50 YEARS OF PURE ADVANTAGE

SPCC POST-CMP CONFERENCE

High Performance, Ceria Post-CMP Cleaning Formulations for STI/ILD Dielectric Substrates

Daniela White*, PhD – Sr. Principal Scientist
Atanu Das, PhD – Scientist
Thomas Parson, PhD – Scientist
Michael White, PhD – Director, Post-CMP Development

ENTEGRIS Inc., R&D Surface Preparation and Integration

7 Commerce Drive, Danbury CT 06810

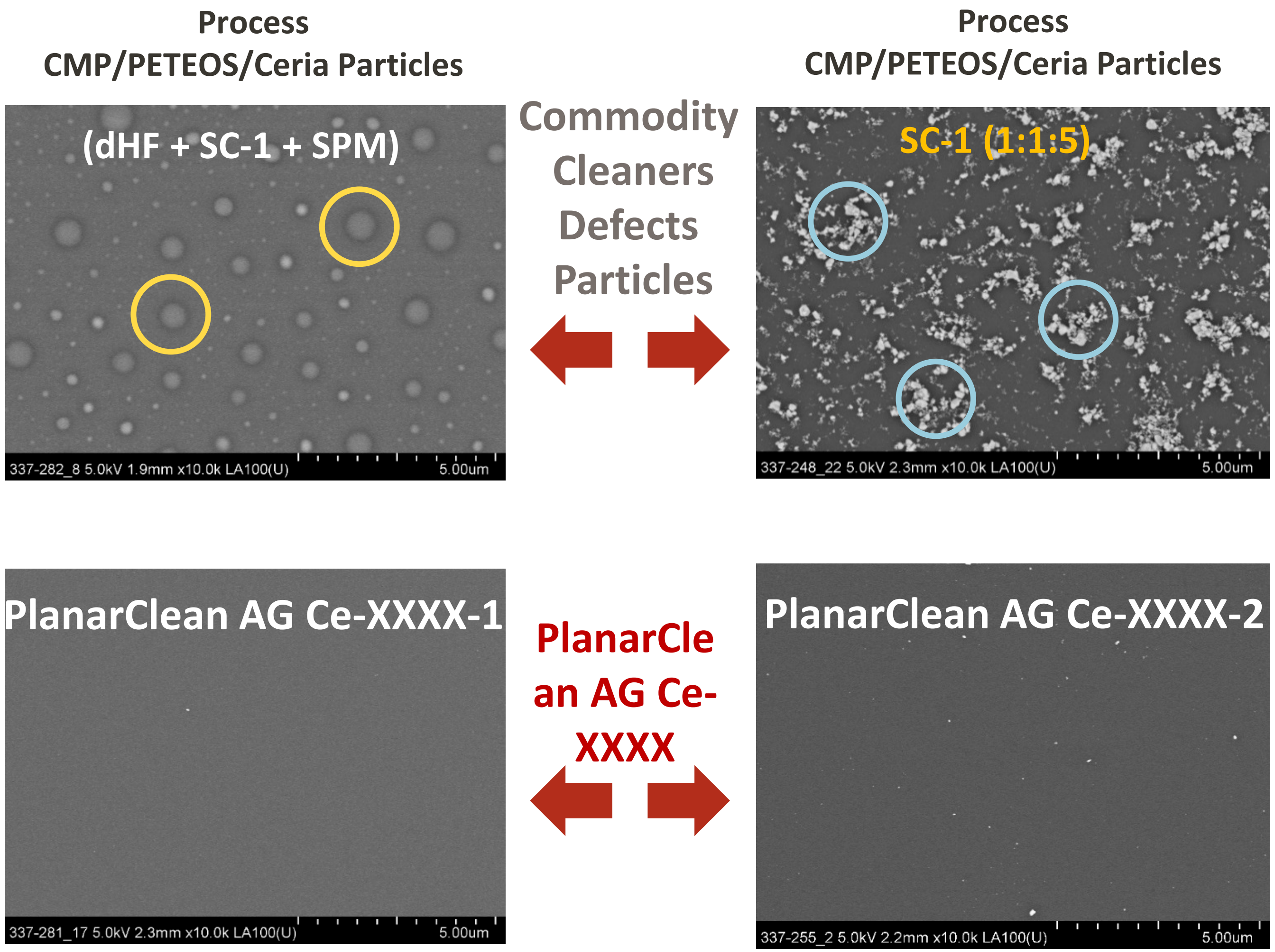
Ph: 203-739-1470, daniela.white@entegris.com

OUTLINE

- Development of a low pH and high pH family of efficient ceria cleaners for STI and ILD dielectric surfaces (PETEOS, SiN, SiC, thermal oxide, etc.), PlanarClean® AG Ce-XXXX
- Mechanistic considerations specific to PlanarClean AG Ce-XXXX formulation design
  - Understanding CeO_2 surface chemistry and CeO_2-SiO_2 interactions: Raman, FTIR
  - Ce^{4+}/Ce^{3+} oxidation state characterization: UV-VIS, Raman, potentiometric titrations
  - $Ce^{4+/3+}$ impact on the ceria cleaning mechanism
- Ceria particle defect count results by SEM, Dark field Microscopy (DFM) and ICP data on dielectric surfaces cleaned with PlanarClean AG Ce-XXXX formulation
- Conclusions and path forward

WHY FORMULATED CERIA CLEANERS VS. COMMODITY?

1. EHS/Safety concerns with traditional cleans (hot SPM, dHF, SC-1, TMAH + dHF)
2. One-step clean process requirement for throughput improvement
3. Need for improved particle removal
4. Need for improved metal removal
5. No damage to dielectric substrates

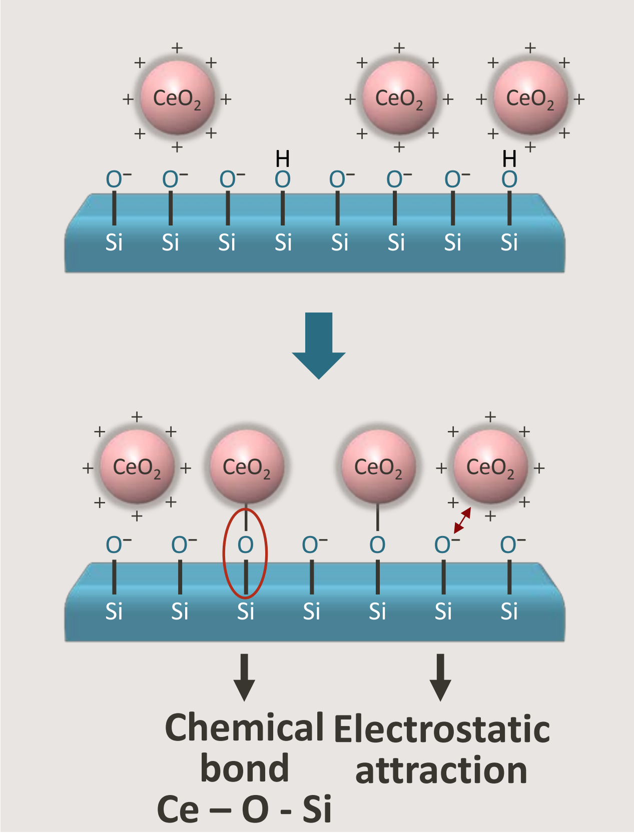


CERIA POST-CMP CLEANING FORMULATION – MECHANIC DESIGN CONCEPT

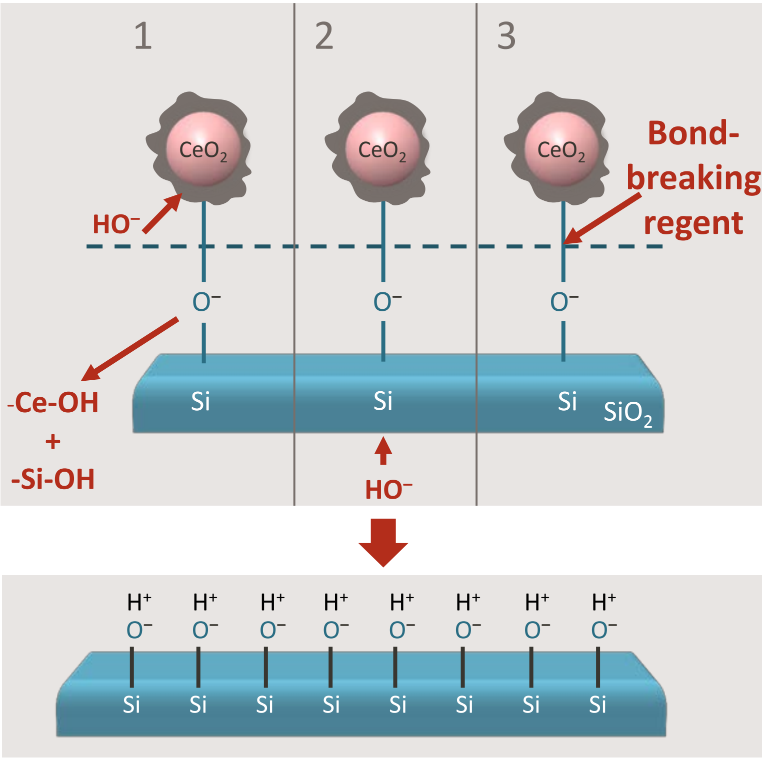
Formulation Design Options

1. High pH hydrolysis of -Ce-O-Si- bonds by HO⁻ nucleophilic attack to Ce^{4+} plus additives needed to stabilize –Ce-OH species and prevent re-deposition
2. High pH partial etch/dissolution of the surface –Si-O-Ce- groups plus re-deposition prevention
3. Bond-breaking additives, followed by CeO_2 complexation, particles stabilization and dispersion

CeO_2-SiO_2 Surface Interactions



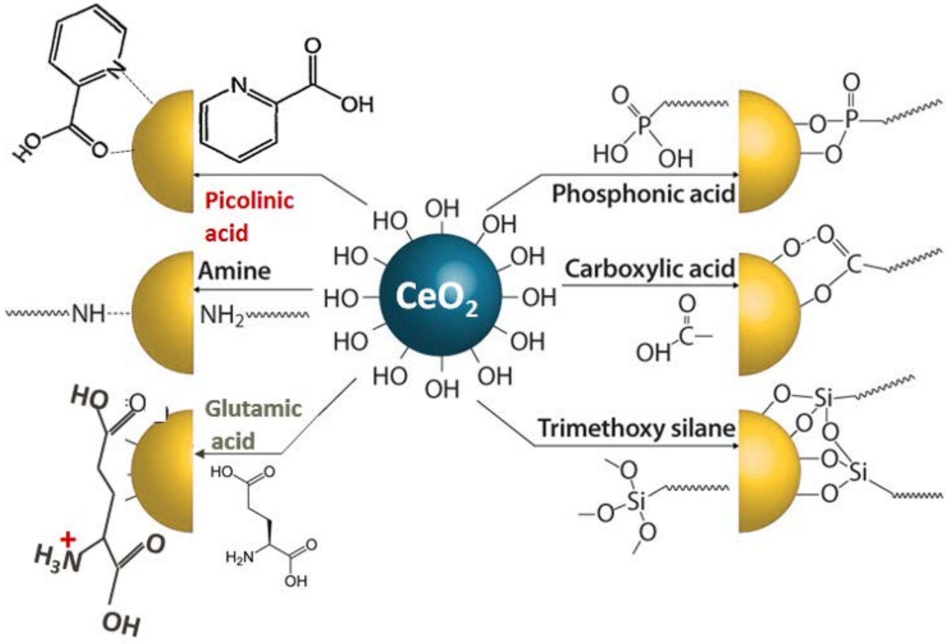
Ce-O Bond-Breaking Mechanisms



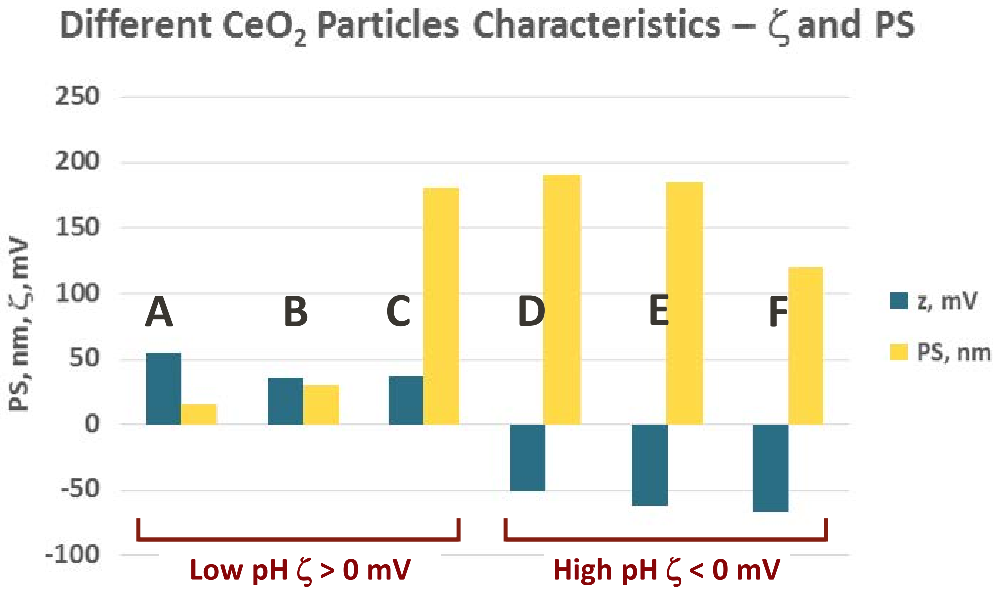
INTERACTIONS OF ORGANIC MOLECULES WITH CERIA SURFACE AND SURFACE CHARGE VS. PH

- Surface modified CeO_2 particles in the CMP slurries: positive or negative surface charge
- Particle size: 15–200 nm
- Need to understand CeO_2 surface chemistry and types of interactions with the dielectric surfaces
- Six different types of CeO_2 particles tested – can we design a universal cleaner?

Surface-Modified Ceria in CMP Slurries



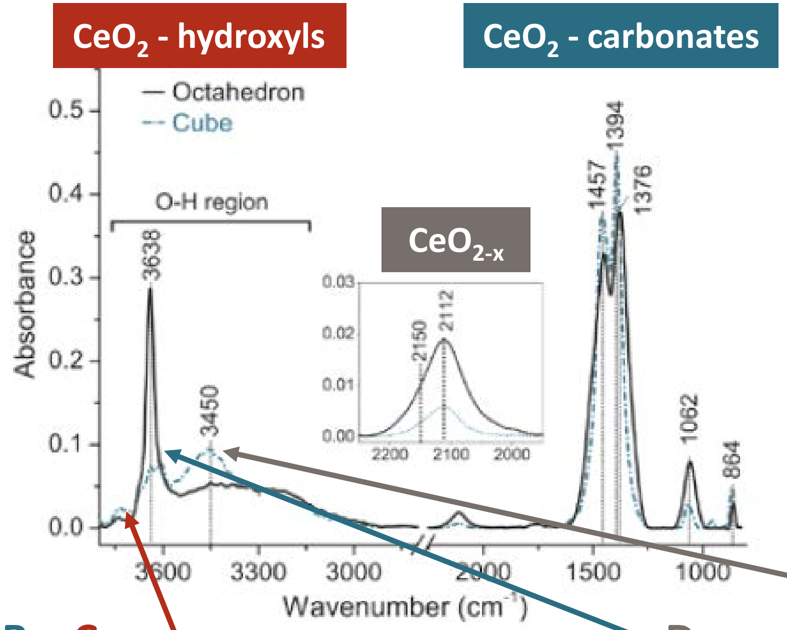
Various CeO_2 Particles (A-F) Tested

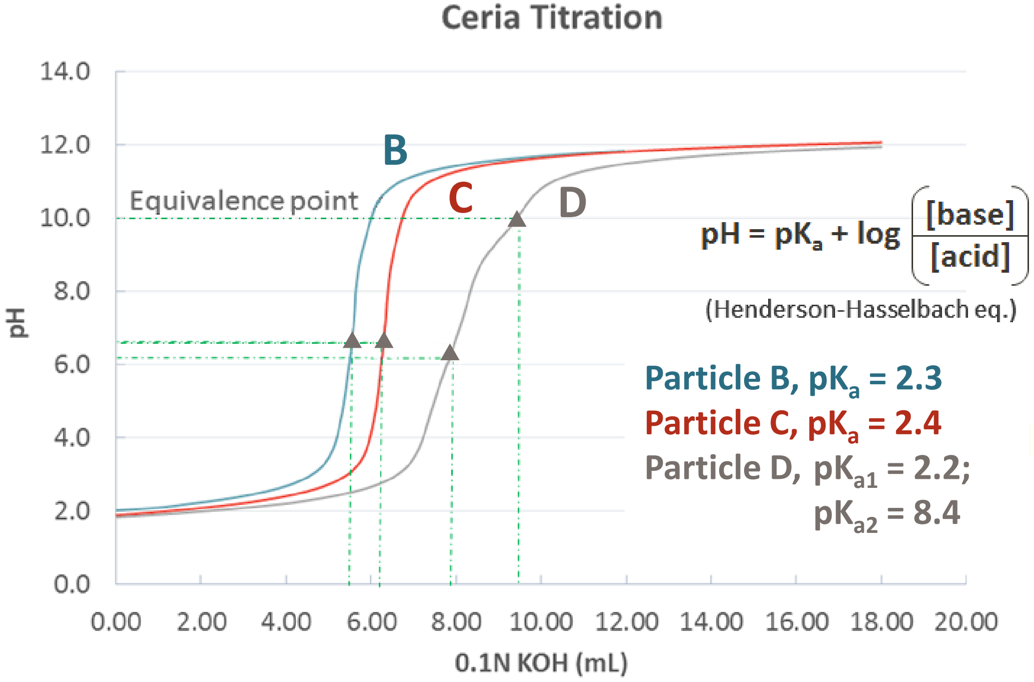


Entegris

TYPES OF CeO_2 SURFACE GROUPS

A. Hydroxyl groups by FTIR[1] and titration





$$pH = pK_a + \log \frac{[base]}{[acid]}$$

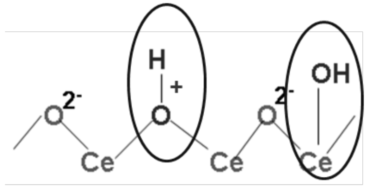
(Henderson-Hasselbach eq.)

Particle B, pK_a = 2.3

Particle C, pK_a = 2.4

Particle D, pK_{a1} = 2.2; pK_{a2} = 8.4

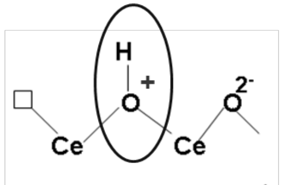
B C



IIA – bridged OH ($3680\ cm^{-1}$)

I – terminal OH ($3700\ cm^{-1}$)

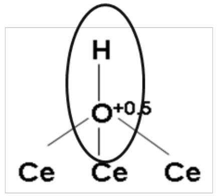
D



[O] vacancy, $3640\ cm^{-1}$

IIB – bridged OH next to a vacancy

D



III - triple-bridged OH ($3470\ cm^{-1}$)

Basic sites, pK_a = 7–10

Acidic sites, pK_a = 3–4

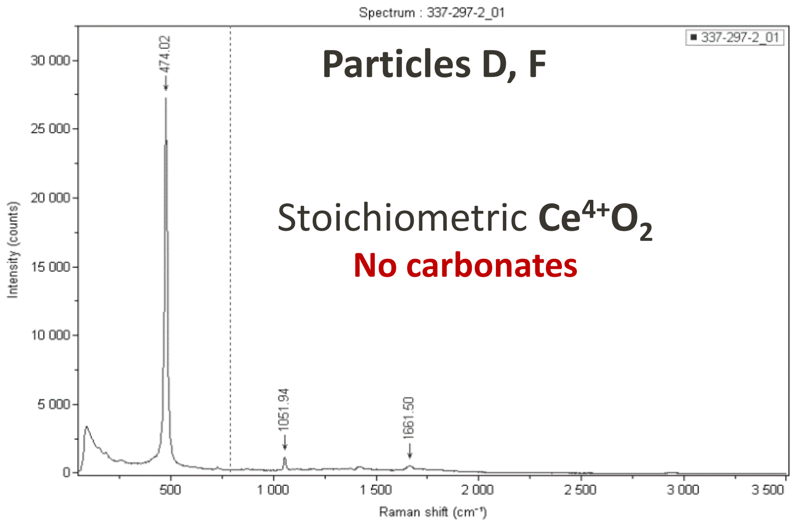
-Ce- HO_2 + OH ⟷ -Ce – OH + H_2O (I)		**PK_{a1} : 8–10 most basic**
-Ce- HO_2 + OH ⟷ -Ce – OH + H_2O (IIA, IIB)		**PK_{a2} : 4–7**
-Ce- HO_2 + OH ⟷ -Ce – OH + H_2O (III)		**PK_{a3} : <3- most acidic**

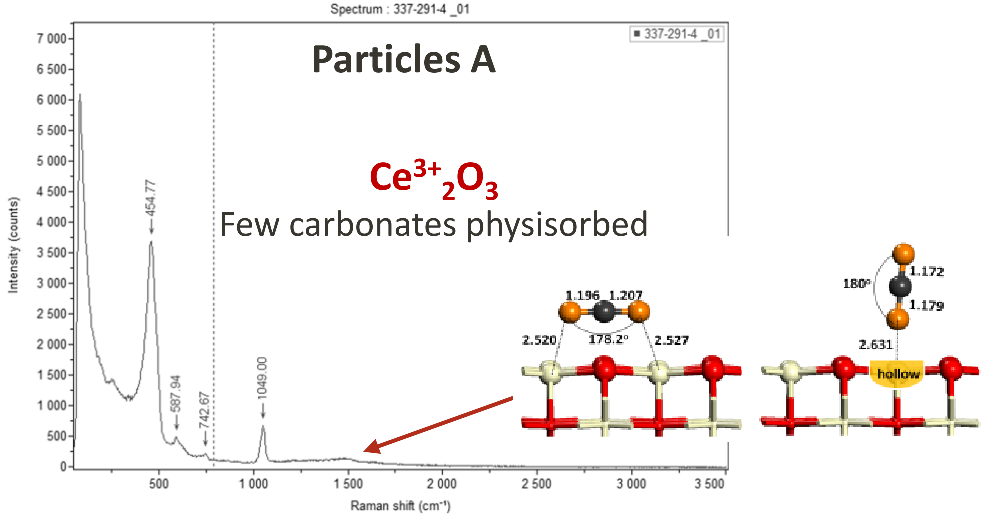
1. Christoph T. Nottbohm, Christian Hess, Catalysis Communications 22 (2012) 39–42

Entegris

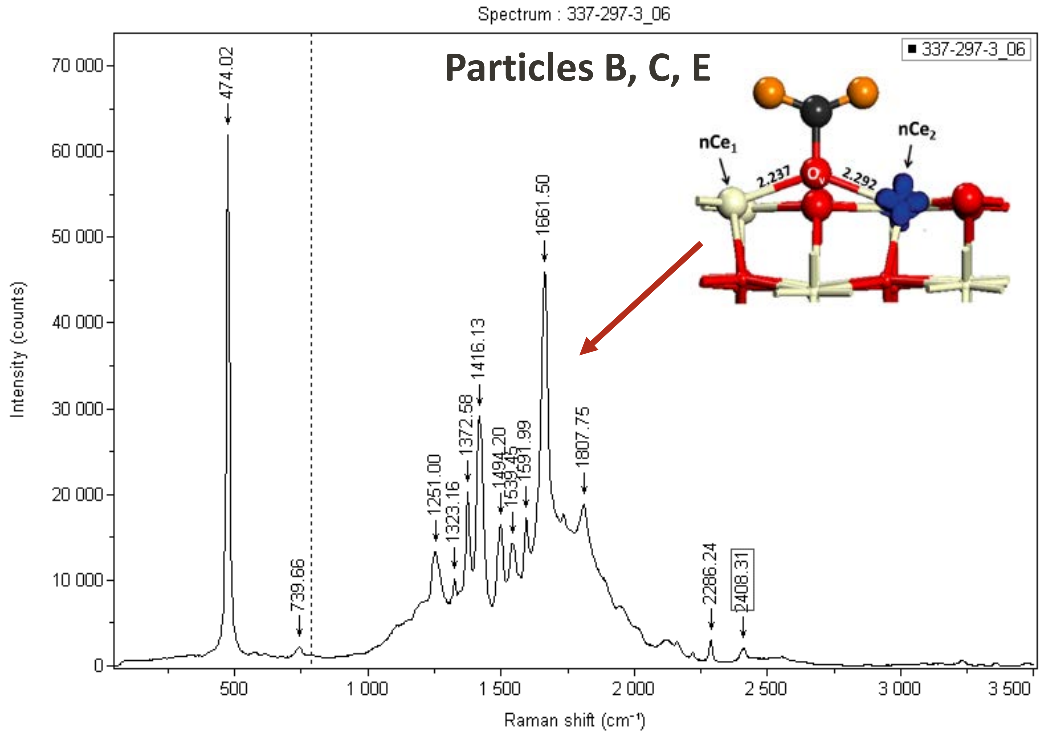
TYPES OF CeO_2 SURFACE GROUPS

B. Carbonates on reduced and stoichiometric ceria nanoparticles[2] (RAMAN)





Expect different CMP (RR) and post-CMP cleaning behavior!

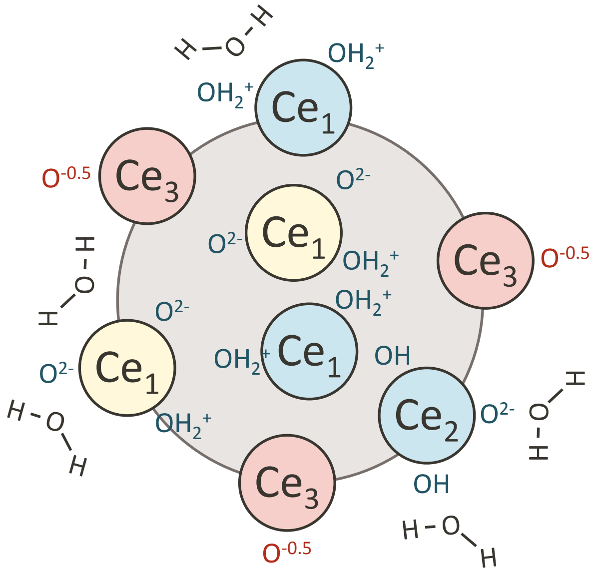


Reduced CeO_x – CO_2 chemisorption → unidentate/bidentate carbonates

2. E. E. Benson, C. P. Kubiak, A. J. Sathrum, and J. M. Smieja, Chemical Society Reviews 38, 89 (2009).

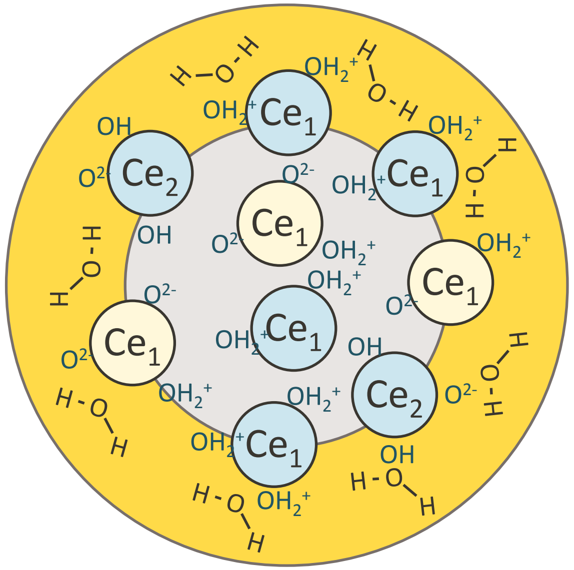
DIFFERENT CLEANING FORMULATIONS FOR DIFFERENT CERIA SURFACE CHEMISTRIES?

Particles E, F



- More acidic surface, partially hydroxylated
- Small amount of surface water H-bonded
- Surface exposed –OH for -Si-O- condensation
- Stronger Ce-O-Si bonds, difficult to break/clean

Particles B, C, D



- More basic surface, more hydroxylated
- Outer-sphere shell of H-bonded water
- Reduced surface reactivity
- Weaker Ce-O-Si bonds, easier to break

Based on the FTIR-ATR UV-VIS and tritation experiments data

CERIA REACTS WITH H_2O_2 BY BOTH REDUCTION AND OXIDATION MECHANISMS

$CeOH^{3+} + H^+ + e \rightarrow Ce^{3+} + H_2O$ … Ered = +1.715 V

$H_2O_2 \rightarrow 2\ H^+ + O_2 + 2\ e$ … Eox = -0.695 V

Ered + Eox > 0, reaction can proceed

Reduction of Ce^{4+} to Ce^{3+}
Oxidation of H_2O_2 to O_2

$Ce^{3+} + H_2O \rightarrow CeOH^{3+} + H^+ + e$ … Eox = -1.715 V

$H_2O_2 + 2\ H^+ + 2\ e \rightarrow 2\ H_2O$ … Ered = +1.776 V

Eox + Ered > 0, reaction can proceed

Oxidation of Ce^{3+} to Ce^{4+}
Reduction of H_2O_2 to H_2O

Commodity cleaners as controls

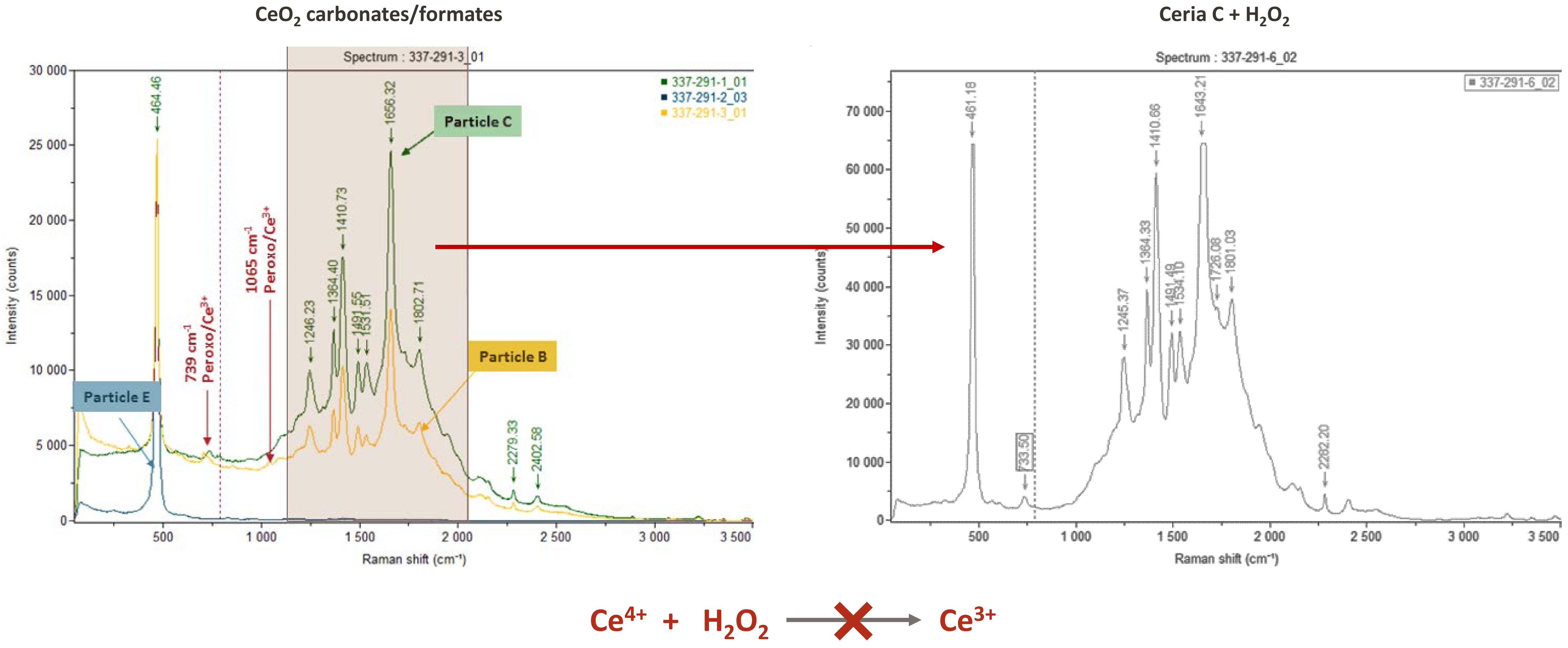
- **SC-1** - H_2O:**H_2O_2**:NH_3 (1:1:5)
- **SPM** – H_2SO_4:**H_2O_2** (1:4), T > 100°C

↓

Why **H_2O_2?**

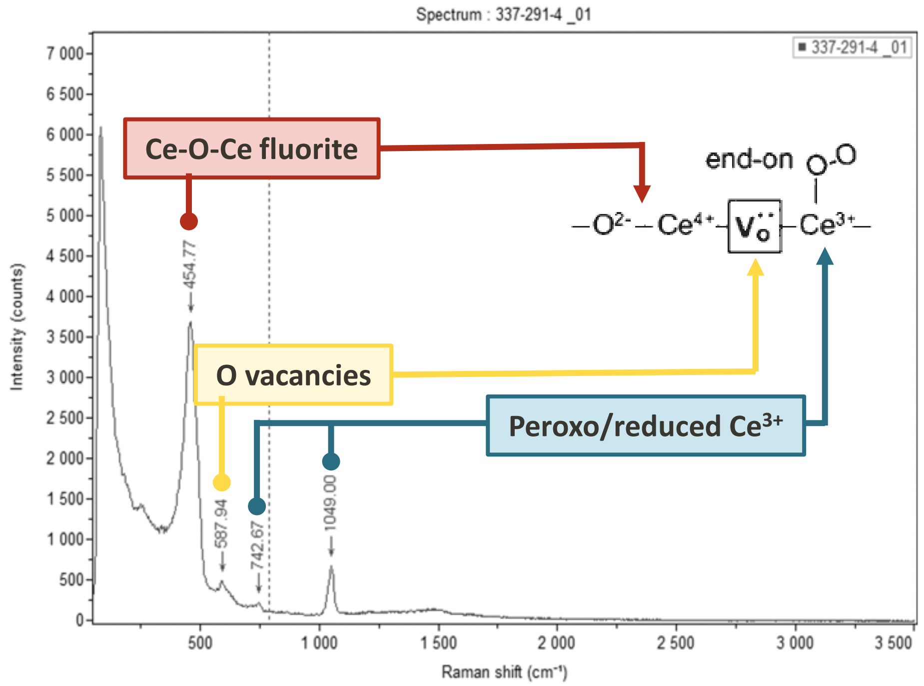
RAMAN SPECTRA FOR BIG CERIA PARTICLES C (>100 nm) IN REACTION WITH H_2O_2/SC-1

No changes on the surface ration Ce^{4+}/Ce^{3+} upon addition of SC-1/H_2O_2

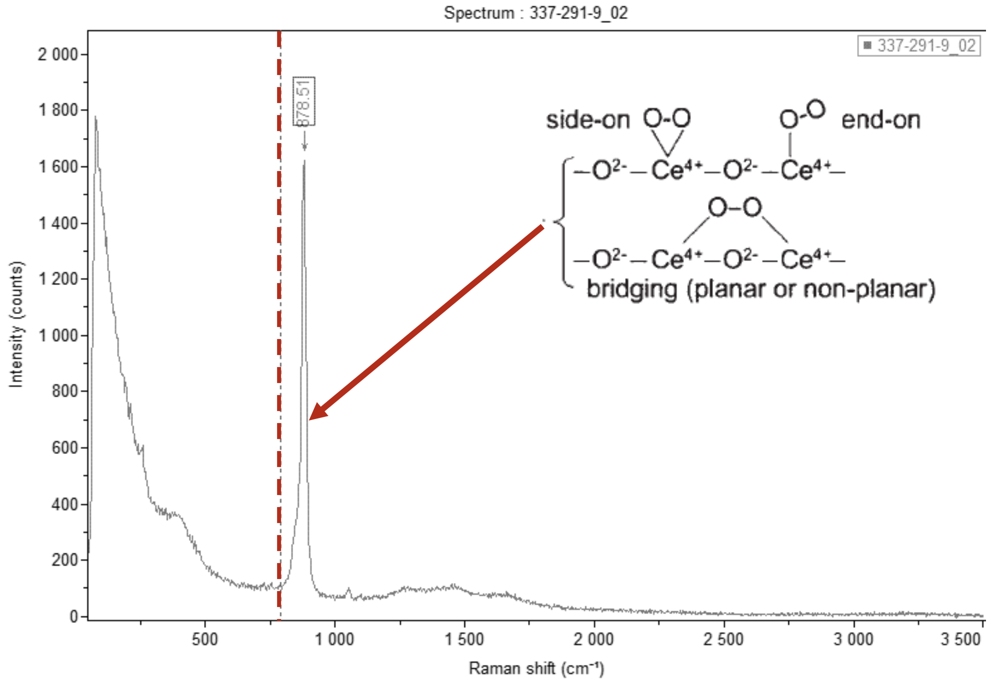


RAMAN SPECTRA FOR SMALL CERIA PARTICLES A (15 nm) IN REACTION WITH H_2O_2/SC-1

Before H_2O_2 addition



After H_2O_2 addition



- Reduced fluorite $Ce^{4+}O_2$ surface species
- Vo.. Vacancies
- Peroxo/reduced Ce^{3+} species

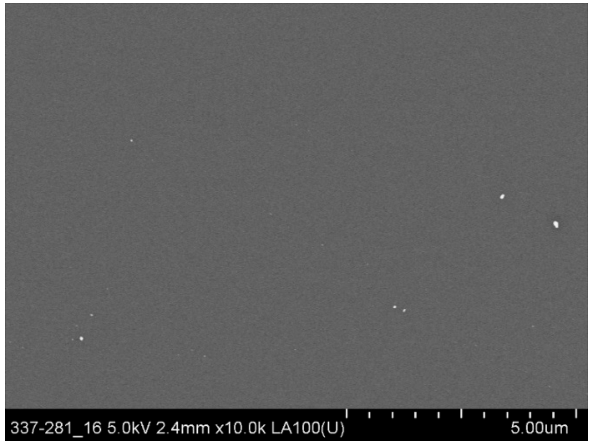
+ H_2O_2

$Ce^{3+} \rightarrow Ce^{4+}$

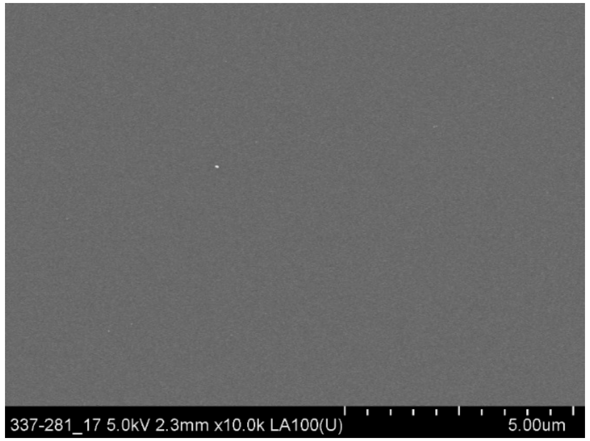
- Fully oxidized Ce^{3+} to Ce^{4+} (only peroxo-Ce^{4+} species)
- No Vo.. vacancies
- No remaining Ce4+-O2--Ce^{4+} fluorite structure
- No remaining reduced peroxo-Ce^{3+} species

THE NEGATIVE EFFECT OF H_2O_2 IN COMMODITY CLEANERS ON DIELECTRIC SUBSTRATES

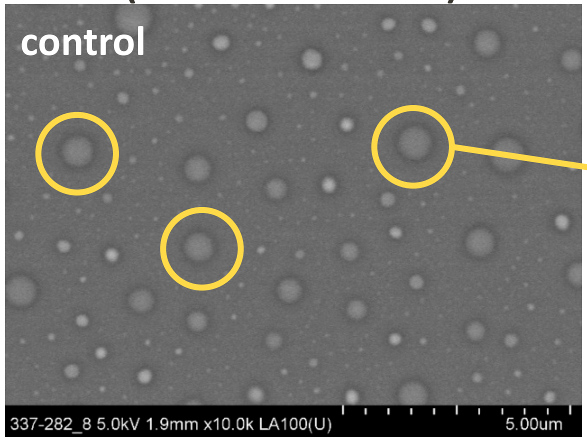
PETEOS/Ceria E/ PlanarClean AG Ce-XXXX-3

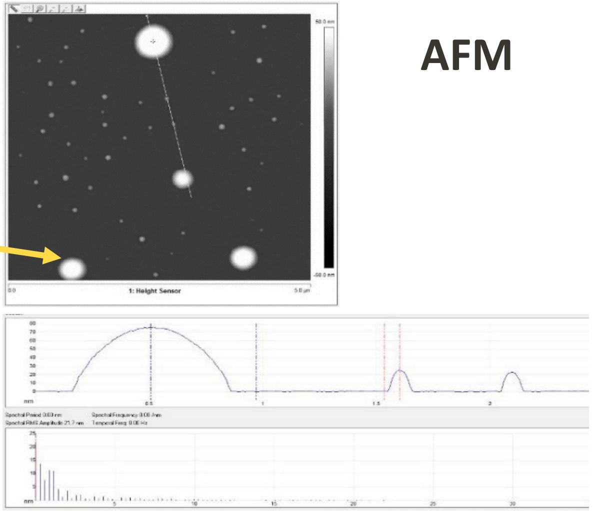


PETEOS/Ceria E/ PlanarClean AG Ce-



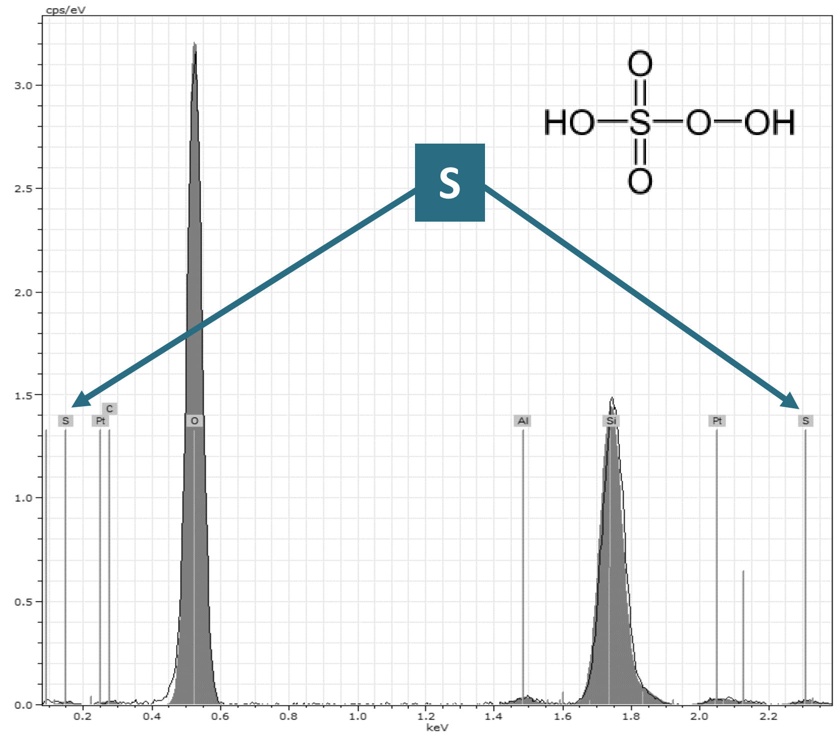
PETEOS/Ceria E/ (dHF + SC-1 + SPM)





AFM

SEM-EDX



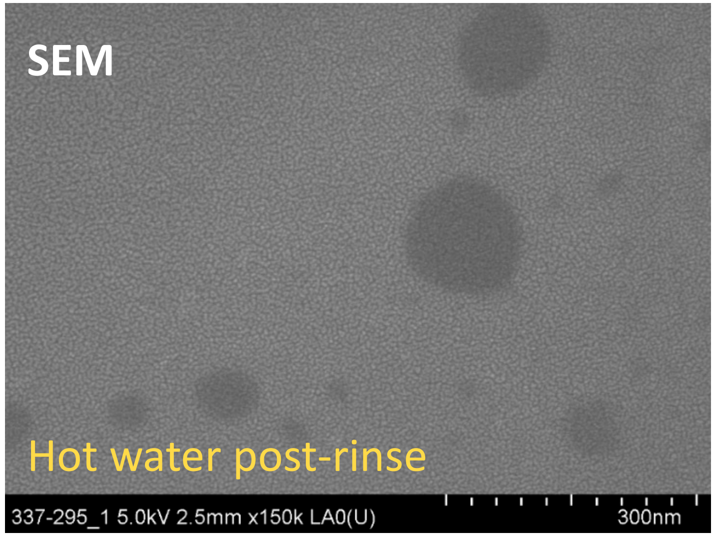
- S spherical deposits from peroxymonosulfuric acid
- PETEOS surface damaged after H_2O hot rinse
- PlanarClean AG Ce-XXXX-1 and -3 leave very clean, undamaged PETEOS surfaces

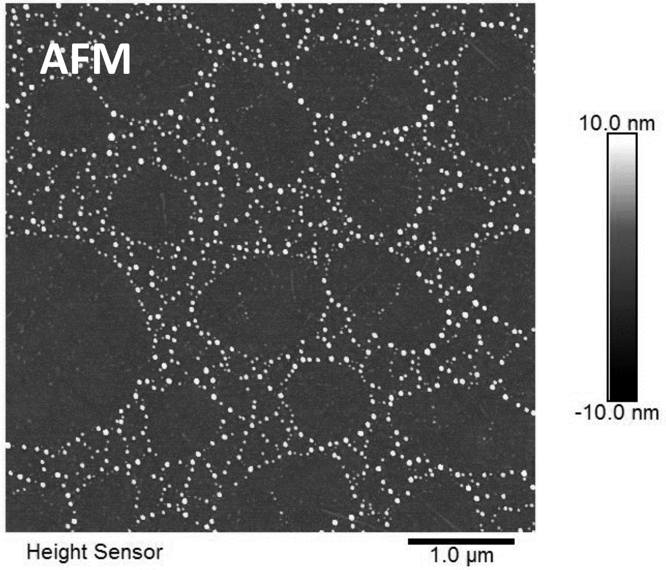
Entegris

PETEOS SURFACE DAMAGE POST-SPM AND SC-1 CLEANED & POST-RINSED WITH HOT WATER

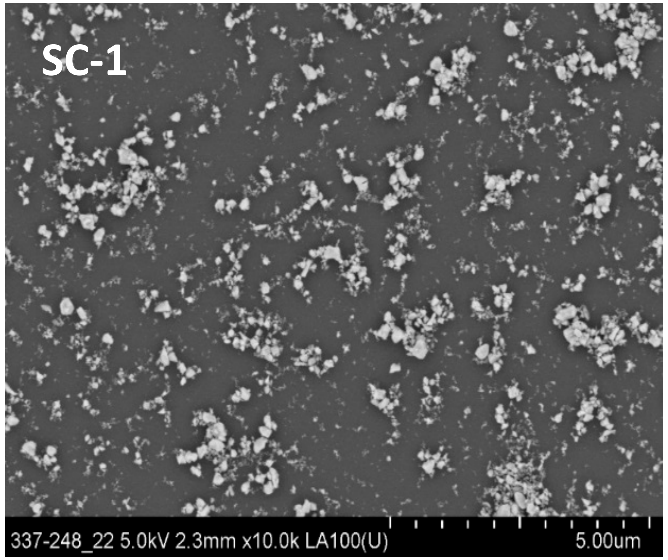
Damaged/etched surface

PETEOS/Ceria E/(dHF + SC-1 + SPM)





Agglomerated ceria particles



Commodity cleaners such as hot SPM and SC-1 potentially damage and leave agglomerated ceria particles and residue on dielectric surfaces

Entegris

PLANARCLEAN AG CE-XXXX FORMULATION ADDITIVES LIST – FUNCTION AND MECHANISM

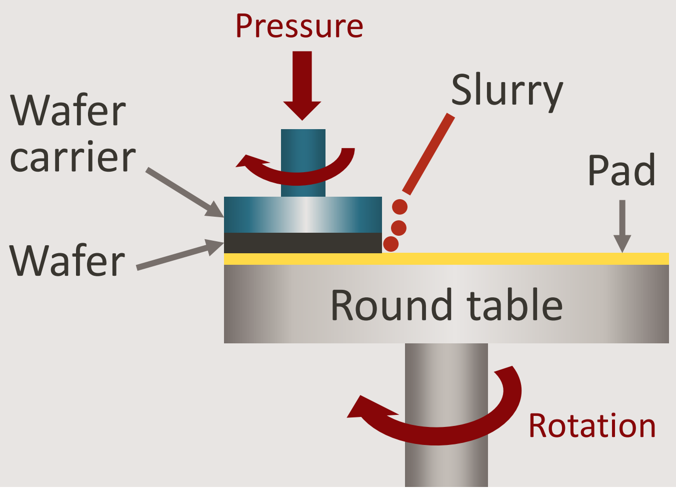
Component	Function	Mechanism
A	Non-TMAH pH adjustor	◦ Provides the hydroxyl anions and adjust pH needed for surpassing CeO_2 pH_{IEP} ◦ Ensures negative surface charge on both dielectric surface and ceria & organic contamination, by being adsorbed on inorganic and organic residues.
B	Complexing reagents Package	◦ Adsorption at the ceria surface ◦ Stabilization of ceria particles via electrosteric repulsion, preventing agglomeration and re-precipitation
C	Bond-breaking reagent	- Ce - O - Si – C - Ce – OH + HO – Si -
D	Cleaning Additives Package	◦ Interacts with particles and dielectrics surfaces to prevent particles aggregation and organics re-deposition

EXPERIMENTAL PROCEDURE

Beaker-dip experiment

PETEOS → (CeO_2 particles A-E, *Beaker dip*) → Ceria contaminated substrate → (AG Ce-XXXX cleaner, *Beaker dip*) → Cleaned substrate

Polishing experiment



Ceria contaminated substrate → (Cleaner, *Beaker dip*) → Cleaned substrate

Metology for Characterization

- Dark Field Microscopy (DFM)
- ICP-MS
- SEM
- AFM
- TOF-SIMS
- XPS
- FTIR-ATR (Mechanism)
- Raman
- UV-VIS (Mechanism)
- NMR (Mechanism)

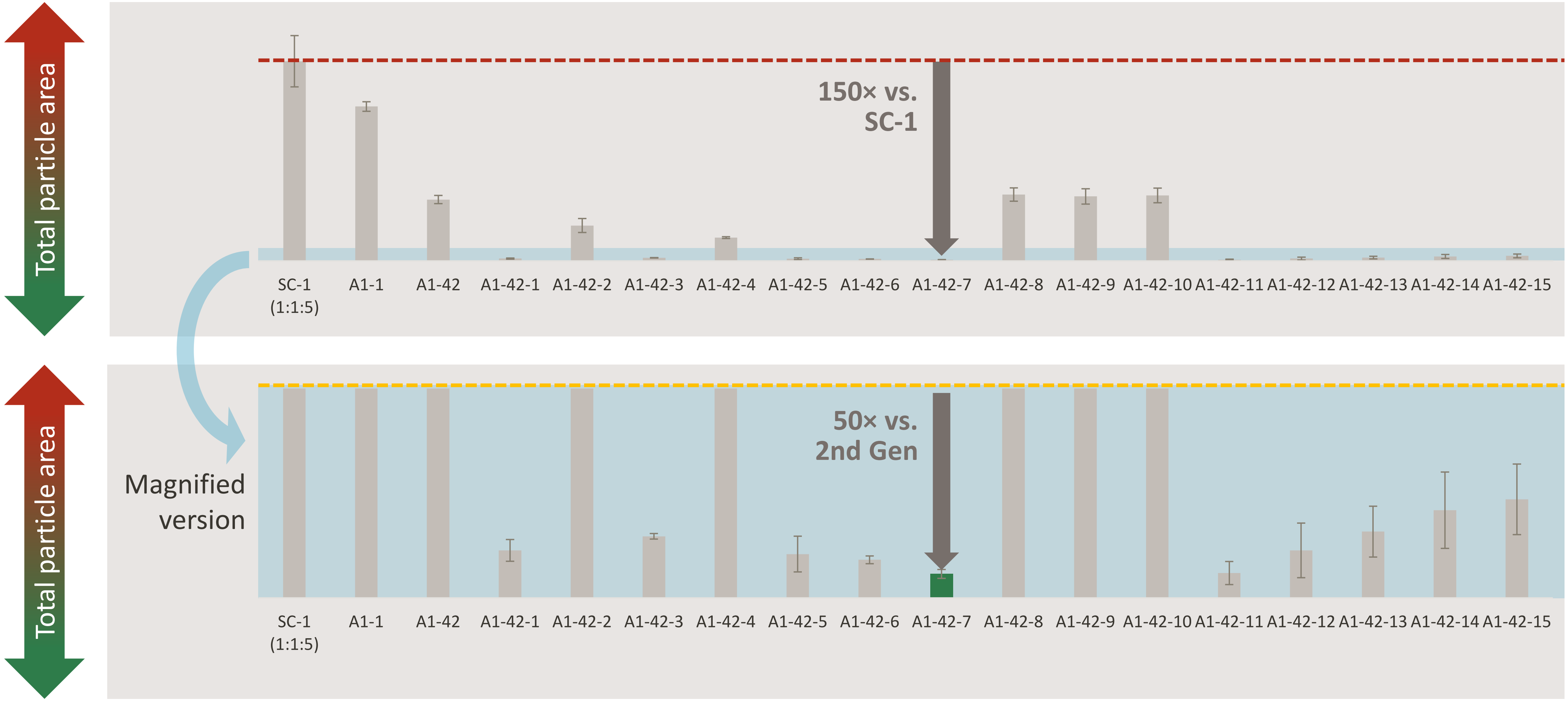
FORMULATION DEVELOPMENT (PERFORMANCE = CERIA CONTAMINATION AFTER CLEANING)

Dark Field Microscopy Data

2nd generation cleaner: 3.5× more efficient than SC-1 and 2× than the 1st generation

Entegris

3RD GEN PLANARCLEAN AG CE-XXXX-2 – 150× BETTER CLEANING PERFORMANCE VS. SC-1 (1:1:5)



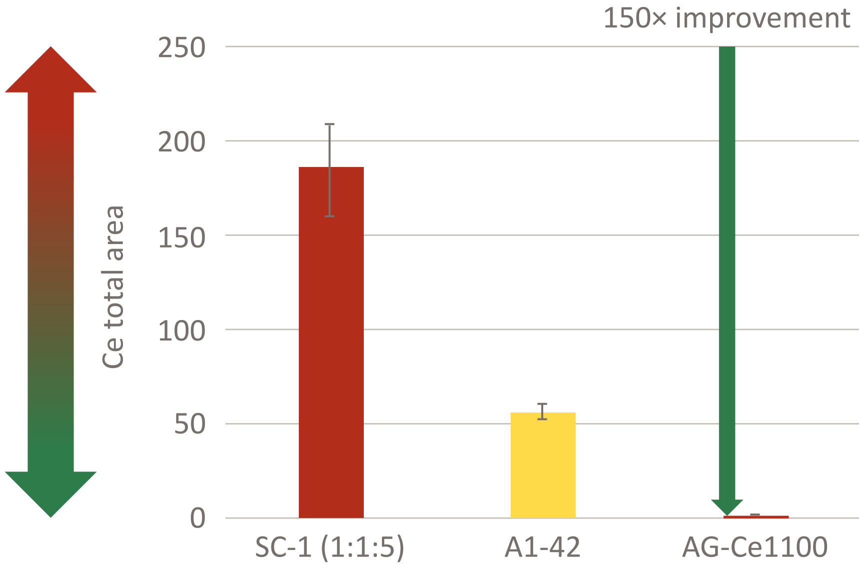
Developed cleaner showed extremely good performance – 150× better than SC-1

Entegris

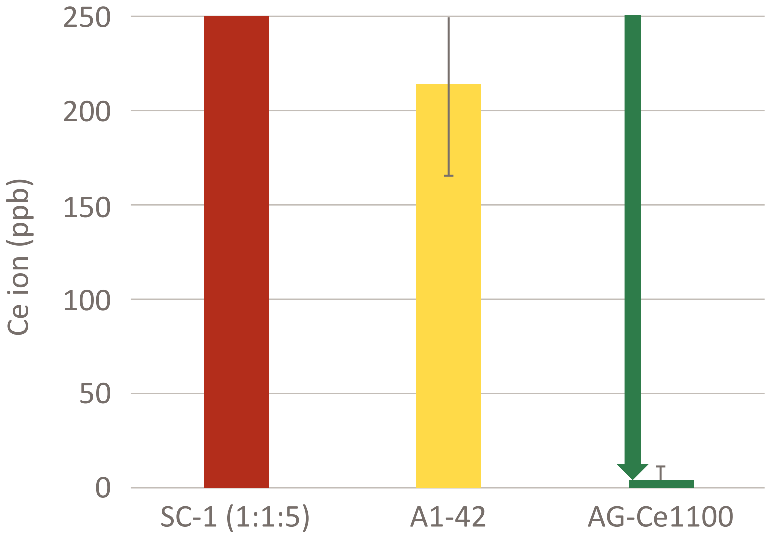
SEM AND ICP-MS CHARACTERIZATION

Process: Beaker dip/PETEOS/Particle C

Dark field microscopy



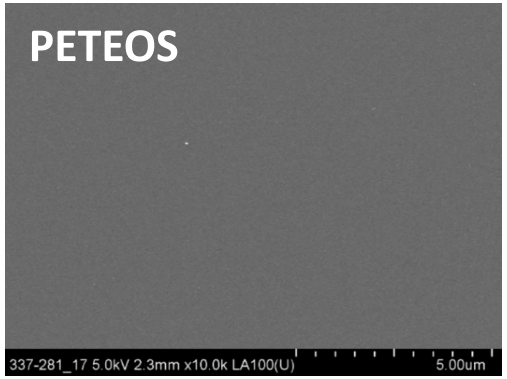
ICP-MS data

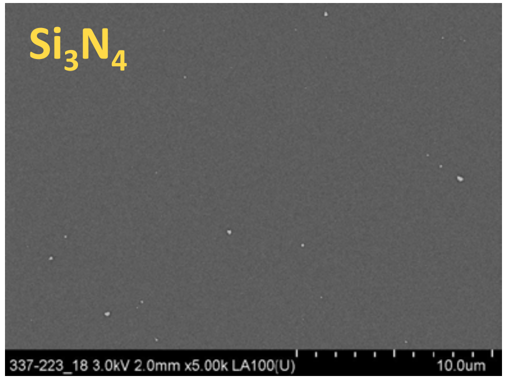


[Ce]/cm^2 = 1.23 × 10^{16}

[Ce]/cm^2 = 2.36 × 10^{13}

CMP/Ceria Slurry/
PlanarClean AG Ce-XXXX-2





- ICP-MS supports the dark field microscopy data and it shows >150× improvement over SC-1
- SEM data strongly supports DFM and ICP data

CONCLUSIONS

- Several low-pH and high-pH high-performance ceria cleaning formulation PlanarClean AG Ce-XXXX were developed at Entegris based on in-depth mechanistic understanding on silica-ceria surface interactions
- All ceria cleaning formulations contain complexing reagents, silica-ceria bond breaking reagents and dispersing reagents for particles agglomeration and re-deposition prevention
- Low-pH PlanarClean AG Ce-XXXX-2 and PlanarClean AG Ce-XXXX-3 formulations perform well on dielectric surfaces polished with both low- and high-pH ceria dispersions
- High-pH PlanarClean AG Ce-XXXX-1 ceria cleaning formulations perform best on dielectric surfaces polished with high-pH ceria dispersions
- We demonstrated that commodity cleaners such as hot SPM and SC-1 are the root cause for defective and damaged dielectrics surfaces, also highly contaminated with ceria aggregated particles
- PlanarClean AG Ce-XXXX formulations show improved ceria particles removal vs. commodities by as much as 150× (ICP-MS)

ACKNOWLEDGEMENTS

- Robin Van Den Nieuwenhuizen – brainstorming and financial support
- Emanuel Cooper – brainstorming and consulting
- Changfeng Chen – Raman Spectroscopy
- Michele Stawasz – AFM and SEM-EDX
- Mike Deangelo – SEM Characterization
- Wonlae Kim – ICP-MS measurements
- Mike Owens – lab formulations, contact angle measurements
- Cuong Tran – marketing advice
- Fadi Coder – sales and marketing advice