

# AVS CMP User Group Meeting

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**4/16/15**

“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

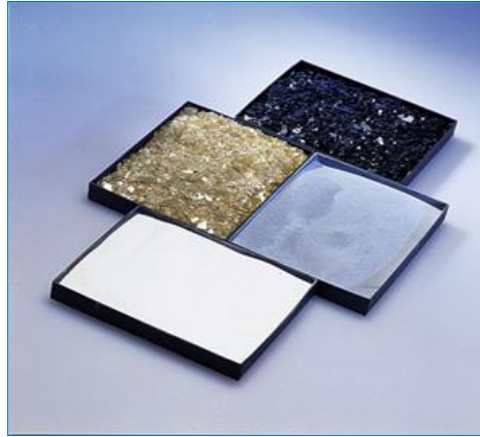
# We are a leading, global producer of performance materials and chemicals




- 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

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- An aerial photograph of the Penn Yan Site, showing a large industrial complex with several large white and grey buildings. A tall water tower is visible in the foreground. The site is surrounded by green fields and dense trees. A road runs along the top of the site, and a parking lot with several vehicles is visible in the foreground.
- ✓ Located on 63 Acres
  - ✓ Lake Frontage of 1100 feet
  - ✓ 320,000 Ft<sup>2</sup> Under Roof
  - ✓ Global R&D Center: Dielectrics and Surface Technologies
  - ✓ Customer Service Center for:
    - Cleveland, OH
    - Vista, California
    - Penn Yan, NY



- **Manufacturer of ceramic powders and slurries**



## Dielectrics



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

## Surface Finishing Material

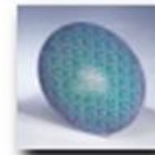


- Zirconia, Ceria and Alumina based powder and slurry formulations for the LCD glass, glass ceramic hard disk, flat glass, cover glass, precision glass, sapphire, plastic lens, metals and automotive polishing applications



## CMP

- Ceria based powders and formulations used in semiconductor applications



# Ferro's Historical Ceria STI Slurries

	Dmean (nm)	D0 (nm)	LPC's > 0.5 um	% Ceria	HDP Removal Rate (A/min.)	Nitride Removal Rate (A/min)
1 <sup>st</sup> Gen STI Slurry	145	450	500,000	4	2000	<20 A/min.
2 <sup>nd</sup> Gen STI Slurry	145	450	400,000	4	2700	<20 A/min.

# 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



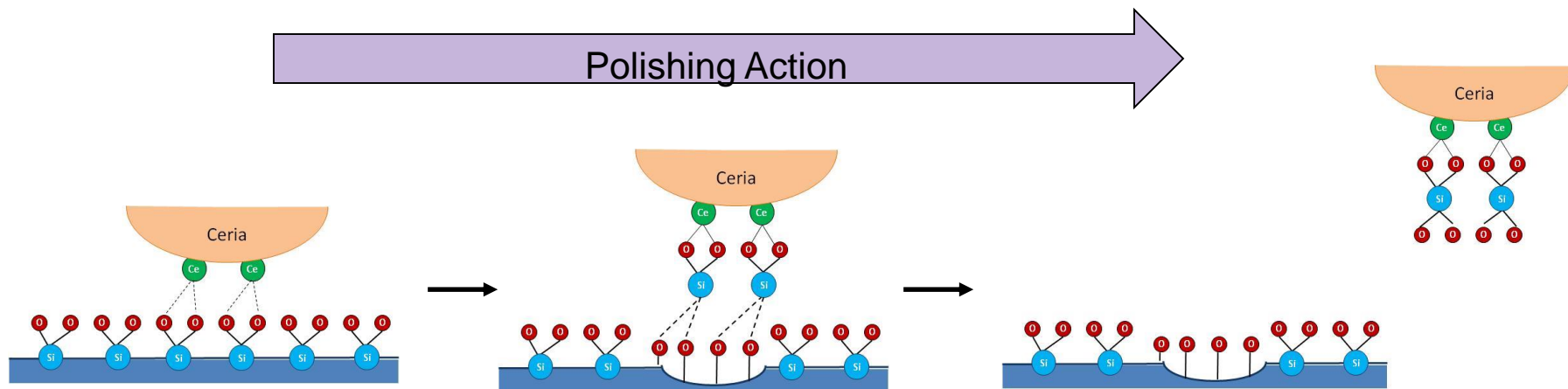


# How do we get there?

◆ Fundamental understanding is key!

# Ceria Polishing Mechanism: Surface Chemical Action

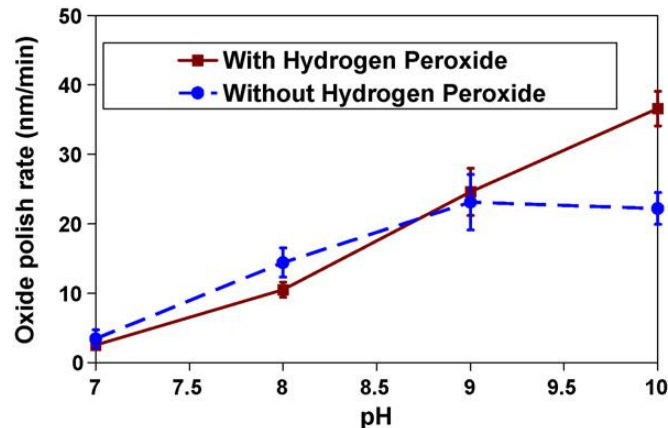
- As opposed to other abrasive types (ie. Silica, alumina, zirconia, etc.), ceria abrasives have a large surface chemical action during glass polishing



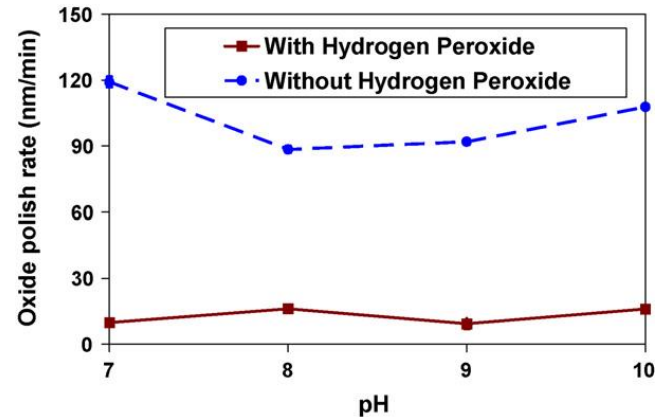
- Lee Cook, Journal of Non-Crystalline Solids 120 (1990), p. 152-171

- 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



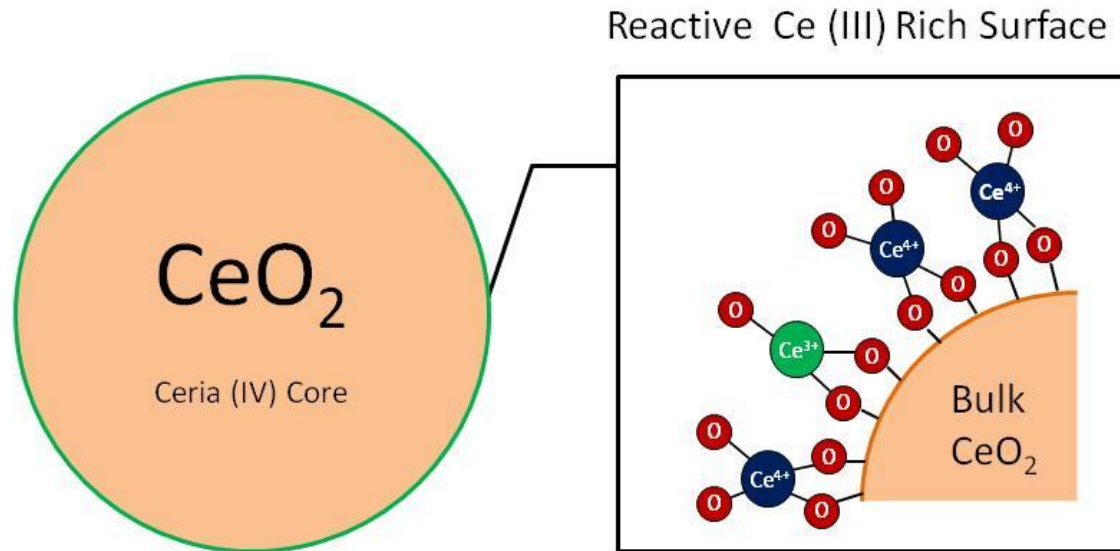
**Silica abrasive**



**Ceria abrasive**

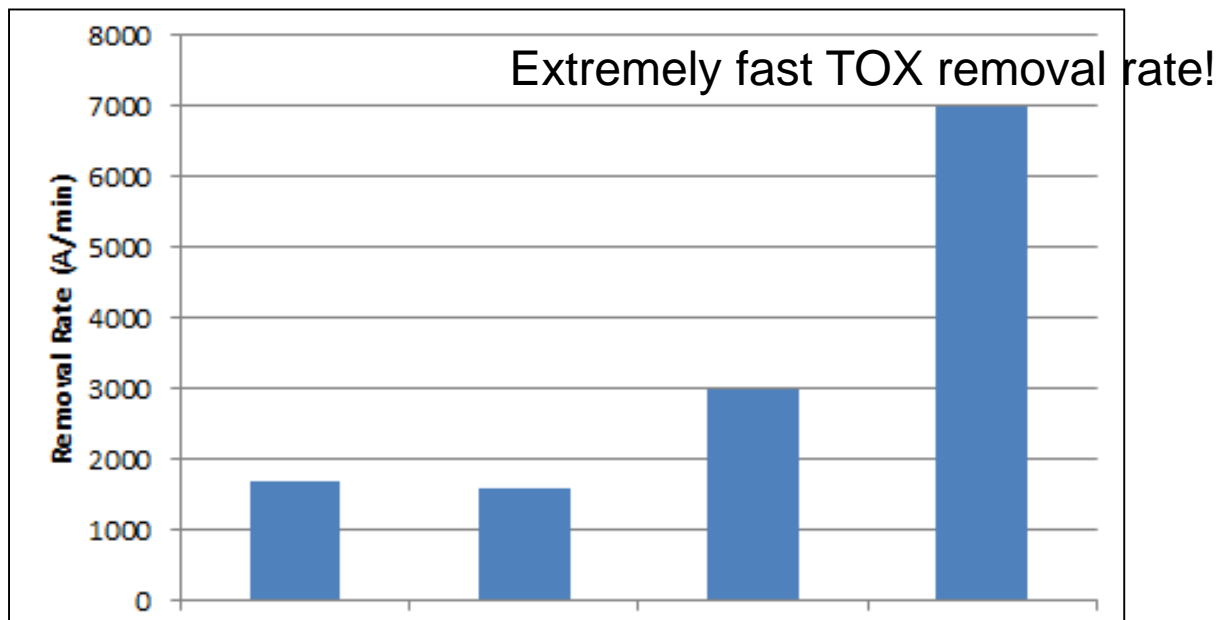
- $H_2O_2$  can shut down oxide removal rates using ceria slurries (more  $Ce^{4+}$  on the surface shuts down oxide removal rates)
  - Effect not seen with other abrasives (silica, zirconia, alumina, titania)
    - R. Manivannan, S. Ramanathan, Applied Surface Science 255 (2009), 3764-3768.
- Further studies have shown that  $Ce^{3+}$  sites on the surface of ceria particles is critical for the silicon dioxide removal rate
  - Veera Dandu (Clarkson thesis, also presented at 17<sup>th</sup> Annual International Symposium on Chemical Mechanical Planarization, August 12<sup>th</sup>-15<sup>th</sup>, 2012, Lake Placid, NY)

# Cerium Surface Oxidation State



- Ferro has developed an additive that stabilizes the Ce<sup>3+</sup> on the surface of the ceria, leading to a higher population of Ce<sup>3+</sup> 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)

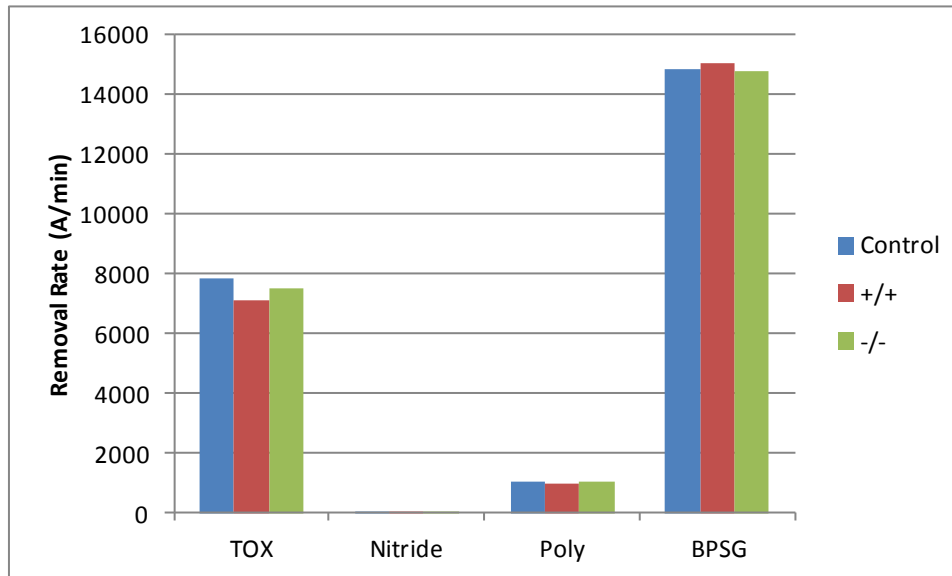
# Novel Rate Accelerant Chemistry



Particle	145 nm ceria	130 nm ceria	130 nm ceria	120 nm ceria
pH	low	low	high	low
Accelerant Package	no	no	no	yes

All systems tested at 3 wt. % ceria

# Current HVM Fast Oxide Slurry



>15,000 Angstroms/minute  
BPSG removal!

- 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



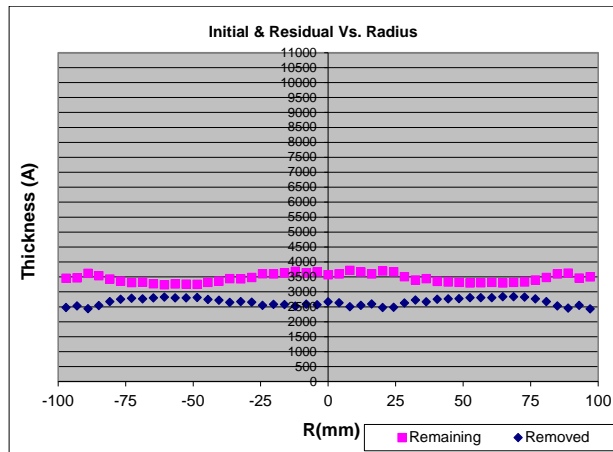
# Ferro's Ceria STI Slurry Evolution

	Dmean (nm)	D0 (nm)	LPC's > 0.5 um	% Ceria	HDP Removal Rate (A/min.)	Nitride Removal Rate (A/min)
1 <sup>st</sup> Gen STI Slurry	145	450	500,000	4	2000	<20 A/min.
2 <sup>nd</sup> Gen STI Slurry	145	450	450,000	4	2700	<20 A/min.
3 <sup>rd</sup> Gen STI Slurry	130	300	<40,000	3	3500	<20 A/min.
4 <sup>th</sup> Gen STI SRS-2092	130	300	<10,000	<0.5	2700	<20 A/min.

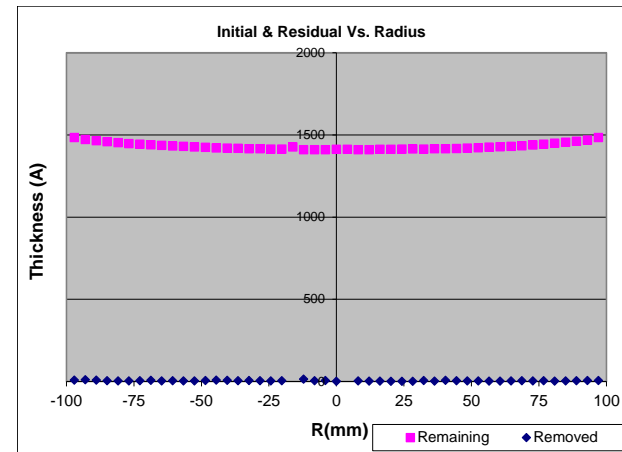
Continuous improvement toward lower ceria loading and lower LPC's for lower wafer level defectivity and lower Fab cost of ownership

# 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

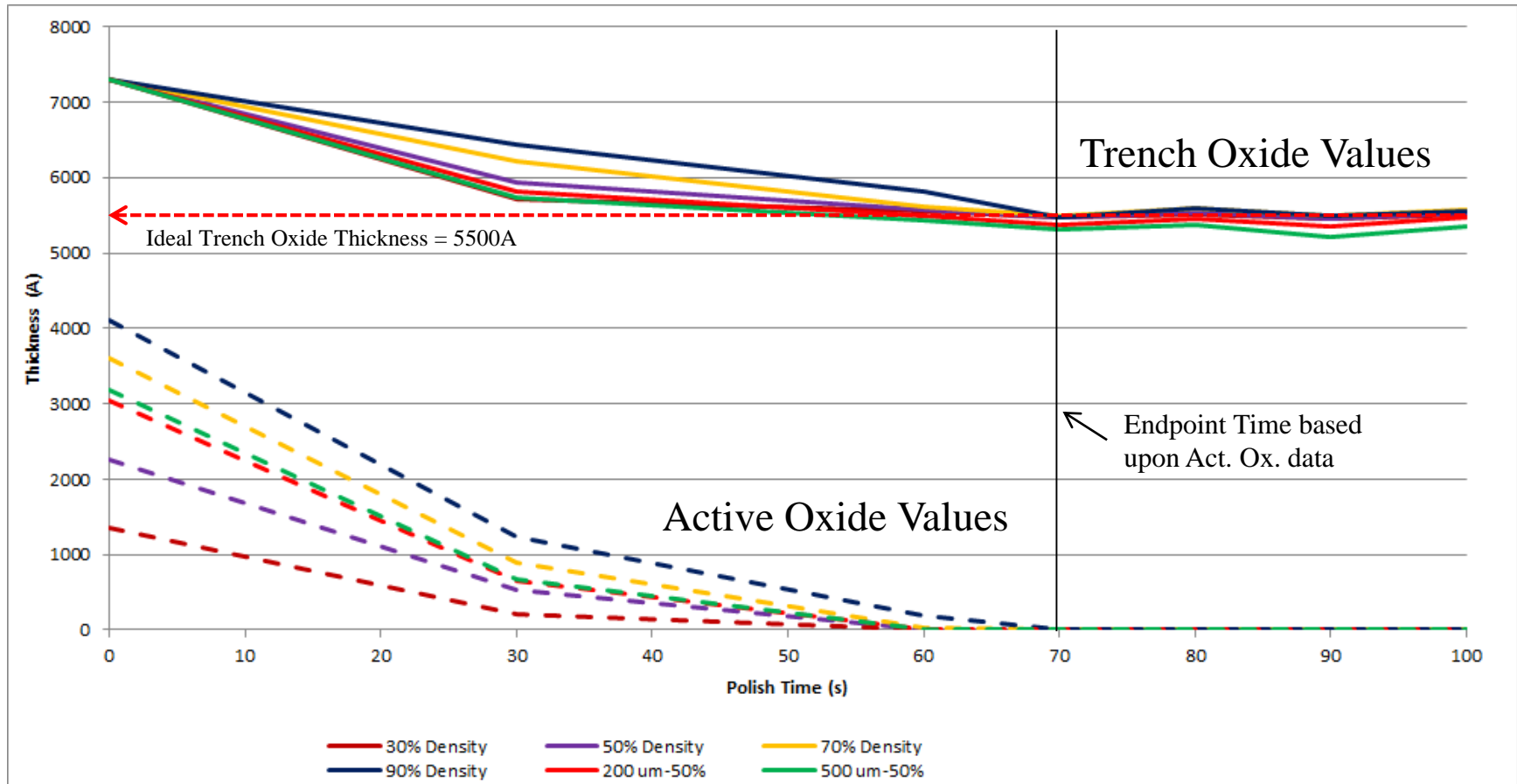


HDP  
2658 A/min RR



Nitride  
4 A/min RR

# SRS-2092 Over-Polish Behavior

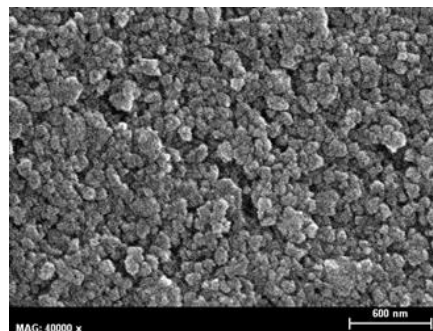
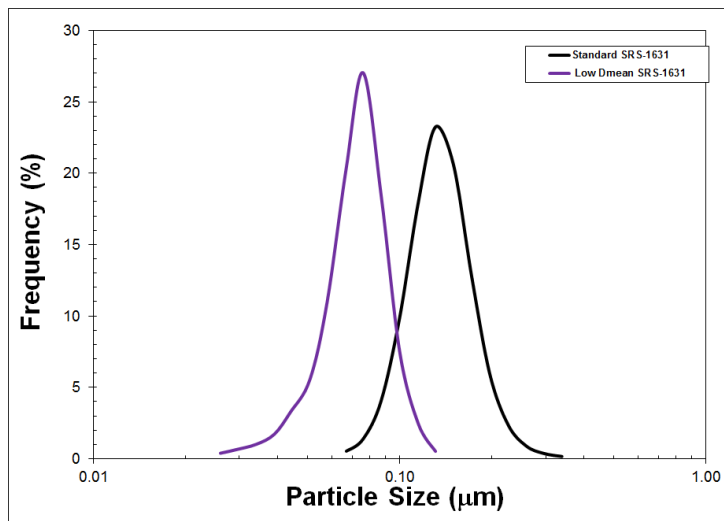


- Extremely long overpolish window with excellent dishing performance!

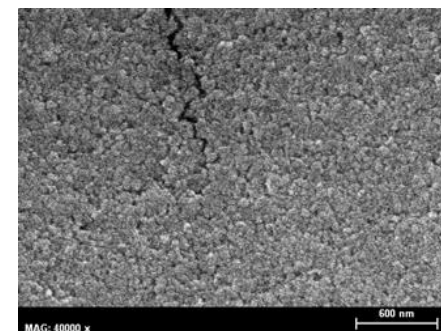
# Where to next?

- ◆ Reduced LPC's/smaller particles to further reduce defects

# Next Generation Fast Oxide Slurry



130 nm ceria



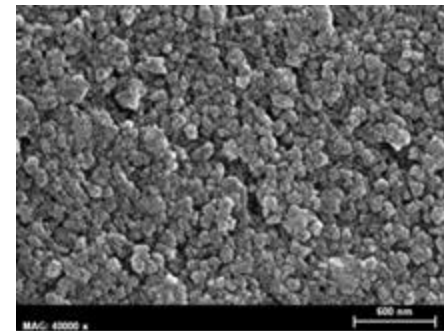
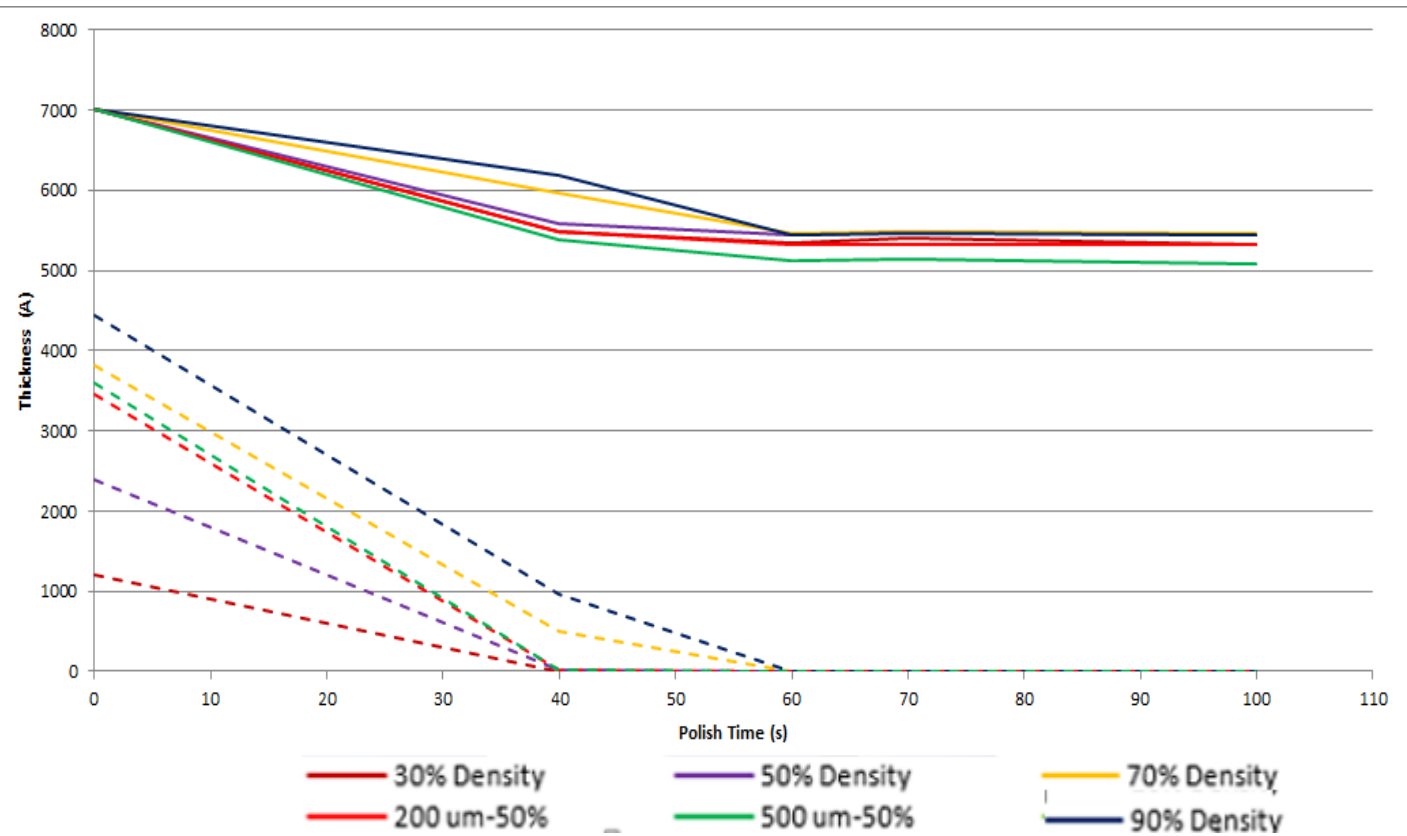
70 nm ceria

	Dmean (nm)	D0 (nm)	LPC's > 0.5 um	TOX RR (Ang./min)	TEOS RR (Ang./min.)	BPSG RR (Ang./min.)
Std. Fast Oxide	130	296	100,000	7189	12,250	14,821
Low Dmean	69	131	1,700	6139	11,651	11,352

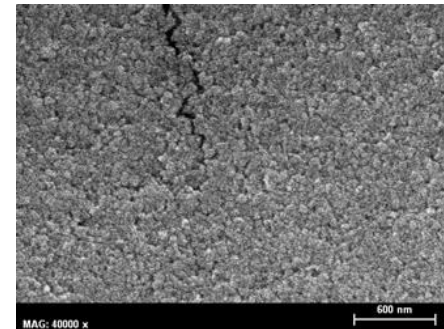
70 nm ceria with extremely fast removal rates

# Low Dmean SRS-2092

- Ferro has developed a low Dmean version of SRS-2092 that has similar polish behavior at approximately half the particle size



SRS-2092  
~ 130 nm



LDM SRS-2092  
~ 70 nm



# Where to next?

- ◆ Further removal rate improvements
  - How will we get there?

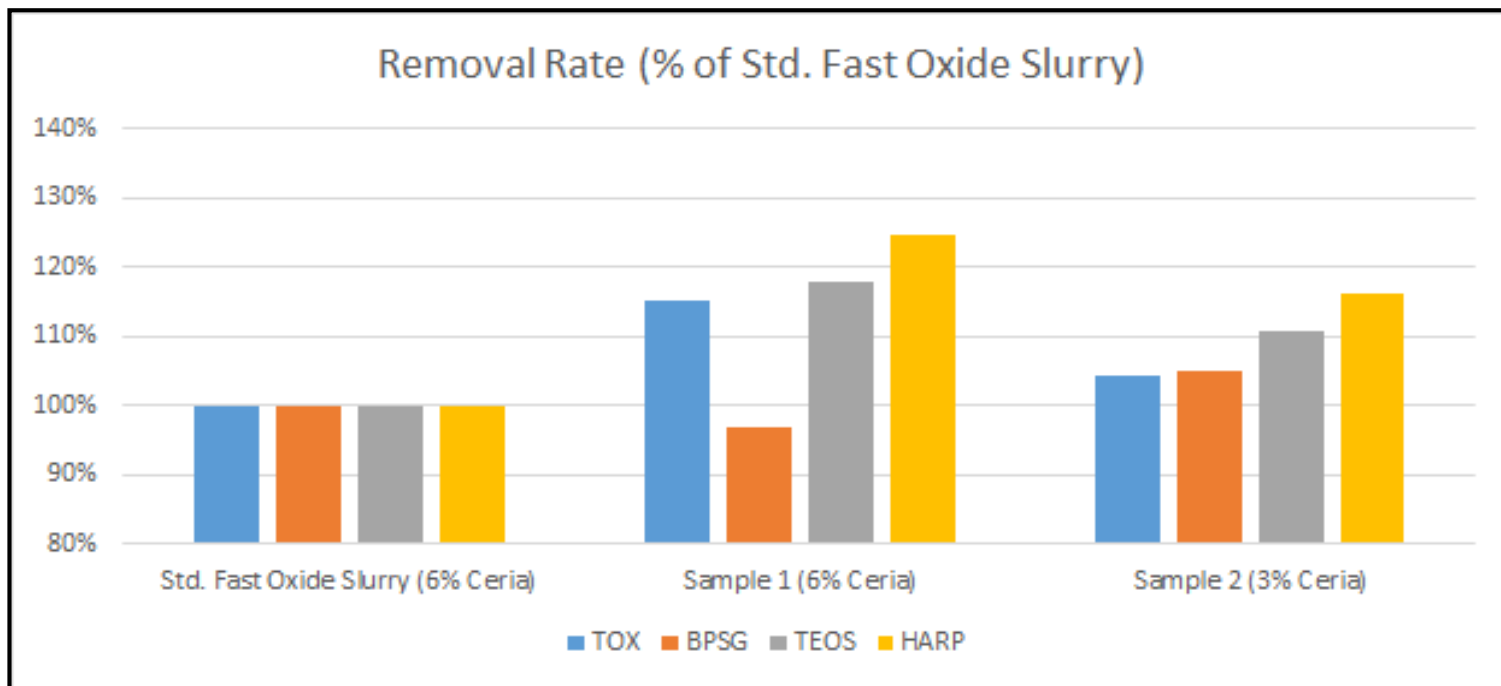
# Ferro's Rate Increase Developmental Program

- ◆ 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 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

- Bob Her
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- Mike Maxwell
- Dave Walker