Advanced CMP Cleaning Solutions

Surfactants, Metal Inhibitors, Oxygen Scavengers & Particle Removers

By

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➢ Background and Principles of CMP Cleaning
➢ New Concepts in CMP Cleaning
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Challenges of CMP Cleaning Solution

- **Multiple materials in Dynamical CMP Systems**
  - Trace metals and ions: Cu, W, Ni, Fe, Ru, Ti, Cr, etc
  - Dielectric material: SiO₂, Al₂O₃, etc
  - Slurry residuals: PSD, MOx
  - Organic polymer materials

- **Cleaning Mechanism for Different Materials**
  - Cleaning chemistry vs. CMP chemistry; pH, corrosion & inhibitors
  - Metal surface cleaning
  - Dielectric surface cleaning
  - Wafer surface topography, structures, macro & micro-scratching

- **Cleaning Tool and Cleaning Functions**
  - Different tools, masonic, rinsibility & dry methods

- **Wafer Quality, CMP Process Performance**
  - Wafer aging, CMP process performance & recontamination
  - Partial dried wafers & wafer surface slurry residual pre-treated
Challenges of CMP Cleaning Solution
Key Issues of Cleaning Chemistry

- **Unbalance of Hydrophilic/Hydrophobic of Surfactants**
  - Poor vehicle of slurry
    - Poor uniformity of slurry across pad
  - Poor surface modification of particles, such as SiO$_2$, CeO$_2$
    - Agglomeration of particles
    - Wide distribution of particles - macro and micro-scratching
  - Residual slurry particles, Al$_2$O$_3$, colloidal SiO$_2$, and CeO$_2$
  - Cleaning residual of BTA in Slurry

- **Incompatible of Metal Inhibitors/Oxygen Scavengers**
  - Non-uniformity of particle dispersion in solution
    - Corrosion of metal, Cu, and W
    - Recontamination
  - Aggressive chemicals, high or low pH
    - Corrosion
    - Macro or micro-scratching
    - Poor rinsibility
Cleaning Fundamentals

- **Cleaning Mechanism**
  - Hydrophilic/Hydrophobic balance
  - Surface tension

- **Metal Cleaning with Inhibitors (BTA)**
  - Better removing particle
  - Corrosion on metal
  - pH range

- **Classic Non-ionic Surfactants (NIS)**
  - Removing particles
  - Removing Organic Contaminations

- **Ionic Surfactants (IS)**
  - Aliphatic phosphorous surfactants
  - Metal surface protection

- **Chelating/Complex Chemicals**
  - Cleaning/removing metal ions and oxides
New Cleaning Concepts
Surfactanized Metal Inhibitors with Cleaning Functions

- **Surfactanized Metal Inhibitors**
  - Hydrophilic metal inhibitor on one side
  - Short aliphatic hydrophobic tail
  - Maximized protection on metals: Cu, W, Ru, Ni, Fe

- **Surfactanized Oxygen Scavengers**
  - Long ethoxylated hydrophilic tail
  - Hydrophobic oxygen scavenger
  - Max scavenged oxygen throughout CMP process

- **Special Surfactants**
  - Ethoxylated hydrophilic tail
  - Short hydrophobic chain with chelating agent
    - Much better vehicle
    - No amines (TMAH) compounds
Briteclean System – How does it work?

Hydrophilic Metal Inhibitor Head + Aliphatic Hydrophobic Tail + Ethoxylated Hydrophilic Tail + Anti-oxidant Hydrophobic Head

Briteclean-0plus/Ultra : Briteclean-Ultra = 1:1 Diluted 50 to 1

Briteclean-0 : Briteclean-1 = 1:1
No dilution
Phase Separation
Briteclean System
pH Control and Application Conditions

- Process Conditions:
  - CMP Tool (8inch): Applied Mirra; Ebara; 6DSSP(Strausbaugh)
  - Slurry: Cabot MH8xx system; ASL system
  - Pad applied: IC1000; Sub IV
  - Cleaning Tool: DNS, SSEC
  - Cleaning solution: Briteclean-1; Briteclean-0plus
    - Mixed: Ratio 1:1 in 1.0% - ~2% Aqueous media
  - Wafer: Cu, W, TiN, TaN, Ni, Fe, Low key, SiOx, Al₂O₃, Ru, etc

Recommendation: BC-0plus/BC-1 = 1:1; Diluted to 1%-2% with DI water

Briteclean-Ultra: pH~9.5
Briteclean-3D: pH~5.0
## Metal and Cl Elements Content in Briteclean products

<table>
<thead>
<tr>
<th>Metal Elements (ppb)</th>
<th>Briteclean-0+</th>
<th>Briteclean-1</th>
<th>Briteclean-ACP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&lt;20</td>
<td>22</td>
<td>53</td>
</tr>
<tr>
<td>Cu</td>
<td>28</td>
<td>&lt;5</td>
<td>25</td>
</tr>
<tr>
<td>Ni</td>
<td>18</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>5</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>As</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;25</td>
</tr>
<tr>
<td>V</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;20</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

1: Cu, Ni, Zn, Ti, Pb, Mn, Co, V, As were analyzed by EPA Method 200.8 on an ICP-MS (Perkin Elmer DRC-e)

2: Fe, Al, Cr were analyzed by EPA Method 200.7 on an ICP-OES (Thermo iCAP 6300 DV)

3: Cl was analyzed by EPA Method 300.0 on an IC (Metrohm 850)

**Note**

1: ICP-MS Analysis
2: “<“ means below detection limit
Corrosion Test – Cu Wafer

**Testing Instrument**
- Solution Fixture
- Std Corrosion testing Cell
- Solartro Electrochemical
- Corrosion testing interface

**Corrosion Test Outputs**
- Tafel/Linear Polarization – Corrosion Rate Measurements
- Galvanic Corrosion Current Measurements
- Electrochemical Impedance Spectroscopy
- Corrosion Rate Measurements under Abration
### Corrosion Testing Results – Cu Wafer

<table>
<thead>
<tr>
<th>Solution</th>
<th>OCV (vs SCE)</th>
<th>RP (Wcm²) (from linear)</th>
<th>io (A/cm²)</th>
<th>ERR (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DI H₂O</strong></td>
<td>-0.0614</td>
<td>10.8</td>
<td>4.18E-06</td>
<td>0.9236</td>
</tr>
<tr>
<td><strong>Best Competitor</strong></td>
<td>-0.242</td>
<td>2135</td>
<td>1.22E-05</td>
<td>2.6845</td>
</tr>
<tr>
<td><strong>Another Competitive</strong></td>
<td>-0.294</td>
<td>685</td>
<td>3.76E-05</td>
<td>8.302</td>
</tr>
<tr>
<td><strong>Briteclean-0+ /Briteclean-1 = 1:1 2% aqueous</strong></td>
<td>0.1017</td>
<td>3645</td>
<td>7.05E-09</td>
<td>0.0016</td>
</tr>
<tr>
<td><strong>Briteclean-0+ /Briteclean-ACP =1:1 2% aqueous</strong></td>
<td>0.1585</td>
<td>2180</td>
<td>1.20E-08</td>
<td>0.0026</td>
</tr>
</tbody>
</table>
Corrosion Testing Results
BC-0plus, BC-1 and BC-Ultra on Cu, TiN, TaN and W Wafer

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Cu</th>
<th>TaN</th>
<th>TiN</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecorr (V)</td>
<td>-0.10764</td>
<td>-0.80145</td>
<td>-0.67662</td>
<td>-0.40374</td>
</tr>
<tr>
<td>Icorr (A/cm²)</td>
<td>2.13E-07</td>
<td>-8.45E-08</td>
<td>1.98E-07</td>
<td>9.31E-06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Cu</th>
<th>TaN</th>
<th>TiN</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecorr</td>
<td>-0.18517</td>
<td>-0.52489</td>
<td>-0.84506</td>
<td>-0.4298</td>
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<tr>
<td>Icorr</td>
<td>2.60E-07</td>
<td>3.29E-07</td>
<td>9.69E-08</td>
<td>9.14E-06</td>
</tr>
</tbody>
</table>
Briteclean System – Applications

- Briteclean products are qualified on 7 Major US fab lines
- Particle Reduction
  - BC cleaning system showed better particle count reduction
  - BC cleaning system showed >40% particle reduction on device production wafers
Principle of Slurry Additive for CMP Applications

- Slurry distribution on polishing pads is a critical factor to achieve better WIW uniformity.

- Adding Brizon products into CMP slurries, the slurry surface extension with IC series CMP pads was modified to form a uniformed slurry layer across the whole wafer.
Surf-Clean Imaging
For Competitor’s Clean Solution

Pre-Treatment

Post-Treatment

Alumina

Cu
Surf-Clean Imaging
For Briteclean Clean Solution

Pre-Treatment

Post-Treatment

Alumina

Cu
Different Slurry Cleanability of BriteClean vs Competitor’s

<table>
<thead>
<tr>
<th></th>
<th>BriteClean mixed Solution</th>
<th>Competitor's Cleaning Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alumina</td>
<td>Cu</td>
</tr>
<tr>
<td>Con-1</td>
<td>-70</td>
<td>190</td>
</tr>
<tr>
<td>Con-2</td>
<td>-22</td>
<td>1571</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
</tr>
<tr>
<td></td>
<td></td>
<td>370</td>
</tr>
</tbody>
</table>
### Different Method Cleanability of BriteClean vs Competitor’s

#### BriteClean mixed Solution

<table>
<thead>
<tr>
<th></th>
<th>Alumina</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roller</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Pencil</td>
<td>-10</td>
<td>-6</td>
</tr>
</tbody>
</table>

#### Competitor's Cleaning Solution

<table>
<thead>
<tr>
<th></th>
<th>Alumina</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roller</td>
<td>318</td>
<td>2985</td>
</tr>
<tr>
<td>Pencil</td>
<td>190</td>
<td>280</td>
</tr>
</tbody>
</table>
Average Particle counts for Briteclean Products on Cu Surface

<table>
<thead>
<tr>
<th>Briteclean Products</th>
<th>AlOx</th>
<th>SiOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Briteclean-0</td>
<td>-20</td>
<td>-6</td>
</tr>
<tr>
<td>Briteclean-0+</td>
<td>-30</td>
<td>-20</td>
</tr>
<tr>
<td>Briteclean-3D</td>
<td>-73</td>
<td>-56</td>
</tr>
<tr>
<td>Briteclean-Ultra</td>
<td>-154</td>
<td>-137</td>
</tr>
</tbody>
</table>

Note: Mixed with BC-1, 1:1 ratio (5%:5% in DI H2O), on Pencil tool
Slurry: Dissolved/Dispersed into Advanced Nonionic Surfactants, Slurry Chemistry

Trace Metals: Dispersed into Advanced Nonionic Surfactants

Metal Ions: Complex to Chelate in the Cleaning System

Aggressive Corrosive High/Low pH: Buffered by the Cleaning Solution

Principle of Cleaning Process for CMP Applications
Briteclean System – Applications

- **Surface Quality improved**
  - Prevent $\text{AlO}_x$ wafer surface without pitting with BC products
  - Metal surface improved

![Full AlOx film pitting – long time in DI water](image1)

![No film pitting – x2 time in DI water + Briteclean](image2)

![Other Cleaning Solution](image3)

![BriteClean Mixture](image4)

![Cu AFM Image](image5)

![Average Roughness (N=3x3): Rms=0.34nm](image6)

![Cu SEM Image](image7)

![Briteclean Cleaner](image8)
Sensor dimension was designed per different usages.
4-point scheme minimizes contact resistance during probing
Briteclean System – Applications

Sensitivity Measurement Trend Chart

Bivariate Fit of Sensor Sensitivity By Probe time

- Briteclean products
- Competitor’s products
Summary

- Briteclean Products use a new surfactanized metal inhibitor and anti-oxidant cleaning approach
- Cleans major metal surfaces, dielectrics materials, slurry & photo residues with one solution
- Highly efficient cleaning with significant particle reduction and better surface quality
- Easier to handle and simpler process on all tools
- Briteclean products in daily use on many fab lines for over 9 years
- Other advanced cleaning products also available