



Asymptotically Approaching Zero Defects: *The Future of Post-CMP Cleaning*

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Roger Luo, Bianzhu Fu, Ruben Lieten and Fadi Coder

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Agenda

Market trends in PCMP

Copper PCMP

W PCMP

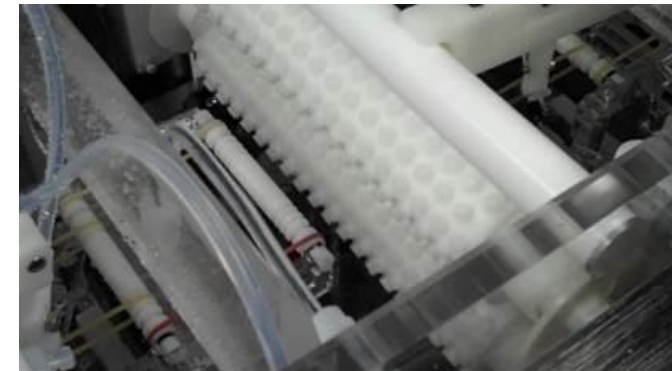
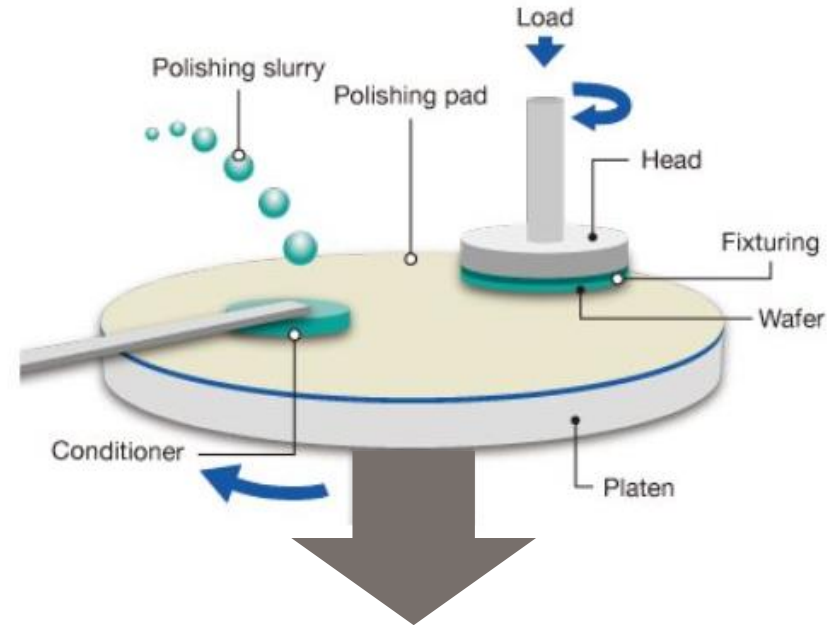
CeO₂ PCMP

Trends in brush technology

The future of PCMP cleaning

Post-CMP Cleaning Challenges

- New materials/film types
 - Diversification of dielectric materials
 - New barrier materials
- Feature size decreasing
 - 10 nm ubiquitous
 - Working on 3-5 nm for most customers
- Increasingly complex CMP slurries
 - New particle types
 - Small particles
 - Advanced organic additives
- Defect detection thresholds decreasing
 - Current state of the art → 18 nm
- Environmental laws/customer EHS more stringent
 - Country to country variations
 - Customer EHS requirements vary
 - Tetramethylammonium hydroxide increasingly forbidden



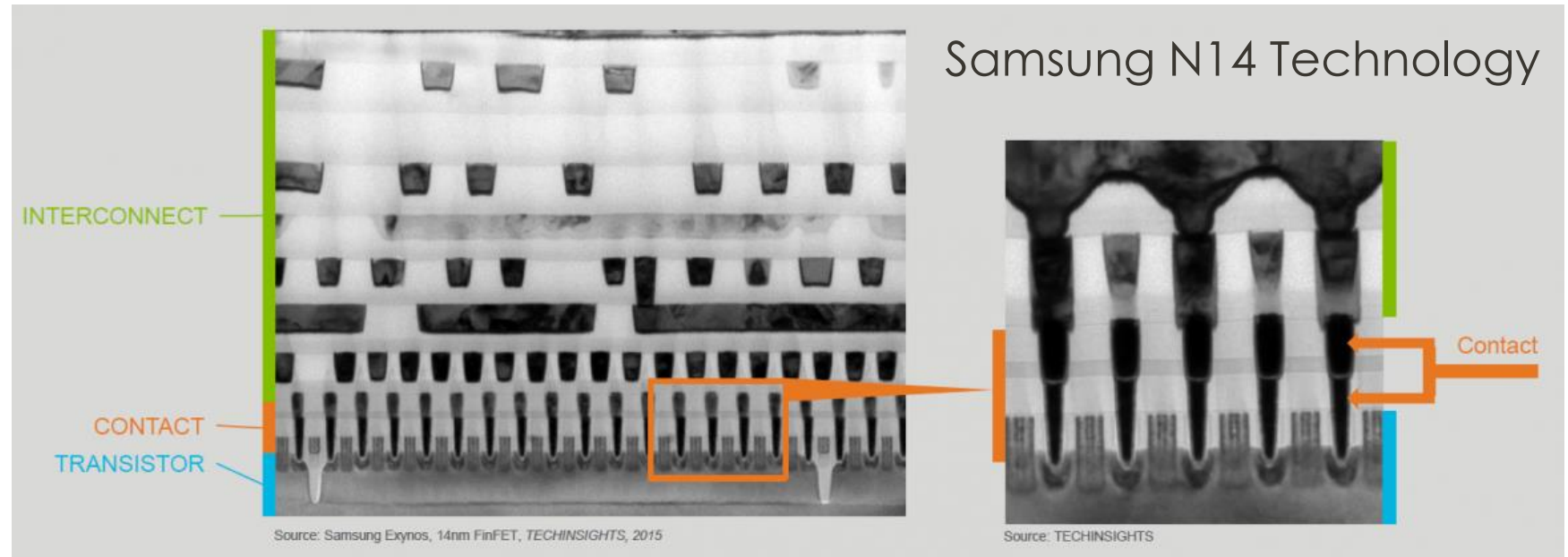
New Materials Lead to Cleaning Complexity

Conductors

- Copper
- Barrier/liners (Ta, TaN, TiN, Co, Ru, Mn)
- Tungsten
- Cobalt
- Ruthenium
- Aluminum
- Molybdenum, Chromium
- Pt Group (Rh, Ir, Ru, Os, Pt, Pd)
- Binary compounds (MoN, Re₂C, ...)

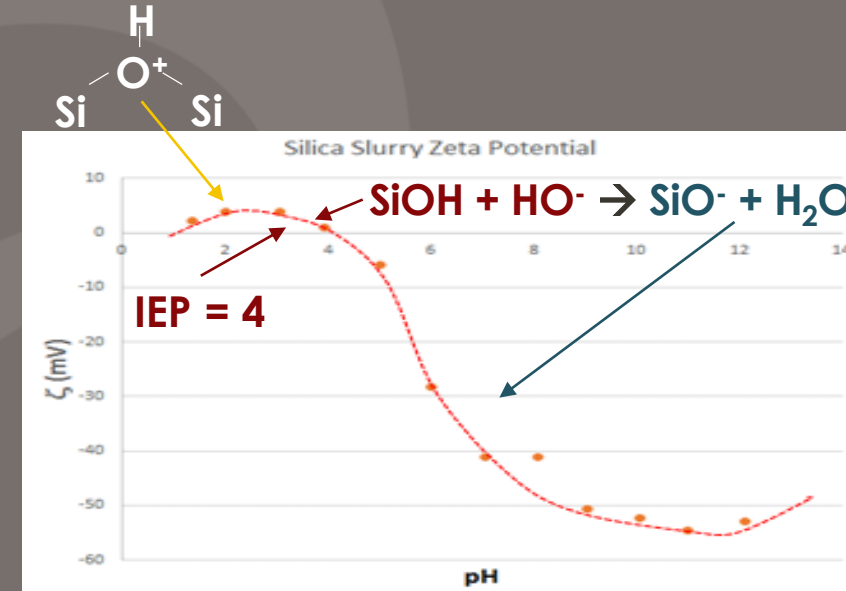
Dielectrics

- TEOS
- Thermal oxide
- Si₃N₄
- Low-k dielectric, SiC (SiOC, SiON, etc.)
- Polysilicon, single crystal silicon (wafer, various doping)
- Doped glass (BPSG, PSG, etc.)

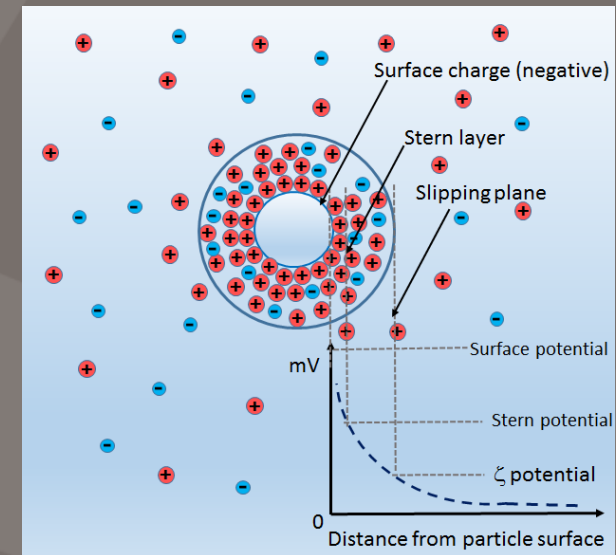


Challenges/Diversity in Particle Cleaning

- Fumed silica (older ILD, W slurries)
- Colloidal silica
 - Controlled growth from “silicic acid”
 - High purity particles via Stober process – controlled hydrolysis of Tetraalkylorthosilicate
- Surface functionalized silica
 - Anionic functionality (carboxyl or sulfonic acid)
 - Cationic (amines, quaternary ammonium)
- Ceria
 - Cationic surface
 - Adsorbed additives for selectivity can modify surface properties
- Alumina
- Titania, zircona
- Nanodiamonds
- SiC



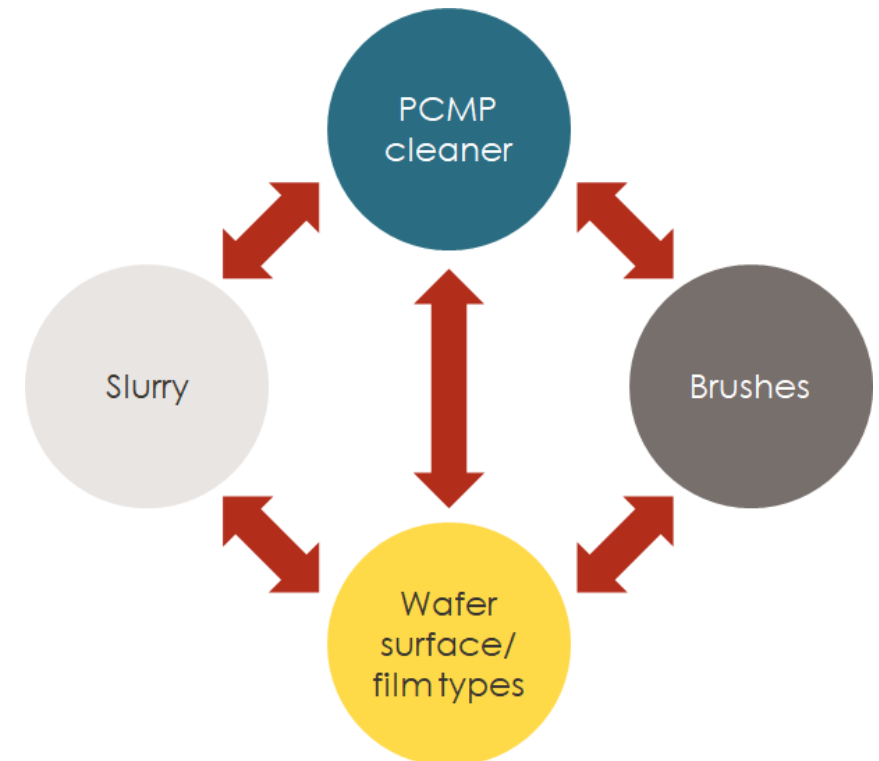
Zeta potential $\zeta = 4\pi\gamma(v/E)/\epsilon$



Formulation Characteristics for Proper Cleaning

- Controlled undercut of particles/dissolution of substrate
 - Break Lewis-acid-base and H-bonding interactions
 - Typically want 1-2 atomic layers
 - No change in low k film dielectric constant
- Dissolution or dispersion of the particles
- Dissolution or dispersion of the organic residue
- Chemical attack on organic residue
- Mechanical action by brushes
- Surface wetting
- Charge repulsion between particles and surface

Complicated 4-way interactions present challenges for Post-CMP cleaning



More predictive simulation/models needed

Challenges in Cu PCMP

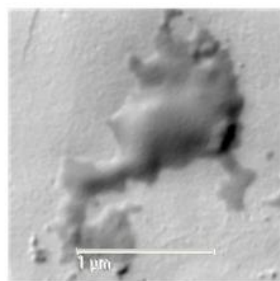
- Advanced generations requiring very low or no defects
 - Organic residue
 - Silica particles
 - Metal particles
- Minimal/zero corrosion to exposed metals (Cu, TaN, Co, Ru)
 - No galvanic corrosion or barrier attack
 - Low Cu recess/etch rates → 3–10 nm technology
- Minimal Cu surface roughness
- Extended queue time
- EHS friendly/green chemistry
 - No TMAH
- Low COO
 - Higher POU dilution
 - Low chemical consumption

Types of organic Residue Encountered in Post-CMP Cleaning

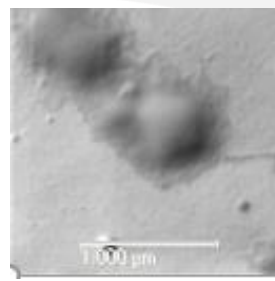
- Corrosion-inhibitor – metal complexes (i.e., Cu-BTA)
- Surfactant residues
- Interactions between slurry additives and cleaning additives
- Pad debris (polyurethane – hydrophobic or hydrophilic)
- Brush debris (crosslinked PVA – hydrophilic)
- Plating additives
- Filter or tubing shedding/residues
- Biological debris (bacterial, skin cells, etc.)



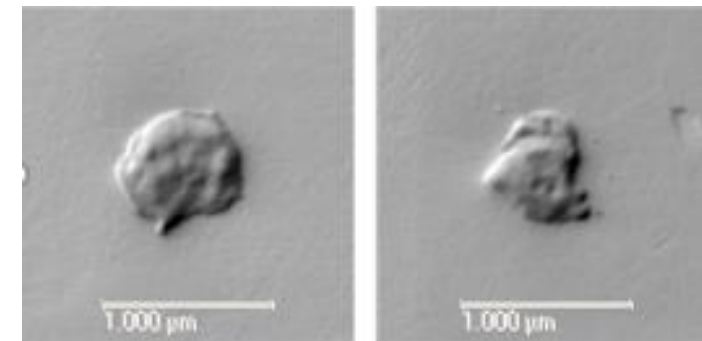
Pad or brush debris
EDX = C, N, O → polyurethane pad
EDX C, O only → brush



Soluble organic
or
surfactant residue



Advanced defect metrology has enabled
detection of smaller defect sizes

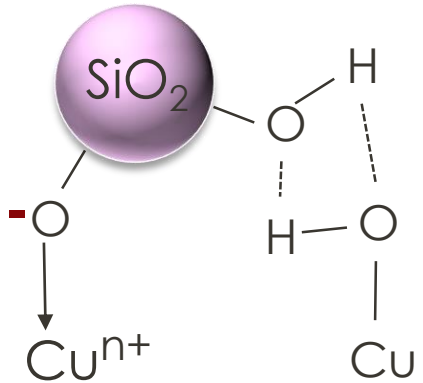


Precipitated organic such as from the interaction
of cleaner with slurry components

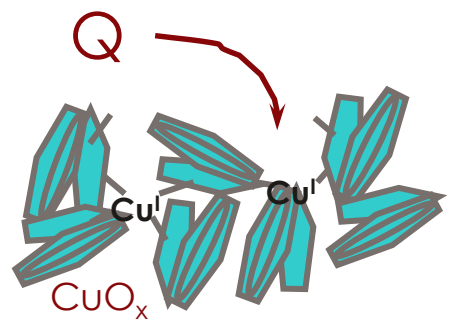
PlanarClean® AG - Advanced Generation Copper Cleaning Mechanism



Etchant for controlled, uniform CuO_x dissolution to undercut particles



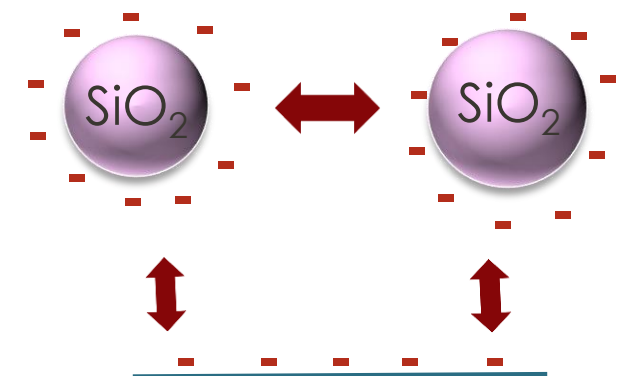
Organic additive attacks and removes Cu-organic residue



Corrosion inhibitor package controls Cu galvanic corrosion



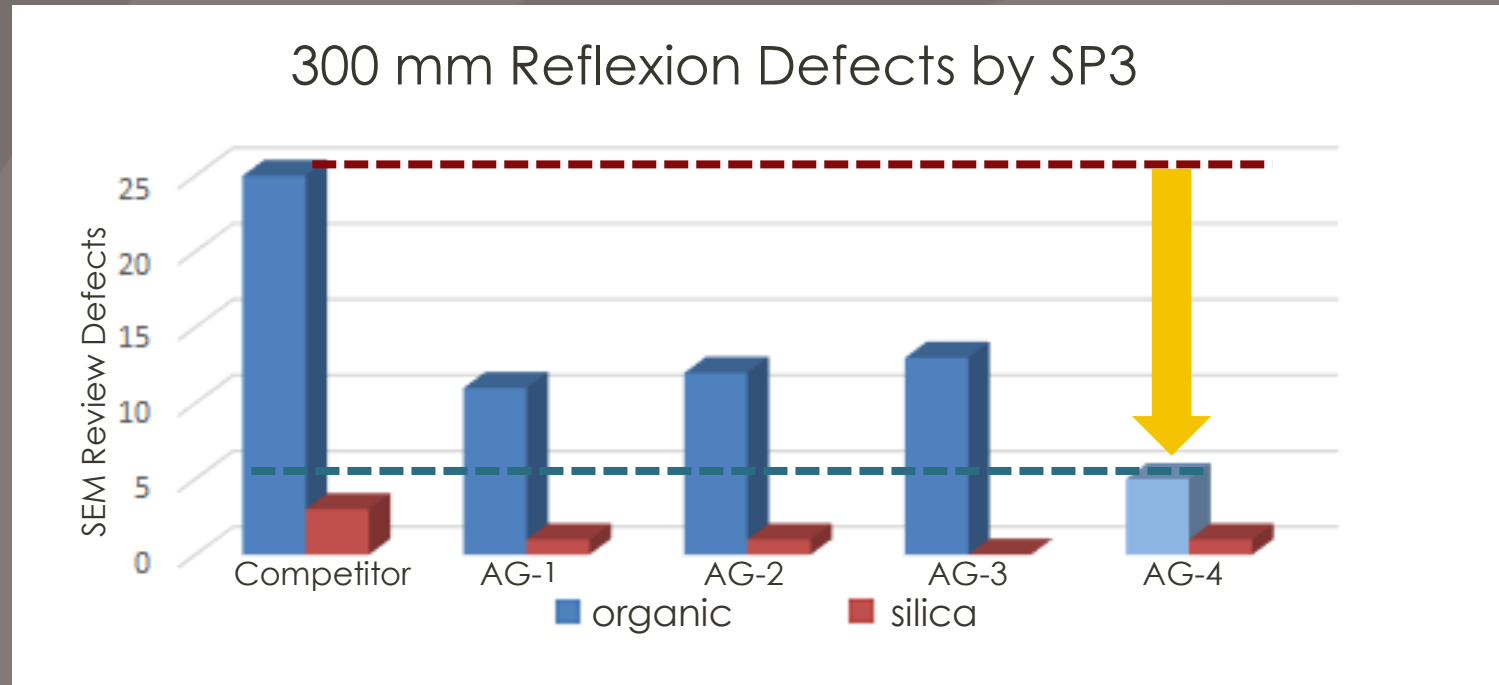
High pH leads to charge repulsion between negatively charged silica and negative copper oxide surface



$\text{Cu}(0)$

IMEC Reflexion Data

Shows lower organic and silica defects compared to the competitor

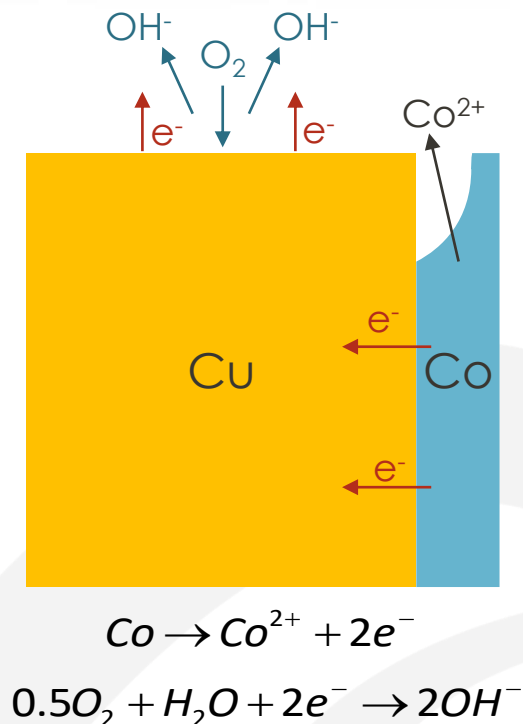


300 mm Reflexion at IMEC w/ SP3 at 80 nm
Threshold, SEM Review

Copper Wafers

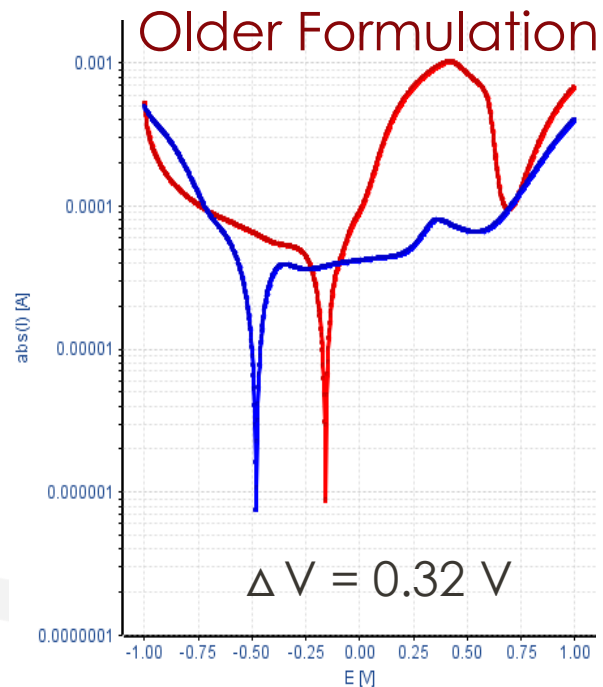
PlanarClean[®] AG Formulations

show improved galvanic corrosion

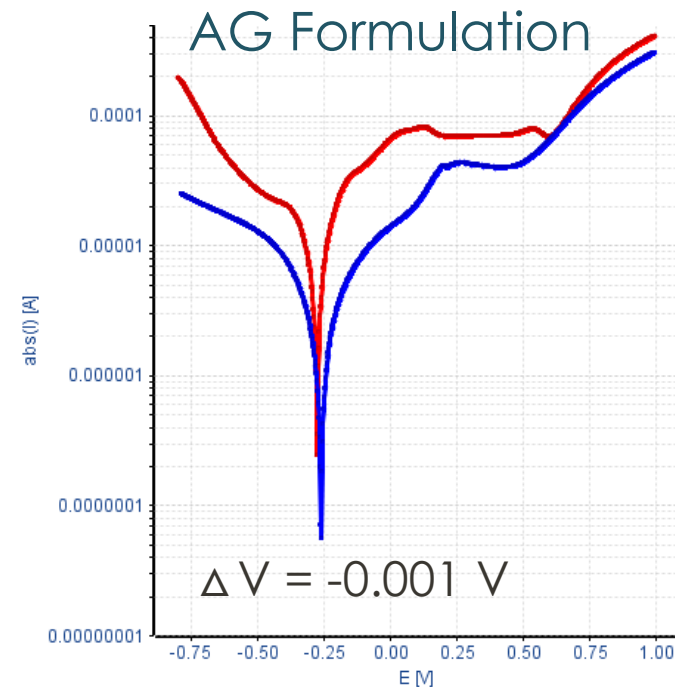


Controlled Electrochemical Properties

- Ligands to control OCP gap
- Passivation to modify resistivity



Anodic Co corrosion



Nearly zero galvanic corrosion

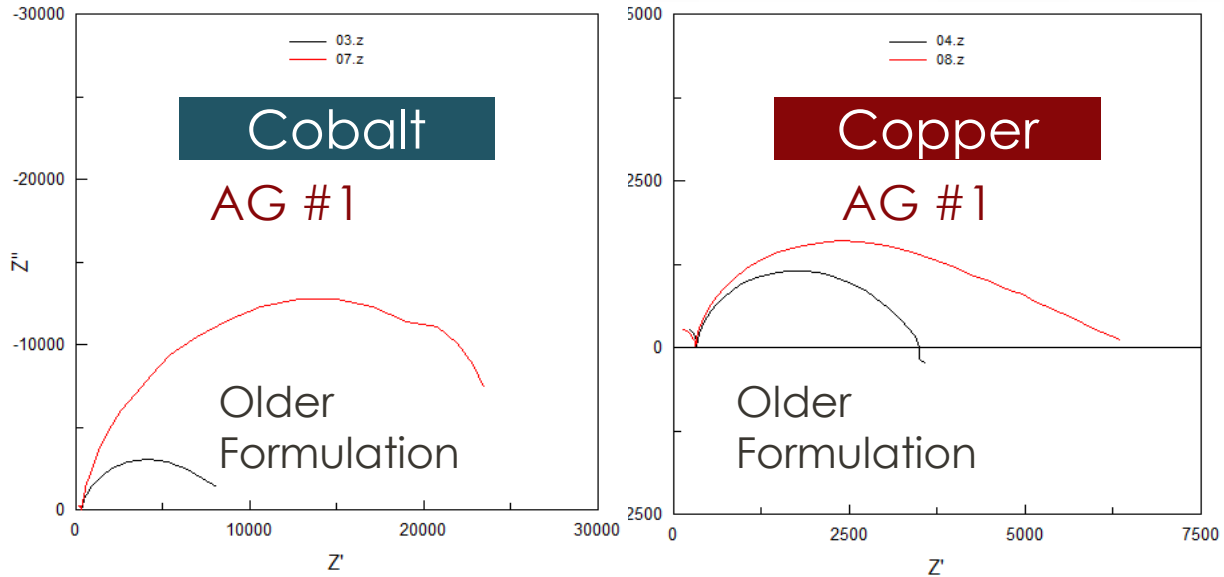
Copper

Cobalt

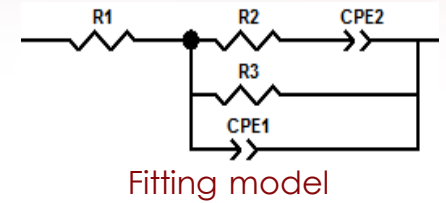
PlanarClean[®] AG Formulations

maintain higher film integrity on both Cu and Co

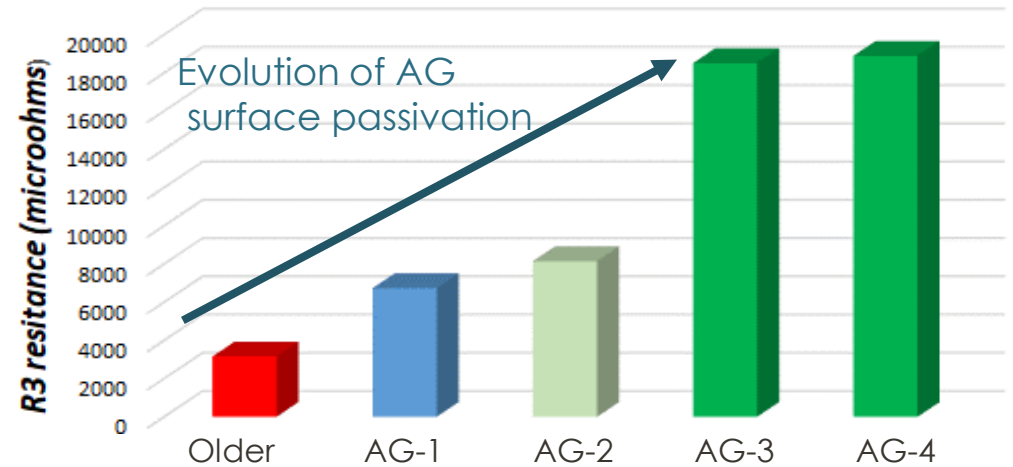
Impedance Spectroscopy



Additional novel Cu inhibitor in AG Formulations improves Cu passivation



Calculated Cu Film Resistance for Various PCMP Formulations



Higher impedance storage and loss components
→ higher film integrity

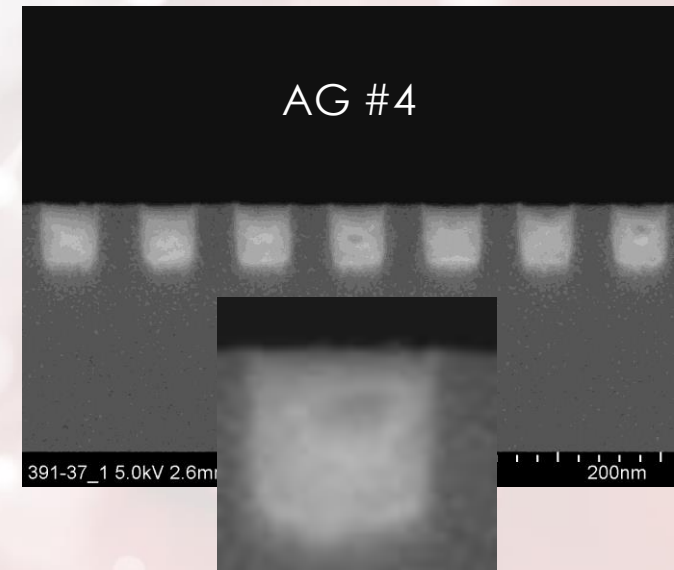
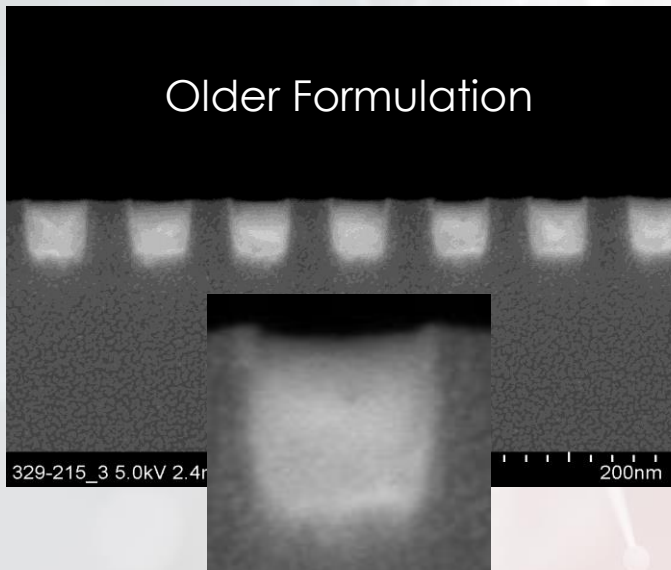
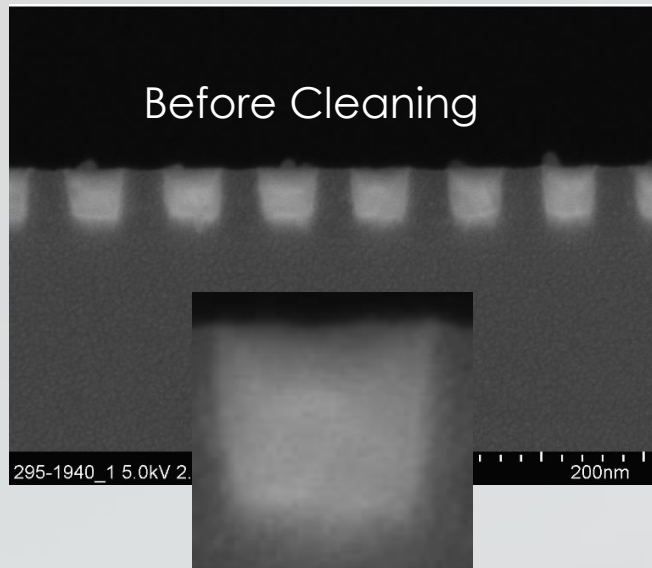
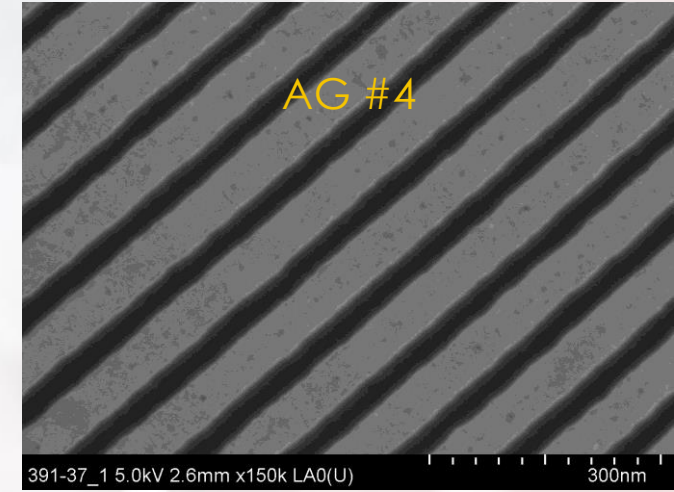
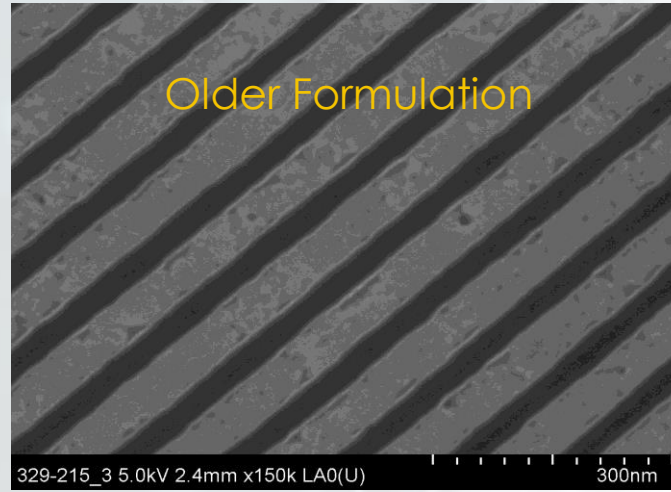
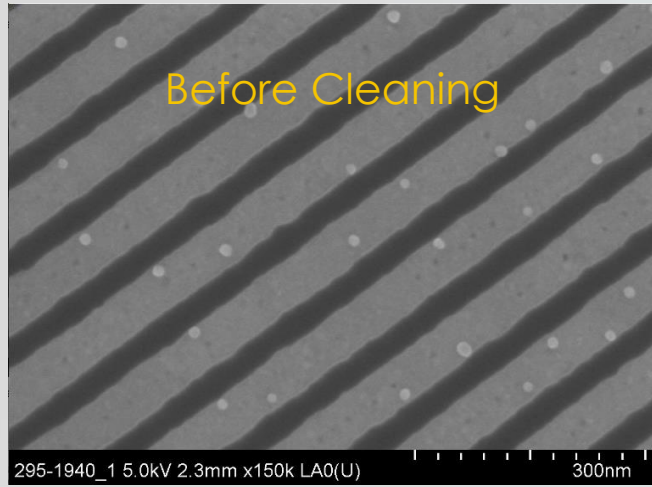
When $\omega \rightarrow 0$

$$Z' = R_{\Omega} + \frac{R_{ct} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma\omega^{-1/2})^2}$$

$$Z'' = -\frac{\omega C_{dl} (R_{ct} + \sigma\omega^{-1/2})^2 + \sigma^2 C_{dl} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma\omega^{-1/2})^2} a$$

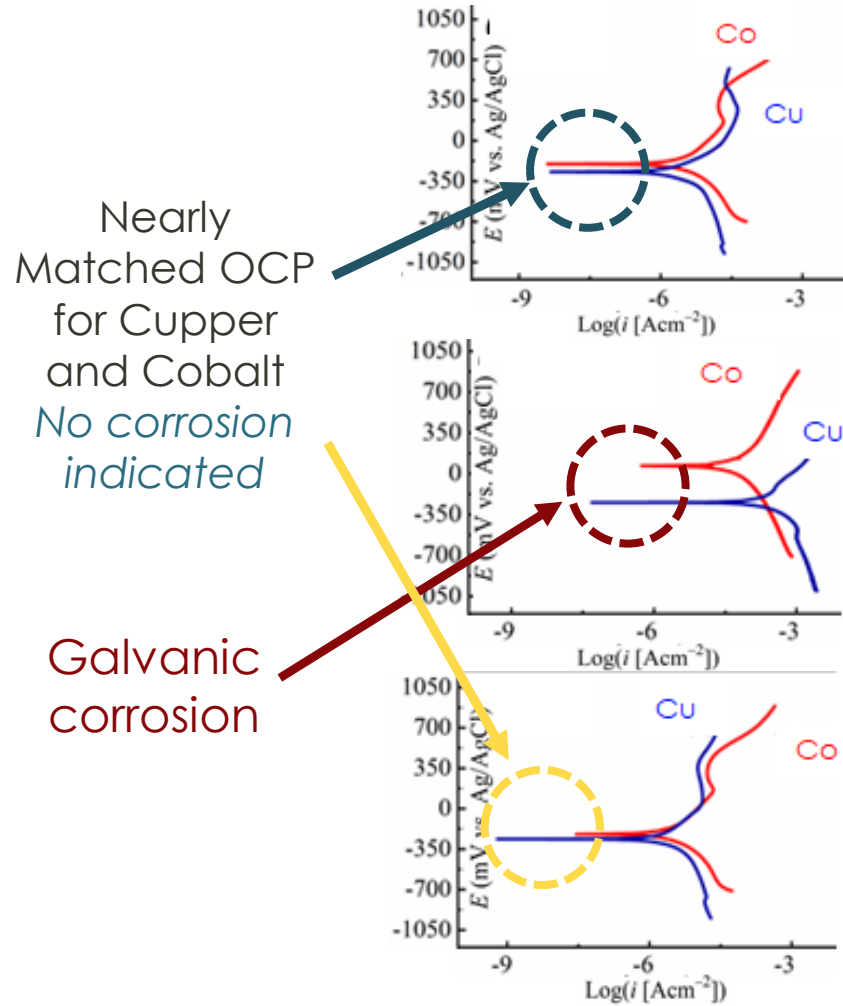
SEM Cross-Section Analysis

IMEC 45nm Cu/Co patterned wafers show no evidence for corrosion



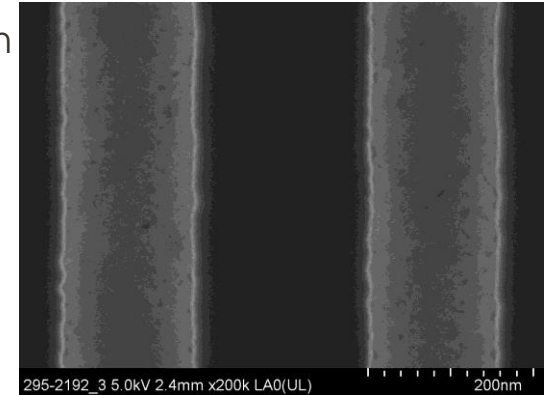
In-Situ Electrochemistry

shows OCP shift under brushing conditions

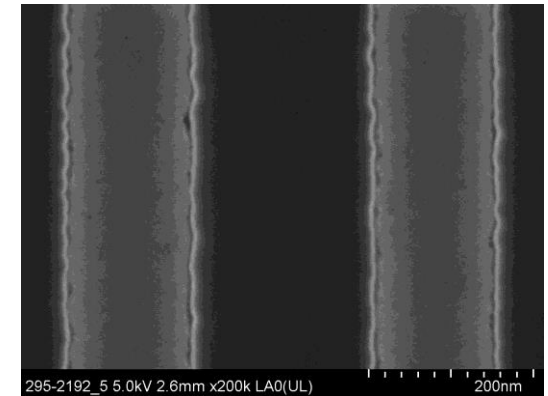


Data indicates the kinetics of the inhibitor reacting with cobalt is critical

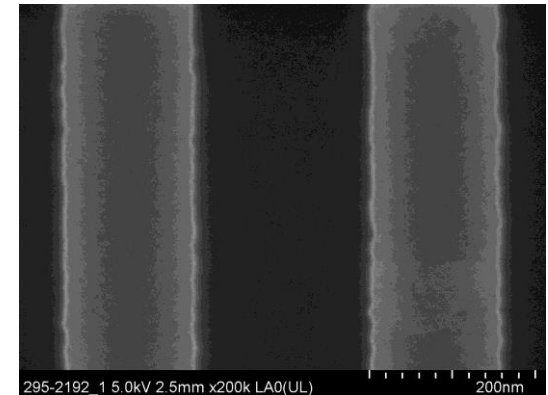
Old formulation - no brush



Old formulation dynamic with 60 RPM brush



Good formulation with 60 RPM brush



Challenges for Ceria

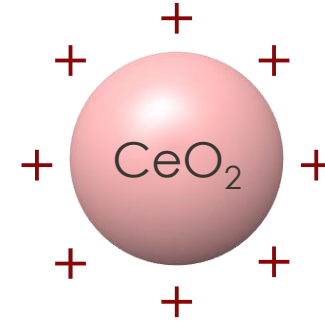
Post-CMP Cleaning Formulations

- Many different ceria types
 - Calcined
 - Precipitated/colloidal
- Organic additives vary depending on goals
 - Rate additives (ILD)
 - Polymeric or small molecule selectivity additives
 - Stop on nitride or poly
 - Reduce feature size dependence

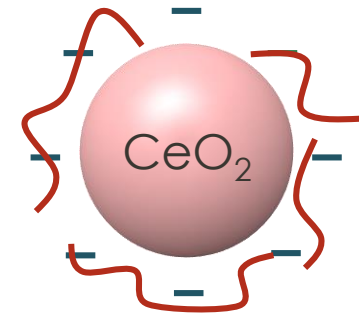
Current industrial POR (commodity clean):
inefficient and environmentally unfriendly

- DHF
- SC-1
- SC-1 + DHF
- SPM ($\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$)
- TMAH + SC-1
- **Highly toxic**
- **Unformulated**
- **Environmentally unfriendly**
- **Damage to dielectric**

Positive Ceria



Negative Ceria

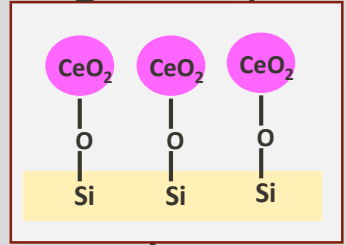


Entegris AG Ce-XXXX formulations

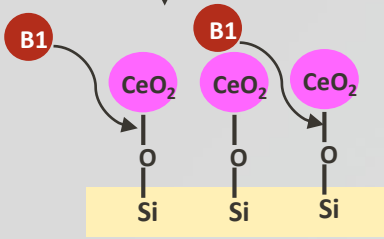
- Improved particle and metal removal
- Replace toxic commodity cleaners
- Environmentally friendly
- No damage to dielectric surfaces
- Ce residue post-CMP cleaning $< 10^{10}$ atoms/cm²

Higher pH vs. low pH Cleaning Mechanism for Negative Ceria

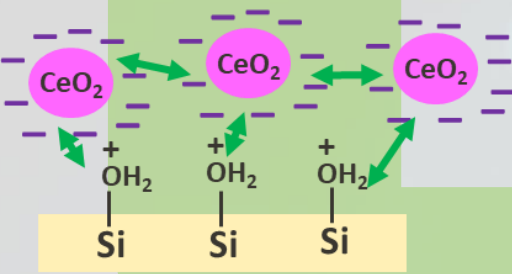
Neutral/Basic Approach
pH = 5-13



Step 1

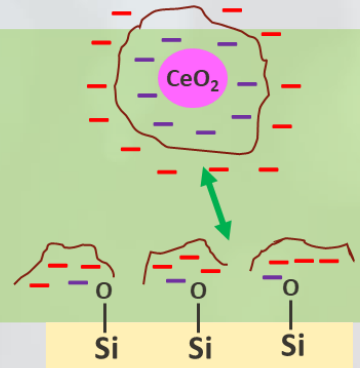


Acidic Approach
pH = 1-4

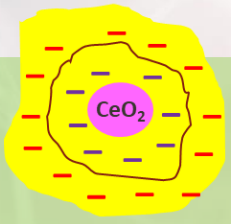


Step 2B

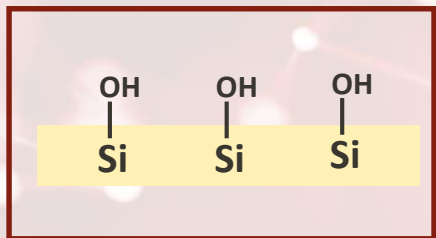
Small molecule charge modifier



Step 3B

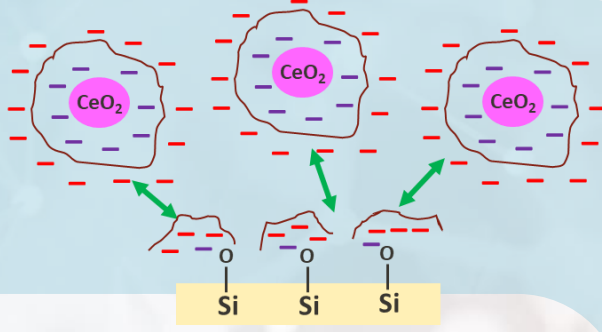
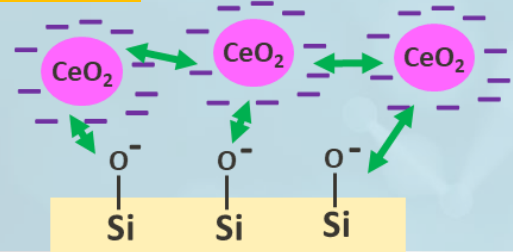


Step 4



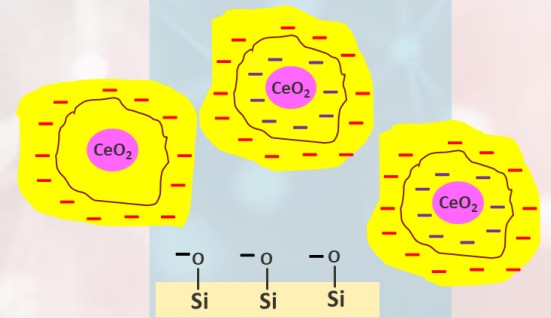
Step 1: bond breaking
Step 2A & 2B: modification of surface charge
Step 3A & 3B: complexation
Step 4: removal of soluble ceria

Step 2A



Strong electrostatic repulsion

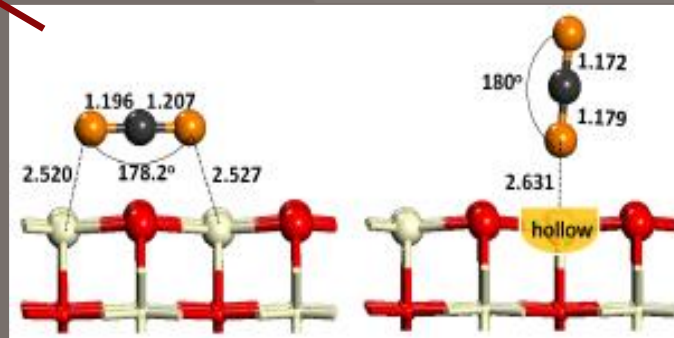
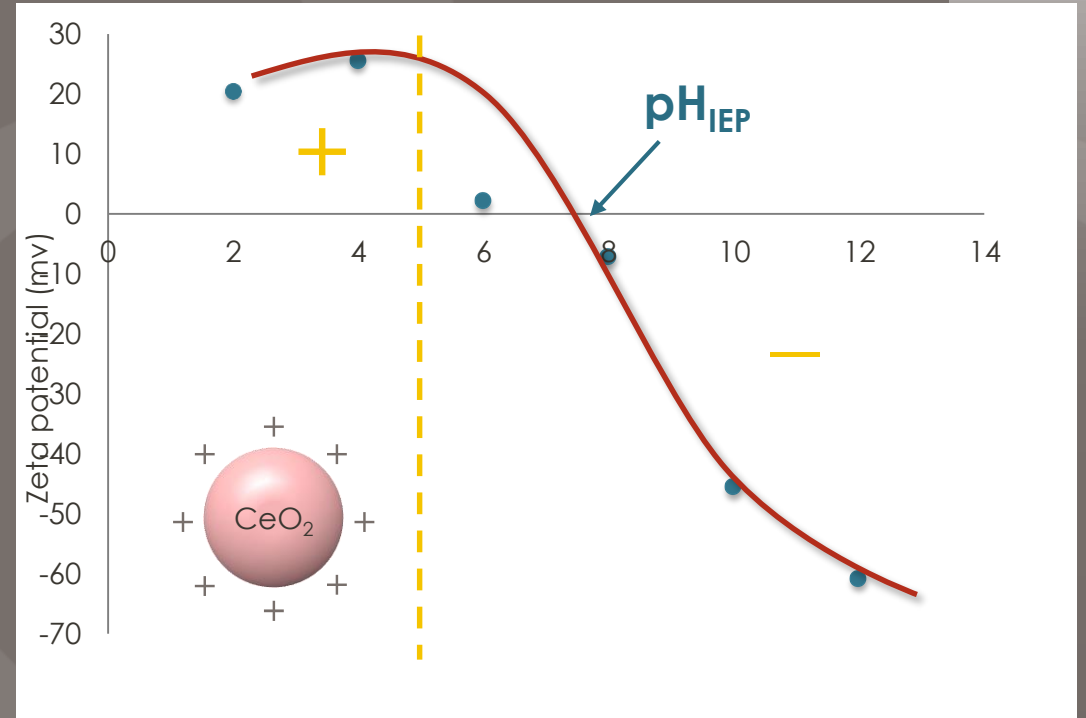
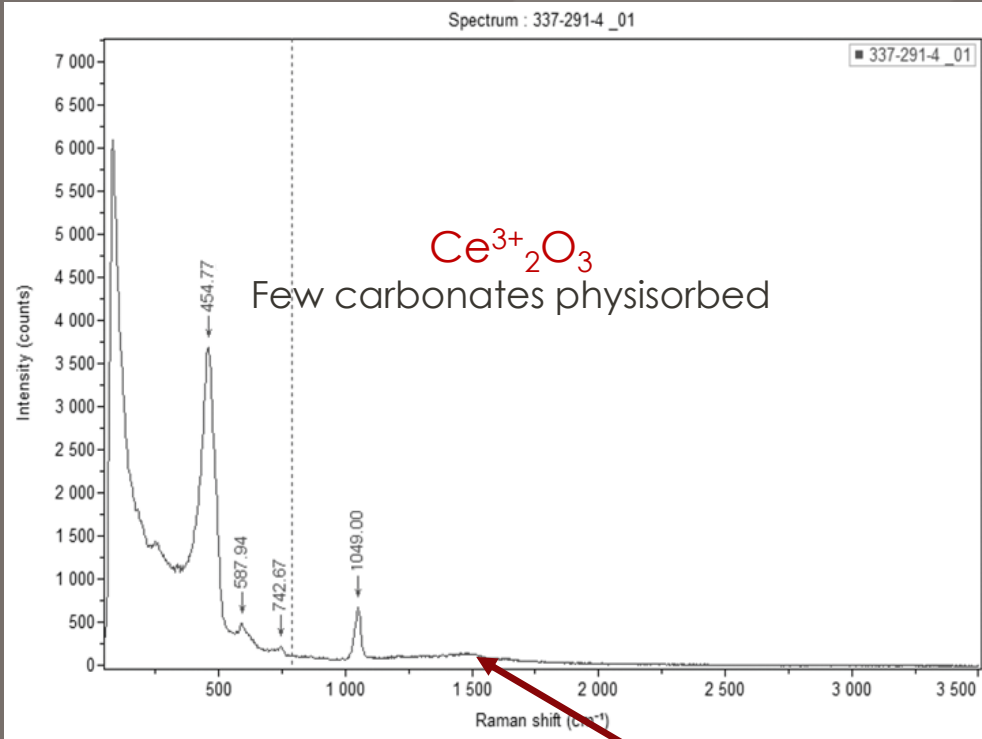
Step 3A



Step 4

Clean surface

Ceria Particle Surface Chemistry Enables the Design of Efficient Ceria Cleaners

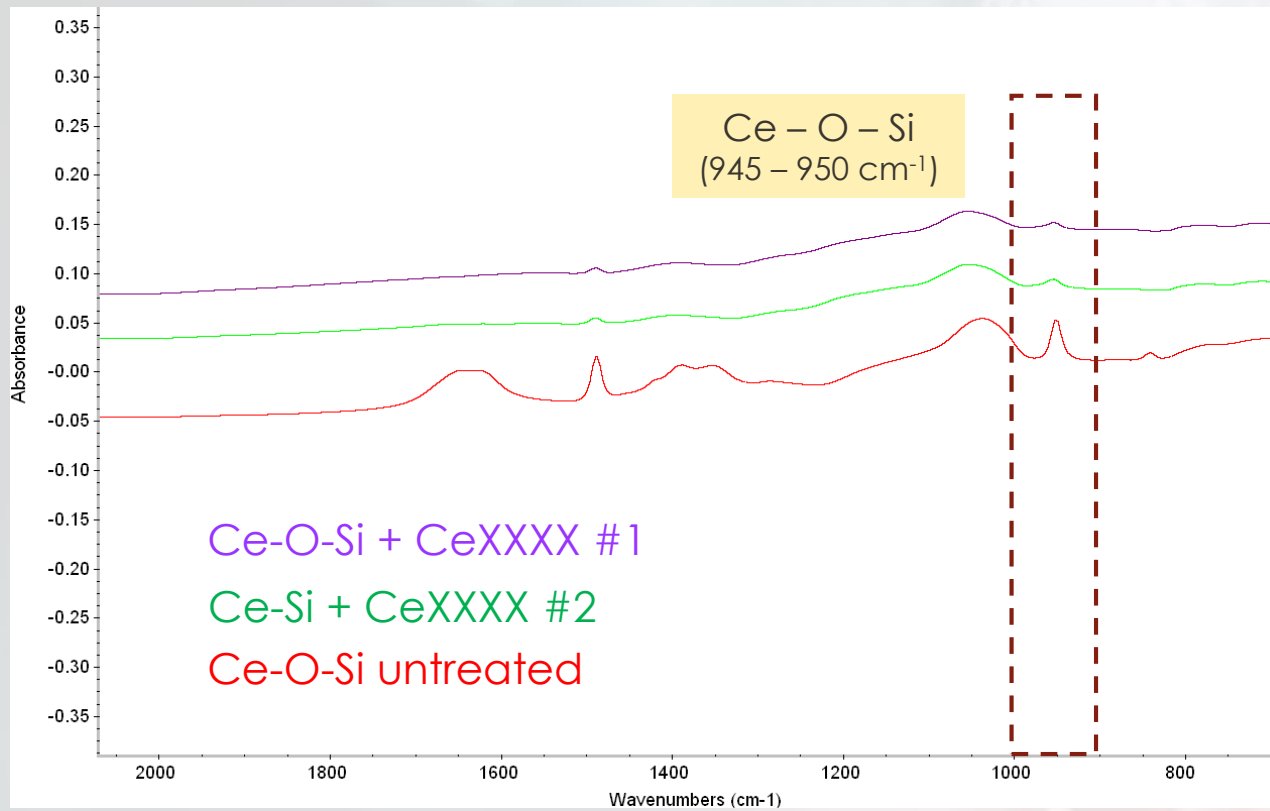


FTIR IR Spectra of Cerium Silicate Shows the Effectiveness Bond Breaking Agent

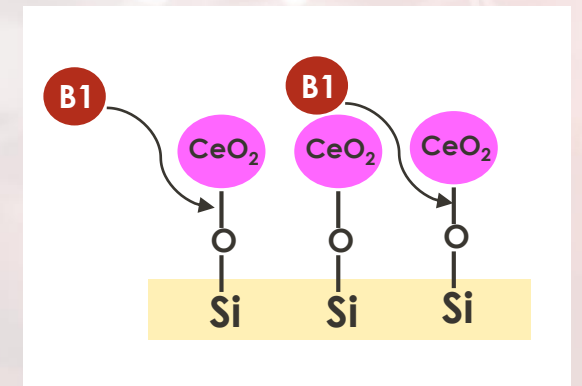
Si – O – Ce solid sample + CeXXXX sample



Solid material isolated + filtrate isolated



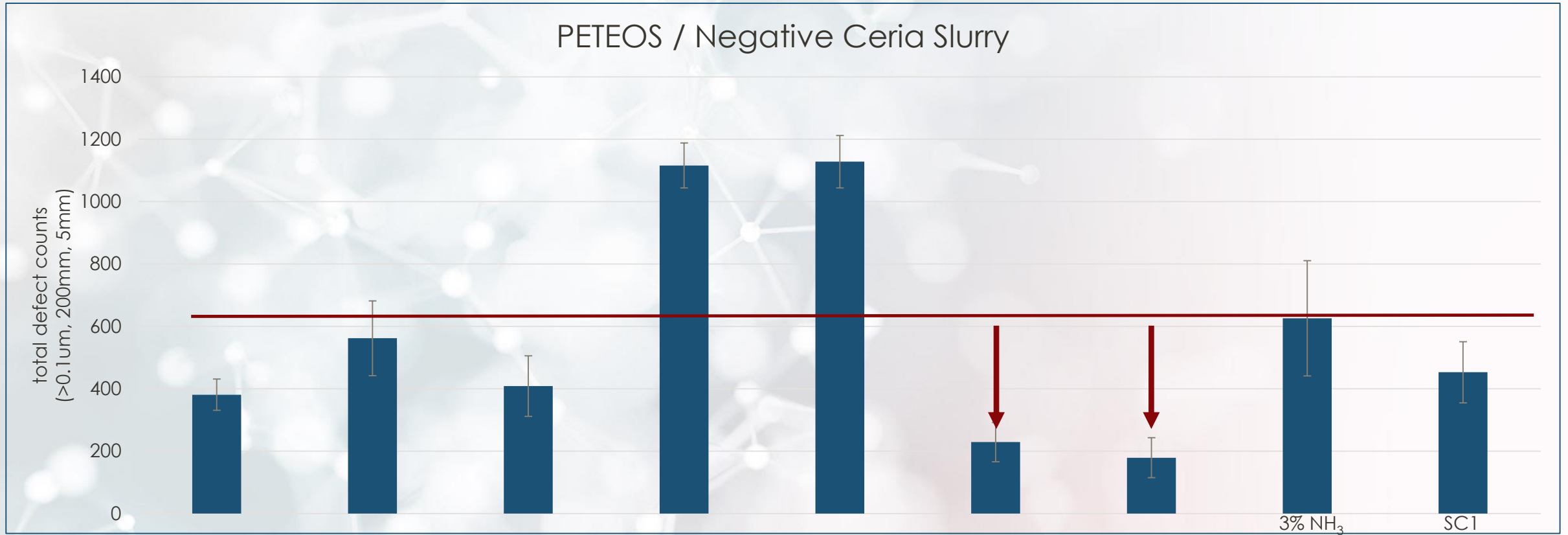
IR of sample before and after treatment



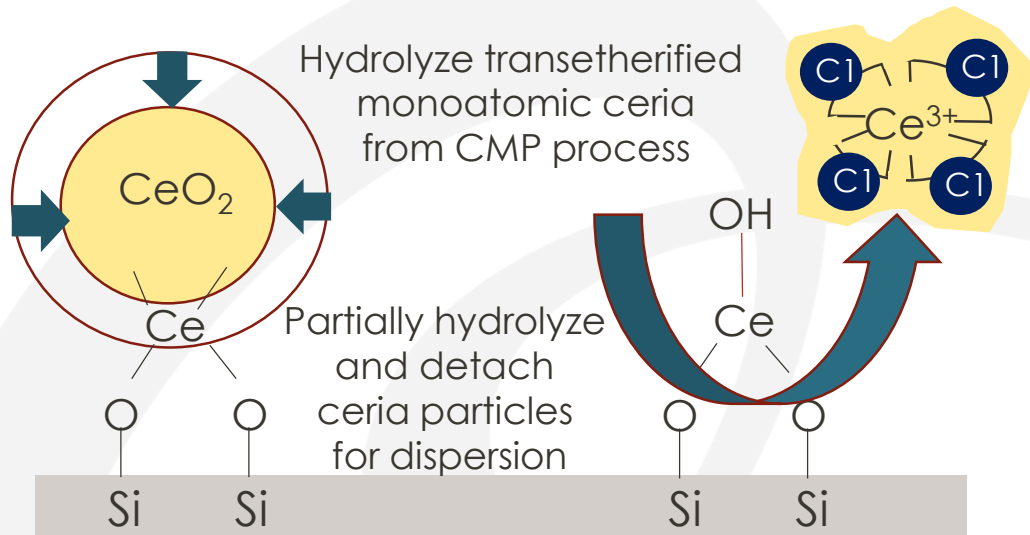
Relative Ce – O – Si intensity is greatly reduced with CeXXXX

Full Wafer Cleaning Data

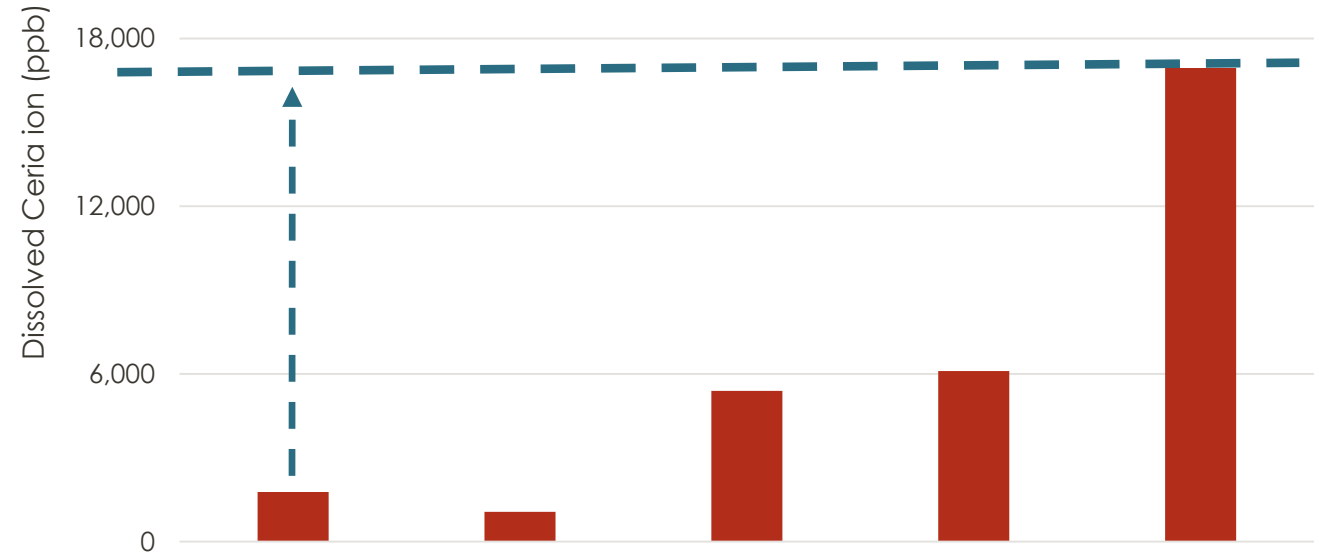
shows significant cleaning improvements



Advanced Products Have Higher CeO₂ Dissolution Efficiency



Ceria-Slurry (CeO₂) Dissolution

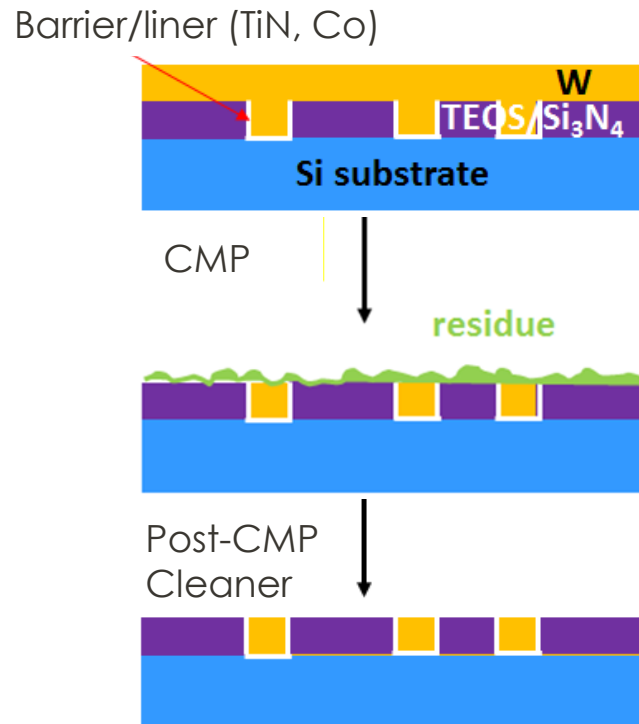


Why is increased ceria dissolution desirable?

Challenges for W Post-CMP Cleaners

Slurry particles and organic residue removal from W and dielectric surfaces (PETEOS, Silicon Nitride, Polysilicon);

Metal residue in any form (Ions, Salts, Metal Oxide)



Cleaning Requirements:

- W ER < 1 Å/min
- TiN ER < 1 Å/min
- Dielectrics ER < 1 Å/min
- Dielectrics: Si₃N₄, TEOS, SiC, etc.
- Defect counts DDC ≥ 0.065 mm lower than commodities: dAmmonia, SC-1
- Low W/TiN galvanic corrosion
- Mt atoms < 10¹⁰ Mt/cm²

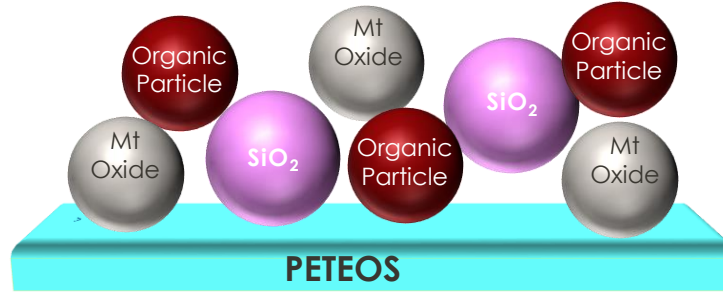
- No increased roughness
- Market increasingly challenged by W recess
 - High pH commodities (SC1, dil NH₃)
 - Traditional low pH cleaners
- Low W etch rates (<2 Å/min) cannot be achieved with commodity cleaners
- No organic Residue Nitride cleaning is particularly problematic
- No silica particles or clusters
- Green chemistry (TMAH free)

Post-CMP W Cleaning Mechanisms vs. pH

Low pH

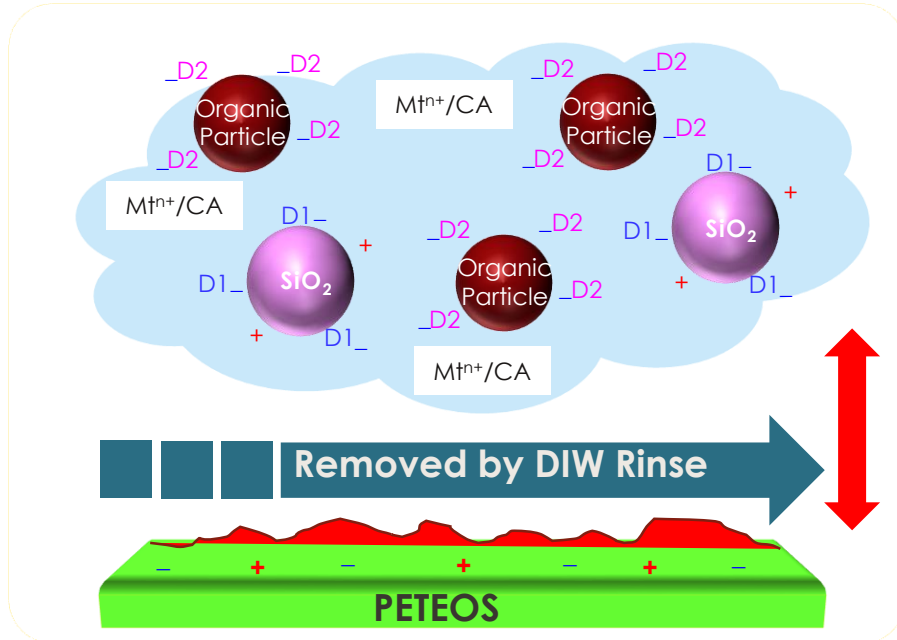
- Silica brush imprints
- Good Mt removal ($\sim 10^{10}$ atoms/cm²)

W CMP residue: silica, Mt oxide, organics



High pH

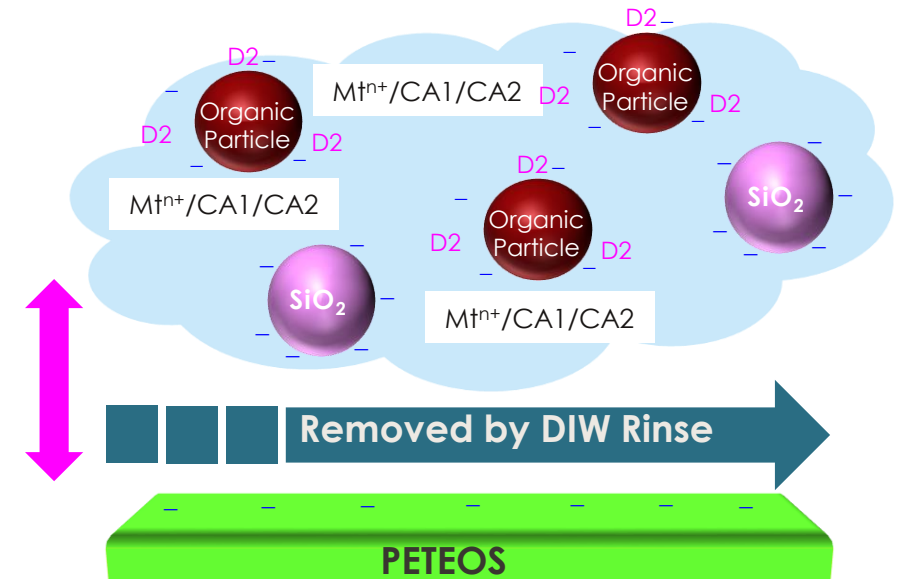
- No Silica brush imprints
- Poor Mt removal ($4-6 \times 10^{10}$ atoms/cm²)



CA = Mt complexing agent
 D1 = SiO₂ dispersant
 D2 = organic residue dispersant

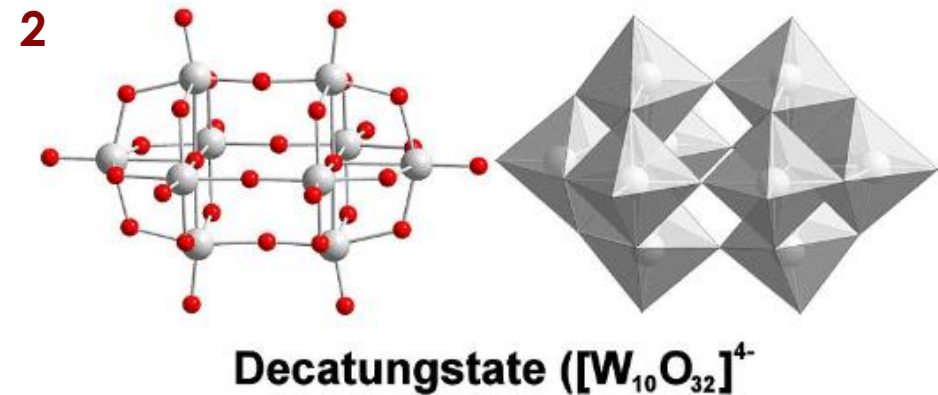
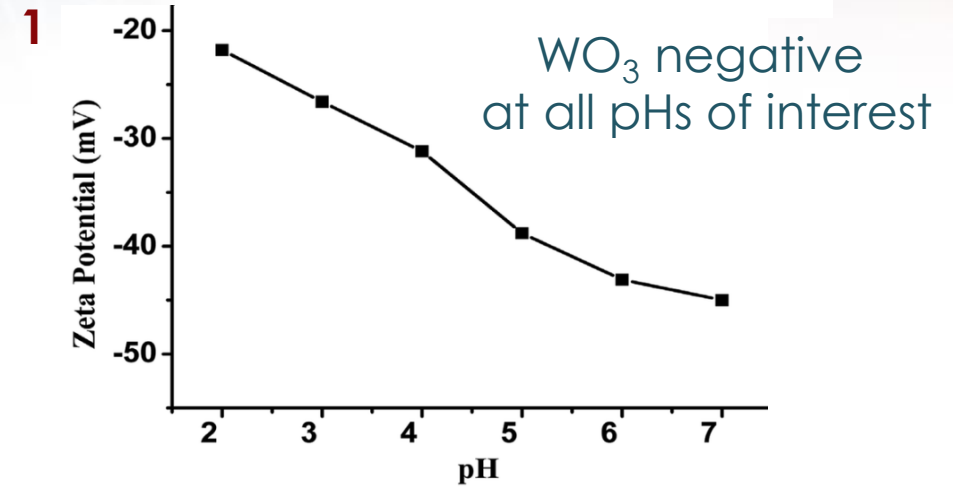
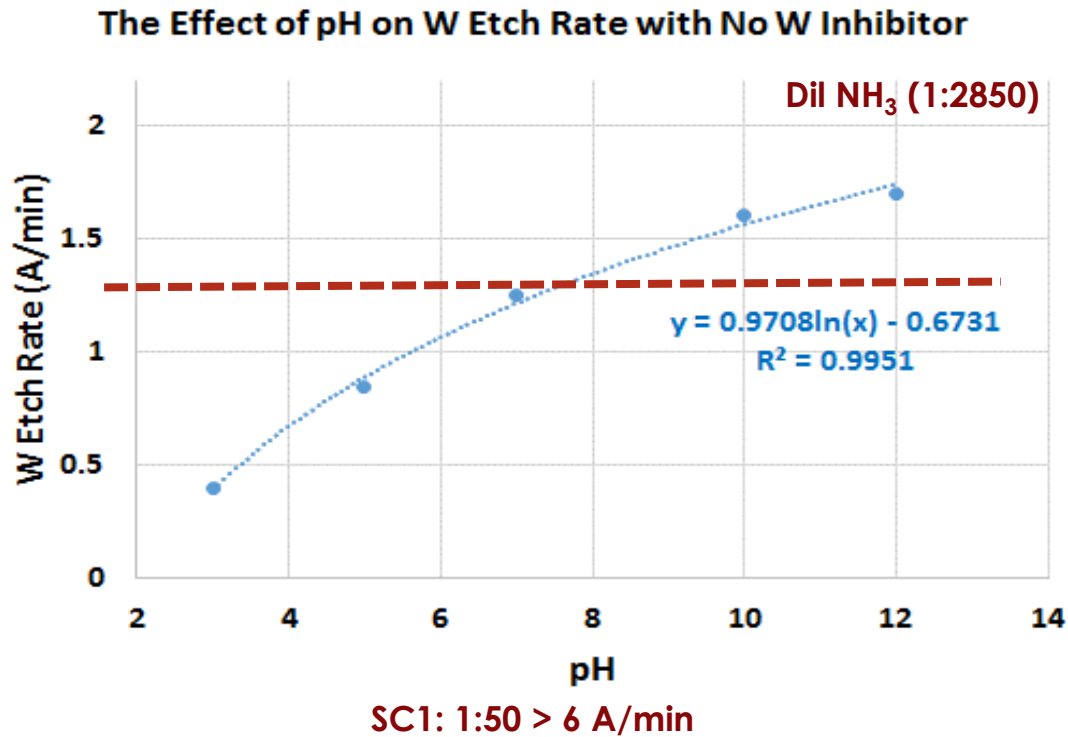
steric repulsion

electrostatic repulsion



Higher Tungsten Etch Rates Observed

Increasing pH due to dissolution as Polyoxotungstate Keggin ions

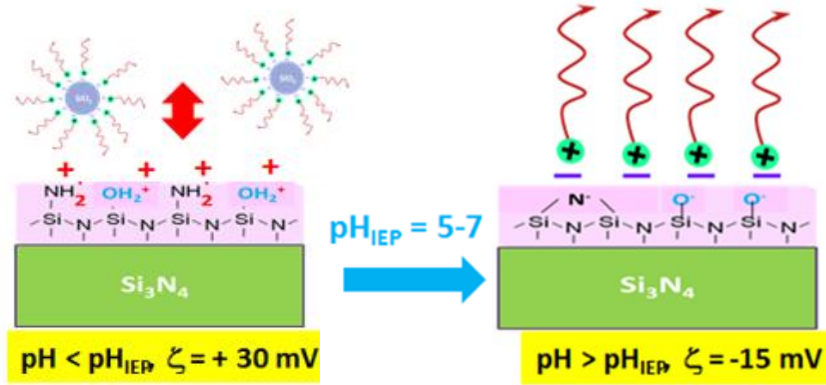


1 - Liu, et al. J. Mater. Chem A, Issue 6, 2014.

2 - "Hetero and lacunary polyoxovanadate chemistry: Synthesis, reactivity and structural aspects". Coord. Chem. Rev. 255: 2270–2280. 2011.

Improving Organic Residue Removal from Si_3N_4 Contact Angle and FTIR

Electrostatic Repulsion during CMP

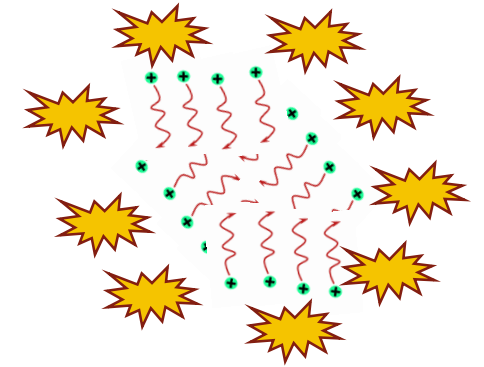


W Post-CMP Cleaner

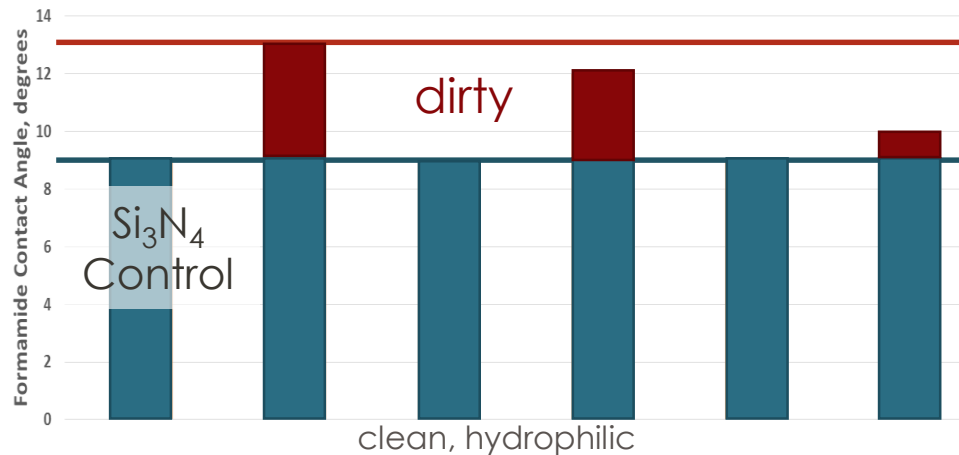
Si_3N_4 surface typically highly contaminated by cationic dishing and erosion control agents



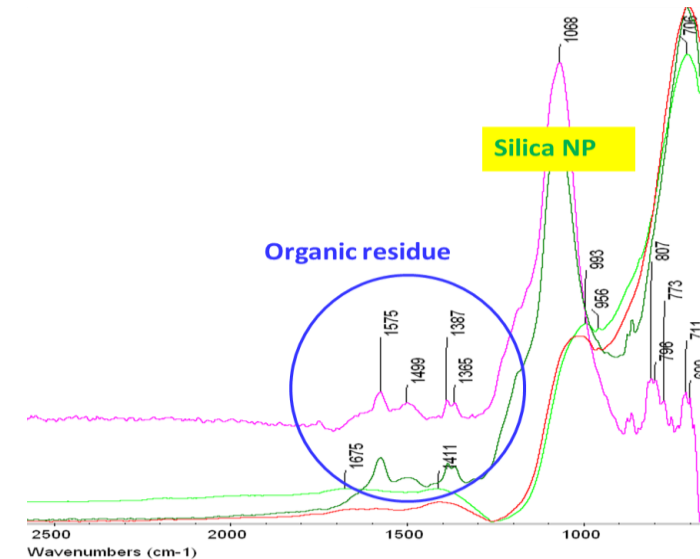
Cleaning additive removes cationic contamination from dielectric surface and disperses



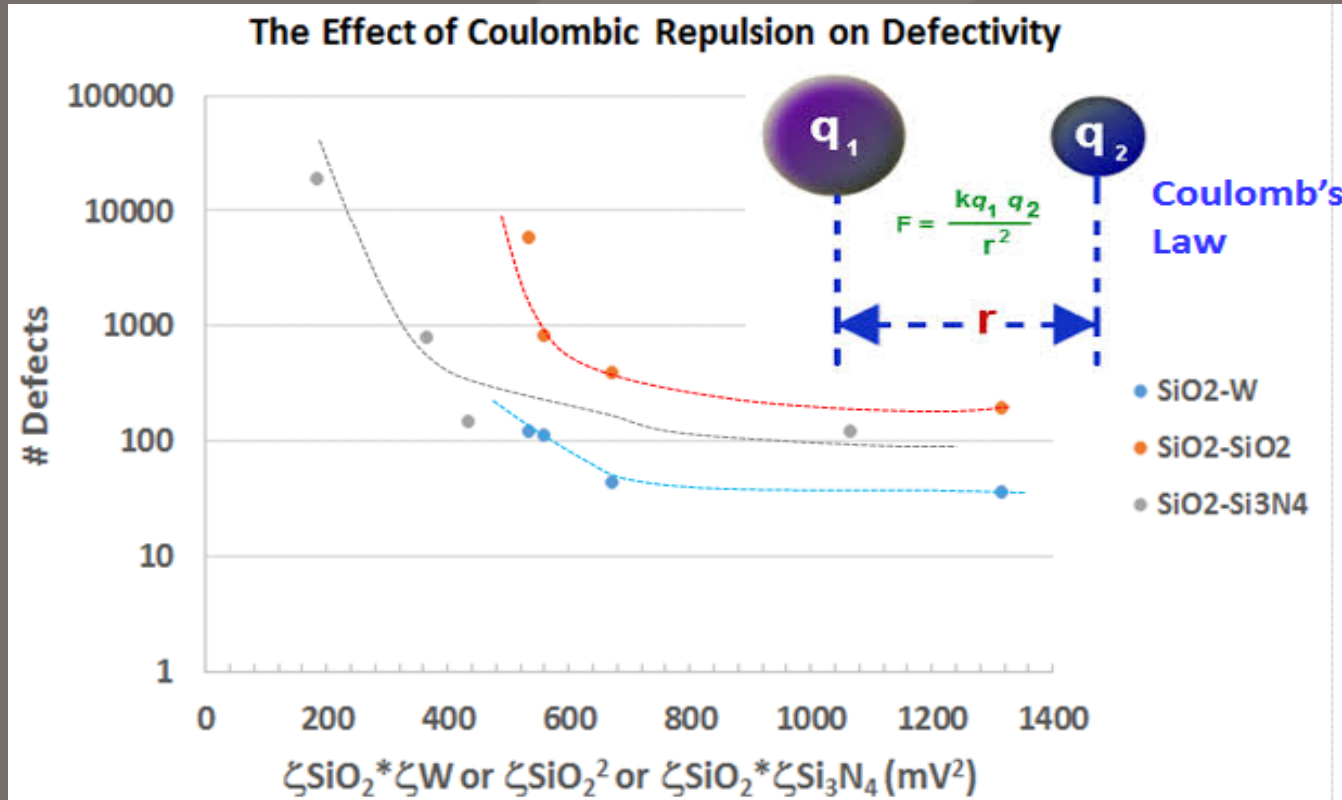
Contact Angle



FTIR



Defectivity Correlated to Charge Repulsion between silica particles and various surfaces (W, SiO₂, Si₃N₄)



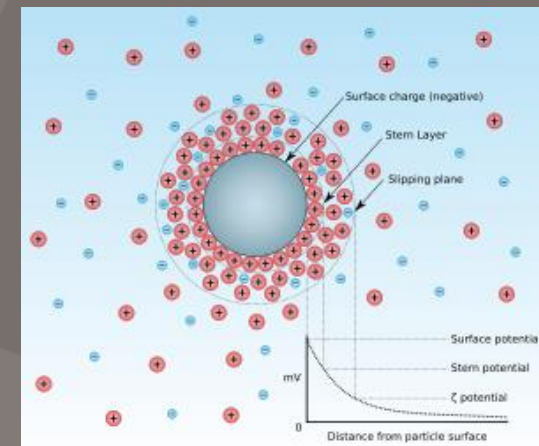
Zeta Potential

(Large-particle approximation for spheres)

$$\zeta \approx \frac{4\pi\eta(v/E)}{\epsilon}$$

↑ Viscosity ↑ Electrophoretic mobility (μ) ↑ Dielectric constant
M. Hubbe

Additive increases negative charge on silica surface



- 1 - White, M. L. et al, *Mater. Res. Soc. Symp. Proc.* 991, 0991-C07-02 (2007)
- 2 - Hedge, S. and Babu, H. V. *Electrochem. Soc. St. Lett.* V7, pp. 316-318 (2008)
- 3 - White, M. L. et al. *Mat. Sc. For.* 1249 E04-07 (2010).

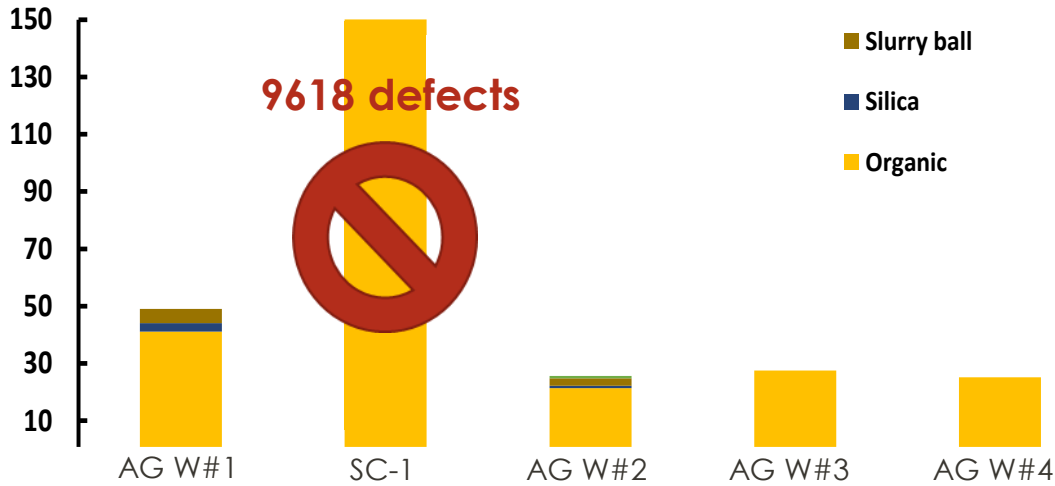
Acknowledgements:
Thomas Parson, Daniela White, Michael Owens

PlanarClean AG-W formulations

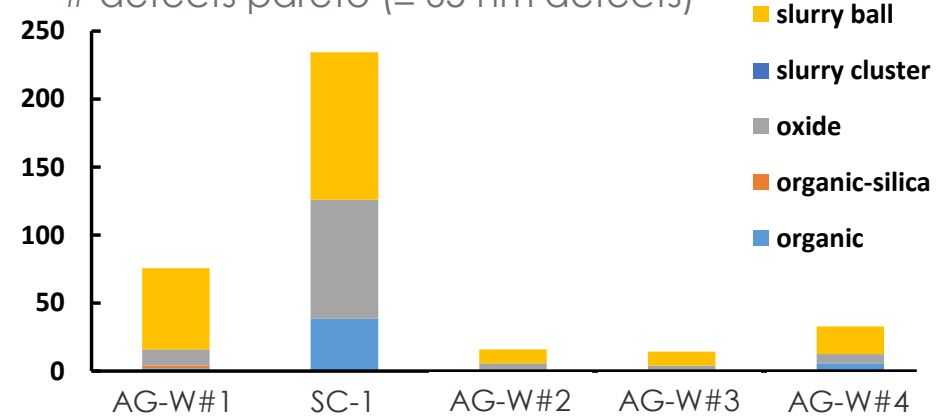
exhibit lower defects and organic residues over traditional cleans



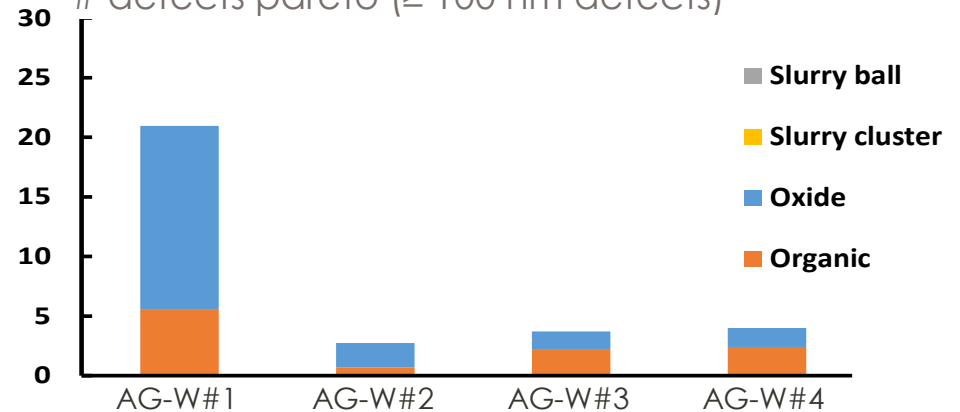
Si₃N₄ – EDR Review – Defect Pareto
defects pareto (≥ 65 nm defects)



SiO₂ – EDR Review – Defect Pareto
defects pareto (≥ 65 nm defects)



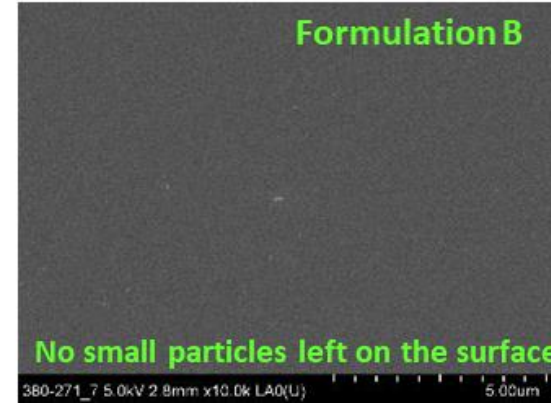
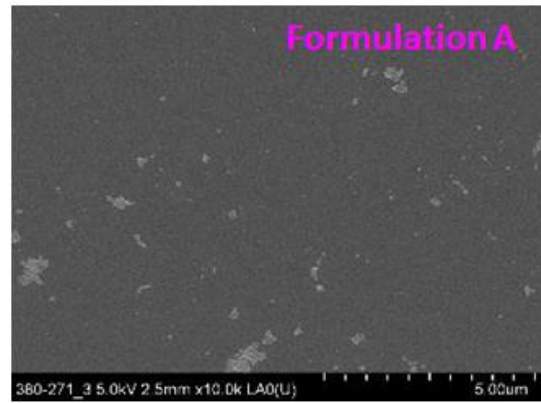
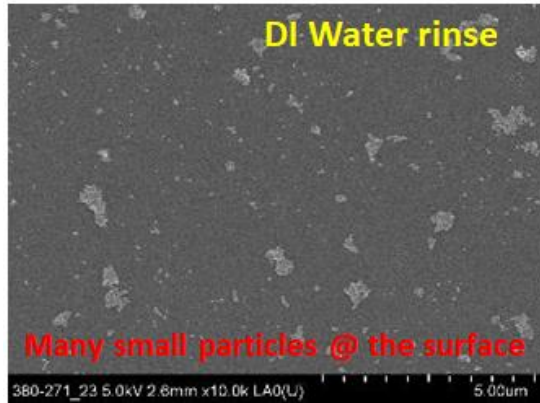
W – EDR Review – Defect Pareto
defects pareto (≥ 100 nm defects)



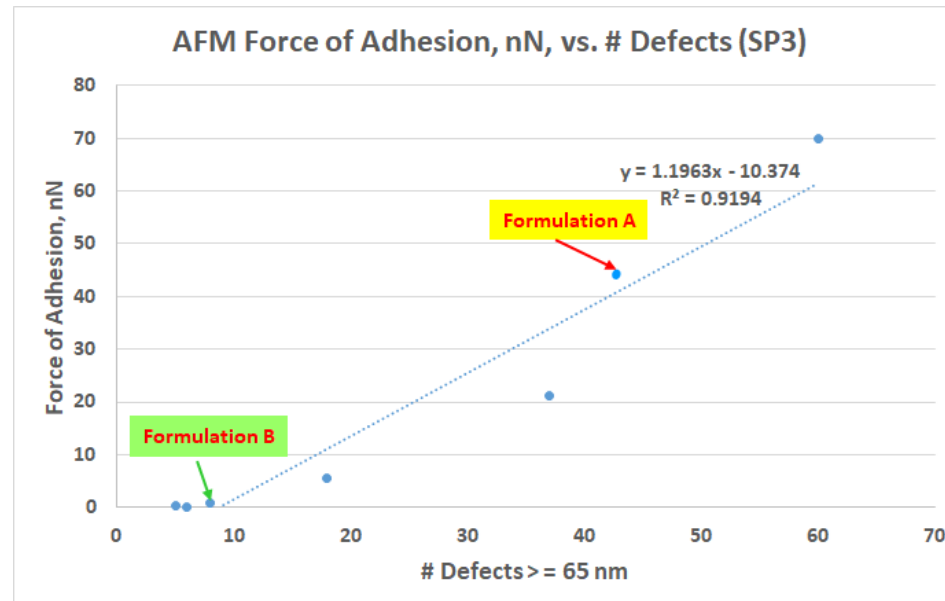
PC AG-W Series show improved performance over SC-1 on all substrates

SEM Images of PETEOS Coupons

Polished with W CMP slurry and cleaned with Formulations A and B

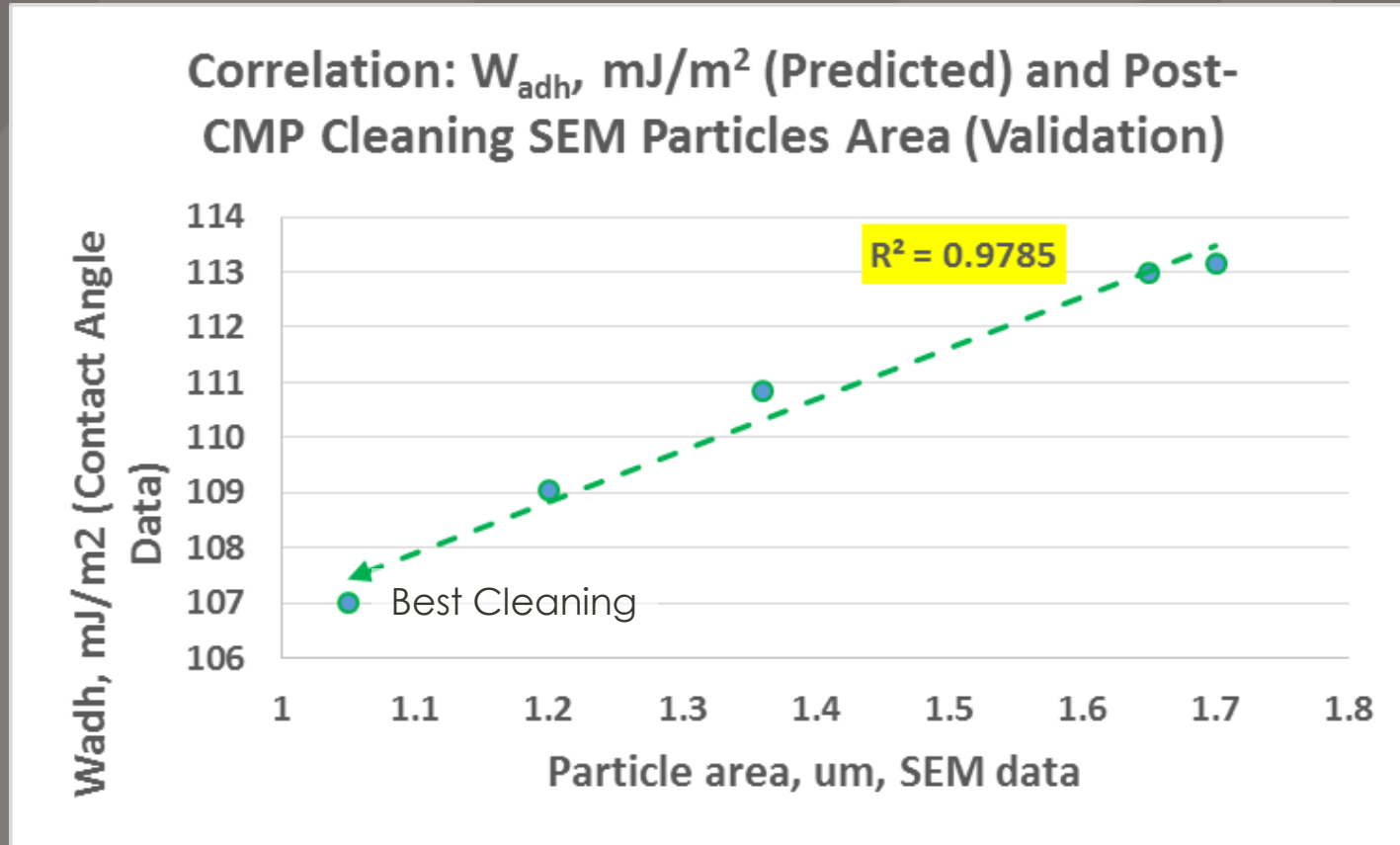


- Tabletop polishing
- Colloidal silica Ludox, PS = 20-30 nm
- pH = 2.3



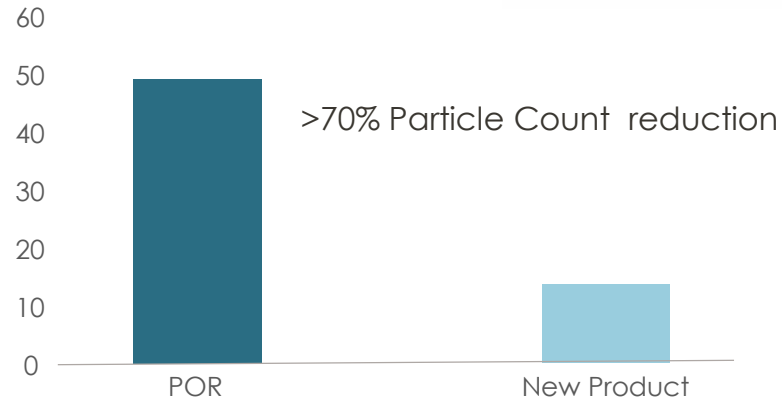
Correlation SEM vs. Calculated Adhesion

Based on contact angle measurements

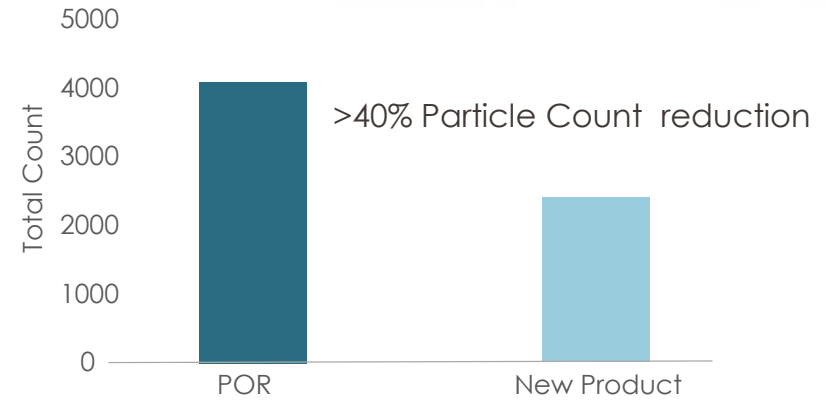


Planarcore® Improved Manufacturing for Reduced Particles

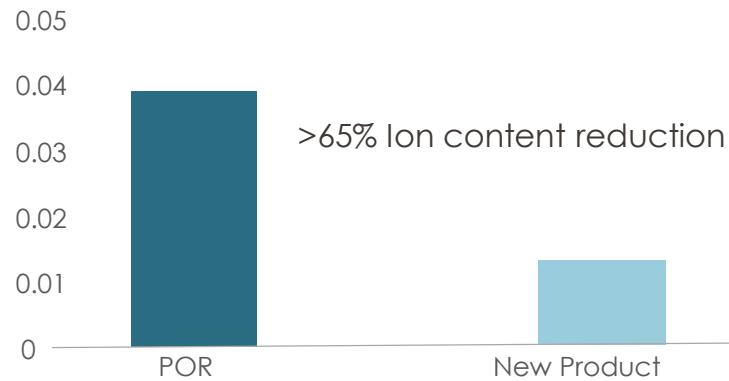
LPC 2.8 Micron



LPC 0.2 Micron



Total IC

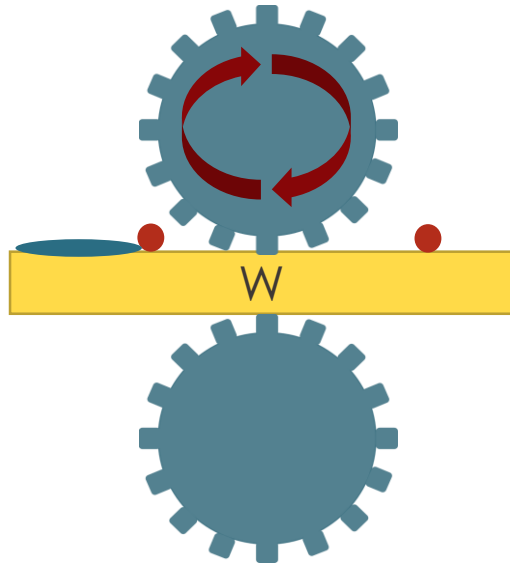


Process Can Often Play a Large Role

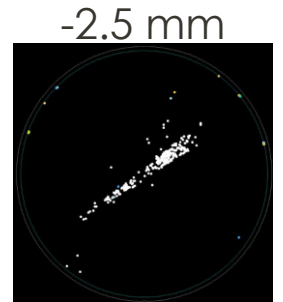
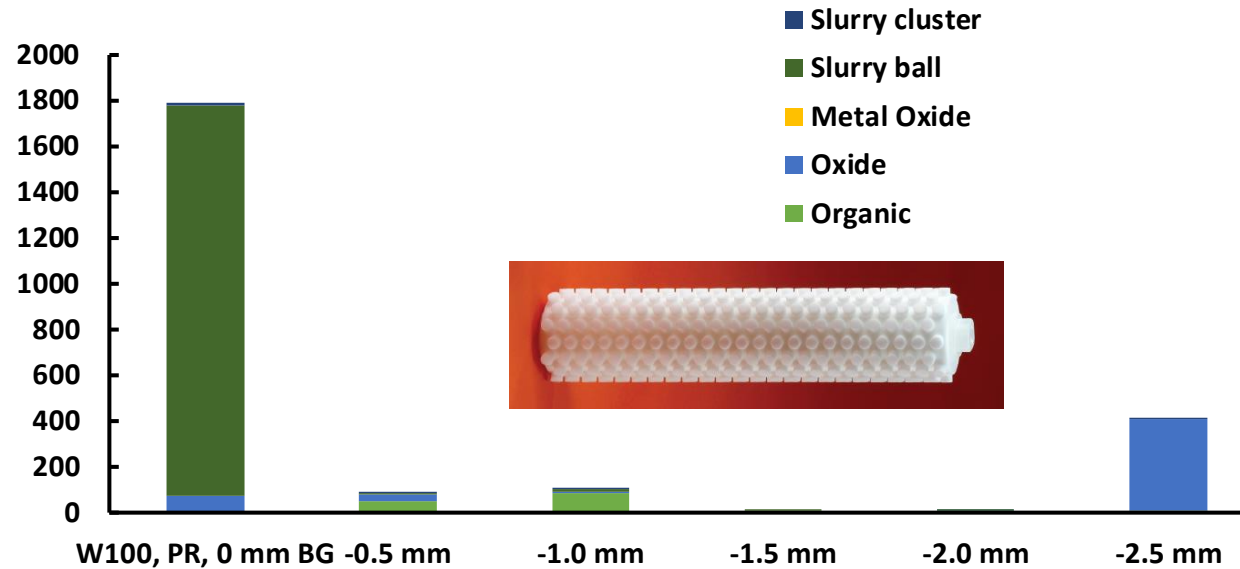
Impact of the Brush Gap

Brush cleaning:

physical + chemical cleaning

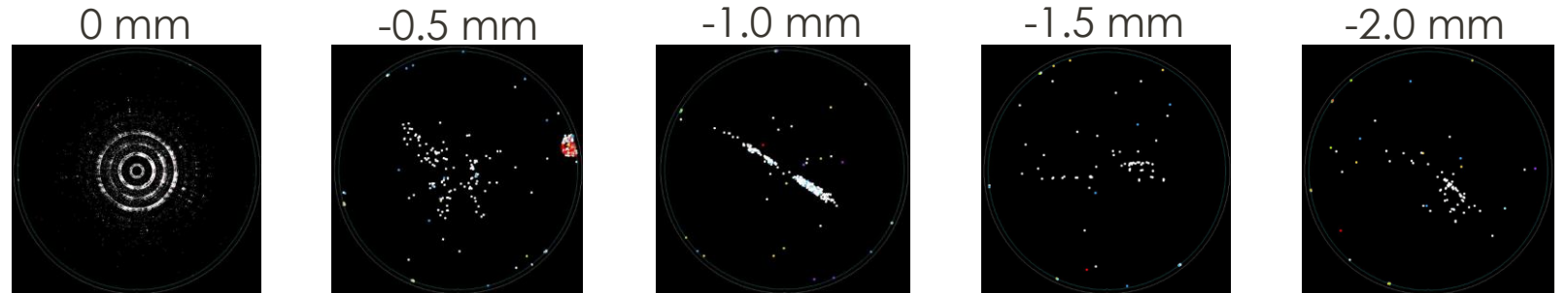


defects pareto (≥ 100 nm defects)



Brush Pressure:

- Too low: insufficient physical cleaning
- Too high: particles stick to PVA brushes and lead to brush marks



Conclusions

Entegris believes that advanced metrology and better simulations of customer processes are the key to designing more effective PCMP cleaners

In situ electrochemistry (Tafel, impedance) under brushing conditions

Model reactions such as cerium silicate bond-breaking studies

Synthesis of Cu-BTA residues

Measurement of particle-wafer interaction energies

Spectroscopic analysis of surfaces, particles and side reactions

(UV-Vis, FTIR, TOF-SIMS, XPS, Raman, $1\text{H}/13\text{C}$ /multinuclear NMR)

Proper mechanistic studies have led to superior defectivity and advanced node patterned wafer corrosion performance

Thank you!

A white speech bubble with a tail pointing down and to the left, containing the text "Q&A". The bubble is centered over a background of silhouetted business professionals in a meeting, with a city skyline and digital data overlays in the background.

Q&A

Appendix

