Poly(ethyleneimine) as a Passivating Agent for Ta Chemical Mechanical Planarization

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We report poly(ethyleneimine) (PEI) as a possible passivating agent for Ta during chemical mechanical planarization (CMP). Studies by electrochemical impedance spectroscopy in a model CMP slurry suggest that PEI forms a polymer film atop a Ta electrode, and voltammetry studies of Ta in 2.5 M HF suggest that PEI films suppress the formation of Ta oxide. Because Ta oxide is mechanically harder than Ta and its oxide may allow reduced downforce or higher removal rates. These observations are consistent with an increase of approximately 3 times in the Ta removal rate in a model CMP slurry upon addition of 3000 ppm PEI.

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When Cu replaced Al and W as the interconnect/via material in Si-based semiconductor devices in the late 1990s, Ta and TaN diffusion barriers were introduced between the interconnect wiring and the active device region because Cu forms a deep level defect in Si. At that time, chemical mechanical planarization (CMP) was introduced for both Cu and Ta removal and nanoscale planarization. Cu is easily chemically etched, so the chemical component of Cu CMP is quite substantial. Cu CMP slurries typically contain benzotriazole, which forms a passive film of the order 10 nm thick that inhibits formation of thicker Cu oxide films. The formation of thick metal oxide films is widely considered to be undesirable as they likely require significant force to abrade. Ta is a much more active metal than Cu, so suppressing Ta oxidation is more difficult. In addition, both Ta and the Ta native oxide (Ta₂O₅) are mechanically harder than Cu and its oxide. For this reason, Ta CMP is predominantly mechanical, requiring higher downforce and/or higher abrasive concentrations than Cu CMP. The Ta native oxide can only be chemically removed in aqueous HF, and Ta CMP slurries containing F ions have been developed. However, polymer CMP additives that restrict the growth of Ta oxide following mechanical abrasion would be desirable. Here, poly(ethyleneimine) (PEI) is studied as a possible additive to Ta CMP slurries, with the goal being to suppress the formation of Ta oxide. PEI enhances the rate of Ta CMP, and in situ studies by electrochemical impedance spectroscopy (EIS) demonstrate that PEI forms an adherent film on Ta. It is believed that this is the first report of polymer film formation atop Ta that increases the removal rate during Ta CMP.

Experimental

Deagglomerated γ-alumina particles (50 nm diameter) were obtained from Alfa Aesar. Semiconductor grade HF (J.T.Baker) was used for all electrochemistry experiments. KCl₀₅ was obtained from J.T.Baker. The pH was adjusted using either potassium hydroxide (KOH) or nitric acid (HNO₃).

All electrochemistry measurements were performed with a three-electrode setup including a Ta rotating disk electrode (RDE), a Pt spiral counter electrode, and a saturated calomel reference electrode (SCE) controlled with an EG&G PAR model 273A potentiostat/galvanostat. EIS was studied by coupling this potentiostat to a Solartron 1250B frequency response analyzer over the frequency range 0.01 Hz–10 kHz using an ac probe voltage of 10 mV. All EIS studies were performed at potentials close to the open-circuit potential (approximately –500 mV vs SCE). For all electrochemistry experiments, 50 mM KCl₀₅ was added to the model slurry to make it electrically conductive. The Ta electrode was rotated at 850 rpm during these experiments.

Ta removal rates were determined on 1 in. diameter Ta disks by measuring the weight change before and after 8 min polishing on a Struers Labopol bench-top polisher. Polishing conditions were 1 psi pressure, 200 mL/min slurry flow rate, and 100 rpm relative table/platen speed using an IC 1000 pad. The rotational speed (850 rpm) of the Ta RDE used for electrochemistry experiments is considerably higher than the relative table/platen speed (100 rpm) used in the Ta CMP experiments. Because the Ta disk is in direct contact with the polishing pad, the extent of convection during Ta CMP is magnified, so the Ta RDE experiments were conducted with a much higher rotational speed to approximate the strong convective forces expected during CMP.

Results and Discussion

Figure 1 illustrates the voltammetry response during anodic scans for the Ta electrode in 2.5 M HF under two different conditions. The solid line was obtained from a bare Ta electrode, showing the characteristic anodic peak we previously observed at about –400 mV vs SCE. The origin of this anodic peak was discussed extensively in Ref. 7, where it is suggested to arise from the formation of a Ta suboxide, perhaps TaO. This argument is based on measurements by EIS that yield a modest charge-transfer resistance (Rₜ) for Ta in 2.5 M HF even at potentials anodic to this current peak. These modest values for Rₜ are in sharp contrast to impedance measurements in 2.5 M NH₄F, where the TaO₅ native oxide is formed, and the impedance response is purely capacitive.

The dotted line in Fig. 1 was obtained from a Ta electrode pretreated with the following procedure: The Ta electrode was pretreated...
by being pressed against a CMP pad with 1000 rpm rotation during immersion into 3000 ppm PEI in water, and the Ta electrode was then transferred to 2.5 M HF for cyclic voltammetry measurements. This pretreatment of the Ta electrode, which should remove the Ta native oxide, completely suppresses the anodic peak, which has previously been ascribed to Ta oxidation, otherwise observed in 2.5 M HF during anodic scans. The anodic peak begins to reappear upon subsequent voltammetric scans. However, the reappearance of this peak is extremely modest, so that even after three repeat voltammetry scans, the anodic peak could not be discerned on the scale of Fig. 1 for the Ta electrode pretreated with PEI.

The absence of the anodic peak in Fig. 1 for Ta electrodes pretreated in PEI, and the very gradual reappearance with time, suggests that PEI forms a polymer film on the surface of the Ta electrode that suppresses Ta oxidation. Figure 2 shows the results of the anodic scans for the Ta electrode in 2.5 M HF, with and without addition of 3000 ppm PEI. These results demonstrate that PEI inhibits Ta oxidation in 2.5 M HF because they do not depend on pretreatment to mechanically abrade the Ta oxide. This hypothesis is further supported by the impedance studies described below. It is believed that this is the first literature report of a polymer film that inhibits Ta oxidation.

This hypothesis was further tested with studies by EIS to understand PEI film formation on Ta in a model CMP slurry containing 50 mM KClO₄ + 3000 ppm PEI at pH 6.5. To test for the attainment of a steady state, the impedance scans were repeated several times, and the results of successive scans were compared. The results of successive impedance scans with and without PEI present are shown in Fig. 3 and 4, respectively, in the form of Nyquist plots. In both cases, only modest changes in the impedance spectrum are seen for successive scans, indicating that the Ta electrodes are close to the steady state.

The impedance results from the outermost arcs (third scan) in Fig. 3 and 4 were fitted to the equivalent circuit in Fig. 5 using standard complex nonlinear least-squares (CNLS) software. This equivalent circuit consists of several impedance elements in series: the model slurry resistance \(R_1\), the capacitive loop for the solid–electrolyte interface \(R_1C_1\), and the capacitive loop for the passive film \(R_2C_2\). However, the capacitances have been replaced with constant phase elements (CPEs) in Fig. 4 to phenomenologically represent the effect of surface heterogeneity. The impedance of a CPE is

$$Z(\text{CPE}) = \frac{1}{(j\omega)^n}$$

where \(T\) is a frequency independent constant, \(\omega\) is the angular frequency, and \(n\) is an exponent within the range \(0.5 < n < 1\). The best-fit circuit elements with and without PEI present are given in Table 1.

The charge-transfer resistance, which corresponds to \(R_1\) in Fig. 4, is the circuit element most sensitive to the presence of PEI in the model CMP slurry. The formation of a PEI film raises the charge-transfer resistance of the Ta electrode from \(8300\) to \(36,000 \, \Omega \, \text{cm}^2\). This appears visually as the diameter of the semicircular Nyquist plots in Fig. 2 and 3, which clearly increases with the addition of PEI to the model CMP slurry. The increase in the charge-transfer resistance at the Ta electrode with an addition of PEI to the model slurry confirms the formation of a PEI film even during a strong convection due to 850 rpm electrode rotation.
One might expect that the impedance results in the presence of PEI could be fitted by including two separate capacitive loops for the Ta oxide and the polymer. However, this yielded a poor data fit, so the capacitive loop for the passive film cannot be understood from the series contribution of Ta oxide and PEI polymer. Thus, when the model Ta CMP slurry does not contain PEI, \( R_1 \) and \( C_1 \) can be attributed mainly to the presence of Ta oxide. However, when the model Ta CMP slurry contains PEI, \( R_1 \) and \( C_1 \) can be attributed mainly to the presence of a PEI film.

The applicability of the Ta electrochemistry results above to Ta CMP can best be studied by measurements of Ta removal rate in a model CMP slurry. If the PEI film formed on Ta during CMP can suppress Ta oxide formation, then one might expect an enhanced Ta removal rate. The isoelectric point of Ta oxide has been reported as 4.2–5.3,\(^{11-13} \) so the Ta surface is negatively charged at pH 6.5. PEI is well known to be positively charged at nearly neutral pH.\(^{14} \) Thus, electrostatic attraction favors formation of a PEI polymer film atop Ta. To form a stable Ta CMP slurry, an abrasive must be chosen, which has a high isoelectric point so that it is positively charged at pH 6.5. Here, aluminum oxide was chosen, which has an isoelectric point of approximately 9.\(^{15} \) Of course, specific chemical interactions of PEI and alumina with the Ta surface may also occur.

Table II summarizes the Ta CMP removal rate studies in a slurry containing 3 wt % alumina at pH 6.5, with and without PEI in the slurry. The addition of PEI increases the Ta removal rate by a factor of more than 3 times. The Ta removal rates in Table II are all quite low because the Ta CMP slurry does not contain any oxidizing agents. The strong effect of PEI on Ta removal rate suggests that PEI indeed forms a polymer film in situ that suppresses formation of Ta oxide, which is quite mechanically hard.

Not surprisingly, the use of PEI in Ta CMP slurries has been previously suggested in the patent literature.\(^{16-19} \) However, several different mechanisms of action have been suggested, including strong bond formation to Cu or SiO\(_2\),\(^{16} \) inhibition of Ta removal,\(^{17,18} \) and abrasive particle coating by electrostatic attractions.\(^{19} \) Only one of these patents reports data for the effect of PEI on the Ta removal rate, and this showed a dramatic suppression of Ta removal, suggesting that PEI is a Ta inhibitor.\(^{17} \) However, the present research reports just the opposite result that PEI forms an effective passivating agent that enhances rather than inhibits the Ta removal rate by suppressing Ta oxide formation. This discrepancy likely arises from differences between the present model slurry composition and the slurries used in Ref. 17, which are commercial slurries that are considerably more complex. These differences include the use of oxidizing agents, polishing agents that increase the removal rate of one or more of the exposed surfaces, pH values of 5 and 7.7, and addition of a surfactant.\(^{17} \) In addition, the detailed nature of PEI and the abrasive used in Ref. 17 were not disclosed.

### Conclusions

When a PEI film is preformed atop a Ta electrode by abrasion against a CMP pad in the presence of PEI and then transferred to 2.5 M HF, the anodic peak that should be observed in 2.5 M HF disappears. The formation of a PEI film atop Ta electrodes is also demonstrated by studies with EIS. The charge-transfer resistance at the Ta–aqueous interface increases from 8300 to 36,000 \( \Omega \) cm\(^{-2} \) upon addition of 3000 ppm PEI to a model Ta CMP slurry at pH 6.5. These electrochemistry results suggest that PEI suppresses the growth of Ta oxide during CMP. This hypothesis is verified by measurements of the Ta removal rate in a model CMP slurry containing 3 wt % alumina at pH 6.5, with and without PEI. The addition of 3000 ppm PEI increases the Ta removal rate by a factor of more than 3 times.

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### References


### Table I. Equivalent circuit parameters from CNLS data fitting.

<table>
<thead>
<tr>
<th>Slurry composition</th>
<th>( R_1 ) (( \Omega ) cm(^2 ))</th>
<th>( T_1 ) (( \mu F ) s(^{-1} ) cm(^{-2} ))</th>
<th>( n_1 )</th>
<th>( R_2 ) (( \Omega ) cm(^2 ))</th>
<th>( T_2 ) (( \mu F ) s(^{-1} ) cm(^{-2} ))</th>
<th>( n_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 nM KClO(_4)</td>
<td>27.6 (1.1)</td>
<td>71.2 (7)</td>
<td>0.93 (0.004)</td>
<td>8263 (83)</td>
<td>96.6 (3.8)</td>
<td>0.88 (0.008)</td>
</tr>
<tr>
<td>50 nM KClO(_4) + 3000 ppm PEI</td>
<td>37.2 (1.0)</td>
<td>34.2 (2.9)</td>
<td>0.82 (0.006)</td>
<td>36,000 (760)</td>
<td>103.4 (2.6)</td>
<td>0.86 (0.008)</td>
</tr>
</tbody>
</table>

### Table II. Ta removal rate during CMP.

<table>
<thead>
<tr>
<th>Slurry composition</th>
<th>Ta removal rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 wt % alumina at pH 6.5</td>
<td>1.0 (0.6)</td>
</tr>
<tr>
<td>3 wt % alumina + 3000 ppm PEI at pH 6.5</td>
<td>3.2 (0.4)</td>
</tr>
</tbody>
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