Susceptibility of Different Slurry Types to Agglomeration

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Introduction

• A variety of types of delivery systems are used to pressurize and circulate CMP slurry to deliver it to the process tools.
• Typically, the slurry passes through the equipment providing the motive force approximately 100 times before it is used to polish wafers.
• Some CMP slurries are susceptible to agglomeration caused by mechanical handling.
  – limits the life of filters
  – reduces yield by causing wafer defects
Experiment performed

- CMP slurry was circulated in a simulated distribution loop using 3 different types of pumps to determine the effect of circulation on slurry health.

- A variety of slurry health parameters were monitored including:
  - Working particle size distribution (PSD)
    - Dynamic light scattering (Particle Sizing Systems NICOMP 380ZLS
    - UFA/SMPS
  - Large particle tail of the slurry PSD ($\geq 0.56 \mu m$)
    - Particle Sizing Systems AccuSizer 780
  - Zeta Potential
  - Total % solids
  - pH
  - Specific gravity
  - Hydrogen peroxide concentration (when applicable)
Silica slurry: Example of UFA/SMPS measurement

- **UFA/SMPS technique**
  - Aerosolize the particles and measure the size using a DMA
  - Measures both size and number concentrations
  - Does not assume a shape of the distribution

Experiment details

- Test system volume: 12 L of slurry
- Pump air supply or speed was adjusted to achieve the following test conditions:
  - Flow rate: 30 Lpm
  - Pump outlet pressure: 30 psig
- Tank blanketed with humidified N₂: RH > 90%
- Slurry temperature: 21 ± 2°C
- Pulse dampener included when applicable
8 CMP Slurries Evaluated

• Slurry Abrasive:
  – Silica (S1-S4)
    • Fumed silica slurry (1)
    • Colloidal silica oxide slurry (3)
  – Alumina oxide slurry (A1-A2)
  – Ceria slurry (C1-C2)

• Slurry Application:
  – ILD (S1)
  – Barrier (S2)
  – W (S3-S4)
  – Copper (A1-A2)
  – STI (C1-C2)
Pumps Evaluated

- Diaphragm pump with pulse dampener
- Bellows pump with pulse dampener
- Levitronix magnetically levitated centrifugal pumps
  - BPS-1
  - BPS-3
  - **BPS-4**
  - BPS-200
  - BPS-600
Pump Comparison

- Working PSD
- Large particle tail
- Other parameters
  - No significant change during any of the tests
Working particle size distributions (PSDs)

- Dynamic Light Scattering (DLS) measurements

<table>
<thead>
<tr>
<th>Slurry Type</th>
<th>Volume-weighted Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>10</td>
</tr>
<tr>
<td>S2</td>
<td>100</td>
</tr>
<tr>
<td>S3</td>
<td>1000</td>
</tr>
<tr>
<td>S4</td>
<td>10000</td>
</tr>
<tr>
<td>A1</td>
<td>Mean Size</td>
</tr>
<tr>
<td>A2</td>
<td>99th Percentile Size</td>
</tr>
<tr>
<td>C1</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td></td>
</tr>
</tbody>
</table>

Relative Volume-Weighted Concentration (%)

Particle Diameter (μm)
S1 slurry: Working PSD measurements (DLS)

As-received slurry plotted at 1.1 turnovers
A1 slurry: Working PSD measurements (DLS)

BPS-4

Diaphragm

Bellows

Error bars represent ± 3σ
## Summary of changes in working PSD

<table>
<thead>
<tr>
<th>Application</th>
<th>Abrasive</th>
<th>Type</th>
<th>Centrifugal</th>
<th>Diaphragm</th>
<th>Bellows</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILD</td>
<td>fumed silica</td>
<td>S1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>barrier</td>
<td>colloidal silica</td>
<td>S2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>colloidal silica</td>
<td>S3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>colloidal silica</td>
<td>S4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>copper</td>
<td>alumina</td>
<td>A1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>copper</td>
<td>alumina</td>
<td>A2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>STI</td>
<td>ceria</td>
<td>C1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>STI</td>
<td>ceria</td>
<td>C2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### Relative Change in Mean Size

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Relative Change in Mean Size</th>
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<tbody>
<tr>
<td>-</td>
<td>&gt; 10% decrease</td>
</tr>
<tr>
<td>0</td>
<td>&lt; 10% change</td>
</tr>
<tr>
<td>+</td>
<td>&gt; 10% increase</td>
</tr>
</tbody>
</table>
Large Particle Tail PSDs in As-Received Slurry

![Graph showing cumulative concentration vs. particle diameter](slide13.png)

- **Cumulative Concentration (#/ml)**
- **Particle Diameter (μm)**

- **S1**
- **S2**
- **S3**
- **S4**
- **A1**
- **A2**
- **C1**
- **C2**
S1 slurry: BPS-200/BPS-600 Pumps

![Graph showing cumulative concentration vs. particle diameter for BPS-200 and BPS-600](CTA pub #86.ppt Slide 14)
S1 slurry: BPS-4, bellows, and diaphragm pumps

**BPS-4**

<table>
<thead>
<tr>
<th>Particle Diameter (μm)</th>
<th>Cumulative Concentration (#/ml)</th>
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<tbody>
<tr>
<td>0.5</td>
<td>$10^2$</td>
</tr>
<tr>
<td>0.6</td>
<td>$10^3$</td>
</tr>
<tr>
<td>0.8</td>
<td>$10^4$</td>
</tr>
<tr>
<td>2</td>
<td>$10^5$</td>
</tr>
<tr>
<td>3</td>
<td>$10^6$</td>
</tr>
<tr>
<td>4</td>
<td>$10^7$</td>
</tr>
<tr>
<td>5</td>
<td>$10^8$</td>
</tr>
<tr>
<td>6</td>
<td>$10^9$</td>
</tr>
<tr>
<td>8</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>10</td>
<td>$10^{11}$</td>
</tr>
</tbody>
</table>

**Bellows**

<table>
<thead>
<tr>
<th>Particle Diameter (μm)</th>
<th>Cumulative Concentration (#/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
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<td>$10^{10}$</td>
</tr>
<tr>
<td>10</td>
<td>$10^{11}$</td>
</tr>
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</table>

**Diaphragm**

<table>
<thead>
<tr>
<th>Particle Diameter (μm)</th>
<th>Cumulative Concentration (#/ml)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3</td>
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<tr>
<td>8</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>10</td>
<td>$10^{11}$</td>
</tr>
</tbody>
</table>
S2 slurry

CTA pub #86.ppt
Slide 16

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S3 slurry

![BPS-4 Graph]

![Bellows pump Graph]

![Diaphragm pump Graph]
S4 slurry

**BPS-4**

**Bellows pump**

**Diaphragm pump**

Particle Diameter (μm)

Cumulative Concentration (#/ml)
A1 slurry

**BPS-4**

- Turnovers:
  - 0
  - 10
  - 20
  - 50
  - 104
  - 202
  - 498
  - 995
  - 3383

**Bellows pump**

- Turnovers:
  - 0
  - 10
  - 20
  - 50
  - 100
  - 202
  - 549
  - 987
  - 3318

**Diaphragm pump**

- Turnovers:
  - 0
  - 10
  - 20
  - 50
  - 100
  - 202
  - 509
  - 995
  - 3334
A2 slurry

BPS-4

Cumulative Concentration (#/ml)

Particle Diameter (μm)

Bellows pump

Diaphragm pump

Particle Diameter (μm)

Cumulative Concentration (#/ml)

Turnovers
C1 slurry

BPS-4

Bellows pump

Diaphragm pump

Turnovers

Cumulative Concentration (#/ml)

Particle Diameter (μm)

Cumulative Concentration (#/ml)

Particle Diameter (μm)

Cumulative Concentration (#/ml)

Particle Diameter (μm)
C2 slurry

- **BPS-4**
- **Bellows pump**
- **Diaphragm pump**
Concentration increases measured after 100 turnovers

S1

S2

S3

S4

Particle Diameter (μm)

Concentration Relative to Initial Concentration

0.1 0.5 0.6 0.8 1.0 2 3 4 5 6 8 10.0

0.1 1.0 10.0 100.0

Particle Diameter (μm)

Concentration Relative to Initial Concentration

0.1 0.5 0.6 0.8 1.0 2 3 4 5 6 8 10.0

0.1 1.0 10.0 100.0

Legend:
- BPS-4
- Bellows
- Diaphragm
Concentration increases measured after 100 turnovers (cont’d)

A1

BPS-4

Bellows

Diaphragm

A2

C1

C2
Concentration increases measured after 1,000 turnovers

S1

S2

S3

S4

Particle Diameter (μm)

Concentration Relative to Initial Concentration

0.1 0.6 1.0 2.0 5.0 8.0 10.0

0.1 0.6 1.0 2.0 5.0 8.0 10.0

Particle Diameter (μm)

0.1 0.6 1.0 2.0 5.0 8.0 10.0

0.1 0.6 1.0 2.0 5.0 8.0 10.0

0.1 0.6 1.0 2.0 5.0 8.0 10.0

0.1 0.6 1.0 2.0 5.0 8.0 10.0

BPS-4
Bellows
Diaphragm

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Concentration increases measured after 1,000 turnovers (cont’d)

A1

BPS-4
Bellows
Diaphragm

A2

C1

C2
### Summary of changes in large particle concentrations

<table>
<thead>
<tr>
<th>Application</th>
<th>Abrasive</th>
<th>Type</th>
<th>Submicron particles (0.56-1.0 µm) after 1000 turnovers</th>
<th>Supermicron particles (&gt; 2.0 µm) after 1000 turnovers</th>
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</thead>
<tbody>
<tr>
<td>ILD</td>
<td>fumed silica</td>
<td>S1</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
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<td></td>
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<td></td>
<td>0</td>
<td>+</td>
</tr>
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<td>barrier</td>
<td>colloidal silica</td>
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<td>0</td>
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</tr>
<tr>
<td>copper</td>
<td>alumina</td>
<td>A1</td>
<td>0</td>
<td>-</td>
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<td></td>
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<td>+</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>STI</td>
<td>ceria</td>
<td>C1</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>0</td>
<td>+</td>
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<td></td>
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<td>0</td>
<td>+</td>
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<tr>
<td>STI</td>
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<td>C2</td>
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<td>NA</td>
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<td></td>
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<td>0</td>
<td>NA</td>
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<tr>
<td></td>
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<td></td>
<td>0</td>
<td>NA</td>
</tr>
</tbody>
</table>

### Symbol

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Concentration change</th>
<th>Concentration ratio after 1,000 turnovers</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Decrease</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>0</td>
<td>None</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>+</td>
<td>Increase</td>
<td>2-10</td>
</tr>
<tr>
<td>++</td>
<td>Large Increase</td>
<td>&gt; 10</td>
</tr>
</tbody>
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Summary

• Most silica slurries are sensitive to handling-induced particle agglomeration, but to varying degrees.
• Some ceria and alumina slurries were also sensitive to handling, while others did not appear to be.
## Summary of effect of pumps on slurry properties

<table>
<thead>
<tr>
<th>Pump Type</th>
<th>PSD</th>
<th>Other Slurry Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Working PSD</td>
<td>Large Particle Tail</td>
</tr>
<tr>
<td>BPS-4 pump</td>
<td>• Significant decrease in 1 slurry (A1)</td>
<td>• Minimal effect</td>
</tr>
</tbody>
</table>
| Diaphragm and Bellows pumps    | • Significant decrease in 1 slurry (A1) | • Significant increase in 6 of 8 slurries  
  • Large increase in 3 of 4 silica slurries  
  • Large increase in at least 1 slurry of each type silica, alumina, and ceria slurry  
  • Large increase with at least 1 slurry in each application area | • Minimal effect |