

Potassium bromate as an oxidizing agent in a titania based Ru CMP slurry

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Abstract: 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 the 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.

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Introduction:

Cu is used as interconnect material in integrated circuits, and a thin barrier layer is used to prevent the diffusion of Cu through the interlayer dielectric^{1,2}. During damascene and dual damascene fabrication of interconnect structures, the excess Cu and barrier are removed by a process of chemical mechanical planarization (CMP). Currently Ta and TaN are used as barrier metals¹ and a thin Cu seed layer is deposited by PVD followed by electrodeposition of Cu. However, as feature dimensions shrink, the PVD Cu is not scalable and Ru is proposed as a suitable seed layer. It has low resistivity as well as negligible solid solubility with Cu^{3,4}.

Although introduction of Ru would likely require the development of chemical mechanical planarization (CMP) techniques, only a few reports have appeared that describe Ru CMP methods⁵⁻¹⁷. Ru is a noble metal with high chemical resistance and mechanical hardness, which makes Ru CMP challenging. Sodium periodate⁵⁻⁹, hydrogen peroxide¹⁰⁻¹², persulfate¹¹, Ce(IV)^{10,13-16}, and perborate¹⁷ have been suggested as suitable oxidizing agents for Ru CMP. Here we report potassium bromate (KBrO₃) as an oxidizing agent and titania as an abrasive for Ru CMP. Titania was chosen as candidate abrasive since it was reported to yield higher Ru removal rate when compared to silica and alumina based slurries¹⁸. The effect of abrasive loading, oxidizing agent concentration and pH is systematically studied.

Experimental:

Ru CMP was studied with a lab-scale polishing instrument (Struers LaboPol-5/LaboForce 3) using a 25-mm diameter, 3-mm thick Ru disc (99.9% purity, William Gregor Ltd, UK). Electrochemical grade copper disc of 25 mm diameter was used for copper CMP. A constant

downward pressure of 5.8 psi was applied, the platen was rotated at 150 rpm, the disc was rotated at 250 rpm, and a slurry flow rate of 100 ml/min was maintained. The slurry contained DI water, titania abrasives (-300 mesh, DCW, India), and the pH was adjusted using HNO₃ or KOH. Each run was conducted for three minutes and at least three runs were performed at each polishing condition. The removal rate was calculated by the weight loss method. The average removal rates along with the standard deviation are reported. For static etch rate experiments, the Ru disc was kept in 100 ml solution for 10 minutes with stirring and the concentration of Ru in the solution was measured using Perkin Elmer Optima 5300DV inductively coupled plasma optical emission spectroscope (ICP-OES).

All electrochemistry experiments were performed with an 11-mm diameter Ru rotating disc electrode (RDE) at 100 rpm in solutions containing 100 mM KClO₄ (supporting electrolyte), Pt spiral counter electrode, and a saturated calomel reference electrode (SCE), controlled with Princeton Applied research 263A potentiostat with 1mV/s sweep rate.. Potentiodynamic polarization experiments were controlled with a Princeton Applied Research (PAR) 263A potentiostat with a sweep rate of 1 mV/s.

Results and Discussion:

Figure 1 shows the removal rate (RR) vs. pH for the Ru disc, with and without KBrO₃. For the blank slurries without an oxidizing agent, the Ru removal rate remains low, in the range of 10 to 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 removal rate. On the other hand, figure 2 shows the Ru static etch rate as a function of 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 RuO should occur at about +350 to 550 mV vs. NHE, but this does not include the effect of KBrO₃ addition¹⁹. In addition, Ru oxide is known to exist at potentials more cathodic to that predicted by the Pourbaix diagram²⁰⁻²². The combination of reasonably high Ru removal rates 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, since the isoelectric points of RuO₂ and TiO₂ have been reported to range from 4-6 and 5-6, respectively²³⁻²⁵. Thus the electrostatic interactions are unlikely to play a significant role in causing a high Ru polish rate with titania.

A high removal rate (about 130 nm/min) for Ru CMP has been obtained using sodium periodate⁷. However, sodium ions can cause reliability issues in microelectronic circuits, so concerns of sodium contamination may preclude its use in CMP slurries. On the other hand, slurries based on potassium periodate are reported to yield a much lower Ru removal rate⁸, perhaps due to the low solubility of potassium periodate in water, about 6 mM at 25° C²⁶. In contrast, KBrO₃ is much more soluble in water, about 0.49 M at 25° C²⁶, and hence is a promising candidate for Ru CMP despite the more modest removal rate.

The effect of changing the abrasive loading is shown in Figure 3. For slurries without any oxidizing agent, the Ru removal rate increases up to 1 wt% titania. At higher abrasive loadings, the Ru removal rate shows saturation. In the presence of 100 mM KBrO_3 , the Ru removal rate 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 a pH of 2. In slurries without KBrO_3 , the removal rate was 7 nm/min. Upon addition of KBrO_3 , the Ru removal rate increases up to 51 nm/min at a KBrO_3 concentration of 0.75 mM, but further increase in KBrO_3 concentration has little effect on the Ru removal rate.

The effects of the concentrations of abrasive (Figure 2) and oxidizing agent (Figure 3) are difficult to understand at a fundamental level due to the complex physico-chemical dynamics during CMP. The effects of abrasive concentration and oxidizing agent concentration have been widely studied for Cu and W CMP²⁷⁻³¹, but not for Ru CMP. The CMP removal rate is expected to increase with the abrasive concentration due to the increased total surface area for mechanical abrasion³². The results of Figure 2 exhibit an initial approximately linear increase in Ru removal rate with abrasive concentration, followed by eventual saturation. Several research groups have reported trends with abrasive concentration similar to those observed in figure 3 for Cu and W CMP²⁷⁻³¹. The limiting value for the removal rate can be increased by changing either the chemical or mechanical parameters governing CMP²⁹. Our results follow this trend, since without an oxidizing agent, the Ru removal rate saturates at 18 nm/min, while upon addition of 100 mM KBrO_3 , the Ru removal rate saturates at 104 nm/min. This effect of reaching a limiting value for the metal removal rate has been proposed to reflect a maximum in the extent of

mechanical abrasion of the metal surface by the abrasive particles³¹ The Cu removal rate in 75mM 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 BTA. Further work is necessary to identify a Cu corrosion inhibitor suitable for this slurry.

The effect of oxidizing agent concentration is more complex, since this depends on the relative rates of metal oxidation and metal oxide dissolution. The observation of a limiting removal rate has been suggested to occur during metal CMP when the overall reaction is rate-limited by mechanical abrasion of the surface film³³.

The results of potentiodynamic polarization experiments are shown in Figure 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 corrosion. As discussed earlier, the Ru static etch rate in these slurries is very low, so the current densities reported in Table 1 do not correspond to Ru electro-dissolution. The dependence of dissolution rate on the KBrO_3 concentration with a reaction order of 0.5 clearly shows that the 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 KBrO_3 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 the KBrO_3 enhances the removal rate at pH values of 2 and below. The removal rate 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 KBrO_3 , despite the low static etch rate. Together, these results indicate that KBrO_3 increases the Ru removal only when the Ru metal is anodized or mechanically abraded.

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Table 1. Effect of KBrO_3 concentration on corrosion potential and corrosion current density.

Electrolyte	Corrosion Potential (mV vs. SCE)	Corrosion current density ($\mu\text{A}/\text{cm}^2$)	Electrochemically predicted Ru etch rates (nm/min)
100 mM KClO_4 at pH 2	280	1.66	<1
100 mM KClO_4 + 0.25 mM KBrO_3 at pH 2	794	4.63	<1
100 mM KClO_4 + 7.5 mM KBrO_3 at pH 2	931	90.2	1
100 mM KClO_4 + 100 mM KBrO_3 at pH 2	1002	1030	13

Figure Captions:

Figure 1. (Color Online) Ru removal rate 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 a pH 2. Note that the axes are in logarithmic scale.

Figure 3. (Color Online) Effect of titania abrasive loading on Ru removal rate, with and without 100 mM KBrO_3 .

Figure 4. (Color Online) Effect of KBrO_3 concentration on the Ru removal rate. 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., 0 mM (A), 0.25 mM (B), 7.5 mM (C) and 100 mM (D) at pH 2.

Figure 1. (Color Online) Ru removal rate vs pH in slurries containing 2 wt% titania abrasives with and without 100 mM KBrO₃.

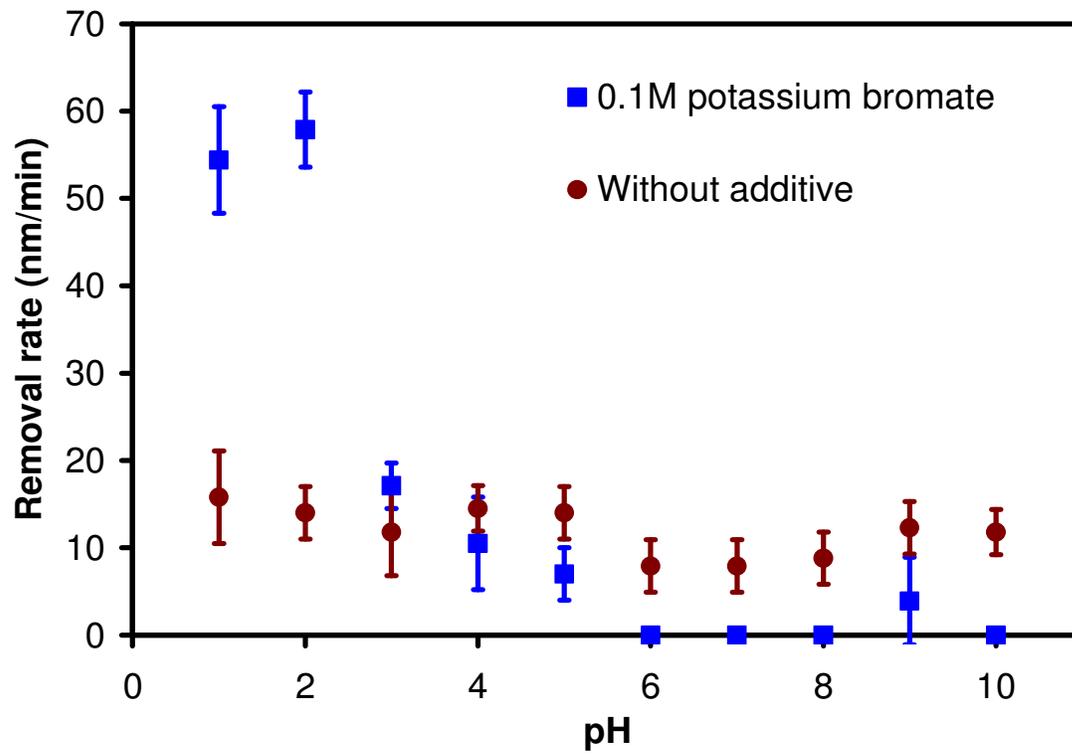


Figure 2. (Color Online) Ru static etch rate vs KBrO_3 concentration at a pH 2. Note that the axes are in logarithmic scale.

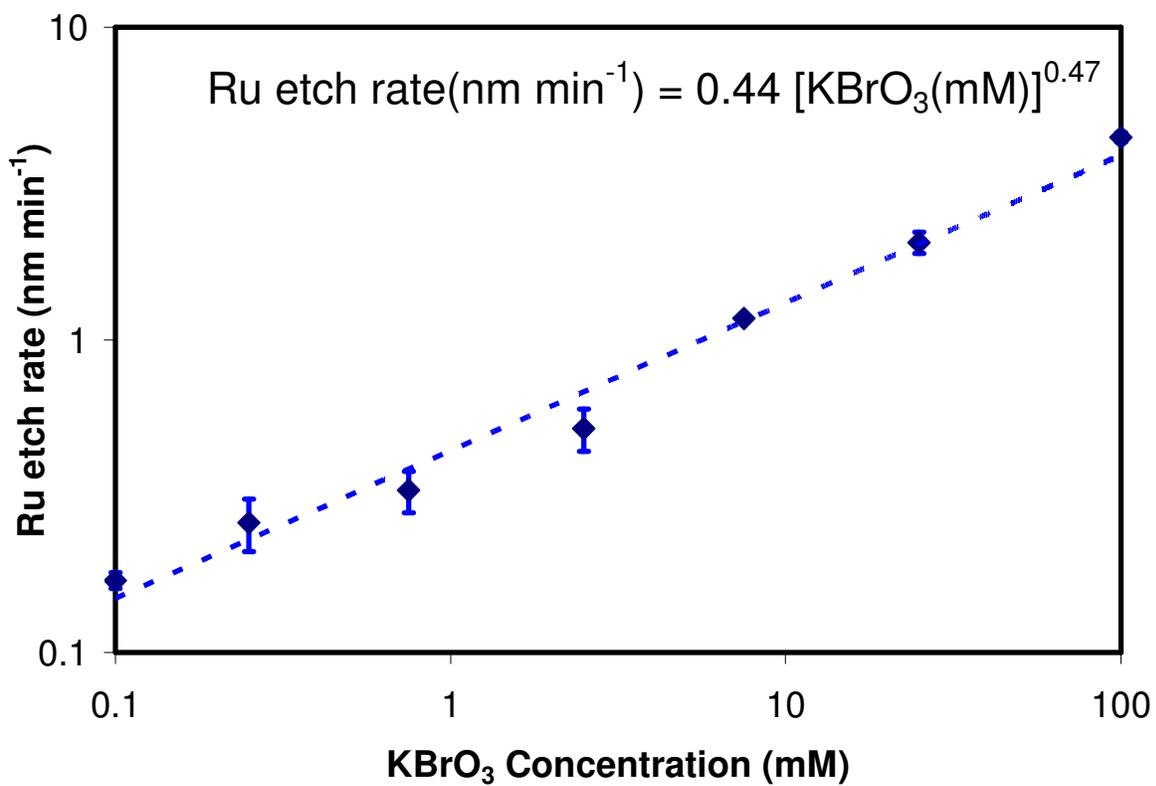


Figure 3. (Color Online) Effect of titania abrasive loading on Ru removal rate, with and without 100 mM KBrO₃.

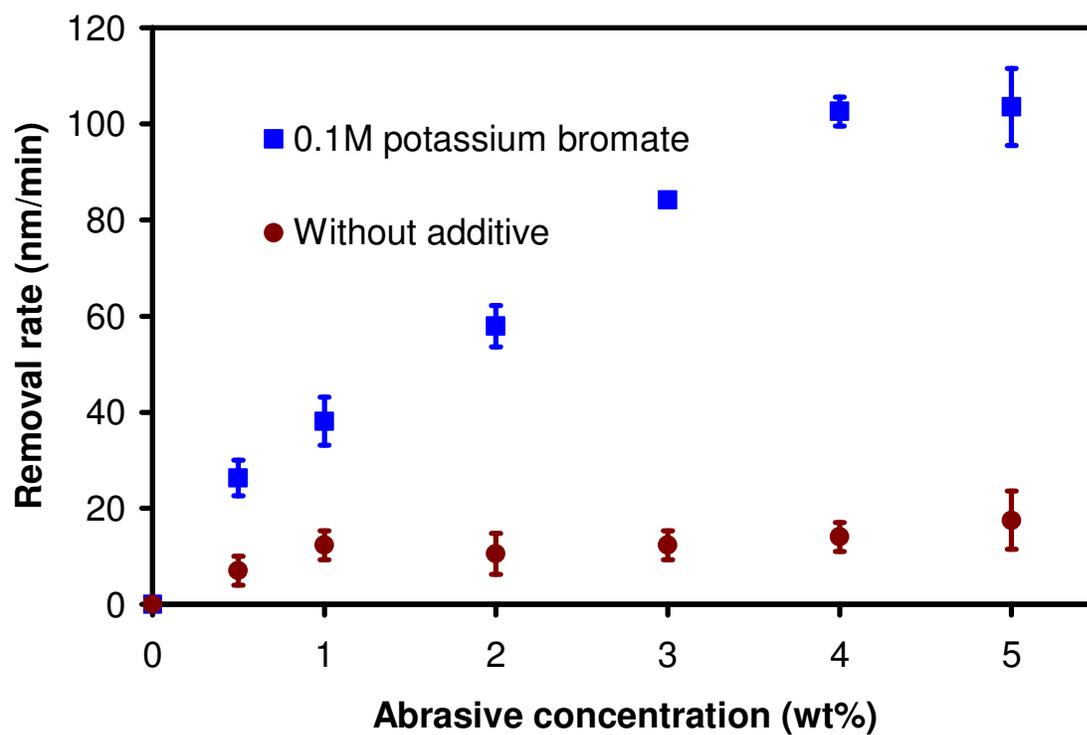


Figure 4. (Color Online) Effect of KBrO_3 concentration on the Ru removal rate. The slurry contained 2 wt% titania at pH 2. Note the break in the abscissa.

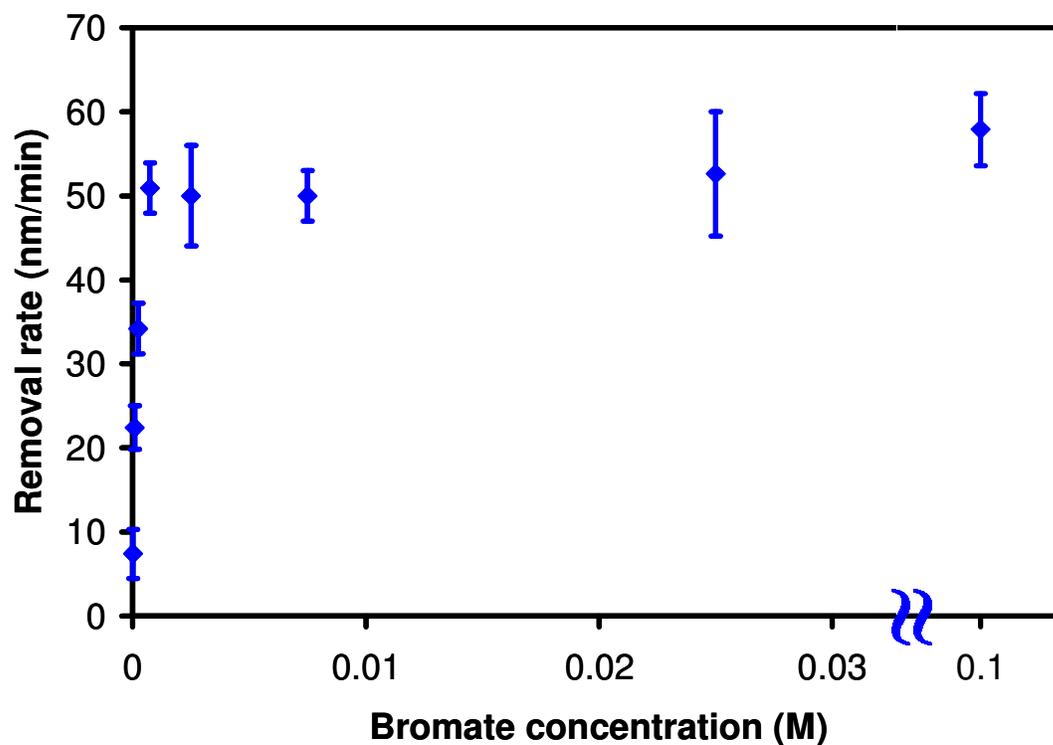


Figure 5. (Color Online) Potentiodynamic polarization curves of Ru in 100 mM KClO_4 and different concentrations of KBrO_3 , i.e., 0 mM (A), 0.25 mM (B), 7.5 mM (C) and 100 mM (D) at pH 2.

