Outline

- Introduction to Ferro
- Shallow trench isolation (STI)
- Silicon nitride passivation
- Ceria polishing mechanism
- Next generation STI slurries
Ferro Overview

- Founded 1919 as Ferro Enameling Company in Cleveland, Ohio USA
- Worldwide leader in production of glass enamels, porcelain enamels, ceramic tile coatings
- Nearly 4,000 associates working in 26 countries
- 2015 sales of $1.1 billion

Approaching centennial as a growing innovator of glass-based coatings and color solutions
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 Ft² 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 sapphire, plastic lens, metals and automotive polishing applications

CMP

• Ceria based powders and formulations used in semiconductor applications
Shallow Trench Isolation (STI)

- Silicon dioxide (SiO$_2$) dielectric used to fill trenches in Si substrate in order to electrically isolate the transistors of an integrated circuit

- STI slurry is required to planarize the deposited SiO$_2$ then stop on an underlying layer of silicon nitride (SiN)

- First CMP process needed in IC fabrication
STI Slurry Challenges

- Wide trench = large dishing
- Narrow nitride = large nitride loss
- Low pattern density: Wide trench + narrow nitride = large dishing + large nitride loss

High (oxide:nitride) selectivity is critical!
STI Slurry Formulation Overview

- Ceria particles
  - Abrasive particle needed for material removal

- Suppressant
  - Amine-based chemistry for passivation of SiN surface

- Other additives
  - Accelerants to boost SiO$_2$ removal rate
  - Dispersants to stabilize particle
  - Rheology modifiers
  - Biocides to promote long slurry shelf life
Mechanism of SiN Passivation

Without suppressant

With amine suppressant
SiN Passivation Model

- Nitride loss is minimal following formation of passivation layer
- High planarization efficiency with long over-polish window
- Dishing and erosion minimized
### Ferro’s Historical STI Slurries

<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>
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<tbody>
<tr>
<td>1st Gen STI Slurry</td>
<td>145</td>
<td>450</td>
<td>500,000</td>
<td>4</td>
<td>2000</td>
<td>&lt;20 A/min.</td>
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<tr>
<td>2nd Gen STI Slurry</td>
<td>145</td>
<td>450</td>
<td>450,000</td>
<td>4</td>
<td>2700</td>
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- SiN passivation chemistry accomplishes high selectivity
New Device Requirements

As devices get smaller and more complex, the demands on the STI slurries that enable their construction increase:

Defects
- Continuous push for reduction in defects
- Large particle count (LPC) control has been demonstrated to be key
How do we get there?

1. Fundamental understanding of ceria polishing

2. Reduction of particle size and LPC’s
Ceria Polishing Mechanism: Surface Chemical Action

- As opposed to other abrasive types, ceria has a large surface chemical action during oxide polishing.

- Studies have shown that $\text{Ce}^{3+}$ sites on the surface of ceria particles are critical for $\text{SiO}_2$ removal rate.
Ferro has developed an additive package that stabilizes the Ce$^{3+}$ on the surface of the ceria, leading to a higher population of Ce$^{3+}$ sites and the subsequent acceleration of SiO$_2$ removal rates.

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

Extremely fast oxide removal rate!

![Graph showing removal rate progressions](image)

<table>
<thead>
<tr>
<th>Particle</th>
<th>145 nm ceria</th>
<th>130 nm ceria</th>
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<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>
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All systems tested at 3 wt% ceria
### Ferro’s STI Slurry Evolution

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<td><strong>3rd Gen STI Slurry</strong></td>
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<td>300</td>
<td>&lt;40,000</td>
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<tr>
<td><strong>SRS-2092</strong></td>
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<td>260</td>
<td>&lt;10,000</td>
<td>0.5</td>
<td>2700</td>
<td>&lt;20 A/min.</td>
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- Same rate/selectivity with significantly lower ceria content
- Lower COO at 0.5% ceria loading
Continuous Improvement for Lower Defects

- 2nd Gen. STI slurry
  LPD Adder = 600

- SRS-2092
  LPD Adder = 100

- Lower defectivity at smaller particle sizes and reduced LPC’s
SRS-2092: Low Solids STI Slurry

- Customer has reported >500:1 selectivity!
SRS-2092: Over-Polish Behavior

- Extremely long over-polish window with minimal trench loss
Where to next?

1. Even further reduction of particle size and LPC’s

2. Colloidal ceria-based STI slurry
Low Dmean SRS-2092

SRS-2092
~ 130 nm

LDM SRS-2092
~ 70 nm

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<td>LDM SRS-2092</td>
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<td>131</td>
<td>1,700</td>
<td>0.5</td>
<td>2800</td>
<td>&lt;20 A/min.</td>
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- Similar polish behavior as SRS-2092 at almost half the size
Colloidal SRS-2092

- Colloidal ceria-based slurry under development with the intent to further reduce particle size and potentially defects

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<td>Colloidal SRS-2092</td>
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<td>0.5</td>
<td>2000</td>
<td>&lt;10 A/min.</td>
</tr>
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- Slightly reduced removal rates with extremely high selectivity
Sub-30nm Ceria

- Ferro is working towards a sub-30nm STI slurry for next generation devices
Conclusions

Ferro has developed next gen. STI slurries with the following considerations:

- **High Selectivity:**
  - Amine passivation chemistry accomplishes the high selectivity needed for STI

- **Rate Enhancement:**
  - Chemical accelerant package allows for high removal rates with low ceria content

- **Defectivity Improvement:**
  - Continuous reduction of particle size and LPC’s
  - Colloidal ceria
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