

## PASSIVATION AND ETCHING BEHAVIORS OF COPPER SURFACE IN COPPER CMP SLURRIES

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Copper has been considered as a candidate for the replacement of aluminum in next generation metal interconnects because of lower resistivity (about  $1.7 \mu\Omega\text{-cm}$  for copper compared to  $3.0 \mu\Omega\text{-cm}$  for aluminum) and higher resistance to electro-migration<sup>(1)</sup>. Cu CMP slurry is commonly composed of abrasive particles, oxidants, etchants and corrosion inhibitors. During CMP process, Cu surface was planarized by the repetitive process of the oxidation by oxidants and the polish behavior by etchant and abrasive particles. In general,  $\text{H}_2\text{O}_2$  and organic acids for oxidant and etchant were used for the formulation of commercial Cu CMP, respectively, slurries at neutral and nearly acidic pH. It has been reported<sup>(2)</sup> that the Cu surface was oxidized and corroded to  $\text{Cu}^{2+}$  ions by  $\text{H}_2\text{O}_2$  due to high redox potential of  $\text{H}_2\text{O}_2$  at neutral and acidic pHs and the organic acids easily reacted with metal ions for formation of complex. The surface reaction of Cu in various slurries is important for the understanding of Cu CMP associated with oxidation, etching and dishing of Cu. In this study, characteristics of Cu surfaces were evaluated in Cu CMP slurries containing various additives.

CMP slurry was formulated with three types of organic acids such as citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ), oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ) and succinic acid ( $\text{C}_4\text{H}_6\text{O}_4$ ) as etchants and  $\text{H}_2\text{O}_2$  as oxidant. Also,  $\text{NH}_4\text{OH}$  and BTA were chosen to add to slurry solution as pH adjustor and corrosion inhibitor, respectively. In order to characterize the Cu surface, types of additive, pH of slurry and abrasive types were selected as slurry variables. The surface oxidation and etching of Cu in various slurries were characterized using XPS, spectroscopic ellipsometer and FESEM. Etch and polish rate of copper were evaluated as a function of slurry composition using a four-point probe method. For the polishing experiments, slurry for copper CMP was prepared by changing the ratio of abrasives, oxidizer ( $\text{H}_2\text{O}_2$ ), corrosion inhibitor (BTA) and organic acids.

Polish rate of Cu was dependent on the types of organic acids as shown in Figure 1. Polish rates linearly increased in citric and oxalic acids added slurries as the concentration increased. In the contrary, succinic acid based slurry cannot remove the Cu effectively due to slurry agglomeration as previously reported<sup>(3)</sup>.

No etching and removal of Cu were observed in citric acid based slurry as shown in Figure 2. The addition of  $\text{NH}_4\text{OH}$  to citric acid slurry did not change them either. Cu removal and etch rates did not increased without the addition of oxidant of Cu such as  $\text{H}_2\text{O}_2$ . However, the addition of  $\text{H}_2\text{O}_2$  to slurry oxidized Cu surface and increased etch and removal rates. The low removal rate of Cu was measured due to slurry agglomeration at pH 2. The addition of  $\text{NH}_4\text{OH}$  enhanced the formation of Cu complexes and increased the removal rate. The decrease of etch rate with the addition of  $\text{NH}_4\text{OH}$  might be due to the rapid decomposition of  $\text{H}_2\text{O}_2$  and the decrease of redox potential in citric acid slurry. The etch rate associated with slurry composition is very important for the control of Cu dishing and corrosion during CMP. Cu

surface was polished for suitable removal and etch rate with constant  $\text{H}_2\text{O}_2$  concentration as a function of pH.

Cu surface was oxidized in  $\text{H}_2\text{O}_2$  added solution and oxidation layer was formed on Cu surface irregularly as shown in Figure 3. The Cu oxide layer could be removed by the addition of organic acids. Oxidation layer thickness was measured using spectroscopic ellipsometer and XPS compared with electrochemical study as functions of  $\text{H}_2\text{O}_2$  concentration and slurry composition. Also, Cu dishing was evaluated after patterned wafer polishing as a function of slurry composition.

### References

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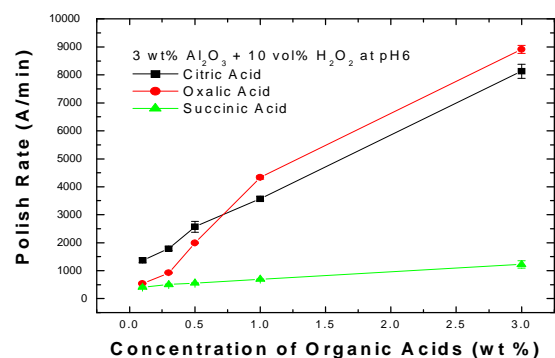


Figure 1. Polish rate of Cu in various organic acids added slurries as a function of organic acids concentration

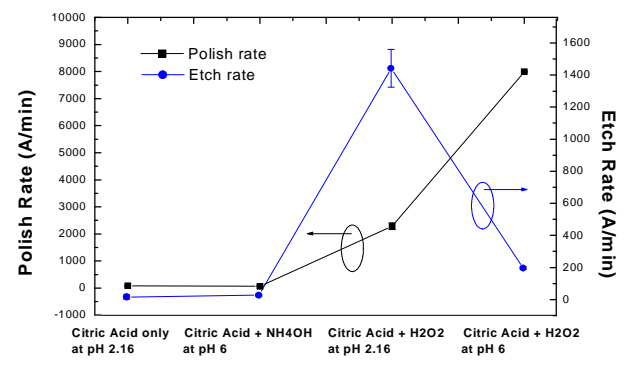


Figure 2. The polish and etch rate of Cu in various slurries with different slurry compositions

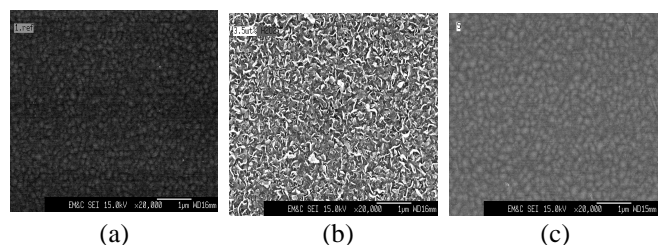


Figure 3. FESEM images of Cu surfaces (a) as electroplated bare Cu and treated in (b) 5 wt%  $\text{H}_2\text{O}_2$ , (c) 10 wt%  $\text{H}_2\text{O}_2$  followed by 3 wt% citric acid