

I. Deliverable:

Name: Report on the novel chemistries for copper and barrier E-CMP

Task ID: 425.014

Task Title: Environmentally Benign Electrochemically-Assisted Chemical-Mechanical Planarization (E-CMP)

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II. Abstract:

A sulfonic acid based chemical system has been developed for the removal of tantalum under electrochemical mechanical planarization (ECMP) conditions. Tantalum as well as copper samples were polished at low pressures (~0.5 psi) under galvanostatic conditions in dihydroxy benzene sulfonic acid (DBSA) solutions maintained at different pH values. At a current density of 0.5 mA/cm^2 and pH of 10, tantalum removal rate of ~ 200 \AA/min with a 1:1 selectivity to copper has been obtained in 0.3M DBSA solutions containing 1.2M H_2O_2 . Presence of a small amount (~ 0.1%) of colloidal silica particles is required to obtain good removal rates.

III. Technical Results:

Electrochemical and polishing studies on tantalum and copper samples were conducted in a modified electrochemical abrasion cell (EC-AC) tool [1]. A three-electrode setup was used for all electrochemical experiments. The reference electrode was a calomel electrode and the counter electrode (cathode) was a stainless steel (316L) disc (diameter ~ 3 cm), to which a perforated polishing pad was affixed. A perforated Rohm and Hass IC1010 pad (with K-grooves) stacked on Suba IV was used for polishing experiments. The polishing pressure was fixed at 0.5 psi for all experiments. The center of the pad/electrode was offset from the center of the wafer sample such that 70% of the sample was polished. The pad (diameter = 3.2 cm) was rotated at 240 rpm and the wafer sample was rotated at 222 rpm using two different computer controlled stepper motors. Electrochemical data were obtained using an EG&G PARC 273A potentiostat.

Tantalum films of thickness 1000 \AA deposited on carbon doped oxide were used for the experiments. Electrodeposited copper films of thickness 1 \mu m on a film stack of tantalum (250 \AA)/ SiO_2/Si were kindly provided by Semitool Corporation.

The I-V characteristics of tantalum films in DBSA solutions were obtained by anodic polarization from open-circuit potential (OCP) to an overpotential of 1V at a scan rate of 5 mV/s. Polishing of tantalum film was carried out in DBSA solutions with and without silica particles (size 80 nm) at various current densities and pH values. After polishing, the solution was collected for tantalum analysis using Perkin Elmer ELAN DRC II inductively coupled plasma-mass spectrometer (ICP-MS). The removal rate was calculated from tantalum concentration in solution. To study the selectivity of the formulation, polishing of electroplated copper films was also carried out under the same conditions. Removal rate of copper was calculated from thickness measurements made with Mitsubishi LORESTA AP super-intelligent four point probe resistivity meter (Model MCP T400).

Anodic Polarization of Tantalum under Abrasion

For preliminary experiments, a pH value of 10 was chosen since conventional CMP is typically carried out at this pH. Fig. 1 displays the anodic polarization curves for tantalum collected during abrasion at 0.5 psi in DBSA solutions at pH 10. The open circuit potential (OCP) of tantalum in 0.1M DBSA solution is -680mV vs. SCE. During anodic polarization, a current density of 0.08 mA/cm² is measured for an overpotential (η) of 1 V. Upon addition of 0.1% SiO₂ to 0.1M DBSA solution, the OCP becomes more negative (-840 mV vs. SCE) likely due to enhanced removal of tantalum oxide from the surface. The current density increases exponentially up to a potential of -400 mV vs. SCE and saturates at 0.15 mA/cm² thereafter. For a solution containing 0.3M DBSA and 0.1% SiO₂ particles, increase in current density with potential is observed up to -600 mV vs. SCE above which it saturates at 0.25 mA/cm². No significant change in OCP is observed upon increasing the concentration of DBSA. Addition of 1.2M H₂O₂ to 0.3M DBSA solution containing 0.1% SiO₂ increases the OCP by 100 mV and the current density is doubled to ~ 0.5 mA/cm² at 1V overpotential. Since the maximum solubility of DBSA is 0.3M, it was decided to use this concentration for further experiments.

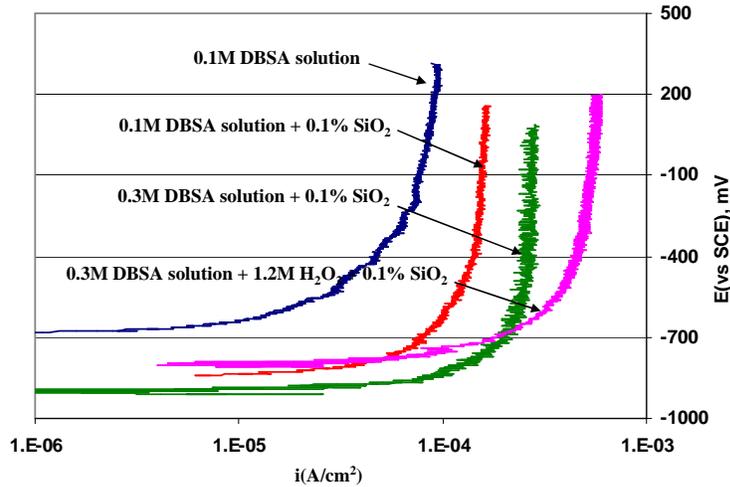


Figure 1: Anodic polarization of tantalum while being abraded with a polyurethane pad in DBSA solution at pH 10.

Effect of Silica and Peroxide Concentration on Removal Rate

The effect of silica and peroxide concentration on the removal rate of tantalum in sulfonic acid solutions was then investigated. Removal rate of tantalum as a function of silica concentration in 0.3M DBSA solution (pH 10) at an applied current density of 0.25mA/cm² is shown in Fig. 2(a). In the absence of silica particles, the removal rate of tantalum is very low ~ 20 Å/min. Addition of 0.05% SiO₂ slightly increases the removal rate to 35 Å/min. Increase in the silica particle concentration to 0.1% nearly triples the removal rate to 90 Å/min. At 4% SiO₂ concentration, the removal rate is found to be 130 Å/min. These results indicate that the presence of a small amount (~ 0.1%) of colloidal silica particles is needed to provide reasonable tantalum removal rates in DBSA solutions.

The effect of peroxide on the removal rate of tantalum in 0.3M DBSA solution containing 0.1% SiO₂ (pH 10) at an applied current density of 0.25mA/cm² is shown in Fig. 2(b). The removal rate of tantalum is 90 Å/min in the absence of peroxide and the addition of 0.6M H₂O₂ increases the removal rate to 120 Å/min. Increase in peroxide concentration to 1.2M further increases the removal rate to 160 Å/min. Peroxide concentration greater than 1.2M increases the removal rate only marginally.

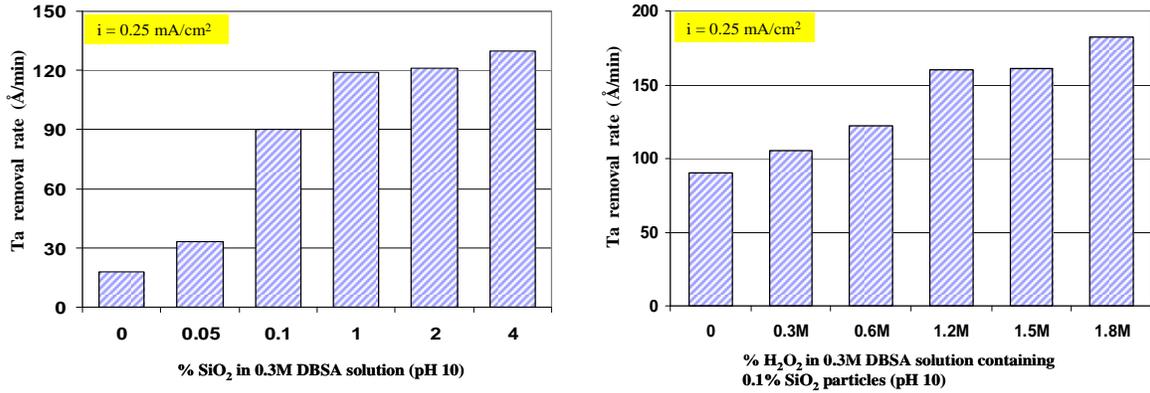


Figure 2: Effect of (a) silica and (b) peroxide concentration on the removal rate of tantalum in 0.3M DBSA solution (pH 10) at a current density of 0.25mA/cm²

Removal Rate vs. pH

Figures 3(a) and (b) show the removal rate of tantalum and copper in 0.3M DBSA solution containing 0.1% SiO₂ as a function of pH in the presence and absence of peroxide at a current density of 0.25 mA/cm². At pH 4, the removal rate of tantalum is 70 Å/min in the absence of peroxide, while the removal rate in the presence of 1.2M peroxide is 95 Å/min. Increasing the pH to 7 results in decrease in tantalum removal rate both in the presence and absence of peroxide. At pH 10, as mentioned previously, higher removal rates of tantalum, of the order of 90 and 160 Å/min are obtained in the absence and presence of peroxide, respectively.

In the case of copper, the highest removal is obtained at pH 4, with removal rate values of 120 and 175 Å/min in the absence and presence of peroxide, respectively. It may be noted that the removal rates decreases with pH. At pH 10, removal rates of 80 and 140 Å/min are obtained in the absence and presence of peroxide, respectively.

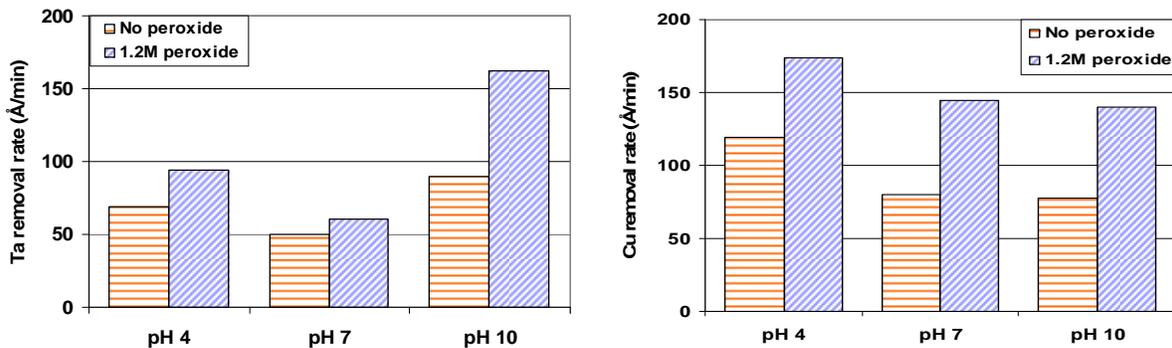


Figure 3: Removal rate of (a) tantalum and (b) copper in 0.3M DBSA solution containing 0.1% SiO₂ as a function of pH at a current density of 0.25 mA/cm².

Effect of Current Density

Since higher removal rates of tantalum were obtained at pH 10, it was decided to investigate this pH in more detail. Fig. 4 shows the removal rate of tantalum as a function of applied current density at pH 10. In a solution containing 0.1% SiO₂ particles, the removal rate is very low ~ 15 Å/min under OCP condition. When a current density of 0.1 mA/cm² is applied, the removal rate doubles to ~ 30 Å/min. However the removal rate plateaus above 0.25 mA/cm².

When 1.2M H₂O₂ is added to the solution containing 0.1% SiO₂ particles, the removal rate increases by 10-20 Å/min for all applied current densities. In order to examine the role of DBSA, the removal rate of tantalum in a solution containing 0.3M DBSA and 0.1% SiO₂ particles was studied. Under OCP condition, the removal rate is 30 Å/min whereas at 0.1 mA/cm², the removal rate is found to be 65 Å/min. This removal rate is nearly twice the value observed in the absence of sulfonic acid. Increasing the current density to 0.25 and 0.5 mA/cm², the removal rate increases to 90 and 120 Å/min, respectively.

Addition of 1.2M H₂O₂ to 0.3M DBSA solution containing 0.1% SiO₂ particles was then examined. Under OCP condition, removal rate of ~ 60 Å/min was obtained. When a current density of 0.1 mA/cm² is applied, the removal rate increases to 85 Å/min. At higher current densities, the removal rate increases yielding a higher rate of 195 Å/min at 0.5 mA/cm².

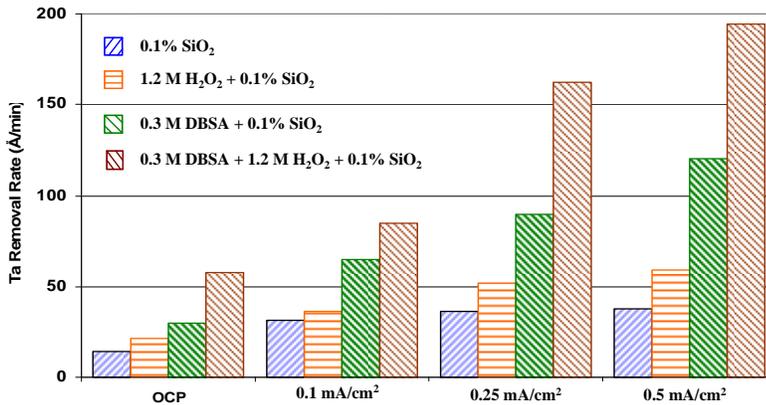


Figure 4: Effect of current density on the removal rate of tantalum at pH 10.

Selectivity

Selectivity between tantalum and copper as a function of applied current density in 0.3M DBSA solution containing 1.2M H₂O₂ and 0.1% SiO₂ at pH 10 is shown in Fig. 5. Under OCP conditions, the selectivity (Ta/Cu) is 0.5. At a current density of 0.25 mA/cm², the selectivity increases to ~ 1.2. Upon further increase of the applied current density 0.5 mA/cm², the selectivity decreases to ~0.85.

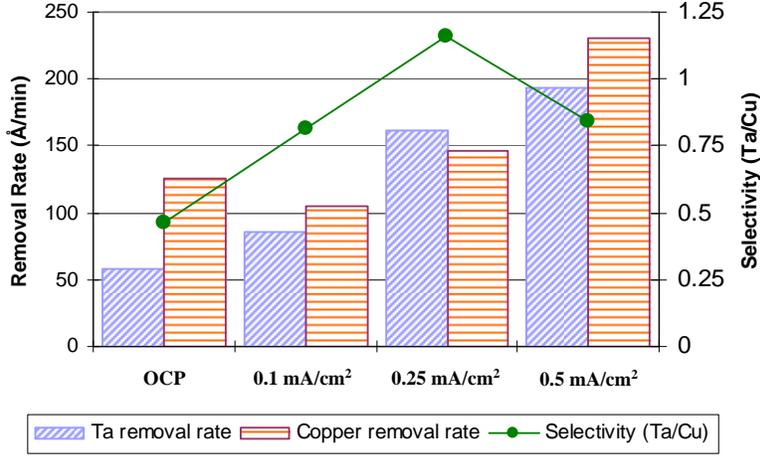


Figure 5: Selectivity between tantalum and copper at different applied current densities in 0.3M DBSA solution containing 1.2M H₂O₂ and 0.1% SiO₂ at pH 10.

Proposed Mechanism and Current Efficiency

The results have shown that both peroxide and DBSA significantly improve the removal rate of Ta under simultaneous application of pressure and current. Under mildly alkaline conditions [2], the most stable form of Ta is Ta₂O₅ (s). However, it is well known that Ta can form metastable oxides such as TaO, Ta₂O₃ and TaO₂ during thermal oxidation [3]. Kerrec et al. [4] and Kerrec [5] have shown by means of XPS and EIS studies that the tantalum oxide film formed under anodic conditions consists of a mixture of TaO and Ta₂O₅. These studies have also shown that TaO forms a significant portion of the surface oxide in the case of thin films ($t < 20$ nm), while in the case of relatively thick tantalum oxide films ($t > 20$ nm), Ta₂O₅ is the dominant oxide formed. Further, it has been shown that mechanical polishing using alumina slurries followed by air exposure induces the formation of a mixed oxide film composed of a mixture of TaO and Ta₂O₅. In this study, since the removal rate of tantalum is of the order of ~ 20 nm/min, it is reasonable to expect that TaO would form a significant portion of the surface tantalum oxide during the ECMP process.

As discussed in the background section, DBSA molecule contains complexing groups. In conjunction with H₂O₂, DBSA may aid the oxidative dissolution of TaO in the form of peroxotantalate complexes such as [Ta (O₂) L₆]³⁻, [Ta (O₂)₂ L₄]³⁻ or [Ta (O₂)₃ L₂]³⁻ where L₂²⁻ represents one ionized DBSA molecule. Such peroxy complexes have been reported by Bayot et al. [6]. As an example, the formation of triperoxotantalate complex, [Ta (O₂)₃ L₂]³⁻ can be represented by the following reaction.



Obviously, detailed spectroscopic analysis is required to determine the exact nature of the complex formed.

In summary, it is proposed that the tantalum ECMP process in DBSA based chemical systems occurs by the following mechanism.

1. Tantalum is oxidized to TaO by an interfacial two electron transfer reaction.

- TaO is oxidized and dissolved by H₂O₂ and DBSA in the bulk solution in the form of complexes of the type [Ta (O₂)_x L_y]³⁻, where x = {1,2,3} with corresponding y = {6,4,2}.

Based on two electron transfer reaction, the current efficiency values calculated from results obtained in 0.3 M DBSA solution containing 1.2 M H₂O₂ and 0.1% SiO₂ at pH 10 are shown in Table 1. It is pertinent to mention the removal rates at different applied current densities were corrected by subtracting rates at OCP conditions. The current efficiency in excess of 100% might be attributed to the analytical errors.

Applied current density (mA/cm ²)	Estimated removal rate (Å/min) of tantalum based on 2 e ⁻ transfer	Actual removal rate of tantalum (Å/min) in 0.3M DBSA + 1.2M H ₂ O ₂ + 0.1% SiO ₂ (pH 10)	Calculated current efficiency (%) after correcting for OCP removal rate
OCP	-	60	-
0.1	34	85	80
0.25	85	160	109*
0.5	169	195	81

Table 1: Current efficiency (%) as a function of pH under different conditions (*: Please see text for explanation of current efficiencies higher than 100%)

Conclusions

DBSA based chemical system has been evaluated for the electrochemical mechanical removal of tantalum. At pH 10, in 0.3M DBSA solution containing 1.2M H₂O₂ and 0.1 % silica particles, tantalum removal rate of ~ 200 Å/min with 1:1 selectivity with respect to copper has been obtained at a current density of 0.5 mA/cm². It has been determined that a small amount (~0.1%) of colloidal silica particles is required to obtain good removal rate of tantalum.

References

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