“Advances in Ceria Slurries to Address Challenges in Fabricating Next Generation Devices”
Outline

- Introduction to Ferro
- Historical Products
- Rate Accelerants
- Fast Oxide CMP Slurry
- Path to Next Generations of STI and Fast Oxide Slurries
We are a leading, global producer of performance materials and chemicals

- Ferro was founded in 1919 in Cleveland, Ohio. Porcelain enamel was the Company’s original business and it remains an important product line today.

- We are a leading, global producer of performance materials and chemicals sold to manufacturers worldwide.

- Our customers represent more than 30 industries and span 100-plus countries.

- We have manufacturing facilities in The Americas, Europe/North Africa and Asia-Pacific.

- Approximately 4,600 employees work at sites in 26 countries.

- Ferro is publicly-owned; our shares trade on New York Stock Exchange under the symbol FOE.
Ferro’s Core Technologies

- Particle Engineering
- Color and Glass Science
- Surface Chemistry and Surface Application
- Formulation
Penn Yan Site

- Located on 63 Acres
- Lake Frontage of 1100 feet
- 320,000 Ft$^2$ Under Roof
- Global R&D Center: Dielectrics and Surface Technologies
- Customer Service Center for:
  - Cleveland, OH
  - Vista, California
  - Penn Yan, NY
Penn Yan Products

- Manufacturer of ceramic powders and slurries

**Dielectrics**
- High purity engineered powders and formulations for the multi-layer ceramic capacitor (MLCC) industry

**Surface Finishing Material**
- Zirconia, Ceria and Alumina based powder and slurry formulations for the LCD glass, glass ceramic hard disk, flat glass, cover glass, precision glass, sapphire, plastic lens, metals and automotive polishing applications

**CMP**
- Ceria based powders and formulations used in semiconductor applications
### Ferro’s Historical Ceria STI Slurrys

<table>
<thead>
<tr>
<th></th>
<th>Dmean (nm)</th>
<th>D0 (nm)</th>
<th>LPC’s &gt; 0.5 um</th>
<th>% Ceria</th>
<th>HDP Removal Rate (A/min.)</th>
<th>Nitride Removal Rate (A/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1st Gen STI Slurry</strong></td>
<td>145</td>
<td>450</td>
<td>500,000</td>
<td>4</td>
<td>2000</td>
<td>&lt;20 A/min.</td>
</tr>
<tr>
<td><strong>2nd Gen STI Slurry</strong></td>
<td>145</td>
<td>450</td>
<td>400,000</td>
<td>4</td>
<td>2700</td>
<td>&lt;20 A/min.</td>
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New Device Requirements

◆ As devices get more complex, the demands (in addition to the basic planarity requirement), on the CMP slurries that enable their construction increase:

Defects

- Continuous push for reduction in defects
- LPC control has been demonstrated to be key

Rate

- More complex designs require:
  - An increase in removal rate due to the number/thickness of layers requiring polishing
  - The ability to polish multiple wafer/layer types with the same slurry
How do we get there?

Fundamental understanding is key!
Ceria Polishing Mechanism: Surface Chemical Action

- As opposed to other abrasive types (i.e., Silica, alumina, zirconia, etc.), ceria abrasives have a large surface chemical action during glass polishing.

- By control of the ceria particle characteristics and the surface active chemical components in a formulation, ceria systems can be highly tunable in terms of oxide removal rates.

Ceria Polishing Mechanism: Surface Oxidation State

- $\text{H}_2\text{O}_2$ can shut down oxide removal rates using ceria slurries (more $\text{Ce}^{4+}$ on the surface shuts down oxide removal rates)
  - Effect not seen with other abrasives (silica, zirconia, alumina, titania)

- Further studies have shown that $\text{Ce}^{3+}$ sites on the surface of ceria particles is critical for the silicon dioxide removal rate
Ferro has developed an additive that stabilizes the Ce$^{3+}$ on the surface of the ceria, leading to a higher population of Ce$^{3+}$ sites and the acceleration of the oxide removal rate

- Additive is stable in solution (beyond 12 month shelf life)
- Additive also buffers pH in low regime (pH=3-4)
### Novel Rate Accelerant Chemistry

**Graph:** Extremely fast TOX removal rate!

**Table:**

<table>
<thead>
<tr>
<th>Particle</th>
<th>145 nm ceria</th>
<th>130 nm ceria</th>
<th>130 nm ceria</th>
<th>120 nm ceria</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Accelerant Package</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

All systems tested at 3 wt. % ceria
Current HVM Fast Oxide Slurry

- Fast Oxide Slurry was formulated with extra ceria and accelerant (+/+) and reduced ceria and accelerant (-/-) and compared to standard.
- Formulation proven to be robust across formulation space studied.

>15,000 Angstroms/minute BPSG removal!
### Ferro’s Ceria STI Slurry Evolution

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</tr>
<tr>
<td><strong>3rd Gen STI Slurry</strong></td>
<td>130</td>
<td>300</td>
<td>&lt;40,000</td>
<td>3</td>
<td>3500</td>
<td>&lt;20 A/min.</td>
</tr>
<tr>
<td><strong>4th Gen STI SRS-2092</strong></td>
<td>130</td>
<td>300</td>
<td>&lt;10,000</td>
<td>&lt;0.5</td>
<td>2700</td>
<td>&lt;20 A/min.</td>
</tr>
</tbody>
</table>

Continuous improvement toward lower ceria loading and lower LPC’s for lower wafer level defectivity and lower Fab cost of ownership
SRS-2092: Low Solids STI Slurry

- Ferro has designed its next generation STI slurry
- It is designed to be diluted (typically 1 part slurry : 2 parts water)
  - Lower COO at <0.5% ceria loading
  - Lower Defectivity at smaller particle sizes

HDP
2658 A/min RR

Nitride
4 A/min RR
- Extremely long overpolish window with excellent dishing performance!

**Trench Oxide Values**

Ideal Trench Oxide Thickness = 5500Å

**Active Oxide Values**

Endpoint Time based upon Act. Ox. data
Where to next?

- Reduced LPC’s/smaller particles to further reduce defects
Next Generation Fast Oxide Slurry

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<tr>
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<th>Dmean (nm)</th>
<th>D0 (nm)</th>
<th>LPC’s &gt; 0.5 um</th>
<th>TOX RR (Ang./min)</th>
<th>TEOS RR (Ang./min.)</th>
<th>BPSG RR (Ang./min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std. Fast Oxide</td>
<td>130</td>
<td>296</td>
<td>100,000</td>
<td>7189</td>
<td>12,250</td>
<td>14,821</td>
</tr>
<tr>
<td>Low Dmean</td>
<td>69</td>
<td>131</td>
<td>1,700</td>
<td>6139</td>
<td>11,651</td>
<td>11,352</td>
</tr>
</tbody>
</table>

70 nm ceria with extremely fast removal rates
Ferro has developed a low Dmean version of SRS-2092 that has similar polish behavior at approximately half the particle size.

- LDM SRS-2092 ~ 70 nm
- SRS-2092 ~ 130 nm
Where to next?

- Further removal rate improvements
  - How will we get there?
Ferro’s Rate Increase Developmental Program

- Ferro is in the middle of a large rate increase developmental program

- A fundamental 3 path approach is being taken:
  - Alternate Ceria’s
  - Alternate Processing
  - Alternate Accelerants
Current State

- Based upon 120 nm Dmean
  - With the intent that defects will be reduced compared to Std. Fast Oxide Slurry
  - LPC’s are a similar order of magnitude as the sub 70 nm particles

- Combination of alternate processing and alternate accelerants
  - Increase in oxide removal rates with smaller particles (even with a reduction in ceria %)

![Removal Rate (% of Std. Fast Oxide Slurry)](chart.png)
Path Forward

- **Removal Rate Improvement:**
  - Optimize best options to date to achieve greater than 40% increase in removal rate vs. Std. Fast Oxide Slurry with improved defect levels
  - Continue fundamental work to lead to breakthroughs necessary to increase removal rates greater than 80% vs. Std. Fast Oxide Slurry while further improving defect levels

- **Defect Improvement:**
  - Integrate the learnings above with 70 nm and smaller particles
  - Incorporate the learnings above in next generation STI Slurries to enable the use of 70 nm and smaller particles and further reduce ceria levels
Acknowledgements

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