Agenda

• Versum Materials’ diverse CMP and pCMP clean product offerings
• W CMP
  • Balance of chemical and mechanical aspects
  • Importance of fundamental and mechanistic investigation
  • W removal kinetics
    • Characteristics of oxidized W surface film and RR model
    • Strong temperature dependence: in-process heat generation, incubation and activation behavior
• Performance table of exemplary VM’s W CMP products
• Conclusive remarks
Versum Materials

FOCUSED PURE PLAY WITH STRONG PORTFOLIO AND CAPABILITIES

• Focus on the semiconductor (IC) materials space where materials provide low cost in use/high value in use

• Leverage technology leadership, global scale, quality and reliability capabilities, and partnership with customers and OEMs to develop and commercialize the next generation technologies which will advance the industry

• Expand into adjacent segments within IC

Versum Materials participates in six of seven key semiconductor process steps
VM’s Broad Product Offerings in FEOL and BEOL Slurries and Post CMP Cleans

**FEOL Dielectrics**
- STI 2100/STI 2113
- STI2401/2910
- STI2402/2910
- HPD platform
- SCN 8966

  - Reduced defectivity
  - High Selectivity (Nitride, oxides and Poly)
  - Low oxide dishing

**MOL MG & Contacts**
- W and Co
  - W5880
  - W5900
  - DP5988; DP1118
  - Co7000 (Co Bulk)
  - Co7200 (Co Barrier)

  - Removal rate and selectivity tunability
  - Topography improvements
  - Low defectivity

**BEOL interconnect**
- Cu Bulk /Barrier
  - Cu3928/3929 (Cu Bulk)
  - Cu3930/Cu3086 (Cu Bulk)
  - Cu4545 (Cu Barrier)
  - BAR6630/BAR6610R (Cu Barrier)
  - BAR6620/6520 (Cu Barrier)

  - Low defectivity
  - Optimized COO
  - Tunable
  - Compatible w. new metals Co/Ru

**CMP Slurries**
- Proprietary Clean
  - STI 2950 (buff)
  - CeClean 2020 (BB)

  - Ceria nano particle removal
  - Reduced Defect
  - Increased PVA brush life

**PCMP Cleans**
- CP72B: Al HKMG
  - WClean 1090/CP98D:W
  - Co7900: Co

  - Corrosion control
  - Metal contamination
  - Reduce Particle Defect

- CP72B: Cu
  - CP98D: Cu/Co
  - CP1002: Cu/Co/Ru

  - Corrosion control
  - Organic residue removal
  - Reduce Par. Defect
Tungsten CMP

Ice

Too hard to deal with

Chemically creates soft surface layer

Mechanically removal of the soft layer

Oxidant + Catalyst

WOxHy

Abrasive particles
Fundamental and Mechanistic Investigation

Differentiated W Products with Speed, Quality and Reduced Cost

- W corrosion/mitigation
- W oxidation kinetics
- Interfacial interactions
- Colloidal chemistry
- Computation modelling
- Fluid dynamics

Electrochemistry: Tafel plots

Corrosion mitigation using corrosion inhibitor
**Layered-structure of an Oxidized W Surface**

- Only the very top metal oxide layer is abraded during CMP.

- W forms protective oxide films

\[
\text{Layer 0: } 100\% \text{ W-OH} \\
\text{Intermediate Layer 1: } 22\% \text{ W} + 78\% \text{ W}_{\text{oxide}} \\
\text{Intermediate Layer 2: } 65\% \text{ W} + 35\% \text{ W}_{\text{oxide}} \\
\text{W Substrate } 100\% \text{ Tungsten}
\]

* Thickness and density of the oxidized tungsten films determined by X-Ray Reflectivity analyses after oxidizing with H$_2$O$_2$ addition and post cleaning in 1 M KOH.

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W Removal Rate Model

• Modified Langmuir-Hinshelwood (LH) model:

❖ n moles of reactant R in the slurry react at rate $k_1$ with tungsten film on the wafer to form a product layer L on the surface

\[
W + nR \xrightarrow{k_1} L \quad k_1 = A \times \exp\left(-\frac{E_a}{kT}\right)
\]

❖ Product layer L is subsequently removed by mechanical abrasion with rate $k_2$

\[
L \xrightarrow{k_2} L \quad k_2 = C_p \times COF \times p \times V
\]

❖ Abraded material L is carried away by the slurry

• RR in this sequential mechanism therefore is a function of both chemical and mechanical attributes of the process

\[
RR = \frac{M_{w}}{\rho} \frac{k_1 k_2}{k_1 + k_2}
\]
W Removal: An Thermally Activated Process

Heat is generated by friction and exothermic oxidation. Temperature at the wafer surface is constantly changing.

\[ W + 3H_2O_2 \rightarrow H_2WO_4 + 2H_2O \quad \Delta H = -1,140 \text{ kJ/mole} \]

Reaction 2,000Å/min = 24 W
Friction = 200-400 W

Heat generation is dominated by friction.

Establishment of Temperature Monitor Capability on an Ebara Polisher
Incubation and Activation Behaviors of W CMP

W RR and max. pad temperature of time-polishing using different W slurries

300mm Ebara Polisher, 1.7 psi, hard pad

<table>
<thead>
<tr>
<th>Polish Time (Second)</th>
<th>W RR (Å/min)</th>
<th>Max Pad Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slurry I - W RR</td>
<td>Slurry II - W RR</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>2,000</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>4,000</td>
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</tr>
<tr>
<td>60</td>
<td>6,000</td>
<td>60</td>
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<tr>
<td>80</td>
<td>8,000</td>
<td>80</td>
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</table>

Ea (eV)

<table>
<thead>
<tr>
<th></th>
<th>Slurry I</th>
<th>Slurry II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ea (eV)</td>
<td>1.7</td>
<td>0.7</td>
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</tbody>
</table>

Versum Materials Confidential
Blanket RRs and W/Oxide Selectivity of VM’s Exemplary W CMP Products

<table>
<thead>
<tr>
<th>Product ID</th>
<th>Down Force (psi)</th>
<th>W RR (Å/min)</th>
<th>Oxide RR (Å/min)</th>
<th>W/Oxide Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>W5880 Bulk</td>
<td>3</td>
<td>2000-2600</td>
<td>480-640</td>
<td>3-6</td>
</tr>
<tr>
<td>DP5988 Bulk</td>
<td>3</td>
<td>2500-3900</td>
<td>&lt;50</td>
<td>50-80</td>
</tr>
<tr>
<td>W5900 Bulk</td>
<td>1.7 – 4</td>
<td>2600-5200</td>
<td>&lt;15</td>
<td>&gt;100</td>
</tr>
<tr>
<td>DP1118 Barrier/Buff</td>
<td>3.4</td>
<td>200~700</td>
<td>700 ~ 1000</td>
<td>0.2 - 1</td>
</tr>
</tbody>
</table>
Conclusive Remarks

• Versum Materials (VM) offers broad spectrum of CMP and pCMP clean products including tungsten (W) slurries.

• Optimal W removal balances chemical oxidation of hard metallic W into softer oxidized surface layer(s) and subsequent removal of the oxidized layer(s) by mechanical motions of abrasive particles.

• W CMP is a highly thermally activated process, showing incubation and activation behaviors that can be tuned by slurry chemistries.

• Fundamental and mechanistic understandings empower VM to develop differentiated W products per customers’ requirements.