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20TH SURFACE PREPARATION AND CLEANING CONFERENCE (SPCC) – 2018

Fundamentals of Post-CMP Cleaning of Dielectric Surface Contaminated with Ceria (Nano-to-Micro) Particles

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AGENDA

01 Fundamentals of Ceria-Silica CMP Process

02 Reactivity Between Ceria and SiO_2 and Si_3N_4

03 Commodity Cleaner vs. Formulated Cleaners

04 Formulation Design Concept and Components

05 Ceria Cleaning Mechanism – Spectroscopic Evidences

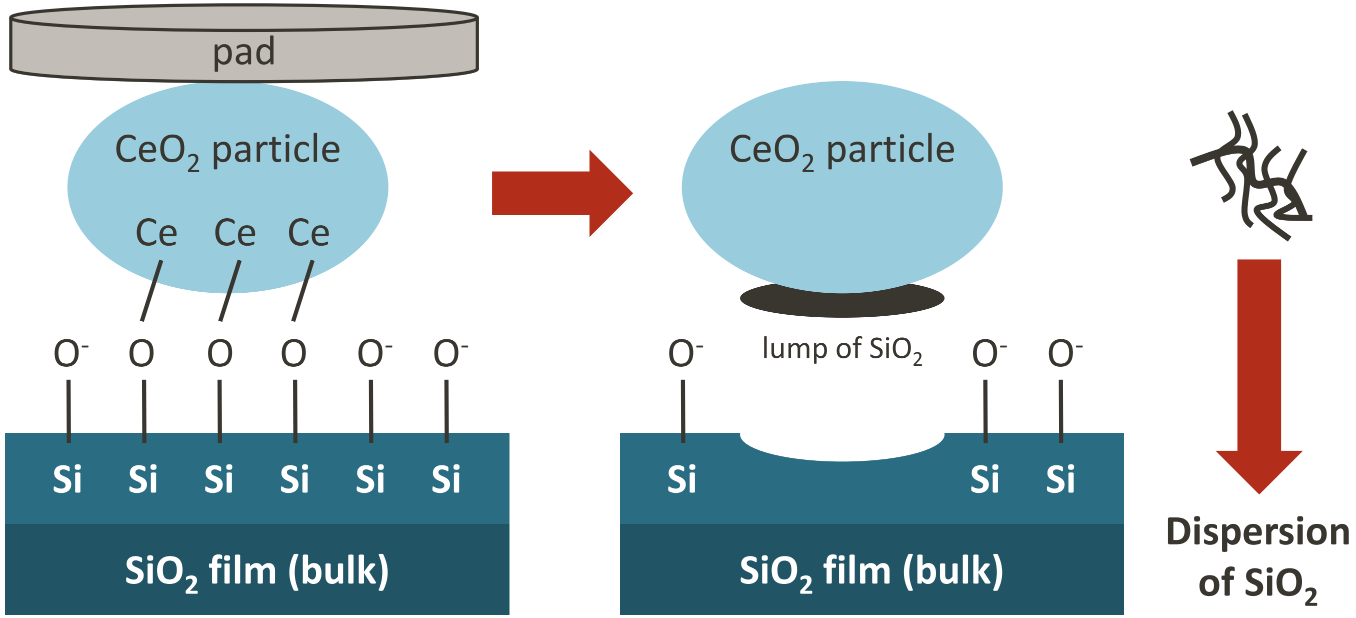
06 Positive vs. Negatively Modified Ceria Cleaners

07 Entegris Recommendations

08 Conclusions

POLISHING OF SiO_2 FILMS BY CeO_2 PARTICLES – PROPOSED MECHANISM

Ceria – CMP process



Overall reaction

$$R-Si-OH + Base \longrightarrow R-Si-O^- + BaseH^+$$

$$R-Si-O^- + HO-Ce-R' \longrightarrow R-Si-O-Ce-R' + OH^-$$

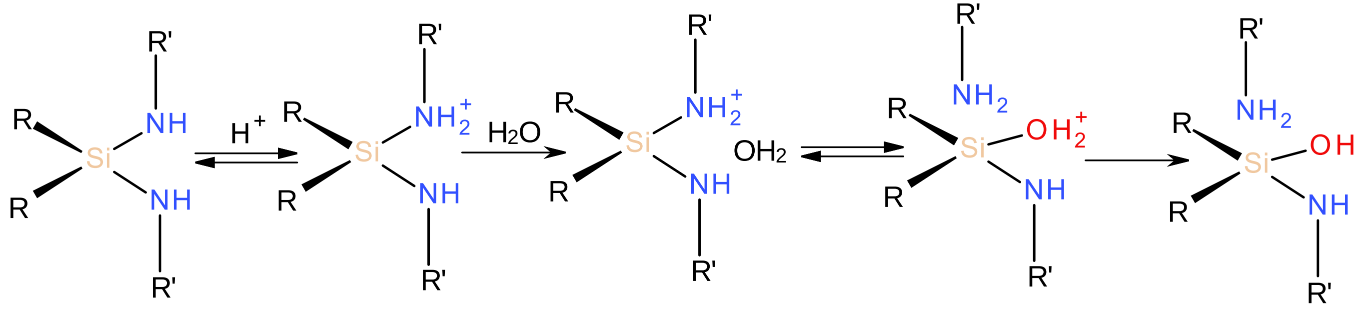
- Key steps and factors determine silica removal:
  - Si–O–Ce bond formation
  - Particle size distribution
  - Hydrodynamic forces acting at the interface
  - Pad properties
  - Fluid Rheology
- Challenges:
  - CMP doesn’t always remove Si – O – Ce from surface
  - An effective post-CMP formulation needed to clean the surface

Ref: T. Hoshino et al. / Journal of Non-Crystalline Solids 283 (2001) 129-136

REACTIVITY BETWEEN CERIA AND SILICON NITRIDE (WHY MODIFY CeO_2?)

CeO_2–Si_3N_4 surface interactions (3 key steps)

Step 1: Silicon nitride hydrolysis

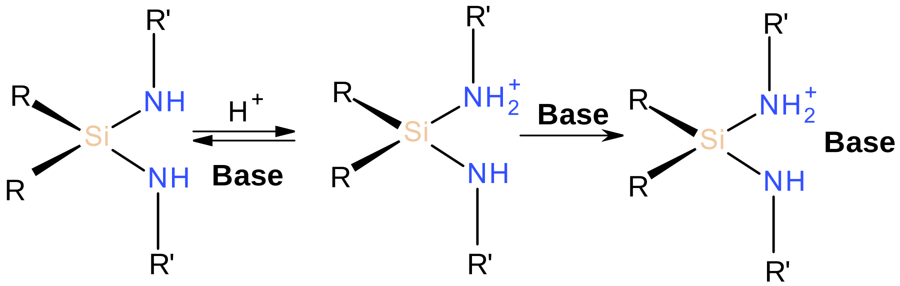


R = subsurface neighboring atom
R' = surface atom covalently bonded to nitrogen (silicon or hydrogen)

Step 2: Reaction of the surface silanols/oxoanions

Step 3: Removal of the surface oxide layer with ceria particle

Appropriate organic base can influence silicon nitride hydrolysis



- Organic base can create a new acid-base equilibrium
- Deprotonate the surface amide
- Site-block water from silicon metal

CeO_2 is modified with appropriate organic base to tune the Si_3N_4 removal

T. P. Johns et al. Electrochemical and Solid-State Letters, 8 q8r G218-G221 (2005)

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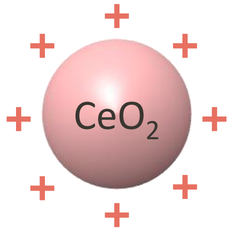
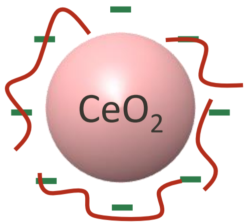
WHY FORMULATED CERIA CLEANERS VS. COMMODITY?

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

Positive Ceria

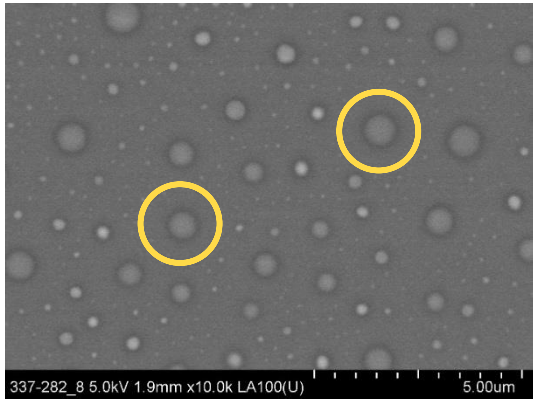


Negative Ceria



1. Many different ceria particles and chemistries are on the market
2. Cleaning challenges vary greatly depending on slurry type → no universal cleaner so far
3. **Best approach is for slurry supplier to collaborate directly with cleaning supplier and customer to develop the best BKM**

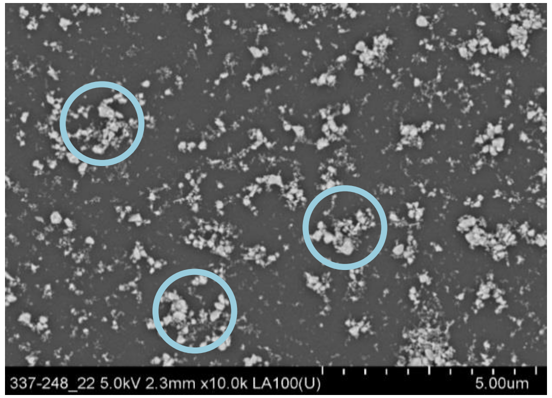
Process CMP/PETEOS/Ceria Particles



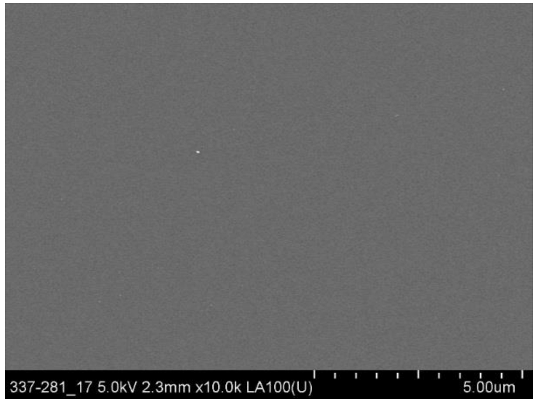
(dHF + SC-1 + SPM)

Commodity Cleaners Defects Particles

Process CMP/PETEOS/Ceria Particles

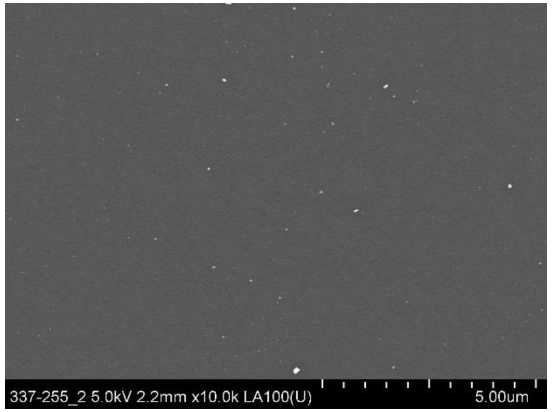


SC-1 (1:1:5)



PlanarClean AG Ce-XXXX-1

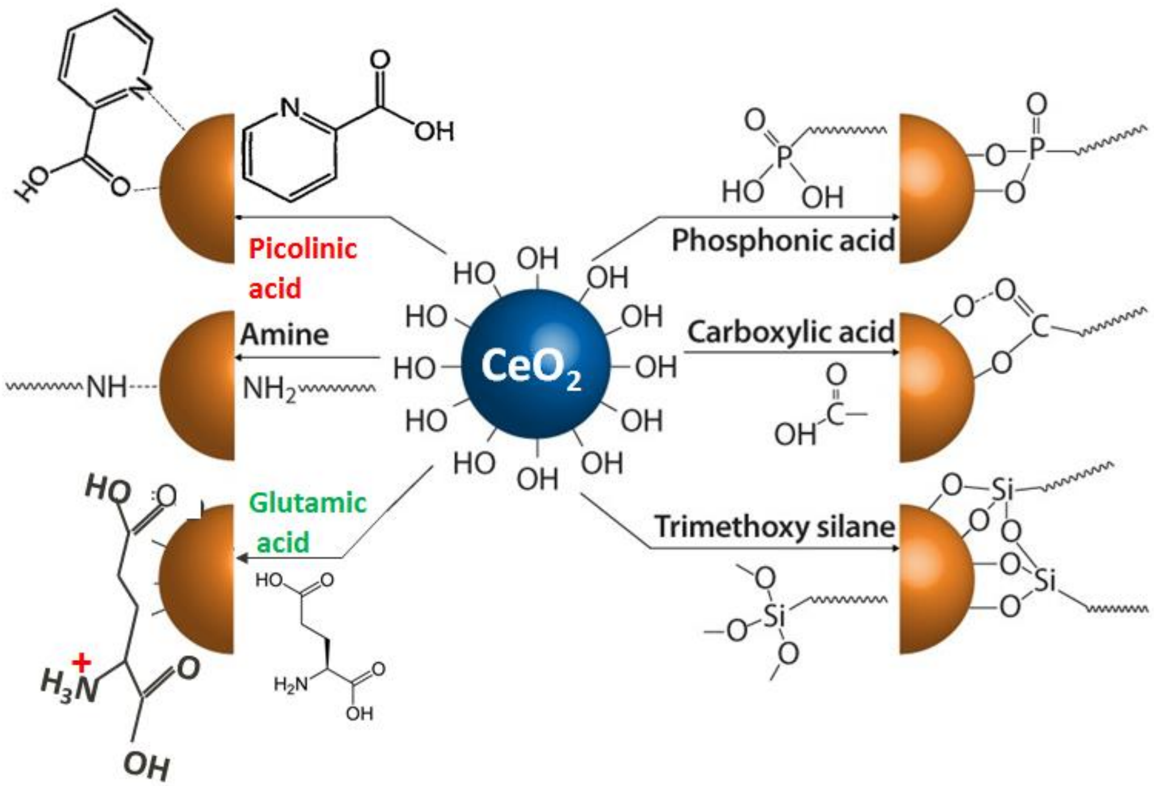
PlanarClean AG Ce-XXXX



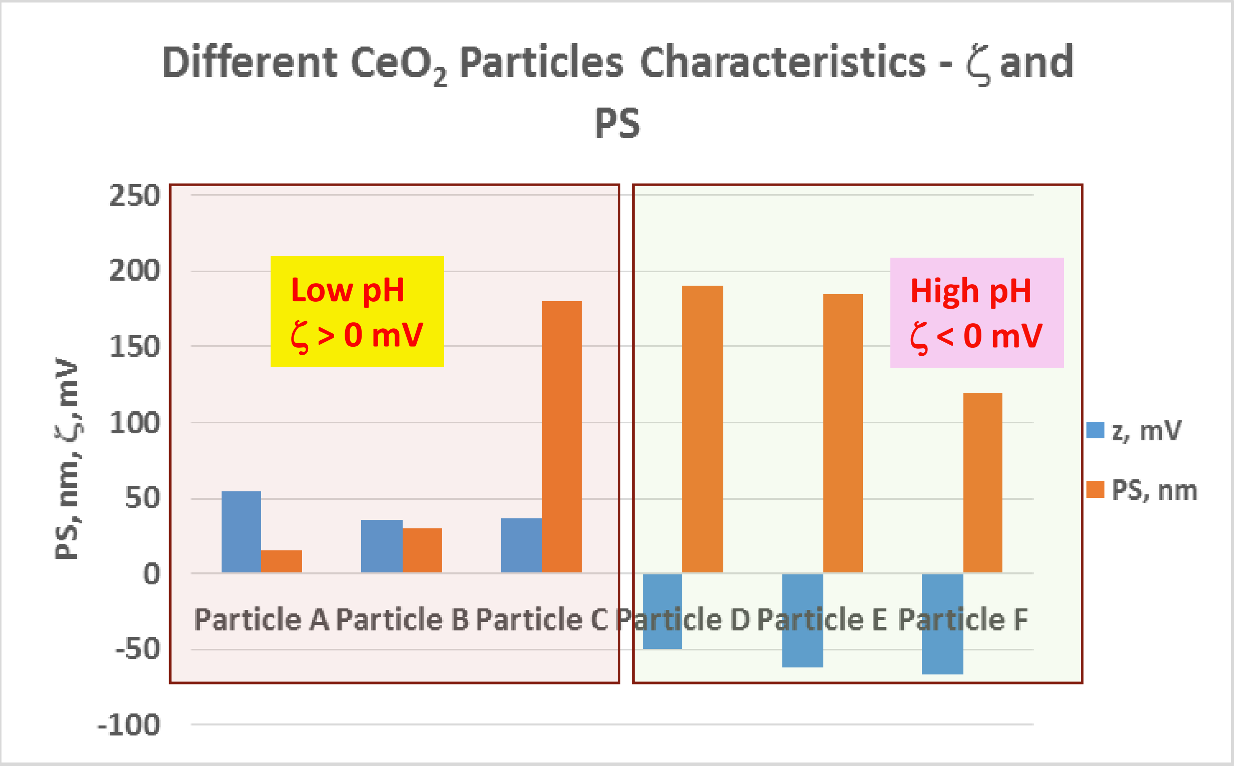
PlanarClean AG Ce-XXXX-2

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

Surface-modified ceria in CMP slurries



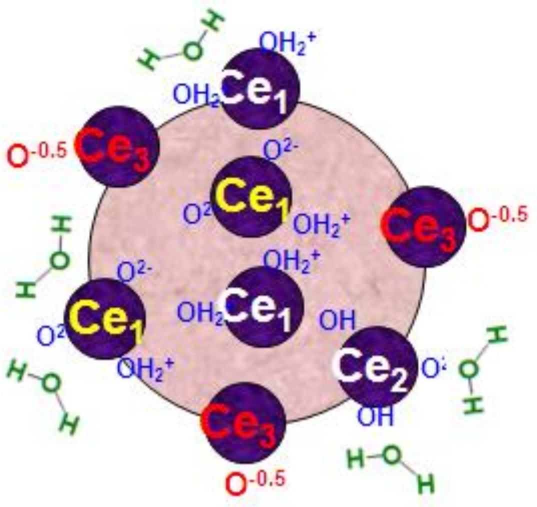
Various CeO_2 Particles Tested



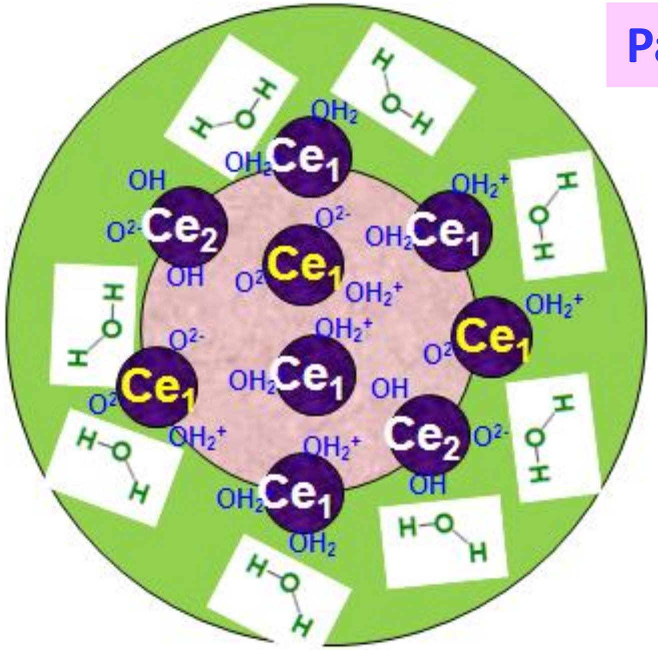
- Surface modified CeO_2 particles in the CMP slurries: positive or negative surface charge;
- Particle size: 15 – 200 nm;
- Need to understand CeO_2 surface chemistry and types of interactions with the dielectric surfaces;
- Six different types of CeO_2 particles tested – can we design an universal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

DIFFERENT CLEANING FORMULATIONS FOR DIFFERENT CERIA SURFACE CHEMISTRIES?

Particles E, F



Particles B, C, D

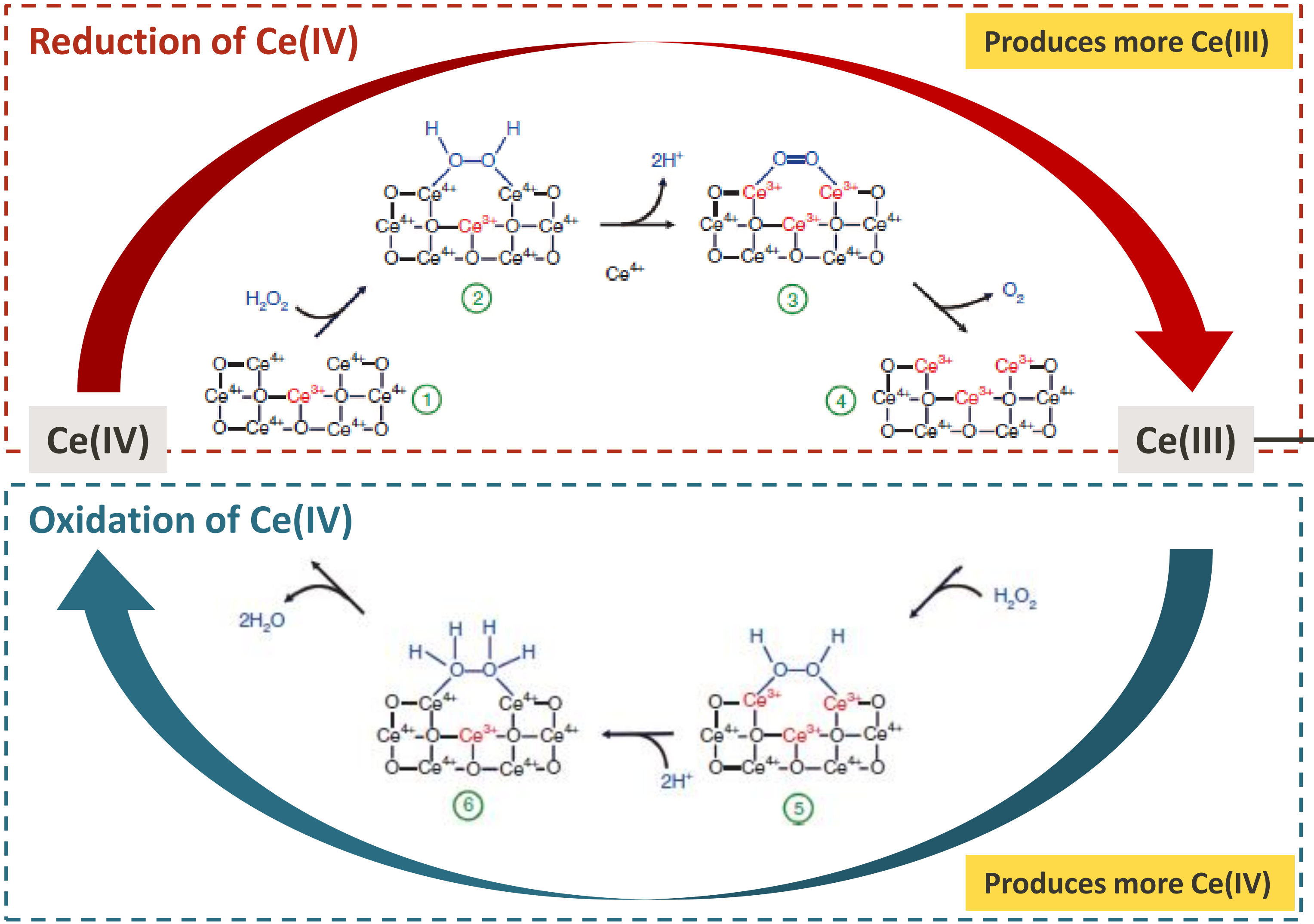


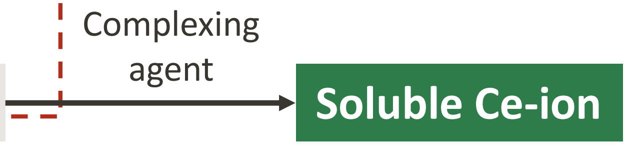
- More acidic surface, partially hydroxylated
- Small amount of surface water H-bonded
- Surface exposed –OH for -Si-O^- condensation
- Stronger Ce-O-Si bonds, difficult to break/clean

- 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 titration experiments data

HOW DOES THE COMMODITY CLEANER WORK? AN EXAMPLE





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

Drawback:

- H_2O_2 can attack to the dielectric
- Basic – H_2O_2 dissolve more oxide
- SPM – additional step needed for leftover sulfur

Overall reaction

$$2\left[Ce^{(IV)}-O-Si\right] + H_2O_2 \longrightarrow 2\left[Ce^{(III)}-O-Si\right] + 2H^+ + O_2$$

H^+ | Complexant (C) ↓

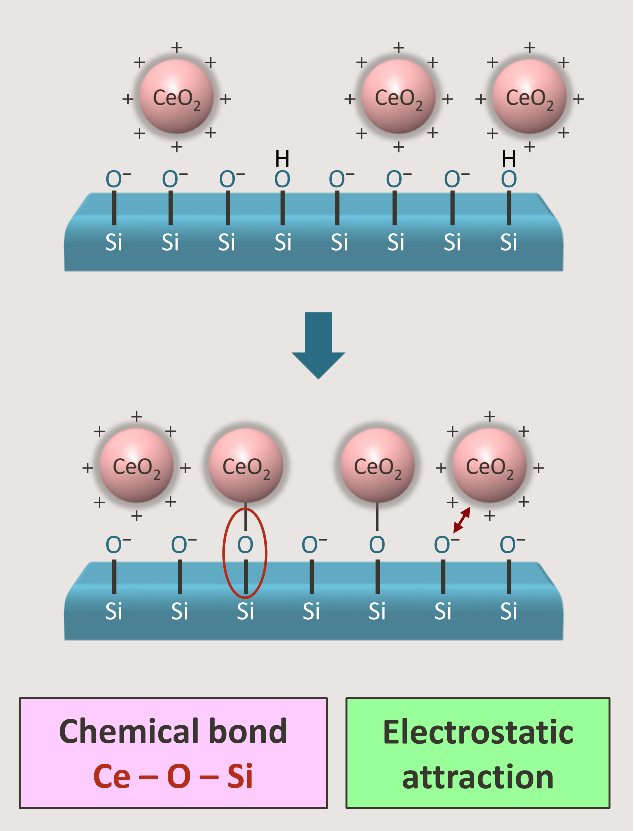
$$\left[Ce^{(III)}-C\right] + HO-Si$$

soluble

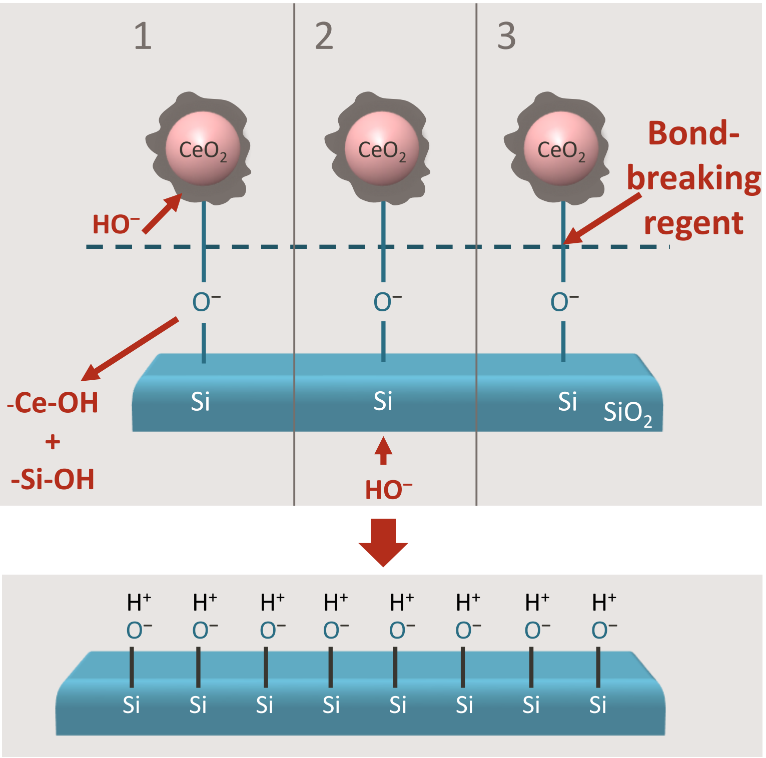
Wei-Tsu T. et al. Journal of Solid state Science and Technology, 6 (10) P7118

SURFACE INTERACTIONS AND KEY BOND-BREAKING STEPS

CeO_2-SiO_2 Surface Interactions



Ce-O-Si Bond-Breaking Mechanisms



Cleaning formulation (low or high pH) can be designed based on types of ceria and its interaction to the surface

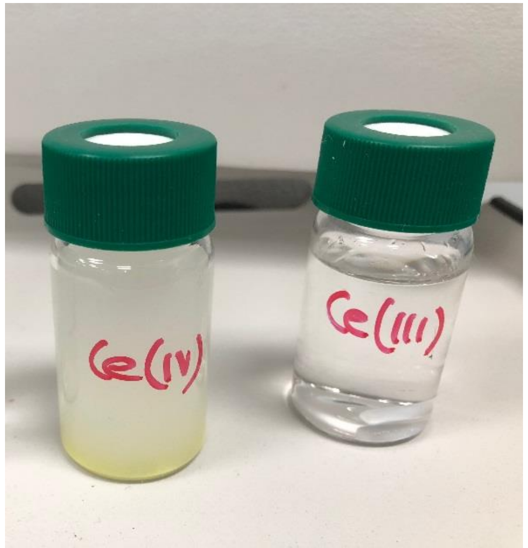
Three possible options:

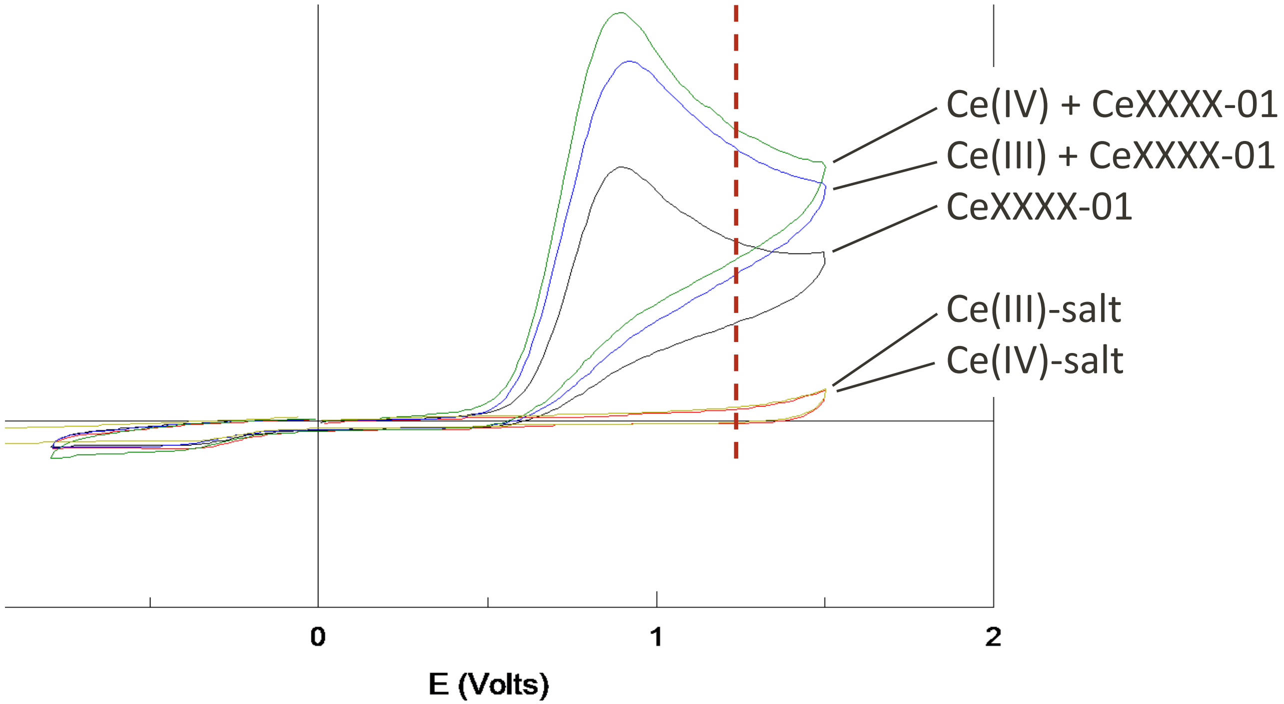
1. Nucleophilic attack of OH- to Ce-center
2. Partial etch of the surface
3. Breaking of (CeO_2)–SiO_2 bond

Formulation design concepts:

1. High pH hydrolysis of -Ce-O-Si- bonds by HO- nucleophilic attack to Ce-center
2. Additives needed to stabilize –Ce-OH species and prevent redeposition
3. High pH partial etch/dissolution of the surface –Si-O-Ce- groups + redisposition prevention.
4. Low pH: Bond-breaking additives, followed by CeO2 complexation, and particles stabilization and dispersion

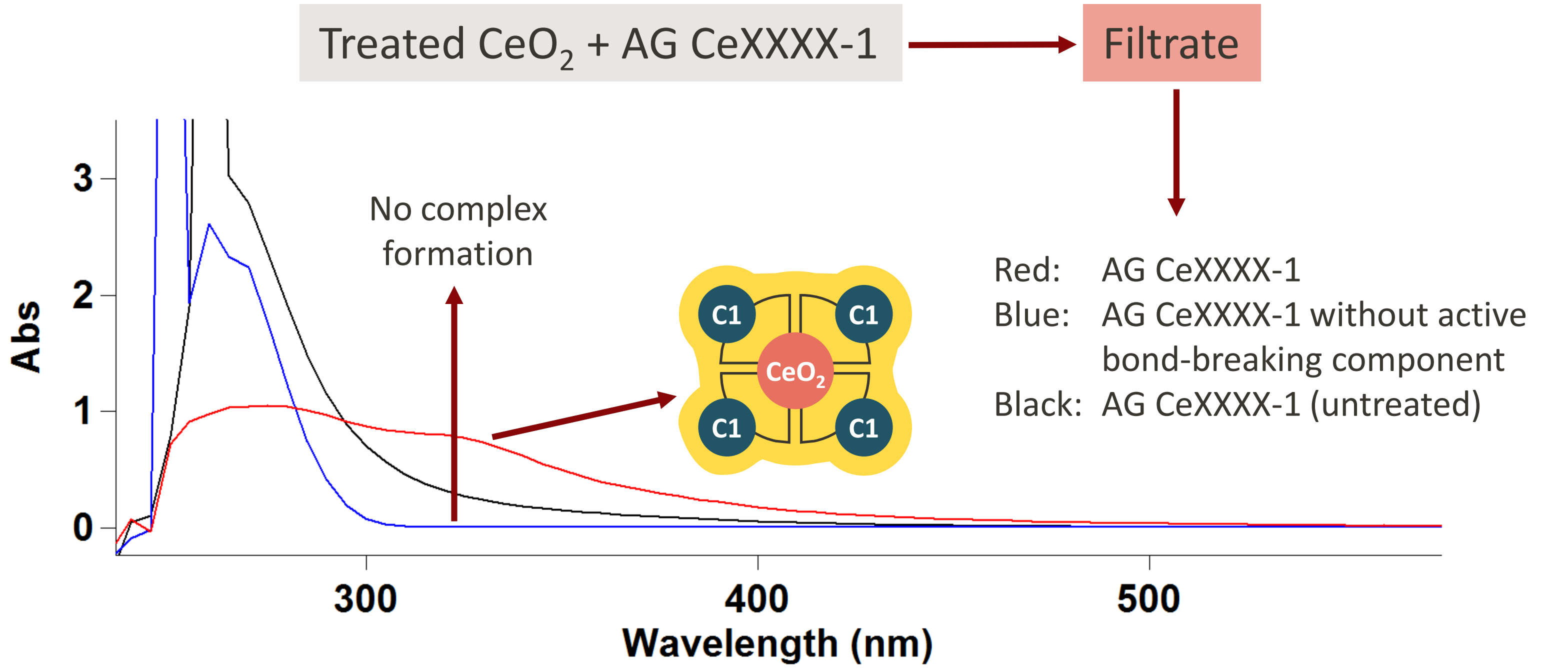
INTERACTIONS OF CE(IV) AND CE(III) SALTS WITH CEXXXX-01: MONITORED BY CV EXPERIMENT





- Ce(IV)/Ce(III) redox couple can't be detected in the solvent potential range
- CeXXXX-01 redox wave remains unchanged after the treatment with Ce(III) or Ce(IV) salts
- Redox property of CeXXXX-01 component remains active for Si – O – Ce bond breaking

SPECTROSCOPIC EVIDENCE OF ACTION OF BOND-BREAKING COMPONENT

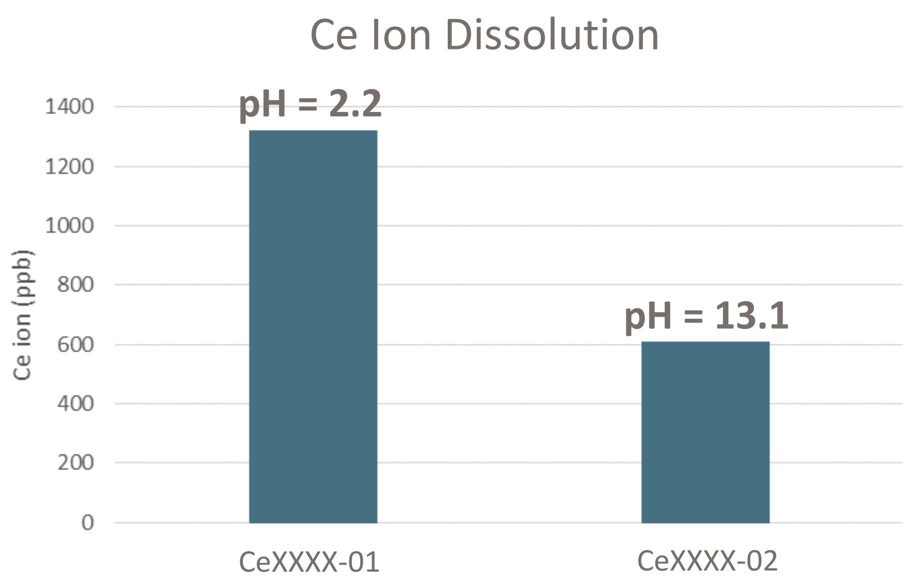


Samples were collected after the PCMP process

Without the active bond-breaking component, no complex formation was observed, indicating component helps to keep the ceria soluble

LOW PH FORMULATION DEVELOPMENT

CeO_2 (powder) + Formulation

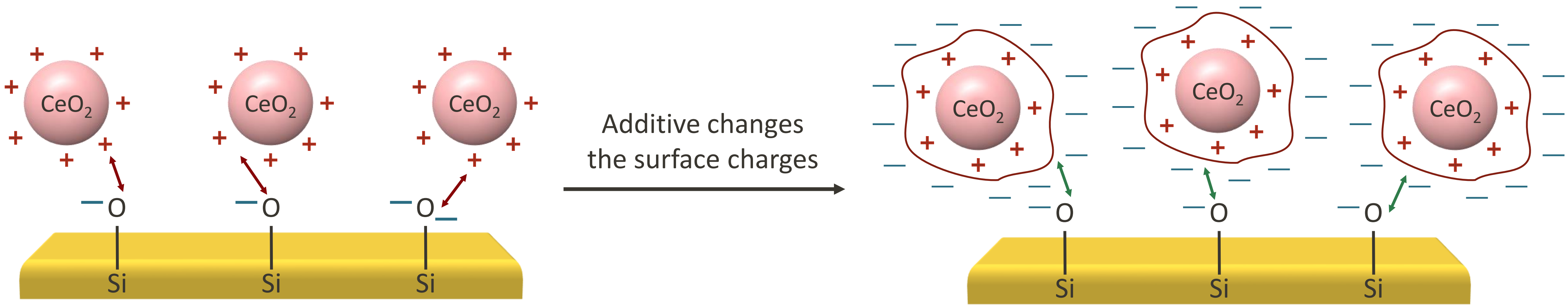


- Purpose
  - Ceria particle dissolution comparison
- Test conditions
  - CeO_2 powder (from Aldrich)
  - Chemistry: CeXXXX-01, CeXXXX-02
  - Chemistry dilution (100:1)
  - Procedure
    - Add CeO_2 in chemistry
    - Stir for 15 min
    - Filter the powder
    - ICP MS analysis for Ce ion

CeXXX-01 and CeXXX-02 can dissolve certain amount of Ceria powder

CeXXX-01 shows better Ceria powder dissolving than CeXXX-02

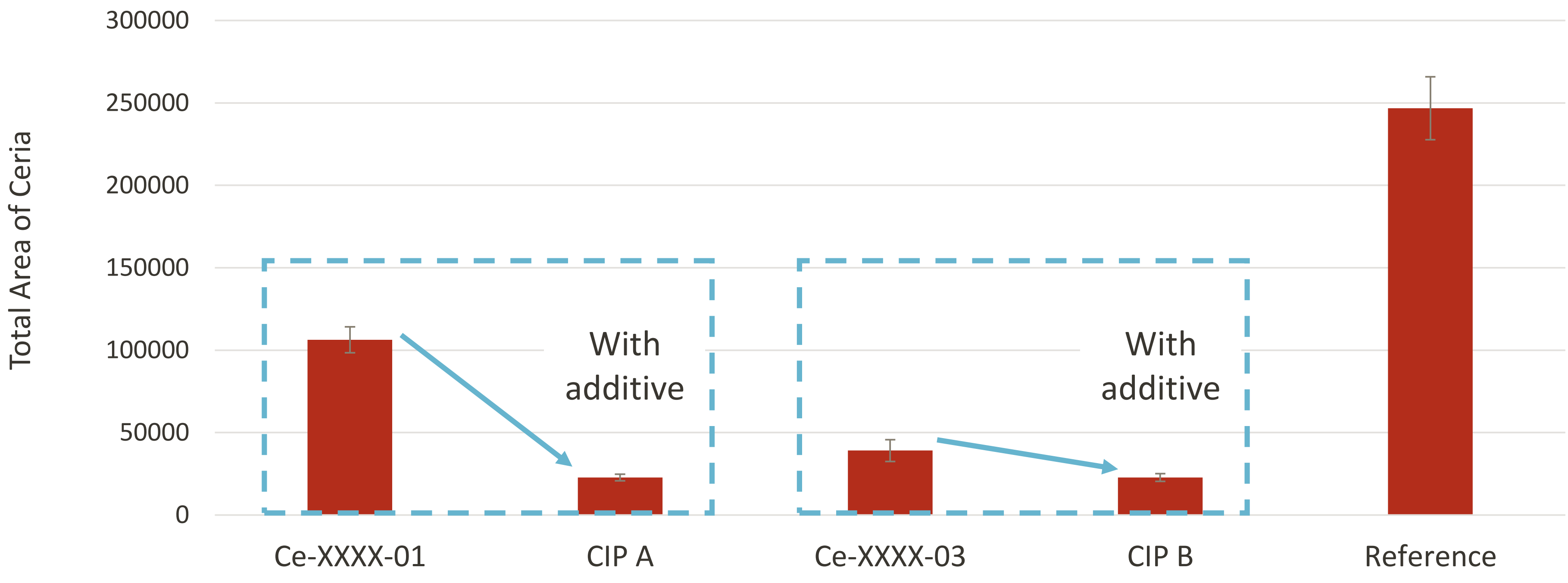
LOW PH FORMULATION FOR NEGATIVE CERIA



Strong ionic attraction leads to poor cleaning

Right additive changes the surface charges.
As a result, strong repulsion leads to better cleaning.

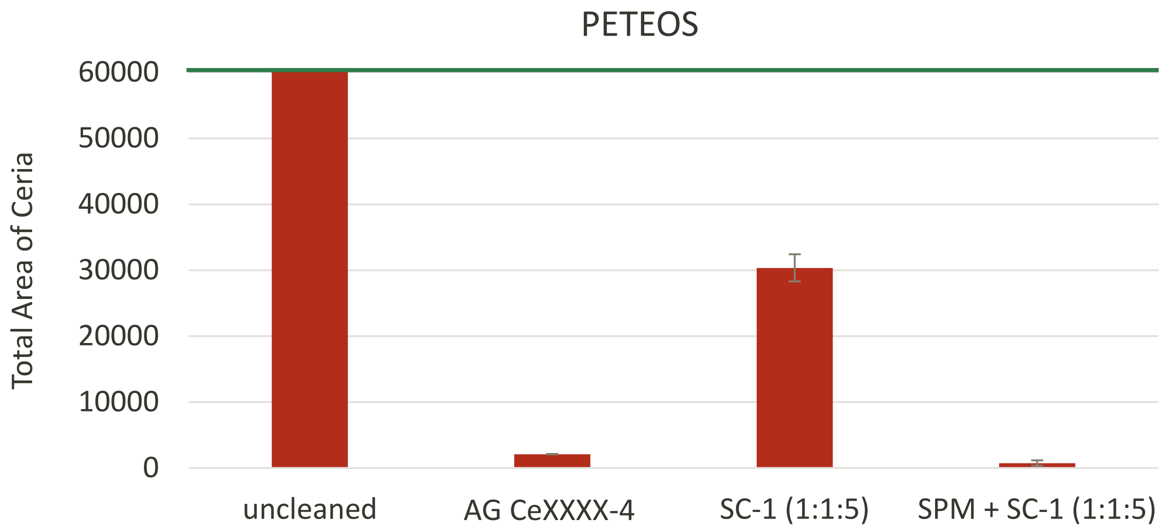
CLEANING PERFORMANCES WITH AND WITHOUT ADDITIVES



Cleaning additive has strong effect in changing the surface property of CeO_2 particles

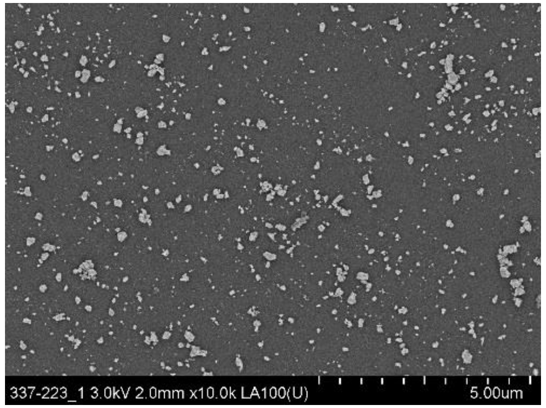
Choosing the right additive is one of the key steps to design efficient formulation

CLEANING OF POSITIVE-CeO_2 ON PETEOS

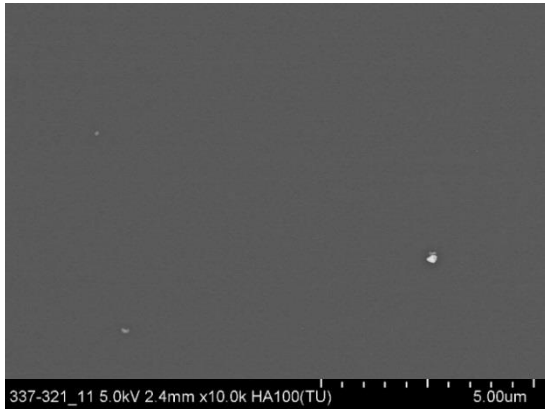


- No H_2O_2 or HF was used in the formulation
- Compare to commodity cleaner (H_2O_2 + NH_4OH), CeXXXX-4 sows 150× improvement
- No CeO_2 agglomeration indicates soluble Ceria-formation or better dispersion after PCMP process

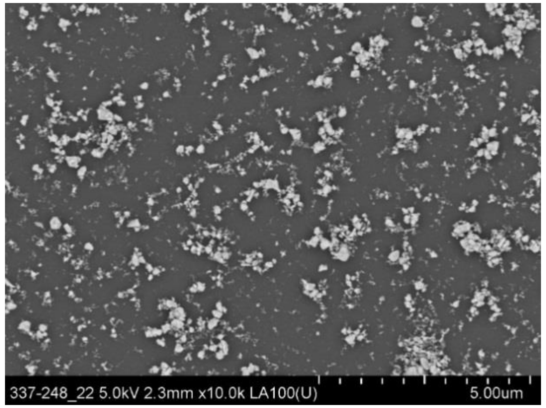
uncleaned



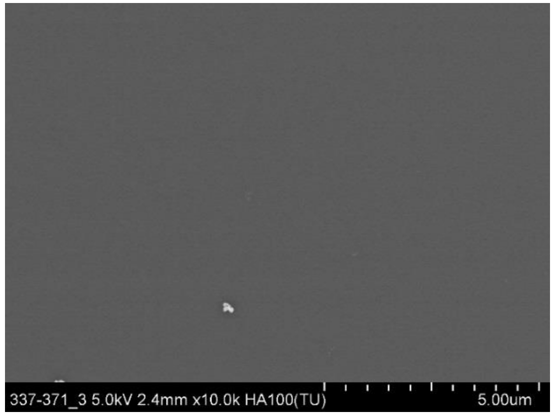
AG CeXXXX-4



SC-1

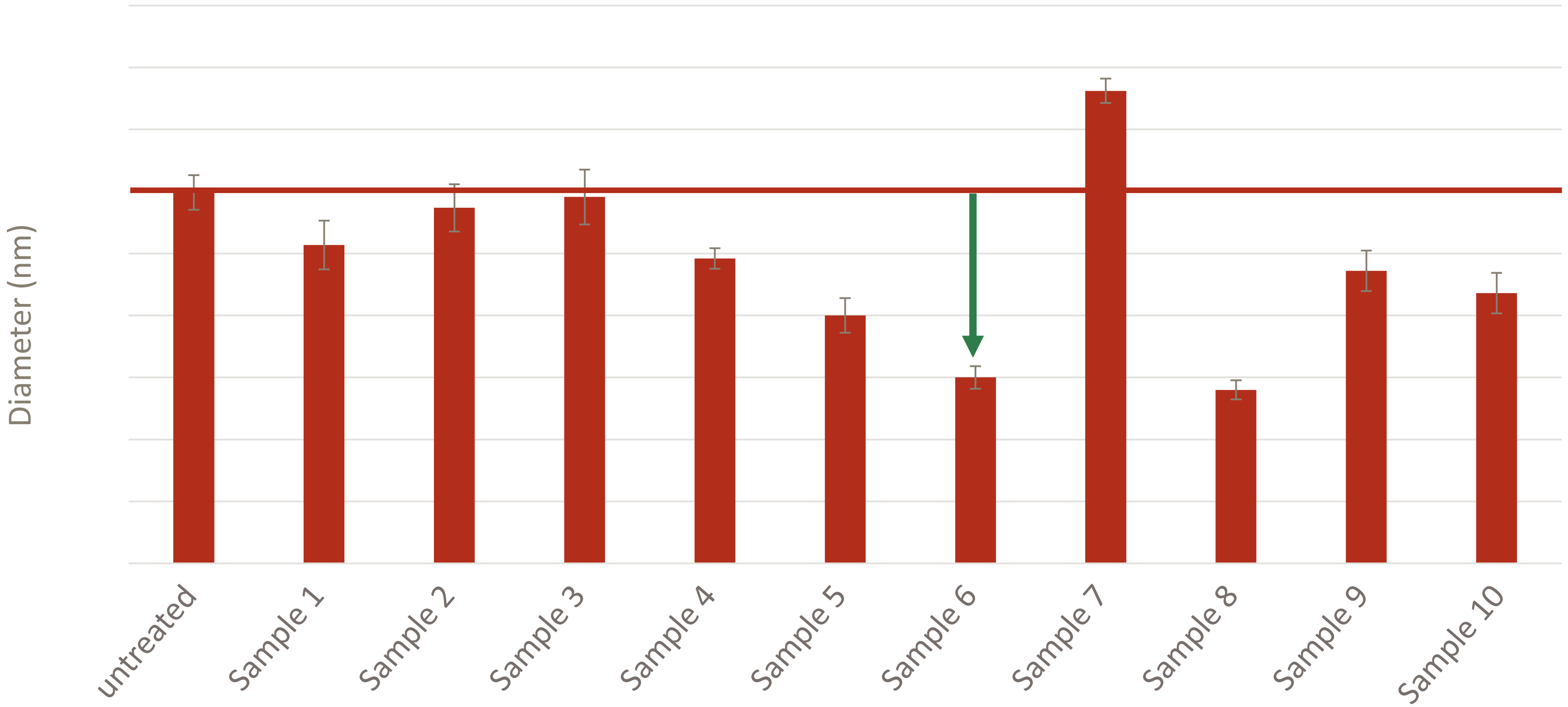


SPM + SC-1



TREATMENT OF POSITIVE-CeO_2 WITH CLEANER SOLUTION

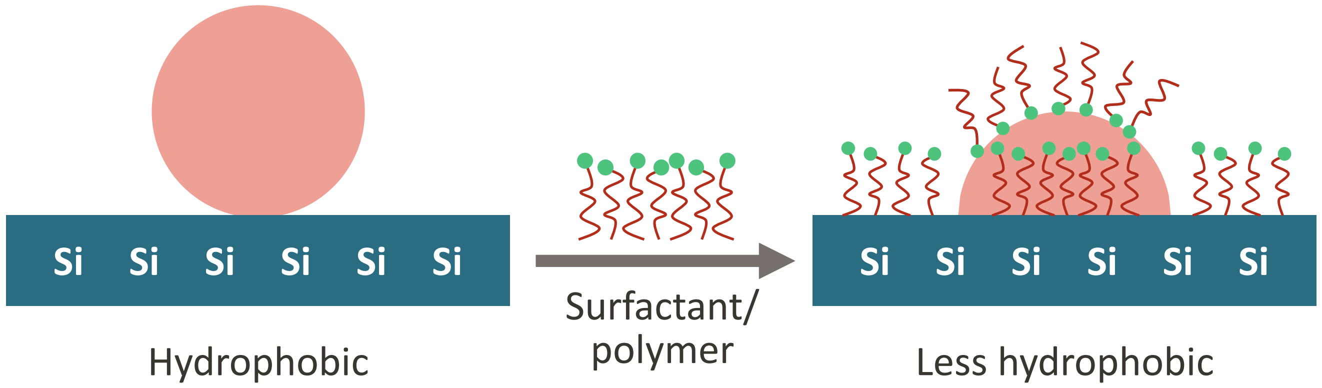
Treated-CeO_2 + Cleaner $\xrightarrow{\text{Stir 5 min}}$ Measure particle size

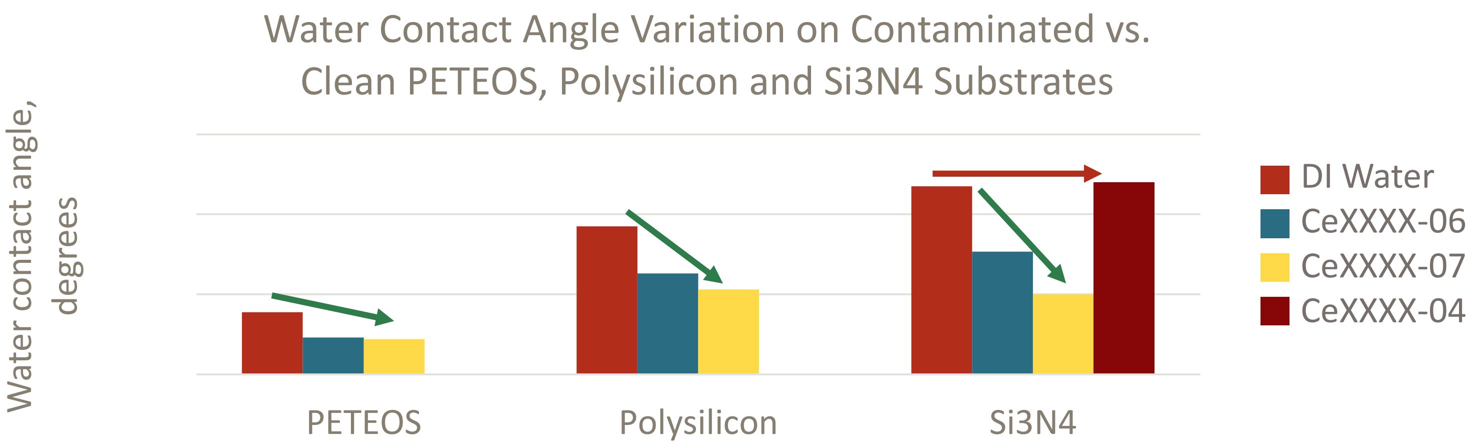


No particle agglomeration was observed

Sample 6 show highest reduction of size; indicates higher degree of surface interaction with the cleaner

CONTACT ANGLE EXPERIMENT TO MONITOR ORGANIC RESIDUE REMOVAL EFFICIENCY





Contact angles are reduced after cleaning with CeXXXX-06 and 07

Surfaces become more hydrophilic, indicates less organic residue leftover after the cleaning

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CONCLUSIONS

- Understanding the nature of Ceria surface and interaction with the Silica surface are the key to designing the proper cleaner
- Spectroscopic evidence suggests that the right bond-breaking component is essential to remove Ceria from surface
- Different bond-breaking reagent are necessary for each type of Ceria at different pHs
- Several low-pH and high-pH high-performance Ceria cleaning formulation, AG-CeXXXX were developed at Entegris, based on in-depth mechanistic understanding on Silica-Ceria surface interactions
- So far there is no universal ceria cleaner

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