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Chemical Mechanical Planarization of Ruthenium with Oxone as Oxidizer

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Potassium peroxymonosulfate (Oxone) was investigated as an oxidizing agent in silica based slurries for chemical mechanical planarization of Ru. Upon addition of oxone, the Ru removal rate increases significantly in the pH range of 1–6. The slurry stability is poor at pH 3 and higher. At pH 2, oxone enhances the Ru removal rate even in the absence of abrasive, indicating that a soft film is formed on the Ru surface. Ru dissolution experiments show that the static etch rate is low. The Ru removal rate variation with pressure and velocity does not follow the Preston equation.
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Transistors within integrated circuits are connected by Cu interconnects formed by the dual damascene process. A thin barrier layer, typically Ta and TaN, prevents Cu diffusion into the dielectric layer,[1,2] but also prevents direct electrodeposition of Cu. In the conventional dual damascene process a thin seed layer of Cu is grown atop the barrier metal layer by physical vapor deposition (PVD), followed by the electrodeposition of Cu. Chemical mechanical planarization (CMP) is used to remove the excess Cu, Ta and TaN materials deposited.[1] However, as the feature dimensions shrink, PVD Cu is not scalable. Hence there is need for an alternate seed layer which allows direct electrodeposition of Cu[3–5] and Ru is proposed as a suitable candidate. Ru also has low resistivity and low solid solubility with Cu, but its introduction would necessitate the development of Ru CMP.

For Ru CMP, oxidizing agents such as periodate,[6–11] hydrogen peroxide,[12–14] persulfates,[12] ceric ammonium nitrate[13,15,16] and bromate[17] has been investigated. The use of potassium peroxymonosulfate (Oxone) along with potassium sulfate for Ru CMP has been suggested, but only a limited set of data is available.[18] In this study, the use of oxone as an oxidizer has been systematically studied. The Ru removal rate as a function of pH, oxidizer concentration, abrasive loading, polishing pressure and velocity was studied. Potentiodynamic polarization studies were also conducted to understand the role of chemical dissolution.

Experimental

The chemical mechanical planarization (CMP) experiments were conducted on a lab scale polisher (Struers Labopol5/Laboforce 3) with a 25 mm diameter Ru disk (William Gregor Ltd, U.K). Unless mentioned otherwise, a pressure of 5.7 psi and a turn table speed of 150 rpm were used for all CMP experiments. The sample was rotated at 250 rpm for all experiments, and a soft pad (SUBA 500 from Rohm & Haas) was used. Fumed silica particles (M5 Cab-o-sil, from Cabot-Sanmar, India) with a surface area of 200 m^2/g were used as the abrasive. The slurry was supplied at a flow rate of 100 mL/min, with pH adjustment using either KOH or HNO_3. Each CMP run was conducted for two minutes, and at least three runs were performed at each polishing condition. The removal rate was calculated by gravimetric method using a balance with 0.1 mg sensitivity, and both the average removal rates and standard deviation are reported. For static etch rate experiments, the Ru disk was immersed in 150 mL solution for 15 minutes with stirring. All electrochemistry experiments were performed in slurries containing 2 wt% silica and 100 mM $NaClO_4$ as the supporting electrolyte at pH 2. The pH adjustment was made by adding either dilute $HClO_4$ or NaOH. A Ru rotating disk electrode (RDE) of diameter 11 mm was used as a working electrode, with Pt and saturated calomel electrodes (SCE) as counter and reference electrodes respectively. The electrode was pressed against the pad and rotated at 100 rpm during the measurement to simulate abrasion during CMP. Voltammetry experiments were controlled with Princeton Applied Research 273A potentiostat at sweep rate of 1 mV/s.

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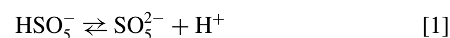
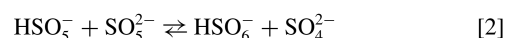
Results and Discussion

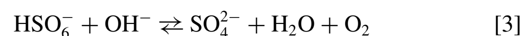
Fig. 1 shows the Ru removal rate (RR) at various pH in a slurry with 2 wt% silica in the presence and absence of 2 wt% oxone. In the absence of 2 wt% oxone, the Ru RR was essentially zero at all pH values investigated. The natural pH of the slurry with 2 wt% oxone and 2 wt% silica is 1.5. Upon addition of oxone, the RR increased to 53 nm/min at pH 1. The Ru RR increased with pH until pH 2, and then remained approximately constant up to pH 6. However, in the presence of oxone, at pH 3 and above, the slurry was unstable, and the pH decreased continuously with time, so it had to be adjusted every 5 minutes. The decrease in pH is probably due to dissociation of oxone by the following reactions[19]



$$HSO_5^- \rightleftarrows SO_5^{2-} + H^+ \quad [1]$$



$$HSO_5^- + SO_5^{2-} \rightleftarrows HSO_6^- + SO_4^{2-} \quad [2]$$



$$HSO_6^- + OH^- \rightleftarrows SO_4^{2-} + H_2O + O_2 \quad [3]$$

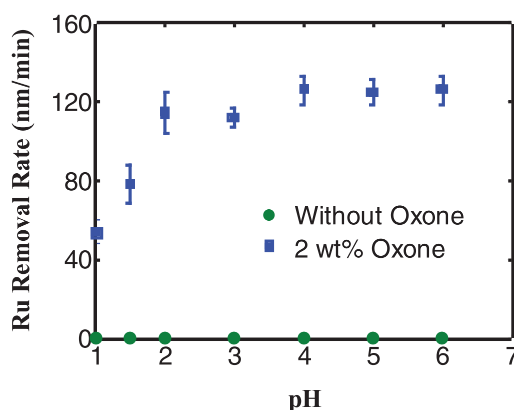


Figure 1. Ru removal rate (RR) vs pH in slurries containing 2 wt% silica with and without 2 wt% oxone.

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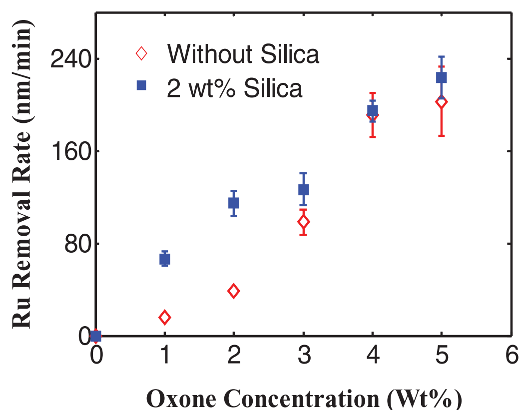


Figure 2. Effect of oxone concentration on Ru removal rate (RR) with and without 2 wt% silica at pH 2.

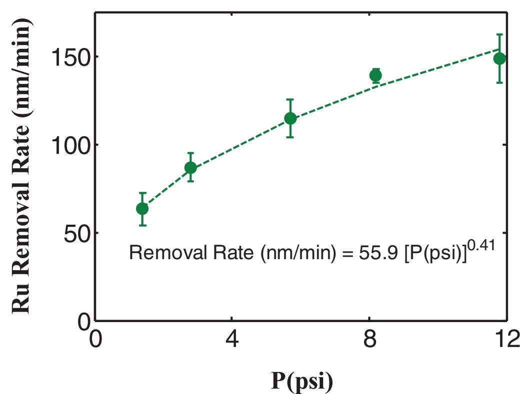
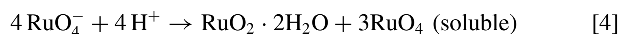


Figure 4. Ru removal rate (RR) vs Pressure. The slurry contained 2 wt% silica and 2 wt% oxone at pH 2.

The slurry stability at pH 2 was tested by monitoring the pH over a few days. The slurry pH decreased to 1.9 and remained stable for at least five more days, so further investigations were carried out in slurries at pH 2.

The Ru RR at various concentrations of oxone, with and without 2 wt% silica abrasive, is presented in Fig. 2. Even in the absence of abrasives, the Ru RR increases with oxone concentration. While the removal rates are higher in the presence of abrasive for oxone concentrations of 1–3 wt%, abrasives have little impact on the Ru RR at oxone concentrations of 4–5 wt%. The results indicate that in presence of oxone, either the static etch rate of Ru is very high, or a soft film is formed that is easily removed by the pad during CMP. To our knowledge, this is the first report of abrasive-free Ru CMP. The open circuit potential of Ru in solutions containing 1 to 5 wt% oxone at pH 2 was found to be 1.07 to 1.105 V vs SCE. In this potential and pH range, the Pourbaix diagram predicts formation of RuO_4 (yellow) and $RuO_2{\cdot}2H_2O$ (black).[7] RuO_4 is soluble in water and will form hyperruthenic acid (H_2RuO_5) by the following reactions.



$$4\,RuO_4^- + 4\,H^+ \rightarrow RuO_2 \cdot 2H_2O + 3RuO_4 \text{ (soluble)} \quad [4]$$

$$H_2O + RuO_4 \rightarrow H_2RuO_5 \quad [5]$$

The static etch rate in 2 wt% oxone solution, measured by weight loss, is very low (<3 nm/min). In 5 wt% oxone solution, the weight loss is 43 nm/min. Hence, at low oxone concentrations, the high Ru RR in oxone CMP slurries is likely due to the formation of a soft film rather than Ru dissolution. At high wt% oxone solution, chemical removal contributes up to approximately 20% of the total removal. During static etch rate measurements in oxone solutions, a black film formed on the surface of the Ru and the solution turned yellow. During CMP measurements in oxone slurries however, only the pad turned black while the surface retained the metallic luster. This suggests that the film is easily removed by the mechanical action. In slurries or solutions without oxone, there was no change in color suggesting that in the absence of oxone, $RuO_2{\cdot}2H_2O$ and RuO_4 do not form.

The variation in Ru removal rate with abrasive concentration is shown in Fig. 3 for a CMP slurry with 2 wt% oxone at pH 2. The Ru RR was zero in slurries without oxone. For slurries with oxone, the Ru RR increased with abrasive loading up to 1 wt% silica, but saturated at higher abrasive loadings. This trend can be explained as follows: at low abrasive loading, the rate of film formation is high, and mechanical removal is the rate limiting step. In this regime, an increase in abrasive concentration causes an increase in the mechanical removal rate, and hence in the overall removal rate. At 2 wt% or more abrasive concentration, film formation is the rate limiting step and hence the overall removal rate remains constant.

In order to understand the mechanical component of Ru CMP, the pressure (P) and table speed (V) were varied, and the results compared to those predicted by the Preston equation:

$$RR = k\,PV \quad [6]$$

where k is a constant. The effect of pressure on Ru RR is shown in Fig. 4. The CMP slurry contains 2 wt% oxone and 2 wt% silica at pH 2, and the turntable rpm was 150. The Ru RR variation with pressure appears to follow a power law trend, with an exponent of 0.41, showing clear non-Prestonian behavior. When film formation is the rate limiting step, a non-Prestonian behavior is expected. Luo

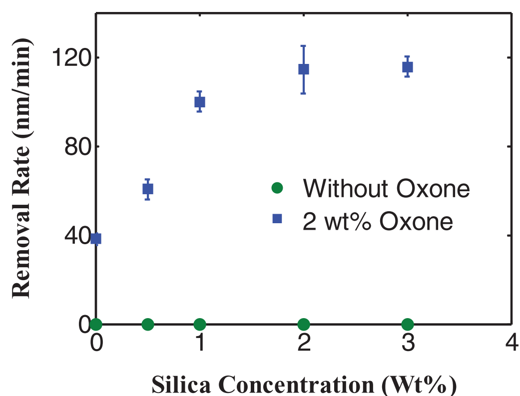


Figure 3. Effect of silica abrasive loading on Ru removal rate (RR) with and without 2 wt% oxone at pH 2.

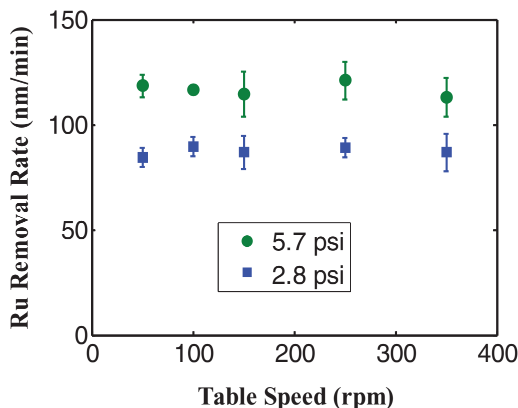


Figure 5. Ru removal rate (RR) vs table rpm. The slurry contained 2 wt% silica and 2 wt% oxone at pH 2.

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Table I. Effect of oxone concentration on corrosion potential and corrosion current density.

Electrolyte	Corrosion potential (mV vs SCE)	Corrosion current density ($\mu A/cm^2$)	Electrochemically predicted Ru etch rates (nm/min)
100 mM $NaClO_4$ + 2 wt% silica	275	6	0.08
100 mM $NaClO_4$+ 1 wt% oxone + 2 wt% silica	964	138	1.75
100 mM $NaClO_4$+ 2 wt% oxone + 2 wt% silica	988	207	2.62

and Dornfeld[20] developed a solid-solid contact mode model accounting for plastic deformations over the wafer-particle and pad-particle interfaces, and estimated that the RR would vary as $\sqrt{P}$. Guo and Subramanian[21] studied the mechanical removal of Cu with alumina abrasives using a SUBA 500 pad, and reported that the RR depended on $\sqrt{P}$. However, no physical explanation was given for the observed trend. Thus, while the Preston equation is used to explain CMP removal rate trends, especially in the absence of dissolution, deviations from Prestonian behavior have been reported for both experimental and modeling studies.

Fig. 5 shows the effect of table speed (rpm) on Ru RR in slurry with 2 wt% silica and 2 wt% oxone at pH 2. At a given pressure, the Ru RR was approximately constant for all turntable speeds employed. As noted above, the Ru removal rate increases with pressure. Since the minimum table speed was 50 rpm in our setup, we could not obtain results for lower speeds. Considering that the dissolution rate is very low, RR vs turn table speed in the region between 0 and 50 rpm (Fig. 5) is likely to show a monotonically increasing trend. Guo and Subramanian[21] reported that the Cu RR on a hard pad (IC 1000) increases at low values of the velocity, and then levels off at velocities above 0.7 m/s. The same trend was observed at higher pressure also, except that the removal rate at the saturation regime was higher. They proposed that at higher velocities, the kinetics of film formation is the rate limiting step. They also proposed that at higher pressure, the temperature and hence the film formation rate would increase, leading to a higher removal rate. A similar hypothesis may be applicable to the results shown in Fig. 5.

Fig. 6 shows the Ru potentiodynamic polarization results in slurries with and without oxone during abrasion. In the slurry without oxone the corrosion current density is quite low. Upon addition of oxone, the corrosion potential shifts in the anodic direction by about 700 mV. The dominant cathodic and anodic reactions appear to have both changed upon addition of oxone. The kink seen in the cathodic branch may be associated with redox reactions of oxone or its dissociation products. The corrosion current densities are summarized in Table I.

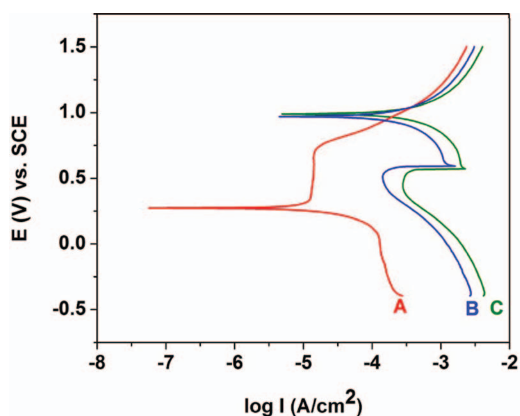

Figure 6. Potentiodynamic polarization curves of Ru in 100 mM $NaClO_4$, 2 wt% silica and different concentrations of oxone i.e. (A) 0, (B) 1 wt% and (C) 2 wt% at pH 2.

The Ru static etch rates in these solutions are quite low, and the Ru electrodissolution rates during abrasion estimated from corrosion current densities (assuming that Ru is oxidized to RuO_4) are also in the same range. Thus the electrochemical results also confirm that chemical dissolution contributes minimally to the overall removal rate.

Since Cu surfaces are also exposed during Ru CMP, and Cu removal rates (RR) are typically much higher than Ru RR, addition of a Cu corrosion inhibitor is likely necessary for commercial applications. The Cu RR in 2 wt% silica and 2 wt% oxone at pH 2 was 1054 nm/min, but was suppressed to 150 nm/min by the addition of 1 wt% benzotriazole (BTA). However, the corresponding Ru RR was practically zero, indicating that BTA is not a suitable inhibitor for this slurry. Further optimization of the slurry, in terms of the abrasive concentration, oxone concentration and the choice of Cu corrosion inhibitor, as well as operating pressure and velocity, will eventually be necessary.

Conclusions

The use of oxone as an oxidizing agent for Ru chemical mechanical planarization (CMP) under various conditions was investigated. CMP experiments showed that oxone enhances the Ru removal rate (RR) in the pH range 1–6, although the slurry stability was poor at pH 3 and above. The RR increases with increased concentrations of oxone and abrasive. The Ru static etch rate in oxone solutions is quite low, but the Ru RR in solutions containing only oxone and no abrasive is high, indicating that it is possible to develop abrasive-free Ru CMP slurries using oxone. The RR is approximately proportional to the square root of pressure, but is independent of table speed in the range employed in this investigation. Potentiodynamic polarization studies also indicate that the chemical dissolution contributes less to the overall removal rate. These results indicate that a soft film is formed on the Ru surface in the presence of oxone, and that the film is removed by the pad and/or the abrasives during CMP.

Acknowledgment

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