and platen velocity can be varied from 50 ~ 250 rpm.

Electrochemical studies of Cu were performed in three electrode cells (flat cell, EG&G) and rotating cell (lab. made) using a computer controlled EG&G model 273A potentiostat. Tafel plots were obtained by scanning at 0.5 mV/sec from 250 mV below the open-circuit potential (E_{oc}) to 250 mV above. SCE electrode (saturated KCl) and platinum mesh were used for the reference electrode and counter electrode, respectively. 3 m thick electroplated Cu wafers on Ta were used as a working electrode. All potentials were reported with respect to the standard hydrogen electrode (SHE).

Also, passivation layer grown on Cu surface was characterized by atomic force microscope (AFM) and field emission scanning electron microscope (FESEM).

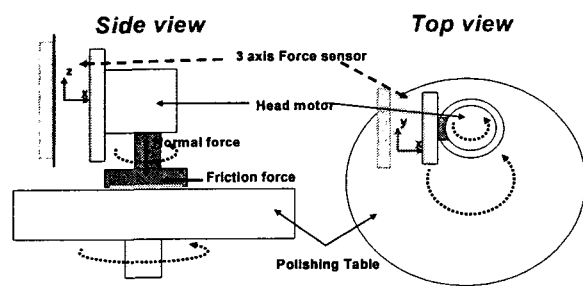


Figure 1. The schematic of equipment for measurement of coefficient of friction during Cu CMP with friction polisher piezoelectric sensors.

3. Experimental Results

In hydrogen peroxide based slurry, Cu surface is dissolved to Cu ions or oxidized to Cu oxide. At low concentration of H_2O_2 solution, dissolution

reaction of Cu is dominant. In the contrary, thick Cu oxide is grown on Cu surface with high concentration of H_2O_2 . Figure 2 shows the etch rate of Cu in citric acid based slurry as a function of H_2O_2 concentration. At high concentration of H_2O_2 solution (up to 10 vol%), etch rate of Cu was not changed even though citric acid concentration increased. In these solution, etch rate of Cu would be dependent on the Cu oxide thickness. However, etch rate of Cu was strongly dependent on the citric acid concentration in low concentration H_2O_2 solution. In this case, Cu etch rate linearly increased as citric acid concentration increased.

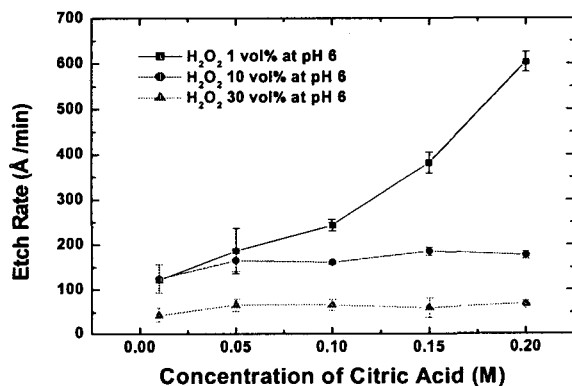


Figure 2. Etch rate of Cu in citric acid based slurry with different concentration of Cu as a function of citric acid concentration

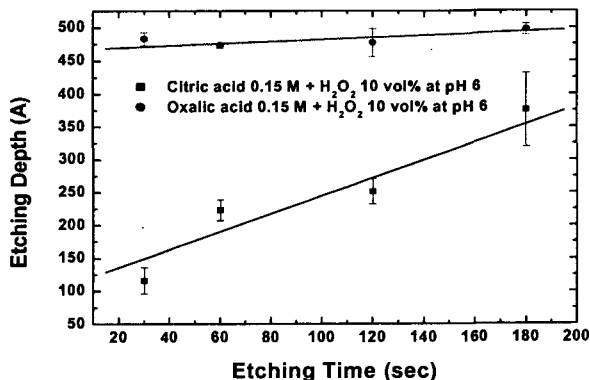


Figure 3. Etching depth of Cu in citric and oxalic acid based slurries with etching time

Figure 3 shows Cu etching rate and depth of Cu in citric and oxalic acid based slurries as a function of etching time. In citric acid based slurry, Cu was continuously dissolved with etching time. Even though the etching time increased, etching depth remained constant in oxalic acid based slurry. From these results, in oxalic acid slurry, it was considered that the passivation layer would be grown on Cu surface.

To confirm the growth of passivation layer, the cross sectional images of Cu after treatment in slurries were taken by FESEM and chemical compositions of treated Cu surfaces were characterized by the Auger Electron Spectroscopy. In oxalic acid based slurry, passivation layer was grown on Cu surface and thickness of passivation layer was about 1 μm as shown in Fig. 4.

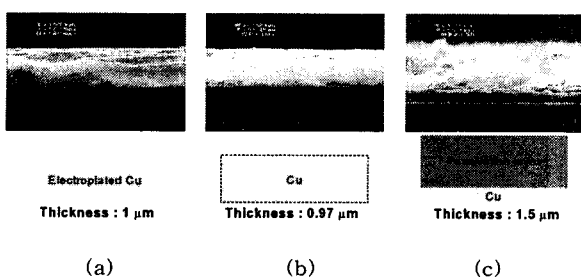


Figure 4. Cross sectional FESEM images and thicknesses of Cu treated in various slurries ; (a) no etch, (b) citric acid and (c) oxalic acid

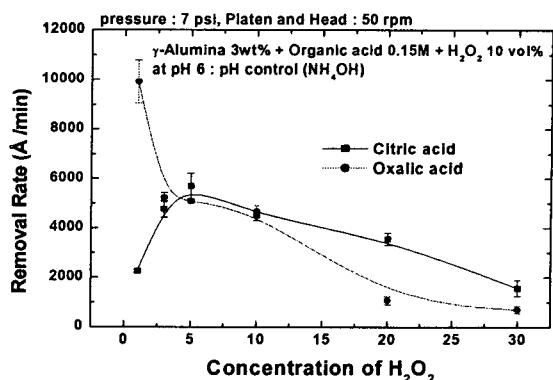


Figure 5. Removal rate of Cu with citric and oxalic acid based slurries as a function of H₂O₂ concentration.

Figure 5 shows the removal rate of Cu with citric and oxalic acids based slurries as a function of H₂O₂ concentration. In citric acid slurry, removal rate increased with 5 vol% H₂O₂ and then remained constant values. In oxalic acid slurry, removal rate drastically decreased as H₂O₂ concentration increased. at low concentration of H₂O₂ solution, etch rate and Cu ion concentration are very high. So removal rate is high value. With high concentration of H₂O₂ slurry, etch rate is low and Cu oxide is thick. So Cu removal rate is low value.

Cu surface was chemically reacted with different ways in the slurry CA and OA. For the characterization of electrochemical behavior of Cu with organic acids, Tafel plots were obtained in various slurry compositions. Figure 6 shows Tafel curves of Cu with citric acid and oxalic acid added solutions with H₂O₂ 10 vol%. Table 1 shows E_{oc}, R_p and i_{oc} in different slurries. Corrosion potential (E_{oc}) and corrosion current (i_{oc}) in the slurry citric acid based slurry was larger than that in the slurry oxalic acid. However, polarization resistance (R_p) was high value in oxalic acid based slurry. the high value of polarization resistance might indicate the thick Cu oxide on surface during treatment in the slurry. So, in oxalic acid based slurry, Cu oxide became thicker than that in citric acid based slurry.

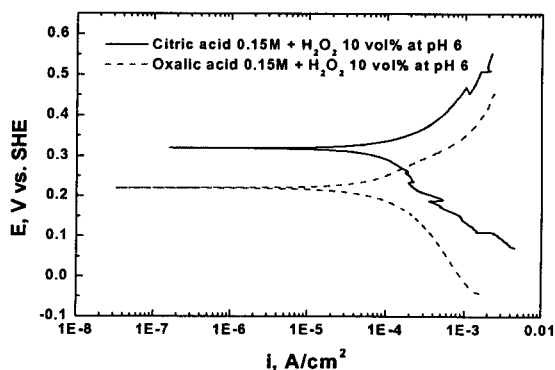


Figure 6. Tafel Curve of Cu in the citric acid and oxalic acid based slurry

Table 1. E_{oc} (open circuit potential), R_p (polarization resistance) and i_{oc} (current density) of Cu in the slurry CA and OA

	CA 0.15M + H ₂ O ₂ 10 vol% at pH 6	OA 0.15M + H ₂ O ₂ 10 vol% at pH 6
E_{oc} (V vs. SHE)	0.318	0.201
i_{oc} (A/cm ²)	5.3×10^{-4}	1.68×10^{-5}
R_p ($\Omega \cdot \text{cm}^2$)	187.7	286.7

Figure 7 shows the COF as a function of Sommerfeld number with citric and oxalic acid based slurries. During Cu CMP process, lubrication regimes couldn't be divided clearly as shown in Fig. 7. COF gradually decreased as Sommerfeld number (transition from direct contact to semi-direct contact), then re-increased (hydro-dynamic lubrication) at certain Sommerfeld number. At the region of circle in Fig. 7, COF was high value with oxalic acid based slurry due to high friction force. On the condition of low pressure and high velocity, COF values re-increased and were similar values in both slurries. So, Cu wafers would be polished in hydro-dynamic lubrication regime in both slurries.

Figure 8 shows the friction forces in different lubrication regimes. In direct contact region, friction force was highest values in both slurries. In direct and semi-direct regimes, high friction forces were measured in oxalic acid based slurry.

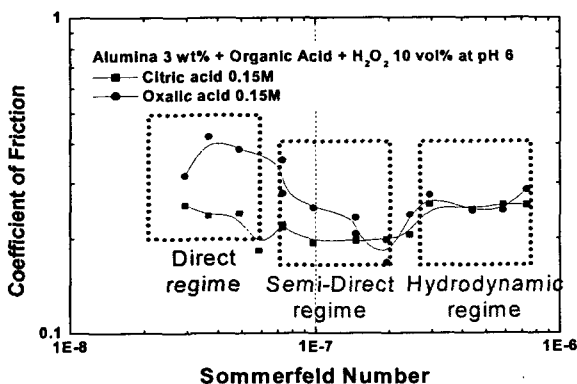


Figure 7. Change of COF as a function of Sommerfeld number (Stribeck curve) in citric and oxalic acid based slurries

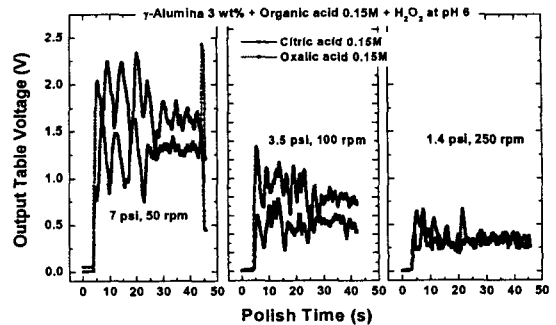


Figure 8. Friction force of Cu in different lubrication regimes with citric and oxalic acid based slurries

4. Summary

In this study, the effect of organic acid on modification of surface charge and slurry stability of alumina based slurry. Also, in-situ characterization of electrochemical and friction force were evaluated using electrochemical cell and frictional polisher. etch rate and removal rate of Cu was strongly dependent on the applied pressure and platen speed. Removal rate increased as pressure increased or platen speed increased. At low pressure and high platen velocity, friction force was small value and Cu friction mode was hydro-dynamic lubrication. When Cu was treated and polished in oxalic acid based slurry, Cu surface became roughened and friction force was larger value than that in citric acid based slurry.

Reference

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