Effect of Oxidizer on the Galvanic Behavior of Cu/Ta Coupling during Chemical Mechanical Polishing

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The effect of oxidizer addition, namely, H₂O₂, KIO₃, and Fe(NO₃)₃, on the galvanic behavior of the Cu/Ta coupling in 0.01 M Na₂SO₄ + 1 wt % Al₂O₃ base slurry was studied. Both open-circuit potentials of the uncoupled Cu and Ta as well as galvanic current of the Cu/Ta were measured in static and under chemical mechanical polishing conditions to analyze the roles of these additives. The results showed that Fe(NO₃)₃ was more effective than H₂O₂ and KIO₃ in promoting the passivation of Ta, which in turn caused the change of polarity between Cu and Ta. The effect of Cu/Ta area ratio on the galvanic behavior of the coupling was also investigated. The results showed that in Fe(NO₃)₃-containing slurry, Ta was the anode with a Cu/Ta area ratio of 5:1 but became the cathode with an area ratio of 1:1.

Experimental

Electrochemical measurements.—A pure Cu (99.99% purity) rod with 2.5 cm diameter was used. This rod was sliced into disks, each with a thickness of 0.8 cm. Each disk was mounted in epoxy resin with one side exposed and with the other connected to a copper wire for electric conduction. The exposed surface area of each Cu disk specimen was 4.9 cm². Similar processes were followed to prepare Ta (99.95% purity) specimens. Two different exposed surface areas, namely, 4.9 and 0.98 cm², were chosen for Ta specimens. These specimens were then ground with SiC paper to 800-grit finish before electrochemical tests. Some of the Cu and Ta specimens were connected with copper wires to investigate the galvanic characteristics between them. This coupling was referred to as the Cu/Ta specimen.

The electrochemical tests were conducted in the base slurries consisting of 0.01 M Na₂SO₄ supporting electrolyte and with 1 wt % Al₂O₃ abrasive particles added. The average particle size of Al₂O₃ powders was 0.05 μm. Three different oxidizers, namely, 10 vol % H₂O₂, 0.1 M KIO₃, and 0.1 M Fe(NO₃)₃, were added in the base slurries. The pH values of the slurries containing the above oxidizers were 4.8, 5.7, and 1.5, respectively.

Electrochemical tests were conducted either in static or under...
CMP conditions. For the latter test, a polisher consisting of an upper carrier and a lower platen with the respective diameters of 7.6 and 20.3 cm was used. The schematic diagram showing the components of this polisher is illustrated in Fig. 1. As shown in this figure, a loading device was attached to the upper carrier. A tank holding the slurry during polishing was bound on the lower platen and a Rodel IC-1400 pad for polishing was also attached to it. During polishing, the lower platen rotated at a speed of 100 rpm, and a downward stress of 3 psi was applied to the specimens which were held in the upper carrier. The inset in Fig. 1 shows the geometry of the specimen arrangement in the carrier. Cu and/or Ta specimens were loaded in positions A and B, respectively. An auxiliary specimen made of epoxy resin was put in position C for weight balance purposes. When galvanic behavior was to be investigated, the Cu and Ta specimens were connected to each other by an external Cu wire.

An EG&G M362 potentiostat was used for the OCP measurement. The OCPs were recorded under static conditions and during CMP. A saturated calomel electrode and the carrier (made of 304 SS) were used as the reference electrode and the counter electrode, respectively. An auxiliary specimen made of epoxy resin was put in position C for weight balance purposes. When galvanic behavior was to be investigated, the Cu and Ta specimens were connected to each other by an external Cu wire.

Results and Discussion

Effect of oxidizer on the OCPs of uncoupled Cu and Ta.—The respective half-cell reactions and potentials for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, $\text{IO}_3^-/\text{I}_2$, $\text{NO}_3^-/\text{N}_2$, and $\text{Fe}^{3+}/\text{Fe}^{2+}$ are given below:\footnote{The potential values are based on the standard electrode potential at 298 K.}

1. $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$
2. $2\text{IO}_3^- + 12\text{H}^+ + 10\text{e}^- = \text{I}_2 + 6\text{H}_2\text{O}$
3. $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- = \text{N}_2 + 6\text{H}_2\text{O}$
4. $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$

The effects of these oxidizers on the OCPs of uncoupled Cu and Ta in 0.01 M Na$_2$SO$_4$ + 1 wt % Al$_2$O$_3$ base slurry under load-free and static condition are demonstrated in Fig. 2. In the slurry containing 10 vol % H$_2$O$_2$, as shown in Fig. 2a, the potential of Cu was constant throughout the whole measurement. In the slurry containing 0.1 M KIO$_3$, the potential of Ta was more active than Cu with a potential difference about 280 mV between them. By comparing Fig. 2a
with 2b, it was found that the OCPs for both Cu and Ta measured in the KIO3-containing slurry were lower than those measured in the slurry containing H2O2. This was attributed to the high oxidizing power of H2O2 as compared with KIO3 present in the slurry.

In the slurry containing 0.1 M Fe(NO3)3, a dramatic change in polarity was found. As shown in Fig. 2c, a constant OCP of Cu (about +45 mV) was observed. However, the potential of Ta became higher than that of Cu. It was initially at +175 mV and further climbed to a steady-state value of +345 mV. The high OCP of Ta indicated that it was passivated in this slurry and became nobler than Cu. It is known that the redox potential of either Fe3+/Fe2+ or NO3−/I2 is lower than that of H2O2/H2O.11 However, the acidic pH (1.5) and high concentration of oxidizing species such as Fe3+ and NO3− in the 0.1 M Fe(NO3)3-containing slurry seemed to have activated the initial dissolution of Ta, which in turn promoted the fast passivation of Ta surface. As a result, the OCP of Ta became higher than that of Cu. Figure 3 shows schematic diagrams illustrating the change of surface Ta5+ ion concentration with time in the slurries containing different oxidizers. Though both H2O2 and KIO3 could promote the dissolution of Ta, the rate was not fast enough to cause passivation. In the presence of 0.1 M Fe(NO3)3 in the slurry, however, the enhanced dissolution could raise the surface Ta5+ ion concentration above the critical concentration for passivation. The transition from active to passive state thus occurred, as commonly found in many passive alloy/environment systems.

By comparing Fig. 2b and c, it was found that the OCPs of Cu in the slurries containing KIO3 and Fe(NO3)3, respectively, were close to each other. This was because the redox potential for IO3−/I2 was close to that of NO3−/N2 but much lower than that of H2O2/H2O. The initial and steady-state OCPs of Cu and Ta measured in the above slurries are summarized in Table I.

Potentiodynamic polarization curves of Ta determined in 0.01 M Na2SO4 + 1 wt % Al2O3 base slurries with different oxidizer additions, under static condition, are demonstrated in Fig. 4.

The corrosion potential of Ta was significantly increased when Fe(NO3)3 was added into the base slurry. Clearly, Fe(NO3)3 was even more effective in passivating Ta in the base slurry considered.

Under CMP, the effect of oxidizer on the OCP of uncoupled Cu and Ta is shown in Fig. 5 and in Table I as well. As shown in Fig. 5a and b, the values of OCP for Cu measured in H2O2- and KIO3-containing slurries were still higher than those of Ta. Compared with those measured in static condition, the potentials were slightly lowered due to polishing. The contact pressure and hydrodynamic condition induced by CMP did impose some effect in changing the surface characteristics of both Cu and Ta. Figure 5c shows the potentials measured in the Fe(NO3)3-containing slurry. The potential of Cu remained almost constant at about +85 mV, which was slightly higher than that in static condition. For uncoupled Ta, the initial potential in Fe(NO3)3-containing slurry was −50 mV, more negative than Cu. However, as shown in Fig. 5c, the potential of Ta increased and eventually became higher than that of Cu as CMP continued. The change of polarity was attributed to the combined effects of accelerating dissolution and mass transfer of Ta ions away from the surface, as illustrated in Fig. 6. With the presence of either H2O2 or KIO3, the dissolution rate was not so fast and the flowing slurry could carry Ta5+ ions away from the surface, as demonstrated in Fig. 6a. Thus, the surface Ta5+ ion concentration could not build up substantially to favor passivation. However, as Fe(NO3)3 was added, the hydrodynamic condition was not in a condition fast enough to remove Ta5+ ions away from the surface. As a result, as depicted in Fig. 6b, the precipitation of Ta2O5 occurred and passivation was attained. The transition of OCP of Ta and the

<table>
<thead>
<tr>
<th>Oxidizer added</th>
<th>Potential measured at static condition (mV vs SCE) Cu</th>
<th>Ta</th>
<th>Potential measured under CMP (mV vs SCE) Cu</th>
<th>Ta</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Initial</td>
<td>Steady state</td>
<td>Initial</td>
<td>Steady state</td>
</tr>
<tr>
<td>10 vol % H2O2</td>
<td>+360</td>
<td>+360</td>
<td>−100</td>
<td>+65</td>
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<tr>
<td>0.1 M KIO3</td>
<td>−10</td>
<td>+30</td>
<td>−280</td>
<td>−250</td>
</tr>
<tr>
<td>0.1 M Fe(NO3)3</td>
<td>+45</td>
<td>+45</td>
<td>+175</td>
<td>+345</td>
</tr>
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reversion of its polarity with respect to Cu were thus explained. All these results indicated that Fe(NO₃)₃ at a concentration of 0.1 M was a stronger oxidizer for Ta. As noted in Table I, the difference between the OCPs of uncoupled Cu and Ta was reduced about 55 mV under CMP as compared with that in static condition (about 300 mV).

**Effect of oxidizer on the galvanic current of coupled Cu/Ta.**—The notable potential difference between the uncoupled Cu and Ta suggests that a significant galvanic current can occur when they are coupled to each other. The theoretical considerations of galvanic corrosion have been discussed by some researchers. The galvanic current through the anode is equal to the difference between the anodic and cathodic currents for the anode at galvanic potential,

\[
I_a = I_a^a(E_a) - I_c^a(E_a)
\]

where \(I_a^a\) and \(I_c\) are the anodic and cathodic current for the anode. Under cathodic diffusion control condition, the galvanic current is equal to the cathodic current at \(E_a\), namely

\[
I_g = I_a^c(E_a) - I_c^c(E_a) = I_c^c(E_a)
\]

where \(I_c\) is the cathodic current at cathode. In this investigation, the galvanic currents for the Cu/Ta couples measured in the base slurry with different oxidizer additions are depicted in Fig. 7. Curves 1 and 2 in Fig. 7 demonstrated the galvanic currents for Cu/Ta couple (both with an exposed surface area of 4.9 cm²) measured under CMP in the slurries containing 10 vol % H₂O₂ and 0.1 M KIO₃, respectively. The negative currents measured indicated that Ta was the anode with respect to Cu cathode in these two different slurries. More specifically, accelerated dissolution of Ta occurred when Ta was coupled to Cu. The results obtained were consistent with the OCP measurements for the uncoupled Cu and Ta as described above. Curves 1 and 2 also demonstrated the variation of galvanic currents with time of the Cu/Ta couples when CMP was terminated at 600 s and thereafter. The negative sign of galvanic current measured still indicated that Ta was the anode in both slurries. The magnitude of galvanic current decreased under static condition, suggesting that the polarity difference diminished perhaps due to the increase of surface Ta⁵⁺ ion concentration. However, the increase in Ta⁵⁺ ion concentration was not high enough to ensure the passivation of Ta.

In Fig. 7, curve 3 represents the galvanic current measured in Fe(NO₃)₃-containing slurry. A negative current was determined initially under CMP, indicating Ta was the anode. However, the negative galvanic current rapidly decreased to zero and became positive for a very short time. The switch of polarity was clearly due to the passivation of Ta in such slurry, in agreement with the potential measurement shown in Fig. 5c. This result again indicated that the addition of Fe(NO₃)₃ could favor and was more effective for the passivation of Ta, even in acidic slurry. When CMP stopped, the galvanic current was further increased due to the increase in the potential difference between Cu and Ta in static condition. The
change of polarity has also been found for the Cu/W coupling in the slurries with different oxidizers. Ernur et al.\(^9\) indicated that W was the anode in H\(_2\)O\(_2\)-containing slurry, yet Cu was the anode in HNO\(_3\) slurry. These results pointed out that the magnitude and polarity of galvanic current strongly depend on material characteristics and slurry composition.

**Effect of Cu/Ta area ratio on galvanic current.**—It is known that the dissolution rate of the anode, as well as the galvanic current density (the galvanic current divided by the anode area) in a galvanic couple depends on the cathode-to-anode area ratio (\(A_c/A_a\)).\(^{14,15}\) The galvanic current densities between Cu/Ta with area ratios of 1:1 (4.9 cm\(^2\)/4.9 cm\(^2\)) and 5:1 (4.9 cm\(^2\)/0.98 cm\(^2\)) in the Fe(NO\(_3\))\(_3\)-containing slurry, were compared as shown in Fig. 8. In the initial stage of CMP, Ta was the anode in the Cu/Ta couple with an area ratio of 1:1 (curve 1) or 5:1 (curve 2). By reducing the area of Ta from 4.9 to 0.98 cm\(^2\), the galvanic current density was increased from about \(-4.1 \times 10^{-6}\) to \(-7.7 \times 10^{-5}\) A/cm\(^2\). The increasing anodic dissolution rate of Ta with increasing Cu/Ta area ratio had also been found in NH\(_4\)OH base slurry.\(^{10}\) In this investigation, it was found that the galvanic current density (with a Cu/Ta area ratio of 5:1) decreased as the time of CMP was increased and

![Figure 6. Schematic diagrams showing the combined effects of anodic dissolution and mass transfer of Ta\(^{5+}\) ions on the surface with (a) H\(_2\)O\(_2\) or KIO\(_3\) addition and (b) Fe(NO\(_3\))\(_3\) addition.](image)

![Figure 7. Effects of (1) 10 vol % H\(_2\)O\(_2\), (2) 0.1 M KIO\(_3\), and (3) 0.1 M Fe(NO\(_3\))\(_3\) on the galvanic currents of the Cu/Ta coupling in 0.01 M Na\(_2\)SO\(_4\) + 1 wt % Al\(_2\)O\(_3\) base slurry during CMP and in static condition.](image)

![Figure 8. Effect of Cu/Ta area ratio on the galvanic current density of the Cu/Ta coupling in 0.1 M Fe(NO\(_3\))\(_3\) + 0.01 M Na\(_2\)SO\(_4\) + 1 wt % Al\(_2\)O\(_3\) slurry during CMP and in static condition.](image)
reached a steady current of about $-5.1 \times 10^{-5}$ A/cm$^2$. However, Ta remained as the anode during the whole period of measurement, dissimilar to that with an area ratio of 1:1. This result indicated that Ta was not passivated during CMP if the Cu/Ta area ratio was reduced to 5:1. The absence of Ta passivation of the Cu/Ta couple was probably due to the insufficient Ta$^{5+}$ concentration on the surface. Though the dissolution of the anode was dependent on the reduction reaction on cathode, the increase in Cu/Ta area ratio seemed not sufficient to raise the Ta$^{5+}$ concentration above the critical value for passivation. However, as soon as CMP was terminated, Ta became the cathode and the reverse of polarity was observed, as demonstrated by curve 2 in Fig. 8.

Figure 9 and 10 show the effect of Cu/Ta area ratio on the galvanic currents measured under CMP in the slurries with 10 vol% H$_2$O$_2$ and 0.1 M KIO$_3$ additions, respectively. In both cases, Ta was the anode regardless of the Cu/Ta area ratio. It was noted that the galvanic current density with a Cu/Ta area ratio of 5:1 was higher than that of 1:1. The results indicated that accelerated dissolution on anode occurred if the area of cathode was increased.

Conclusions

The electrochemical behavior the Cu/Ta galvanic couple in 0.01 M Na$_2$SO$_4$ + 1 wt % Al$_2$O$_3$ base slurry with the presence of different oxidizers, in static or under CMP, was investigated. In static condition and under CMP, the OCP of Cu was higher than that of Ta in 0.01 M Na$_2$SO$_4$ + 1 wt % Al$_2$O$_3$ base slurry with the addition of either 10 vol% H$_2$O$_2$ or 0.1 M KIO$_3$. However, the addition of 0.1 M Fe(NO$_3$_)$_3$ into the 0.01 M Na$_2$SO$_4$ + 1 wt % Al$_2$O$_3$ base slurry made the OCP of Ta nobler than Cu in static condition. Under CMP, the potential of Ta was initially lower than that of Cu but became higher at a latter stage. The presence of Fe(NO$_3$_)$_3$ promoted the passivation of Ta. The results of galvanic current measurements showed that the direction of current flow was consistent with the results obtained in OCP measurement. The magnitude and polarity of the galvanic current also depended on the Cu/Ta area ratio. In the Fe(NO$_3$_)$_3$-containing slurry, Ta was the anode with a Cu/Ta area ratio of 5:1, while a switch of polarity from anode to cathode was observed if the area ratio was 1:1. The dependences of galvanic behavior on the type of oxidizer, polishing condition, and area ratio were clearly demonstrated.

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