Analysis of Post-Chemical-Mechanical-Polishing Cleaning Mechanisms for Improving Time-Dependent Dielectric Breakdown Reliability

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Using Cu/SiOC interconnects, we investigated the relationship between the time-dependent dielectric breakdown (TDDB) reliability and the cleaning process in copper chemical-mechanical polishing (CMP). We found that the formation of a nonuniform copper oxide film during post-CMP cleaning causes TDDB degradation when a barrier metal slurry that does not contain benzotriazole is used. We also found the reformation of a nonuniform copper oxide layer that accompanies the deionized water rinse is due to the dissolution of too much of the copper oxide film during the post-CMP cleaning process. For improved TDDB reliability, the uniform copper oxidation during the post-CMP cleaning process is important in the Cu/low-k damasene integration process.

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We focused on the relation between the TDDB degradation and post-CMP cleaning solutions when a commercially available barrier...
metal slurry without BTA was used. The three post-CMP cleaners listed in Table I were used to investigate the cleaning mechanism for improving the TDDB reliability.

Experimental trial 1: Evaluation of copper contamination on SiOC surface.—First, we prepared 200 mm blanket wafers with a 500 nm thick SiOC film that had been immersed in 1000 ppm copper sulfate solution. We compared the copper removal efficiency on the SiOC film surface of the three post-CMP cleaning solutions by using a wafer scrubber. The remaining copper on the wafer surface was extracted, contacting with nitrohydrochloric acid in a short time, and then the Cu contamination level on the SiOC film surface was measured by an inductively coupled plasma-mass spectrometry (ELAN 6100-DRC, Perkin Elmer, Inc.).

Experimental trial 2: Evaluation of copper oxide formation during post-CMP cleaning process.—Next we prepared blanket wafers embedded in a SiOC/cap-SiO bilayer dielectric stack (500/50 nm). A 15 nm thick tantalum nitride (TaN)/a 15 nm thick tantalum (Ta) barrier metal and a 80 nm thick Cu seed were sputtered, and a 1000 nm thick electroplated Cu film was deposited on every sample. Then, Cu CMP was performed. For the Cu-CMP process, we used a rotary-type polishing system for both Cu and barrier metal polishing. A commercially available Cu slurry was used to remove the Cu embedded in a SiOC film, with a removal amount of 200 nm. We used a low-selective-type barrier metal slurry containing a soluble inhibitor with a copper removal amount of 100 nm. In this experimental trial, we used three kinds of cleaning solution listed in Table I for the post-CMP cleaning. We evaluated the state of the copper oxide formed after the post-CMP cleaning process by an X-ray photoelectron spectroscopy (XPS), ESCALAB 220i, Thermo Fisher Scientific K.K.). Cu oxidation film thickness after the post-CMP cleaning process was measured by cyclic voltammetry (CV) (HZ-5000 potentiostat, Hokutodenko Co., Ltd.). The potential scan rate was 10 mV/s. The electrolyte solution was an aqueous solution including ingredients to be able to suppress copper corrosion (pH 9.1). No deairation was used because of using such an effective electrolyte solution. Figure 5 shows a typical CV measurement. The cathodic wave appearing at a negative potential (−0.6 to −0.7 V) was due to the reduction of cuprous copper (Cu$_2$O) to copper.$^7$

Reduction of Cu$_2$O:

$$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Cu} + 2\text{OH}^-$$  \[1\]

A well-developed peak due to reduction of Cu$_2$O is observed on the first scan, and no peak appeared on the second scan. Subtraction of the current on the second scan from that on the first scan yielded the net current for the reduction of Cu$_2$O (shaded parts of peak area in Fig. 5). The thickness of Cu$_2$O was calculated as follows$^1$

Cuprous copper thickness = $\frac{Q MV}{n FS}$  \[2\]

where $Q$ is the quantity of electricity (C), $F$ is Faraday constant (96500C/mol), MV is the molar volume (Cu$_2$O:23.9 cm$^3$/mol), $n$ is the number of electrons required for the reduction of one molecule of oxide ($n = 2$ for Cu$_2$O), and $S$ is the surface area of the copper sample (in centimeters squared).

Experimental trial 3: Evaluation of copper in dissolution during post-CMP cleaning.—We prepared blanket copper wafers that were polished by using a barrier metal slurry and cleaned by deionized (DI) water rinse. We compared the copper dissolution level on the wafer treated during each cleaning by using the wafer scrubber. We extracted waste solution during the post-CMP cleaning process and

![Figure 2: Comparison of TDBD lifetime dependence on post-CMP cleaning solutions.](image1)

![Figure 3: Dependence of I-V curves on post-CMP cleaning solution.](image2)

![Figure 4: Dependence of leakage current on bias stress time with different post-CMP cleaning solutions.](image3)

Table I. Post-CMP cleaning solutions used in this study.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Contents</th>
</tr>
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<tbody>
<tr>
<td>Organic acid</td>
<td>Citric acid base with surfactants, pH 2</td>
</tr>
<tr>
<td>Organic acid salt</td>
<td>Citric salt base, pH 3.6</td>
</tr>
<tr>
<td>Organic alkali</td>
<td>Tetramethylammonium hydroxide base with surfactants and chelates, pH 10.5</td>
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</table>
investigated the amount of copper in dissolutions by using an inductively coupled plasma-optical emission spectrometry (ICP-OES), 730ES, Varian, Inc.

**Experimental trial 4: Evaluation of copper surface roughness after post-CMP cleaning.** — The blanket copper wafers polished by using a barrier metal slurry and cleaned by each cleaning solution were prepared. The copper surface roughness after the post-CMP cleaning was measured by an atomic force microscopy (AFM), E-sweep/SP4000, SII NanoTechnology Inc., and the roughness of these samples was measured again in acetic acid solution. We confirmed the existence of copper on the SiOC film surface by an energy-dispersion X-ray (EDX) observation (INCA, Oxford Instruments plc). Sematech 854 pattern wafers were used in this experiment.

**Results and Discussion**

**Amount of copper on SiOC surface.** — First, the number of trace copper atoms on the SiOC film surface after the post-CMP cleaning is shown in Fig. 6. The copper ion removal capability of the organic alkali solution or the organic acid salt solution is higher than that of the organic acid. However, we think that TDDB degradation in Fig. 2 is little related to the number of remaining copper ions on the SiOC film surface.

**State of copper oxide formed after post-CMP cleaning process.** — We investigated the existence of other factors that may degrade the TDDB lifetime besides the number of remaining Cu ions. We analyzed the state of the copper oxidization after the post-CMP cleaning process by XPS. Figure 7 shows the XPS intensity (Cu2P) of Cu surface after the post-CMP cleaning with the three cleaning solutions. The copper oxidization state seems not to be dependent on the kind of cleaning solution. Using CV, we measured the thickness of the Cu2O film after the post-CMP cleaning process. Figure 8 shows results of the CV measurement after the post-CMP cleaning process. About 1.5 nm of cuprous oxide were on the copper films. We found no large differences among the samples with similar cuprous oxide thickness after the post-CMP cleaning process.

**State of copper oxide formed during chemical clean.** — In the post-CMP cleaning processes, a DI water rinse process was used after brush cleaning with cleaning solutions. Then, we again measured the Cu oxidization film thickness with CV, excluding the influence of the oxidization film formation that occurs during the DI water rinse process. After the polished copper sheet had been immersed in each cleaning solution, we measured the thickness of their cuprous oxide film. Figure 9 shows current-potential curves for copper sheets that were not rinsed with DI water. We observed the reduction peaks for Cu2O appearing at different potentials. However, the assignment of these voltammetric peaks was achieved with the help of a XPS analysis. Because the copper sheet processed with cleaning solution is not rinsed with DI water before the CV mea-
measure, we thought that the cleaning solutions remaining on the surface of the sample had some influence on reduction-oxidation reaction during the CV measurement, and then the reduction peak for Cu$_2$O shifted. At the step before the DI water rinse, the thickness of the cuprous oxide that remained is different for each sample. Particularly, the cuprous oxide was not etched by the organic alkali solution.

**Amount of copper in dissolution during post-CMP cleaning.**—We extracted the waste solution during the post-CMP cleaning process and performed an ICP-OES analysis to investigate the amount of copper in dissolutions. The Cu concentrations in the waste solution at the time of each post-CMP cleaning are listed in Table II. The organic alkali solution shows a lower etching amount than the others. These results are consistent with the results of the CV measurement without the DI water rinse, suggesting that Cu was oxidized at the DI water rinse step after cleaning with organic acid or organic acid salt solution.

**Copper surface roughness after post-CMP cleaning.**—Next, we measured the Cu surface roughness after post-CMP cleaning. Then, the samples were immersed in acetic acid solution. The oxidized copper film was removed completely, and the roughness on the surface of Cu was measured again. Figure 10 shows the copper surface root-mean-square (rms) roughness after the post-CMP cleaning.

The Cu roughness ratio (after/before copper oxide removal) defines the uniformity of the removed copper oxide thickness (a lower ratio means more uniformity). We think the Cu$_2$O layer thickness produced in the polish process has good uniformity. The rms roughness with acidic cleaner after the oxidized copper removal increases by about four to five times. The uniformity of copper oxide thickness after the organic alkali solution cleaning is superior to that for the other cleaners. After the organic alkali solution cleaning, the Cu$_2$O layer formed during the polish process remained on the copper surface, while the others were produced during the DI water rinse process. Figure 11a shows the AFM images during post-CMP cleaning. We found no large differences among the samples with similar roughness images during the chemical cleaning between the organic alkali solution and the organic acid solution. However, we observed a lot of white dots on the copper surface treated with the organic acid solution during the DI water rinse in the image. The white dots indicate microprojections. Figure 11b shows the scanning electron microscope (SEM) images of the copper surface after post-CMP cleaning. We also observed that white dots on the copper surface treated with the organic acid solution remained. We believe that these dots on the copper surface with organic acid solution cleaning suggest a possibility of nonuniform distribution of Cu$_2$O.

**Cu oxide nonuniform model.**—From these results, we propose the following mechanism of the formation of oxidized copper of film under post-CMP cleaning shown in Fig. 12, which causes TDDB degradation when the barrier metal slurry does not contain BTA.

- **Alkaline cleaner.**—The Cu$_2$O layer remained thick and uniform after chemical clean. Oxygen penetrates through the Cu$_2$O layer after DI water rinse. However, the uniform Cu$_2$O layer intercepts oxygen. Then, oxygen concentration is very low at Cu/Cu$_2$O interface.

- **Acidic cleaner.**—The acidic cleaner etches most of the Cu$_2$O layer produced in the CMP process. Then, the Cu$_2$O thickness is not uniform after the chemical clean. Oxygen penetrates in the copper surface after the DI water rinse. The oxygen concentration has some distribution at the Cu/Cu$_2$O interface. This difference of oxygen concentration might lead to the formation of discrete anode and cathode regions on the copper surface (an oxygen concentration cell). Figure 13 shows an illustration of copper dissolution due to an oxygen concentration cell. Then, Reactions 3 and 4 might be observed due to an electromotive force of an oxygen concentration cell.

In the higher oxygen concentration region at Cu/Cu$_2$O interface

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad [3]
\]

In the lower oxygen concentration region

\[
Cu \rightarrow Cu^{2+} + 2e^- \quad [4]
\]

In order to prove this hypothesis, we performed the experiment shown as follows. We prepared three samples that were cleaned by different cleaning solutions after Cu CMP. These samples were left in the atmosphere for eight days, and we analyzed the surface of them using EDX at intervals of four days. Figure 14 shows results of EDX mapping of copper on patterned wafers. White indicates the area where copper is detected. Regarding samples left in the atmosphere for eight days, copper was detected in the entire area, even on the dielectric film between Cu lines in the samples cleaned with the organic acid or the organic salt solution. A uniform cuprous oxide

![Figure 9](image_url)  
**Figure 9.** (Color online) Current-potential curves of CV (no DI water rinse).

![Figure 10](image_url)  
**Figure 10.** (Color online) Cu surface rms roughness after post-CMP cleaning.

### Table II. Results of Cu concentration in waste solution.

<table>
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<tr>
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<th>Organic acid</th>
<th>Organic acid salt</th>
<th>Organic alkali</th>
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<tbody>
<tr>
<td>Cu concentration in waste solution (ppb)</td>
<td>230</td>
<td>212</td>
<td>72</td>
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</table>
layer formed after cleaning with the organic alkali solution can efficiently prevent copper diffusion due to the above-mentioned electromotive force of an oxygen concentration cell. We think that this result supports the validity of the cleaning mechanism model discussed above.

**TDDB degradation mechanism.**— On the basis of our copper surface roughness after post-CMP cleaning result, we explain the TDDB degradation mechanism as follows. Figure 15 shows an illustration of the TDDB degradation mechanism when using both barrier metal slurry without BTA and an organic acid cleaning solution. A leakage path exists along the CMP surface due to the formation of nonuniform oxidized copper film under post-CMP cleaning. Metal ion penetration has a two-step process: emission of ion and the metal ions movement under the influence of electrical bias and temperature through the dielectric. Copper can ionize when in contact with interfacial oxygen and moisture. The oxygen concentration cell, plus applied electric field and temperature during bias-temperature stress, create a driving force of electrochemical reaction for copper ionization and migration at the edge of Cu lines, where the electric field is more intense. Hence, the leakage path along the CMP surface connects two adjacent Cu lines and subsequently triggers the dielectric breakdown. To enhance the TDDB reliability of Cu/low-k structures, a rigid and uniform interface must be formed on defect-free low-k films.

<table>
<thead>
<tr>
<th>Cleaning process flow</th>
<th>Organic alkali solution</th>
<th>Organic acid solution</th>
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<tbody>
<tr>
<td>(1) Chemical cleaning</td>
<td>(a) AFM images</td>
<td></td>
</tr>
<tr>
<td>(2) DI water rinse</td>
<td>(b) SEM images</td>
<td></td>
</tr>
<tr>
<td>(3) Spin rinse dry</td>
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**Figure 11.** (Color online) (a) AFM and (b) SEM images during post-CMP cleaning.
The cuprous oxide film thickness on the surface of copper after the post-CMP cleaning process has little dependence on cleaning solutions. However, oxide formation during the post-CMP cleaning causes TDDB degradation when the barrier metal slurry does not contain BTA but does contain a soluble inhibitor. We also found that the reformation of nonuniform oxide layer that accompanied the DI water rinse is due to the dissolution of too much copper oxide during the post-CMP cleaning process. For the improvement in the TDDB reliability, uniform copper oxidization during the post-CMP cleaning process is an important factor in the Cu/low-k damascene formation process.

**References**