Understanding Interfacial Surface Interactions

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Challenges for W Post-CMP Cleaners

Slurry particles and organic residue removal from W and dielectric surfaces (PETEOS, Silicon Nitride, Polysilicon);

Metal residue in any form (Ions, Salts, Metal Oxide)

Cleaning Requirements:

- W ER < 1 Å/min
- TiN ER < 1 Å/min
- Dielectrics ER < 1 Å/min
- Defect counts DDC ≥ 0.065 mm lower than commodities: dAmmonia, SC-1
- Low W/TiN galvanic corrosion
- Mt atoms < $10^{10}$ Mt/cm$^2$

- No increased roughness
- Market increasingly challenged by W recess
  - High pH commodities (SC1, dil NH$_3$)
  - Traditional low pH cleaners
- Low W etch rates (<2 Å/min) cannot be achieved with commodity cleaners
- No organic Residue
- Nitride cleaning is particularly problematic
- No silica particles or clusters
- Green chemistry (TMAH free)
Post-CMP W Cleaning Mechanisms vs. pH

**Low pH**
- Silica brush imprints
- Good Mt removal (\(\sim 10^{10}\) atoms/cm\(^2\))

**High pH**
- No Silica brush imprints
- Poor Mt removal (4-6 \(10^{10}\) atoms/cm\(^2\))

**CA** = Mt complexing agent
**D1** = SiO\(_2\) dispersant
**D2** = organic residue dispersant

PETEOS

steric repulsion

**Removed by DIW Rinse**

**Removed by DIW Rinse**
Higher Tungsten Etch Rates Observed

Increasing pH due to dissolution as Polyoxotungstate Keggin ions

Surface Residue PCMP Cleaning with W Slurries

- Fe$^{2+}$/CA (complexing agent) on the silica surface and in the CMP slurry at pH = 2.5;
- End of polishing, soluble Fe$^{2+}$ complexes on the wafer surface;
- DI water rinse and high pH post-CMP W cleaners precipitate Fe$^{3+}$ as insoluble Fe(OH)$_3$ on the PETEOS/SiN surface

W CMP slurry - 15-32 ppm Fe

- W(0) is oxidized to W(VI)O$_3$ (pp) and W(VI)O$_4$$^2$ (s);
- WO$_4$$^2$ (s) is adsorbed on the surface of the Fe$^{3+}$/CPE coated, positively charged Si particles;
- WO$_4$$^2$ precipitates @ pH < 3 as (N$^+$R$_4$)$_n$(H$_x$W$_6$O$_y$)$_m$/silica aggregates that act as additional abrasive during polishing.

FeOx Very difficult to remove

Improving Organic Residue Removal from Si₃N₄ Contact Angle and FTIR

**Electrostatic Repulsion during CMP**

- Cleaning additive removes cationic contamination from dielectric surface and disperses cationic dishing and erosion control agents.
- Si₃N₄ surface typically highly contaminated by cationic dishing and erosion control agents.

**Contact Angle**

- pH < pH_{IEP}, \( \zeta > +30 \text{ mV} \) for Si₃N₄ control.
- pH > pH_{IEP}, \( \zeta < -15 \text{ mV} \) for clean, hydrophilic Si₃N₄.

**FTIR**

- Organic residue peaks at certain wavenumbers.
- Silica NP peaks at different wavenumbers.

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*Image source: Entegris*
Defectivity Correlated to Charge Repulsion Between Silica Particles and Various Surfaces (W, SiO$_2$, Si$_3$N$_4$)

Additive increases negative charge on silica surface

PlanarClean® AG-WXXX Exhibits

No bulk corrosion and no OCP gap between W and TiN

<table>
<thead>
<tr>
<th></th>
<th>TiN</th>
<th>Galvanic Corrosion</th>
<th>W</th>
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</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>-0.622</td>
<td>-0.626</td>
<td>-0.625</td>
</tr>
<tr>
<td>Anode</td>
<td>1.76 x 10^-06</td>
<td>2.35 x 10^-05</td>
<td>1.13 x 10^-05</td>
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<tr>
<td>Corrosion Current (A)</td>
<td>0.167</td>
<td>0.013</td>
<td>0.642</td>
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<tr>
<td>Corrosion Rate (Å/min.)</td>
<td>0.013</td>
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</tbody>
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Low pH PCMP W Cleaners
Further reduce metal defects after CMP

- Complexing reagents: to keep in solution soluble Fe\(^{2+}\) species
- Cleaning additives: able to eliminate silica brush marks at pH = 2

TXRF – SiO\(_2\) blankets

![Graph showing concentration of Fe in SiO\(_2\) blankets](image)
Force of Adhesion – AFM Measurements

\[ dF = k_c \, dZ_c + \frac{dF_{\text{surf}}}{dD} \, dD = \left( k_c - \frac{dF_{\text{surf}}}{dD} \right) dZ_c \]

- **F** = force of adhesion
- **k_c** = spring constant of the cantilever
- **Z_c** = cantilever deflection
- **F_{\text{surf}}** = distance-dependent surface force
- **D** = separation distance

Example of Cleaning Performance Prediction via AFM force of adhesion measurements

Main adhesion forces:
- Van der Waals
- Electrostatic double layer
- Hydration repulsion
- Hydrophobic attraction

Formulations A & B, pH = 2

- DI water $F_{\text{ad, water}} = 70$ nN
- Formulation A $F_{\text{ad, A}}$
- Formulation B $F_{\text{ad, B}}$

+ additive X

Formulations A & B, pH = 2
- $F_{\text{ad, B}} << F_{\text{ad, A}}$
- Best cleaning performance
SEM Images of PETEOS Coupons

Polished with W CMP slurry and cleaned with Formulations A and B

- Tabletop polishing
- Colloidal silica Ludox, PS = 20-30 nm
- pH = 2.3

Formulation A

Formulation B
Correlation SEM vs. Calculated Adhesion

Based on contact angle measurements
PlanarClean AG-W formulations exhibit lower defects and organic residues over traditional cleans.

PC AG-W Series show improved performance over SC-1 on all substrates.

Si₃N₄ - EDR Review - Defect Pareto
# defects pareto (≥ 65 nm defects)

W - EDR Review - Defect Pareto
# defects pareto (≥ 100 nm defects)
Summary

Organic contamination reduction studied by FTIR and contact angle

Work of adhesion and AFM force of adhesion show that less energy is needed to remove silica slurry particles in the presence of the cleaner.

Entegris AG-W Formulations show significantly lower defects on Si3N4, TEOS and W wafers compared to commodity cleans.
Thank you!

Q & A
Appendix