Synergistic Effect of Megasonic Action and Supramolecular Assemblies on STI p-CMP Cleaning

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April 15th, 2021
p-CMP for Dielectric Materials

Standard Clean 1 (SC-1)

H₂O : NH₄OH : H₂O₂
5:1:1

Striking a balance: Role of supramolecular assemblies on the modulation of the chemical and mechanical contributions during Post-STI CMP cleaning

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Brush vs. Megasonic Cleaning

<table>
<thead>
<tr>
<th>Cleaning Method</th>
<th>Brush</th>
<th>Megasonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-1</td>
<td><img src="SC-1.png" alt="Boxplot" /></td>
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</tr>
<tr>
<td>P-103</td>
<td><img src="P-103.png" alt="Boxplot" /></td>
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<tr>
<td>PE-1198LA</td>
<td><img src="PE-1198LA.png" alt="Boxplot" /></td>
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</tr>
<tr>
<td>Tween 20</td>
<td>![Boxplot](Tween 20.png)</td>
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<td>PSSA</td>
<td><img src="PSSA.png" alt="Boxplot" /></td>
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</table>

Particle Count

0  500  1000  1500  2000  2500  3000  3500
2nd Order Kinetic Model for Cleaning

\[
\frac{d \text{ [Particle Count]}}{dt} = k \text{ [Adsorption] [Power]}
\]

**Polyelectrolyte**
Bulk/Immobile and has localized charge

**Micelle**
Mobile but relies on a deformation/reformation mechanism
SC-1 2\textsuperscript{nd} Order Kinetics

\begin{align*}
\text{Time (s)} &
0 & 100 & 200 & 300 & 400 & 500 & 600 \\
I / (\text{Particle Count}) &
0.000 & 0.003 & 0.006 & 0.009 & 0.012 \\
- 0.5 \text{ Watt/cm}^2 & \\
- 1.0 \text{ Watt/cm}^2 & \\
- 1.5 \text{ Watt/cm}^2 & \\
\end{align*}

Graph showing the relationship between time (s) and \( I / (\text{Particle Count}) \) for different power densities:
- 0.5 Watt/cm\(^2\)
- 1.0 Watt/cm\(^2\)
- 1.5 Watt/cm\(^2\)

Equation:
\[ \text{Ce}^{3+} + \text{Ce}^{4+} + \text{CeO}_2 \]

Mixture of Ce\(^{4+}\) and Ce\(^{3+}\)
Ce\(^{4+}\)/Ce\(^{3+}\) ratio of CeO\(_2\): 1.183 ± 0.003

Reaction:
\[ \text{O}_2 \rightarrow \text{O}_2^- \]

O\(_2\) to O\(_2\)\(^-\)

Chemical structures showing the reaction mechanism:
- Ce\(^{3+}\)
- Ce\(^{4+}\)
- CeO\(_2\)
- TEOS

Oxygen atoms and silicon atoms are also shown.
Cleaning performance for Supramolecular Cleaning Chemistries

- **PE-1198LA**
- **P-103**
- **PSSA**
- **Tween 20**
ROS Species for Megasonic Cleaning Conditions

![Chemical structure of p-nitrosodimethylaniline (PNDA)](image)

<table>
<thead>
<tr>
<th>Amino acid present in solution</th>
<th>Pseudo-first-order rate constant ($k \times 10^3$) (1/min)</th>
<th>$[^{14}OH] \times 10^{-14}$ [M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. No amino acid</td>
<td>2.4</td>
<td>0.32</td>
</tr>
<tr>
<td>2. Arginine</td>
<td>2.5</td>
<td>0.33</td>
</tr>
<tr>
<td>3. Phenyl alanine</td>
<td>4.2</td>
<td>0.56</td>
</tr>
<tr>
<td>4. Glutamine</td>
<td>6.1</td>
<td>0.81</td>
</tr>
<tr>
<td>5. Glutamic acid</td>
<td>6.6</td>
<td>0.88</td>
</tr>
<tr>
<td>6. Glycine</td>
<td>13.8</td>
<td>1.84</td>
</tr>
<tr>
<td>7. Serine</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>8. Cysteine</td>
<td>25.7</td>
<td>3.4</td>
</tr>
</tbody>
</table>

p-nitrosodimethylaniline (PNDA)

https://doi.org/10.1149/1.1393979.
ROS Species for Megasonic Cleaning Conditions

0.5 Watt/cm²
60 s Clean
ROS Species for Megasonic Cleaning Conditions

p-nitrosodimethylaniline (PNDA)

PNDA Degradation in the Presence of ROS Species

Absorbance at 440 nm vs. Time (min)

- **H₂O₂**
  - Sonication
  - Dynamic
  - Static

- **Cu²⁺**
  - Sonication
  - Dynamic
  - Static
  - 0.32 x 10⁻¹⁴ M *OH

- **Arginine**
  - Sonication
  - Dynamic
  - Static
  - 0.33 x 10⁻¹⁴ M *OH

- **Serine**
  - Sonication
  - Dynamic
  - Static
  - 2.00 x 10⁻¹⁴ M *OH
Cleaning Performance with PSSA and ROS Species

<table>
<thead>
<tr>
<th>Additive</th>
<th>H2O2 Only</th>
<th>Cu Control</th>
<th>Serine</th>
<th>Arginine</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSA + H2O2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSA + Cu + H2O2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSA + Cu/Ser + H2O2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSSA + Cu/Arg + H2O2</td>
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Cleaning Performance with PSSA and ROS Species
Cleaning Chemistry Adsorption

\[ \Delta f = \text{Rate to Crystal Equilibrium} (\text{DMass/dt}) \]

\[ \Delta \text{Mass} \]

Time (s)

Control H2O2 Cu + H2O2 Cu/Ser + H2O2 Cu/Arg + H2O2
Cleaning Chemistry Adsorption

<table>
<thead>
<tr>
<th>Polyelectrolyte</th>
<th>Without PSSA</th>
<th>With PSSA</th>
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**Graphical Data**

- X-axis: Cleaning Formulation
  - Control
  - H2O2
  - Cu + H2O2
  - Cu/Ser + H2O2
  - Cu/Arg + H2O2

- Y-axis: Rate to Crystal Equilibrium (DMass/dt)
  - Values range from 0 to 6.
Acknowledgements

• Keleher Research Group – Lewis University

• Don Watson & Don Dussault – ProSys