Potassium Bromate as an Oxidizing Agent in a Titania-Based Ru CMP Slurry

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Ru chemical mechanical planarization (CMP) was studied in slurries containing titania and potassium bromate at different pH values, showing that the Ru removal rate is enhanced at pH 2 or less. Potentiodynamic polarization studies indicate that the corrosion current is enhanced in the presence of bromate, while the static etch rate experiments show that the etch rate is low. Potassium bromate increases Ru removal only at anodic potentials or during mechanical abrasion. Studies at different concentrations of abrasive and oxidizing agent reveal that the removal rate enhancement saturates at 0.75 mM bromate and 4 wt % titania.

Results and Discussion

Figure 1 shows the RR vs pH for the Ru disk with and without KBrO3. For the blank slurries without an oxidizing agent, the Ru RR remains low in the range of 10–20 nm/min at all values of pH. In the presence of 100 mM KBrO3 at pH values ≤2, there is a dramatic increase in the Ru RR. Figure 2 shows the Ru static etch rate as a function of the KBrO3 concentration at pH 2. The etch rate is approximately proportional to the square root of the KBrO3 concentration, implying that Ru dissolution is a multistep process with an intermediate species participating in a second-order reaction. The etch rates are much lower than the CMP rates, indicating that direct dissolution has very little contribution to the overall polish rate. The Pourbaix diagram for Ru predicts that at pH 2, Ru oxidation to RuO2 should occur at about +350 to 350 mV vs normal hydrogen electrode, but this does not include the effect of KBrO3 addition.18 In addition, Ru oxide is known to exist at potentials more cathodic than that predicted by the Pourbaix diagram.20-22 The combination of reasonably high Ru RR with extremely low static etch rate suggests that KBrO3 oxidizes Ru to a partially soluble or relatively soft oxide film that is more easily removed by abrasives. This partially soluble or relatively soft Ru oxide film appears to form only at low pH (≤2), whereas a harder Ru oxide film appears to form at higher pH. At pH 2, both the Ru and titania surfaces are likely positively charged, because the isoelectric points of RuO2 and TiO2 have been reported to range from 4 to 6 and from 5 to 6, respectively.23-25

Thus, the electrostatic interactions are unlikely to play a significant role in causing a high Ru polish rate with titania.

A high RR (~130 nm/min) for Ru CMP has been obtained using sodium periodate.1 However, sodium ions can cause reliability issues in microelectronic circuits, so concerns of sodium contamination may preclude its use in CMP slurries. slurries based on potassium periodate are reported to yield a much lower Ru RR,8 perhaps due to the low solubility of potassium periodate in water, ~6 mM at 25°C.26 In contrast, KBrO3 is much more soluble in water, ~0.49 M at 25°C,25 and hence, is a promising candidate for Ru CMP despite the more modest RR.

The effect of changing the abrasive loading is shown in Fig. 3. For slurries without any oxidizing agent, the Ru RR increases up to 1 wt % titania. At higher abrasive loadings, the Ru RR shows saturation. In the presence of 100 mM KBrO3, the Ru RR is clearly much higher and increases with titania loading, but this effect saturates at 4 wt % titania loading. Figure 4 shows the effect of changing the concentration of oxidizing agent in slurries containing 2 wt % titania at pH 2. In slurries without KBrO3, the RR was 7 nm/min.
Upon addition of KBrO$_3$, the Ru RR increases up to 51 nm/min at a KBrO$_3$ concentration of 0.75 mM, but a further increase in KBrO$_3$ concentration has little effect on the Ru RR.

The effects of the concentrations of abrasive (Fig. 2) and oxidizing agent concentration (Fig. 3) are difficult to understand at a fundamental level due to the complex physicochemical dynamics during CMP. The effects of abrasive concentration and oxidizing agent concentration have been widely studied for Cu and W CMP, but not for Ru CMP. The CMP RR is expected to increase with the abrasive concentration due to the increased total surface area for mechanical abrasion. The results of Fig. 2 exhibit an initial approximately linear increase in Ru RR with abrasive concentration, followed by eventual saturation. Several research groups have reported trends with abrasive concentration similar to those observed in Fig. 3 for Cu and W CMP. The limiting value for the RR can be increased by changing either the chemical or mechanical parameters governing CMP. Our results follow this trend, because without an oxidizing agent, the Ru RR saturates at 18 nm/min, while upon addition of 100 mM KBrO$_3$, the Ru RR saturates at 104 nm/min. This effect of reaching a limiting value for the metal RR has been proposed to reflect a maximum in the extent of mechanical abrasion of the metal surface by the abrasive particles. The Cu RR in 75 mM KBrO$_3$ and 2 wt % titania at pH 2 was 285 nm/min, and was not suppressed to a significant extent by the addition of 65 mM benzotriazole. Further work is necessary to identify a Cu corrosion inhibitor suitable for this slurry.

The effect of the oxidizing agent concentration is more complex, because this depends on the relative rates of metal oxidation and metal oxide dissolution. The observation of a limiting RR has been suggested to occur during metal CMP when the overall reaction is rate-limited by the mechanical abrasion of the surface film. The results of the potentiodynamic polarization experiments are shown in Fig. 5. The corrosion current density is quite low in solutions without KBrO$_3$. In solutions with KBrO$_3$, the corrosion potential is significantly shifted in the anodic direction. The plots show that the dominant anodic and cathodic reactions have changed upon addition of KBrO$_3$. However, the corrosion current densities at high concentrations of KBrO$_3$ greatly exaggerate the extent of Ru corro-

**Figure 1.** (Color online) Ru RR vs pH in slurries containing 2 wt % titania abrasives with and without 100 mM KBrO$_3$.

**Figure 2.** (Color online) Ru static etch rate vs KBrO$_3$ concentration at pH 2. The axes are in logarithmic scale.

**Figure 3.** (Color online) Effect of titania abrasive loading on Ru RR with and without 100 mM KBrO$_3$.

**Figure 4.** (Color online) Effect of KBrO$_3$ concentration on the Ru RR. The slurry contained 2 wt % titania at pH 2. Note the break in the abscissa.

**Figure 5.** (Color online) Potentiodynamic polarization curves of Ru in 100 mM KClO$_4$ and different concentrations of KBrO$_3$, i.e., (A) 0, (B) 0.25, (C) 7.5, and (D) 100 mM at pH 2.
ission. The Ru static etch rate in these slurries is very low, so the current densities reported in Table I do not correspond to Ru electrodeposition. The dependence of dissolution rate on the KBrO₃ concentration with a reaction order of 0.5 clearly shows that Ru dissolution is a complex multistep phenomenon and may not be explained by one dominant anodic and another dominant cathodic reaction. The identification of the intermediate species and the complete mechanism of dissolution are beyond the scope of this study. An extensive analysis of the Ru and titania surfaces to understand these interactions would be helpful. Electrochemical impedance spectroscopy and other techniques are currently being employed to fully characterize the Ru CMP in KBrO₃-based slurries.

Conclusions

Potassium bromate as an oxidizer and titania as an abrasive are reported and studied for Ru CMP slurries. CMP experiments show that KBrO₃ enhances the RR at pH values of 2 and below. The RR increases with increasing concentrations of bromate and titania, but saturates at concentrations of 0.75 mM and 4 wt %, respectively. Static etch rate experiments show that the dissolution rate is very low and the order of the reaction is 0.5 with respect to the oxidizer. Potentiodynamic polarization experiments show that the corrosion current is high in the presence of KBrO₃ despite the low static etch rate. Together, these results indicate that KBrO₃ increases the Ru removal only when the Ru metal is anodized or mechanically abraded.

Acknowledgment

We thank the Coulter School of Engineering (CSOE) at Clarkson University for funding this project.

Clarkson University assisted in meeting the publication costs of this article.

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