Asymptotically Approaching Zero Defects:

The Future of Post-CMP Cleaning

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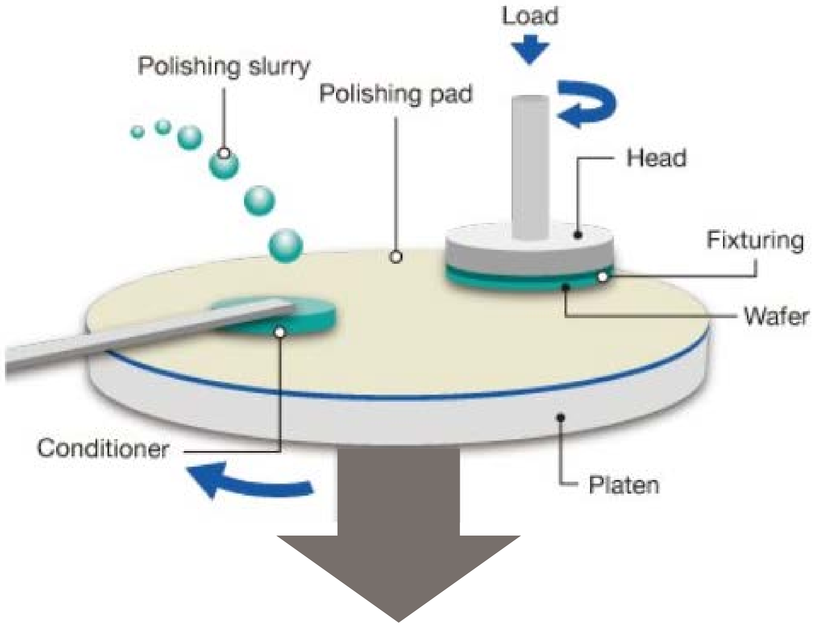
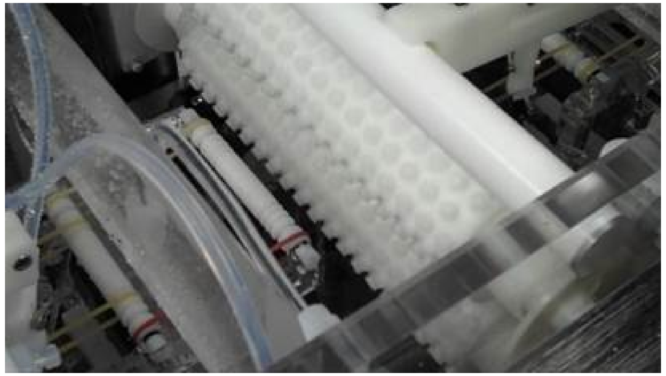
Agenda

- Market trends in PCMP
- Copper PCMP
- W PCMP
- CeO_2 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





Graphic source: http://www.azom.com/article.aspx?ArticleID=12527

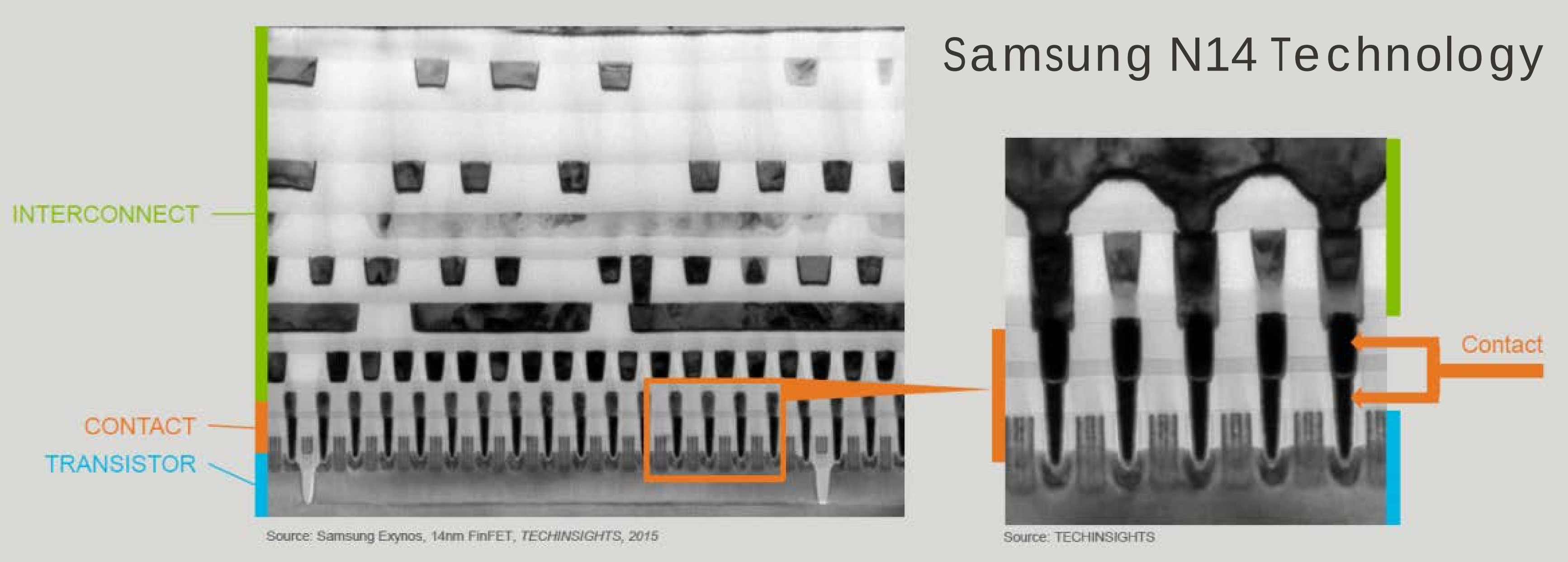
New Materials Lead to Cleaning Complexity

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, Re_2C, ...)

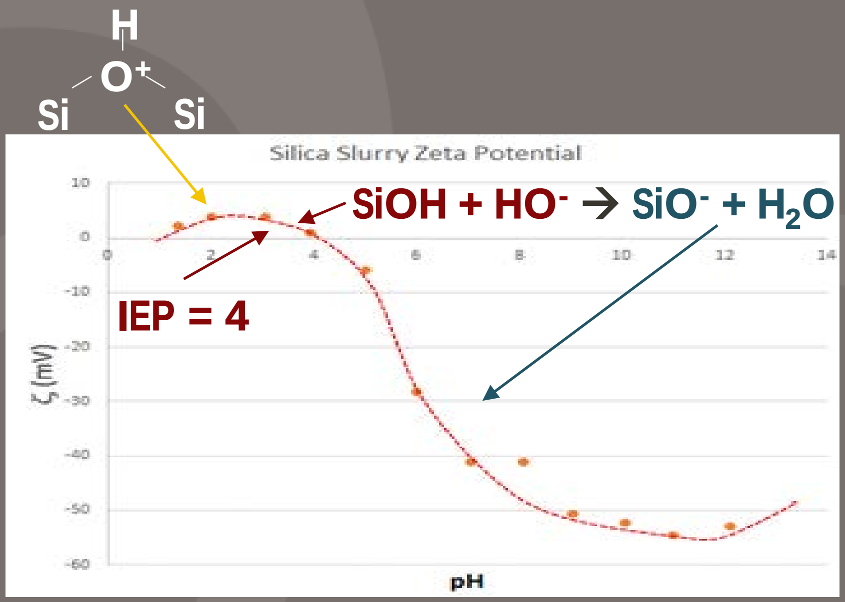
Dielectrics

- TEOS
- Thermal oxide
- Si_3N_4
- Low-k dielectric, SiC (SiOC, SiON, etc.)
- Polysilicon, single crystal silicon (wafer, various doping)
- Doped glass (BPSG, PSG, etc.)

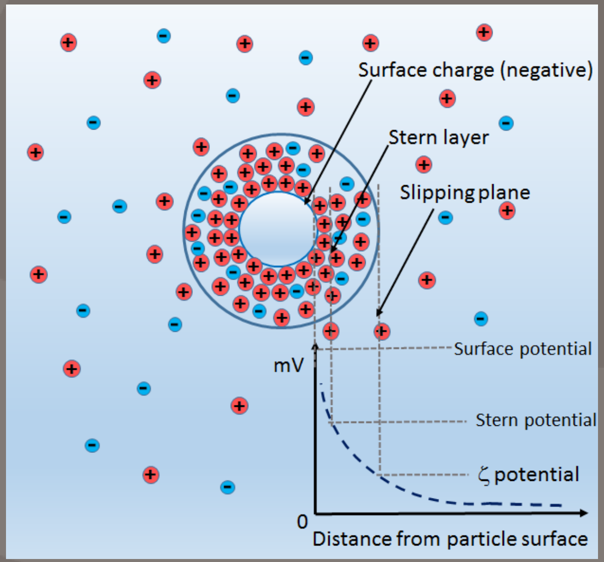


Challenges/Diversity in Particle Cleaning

- 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



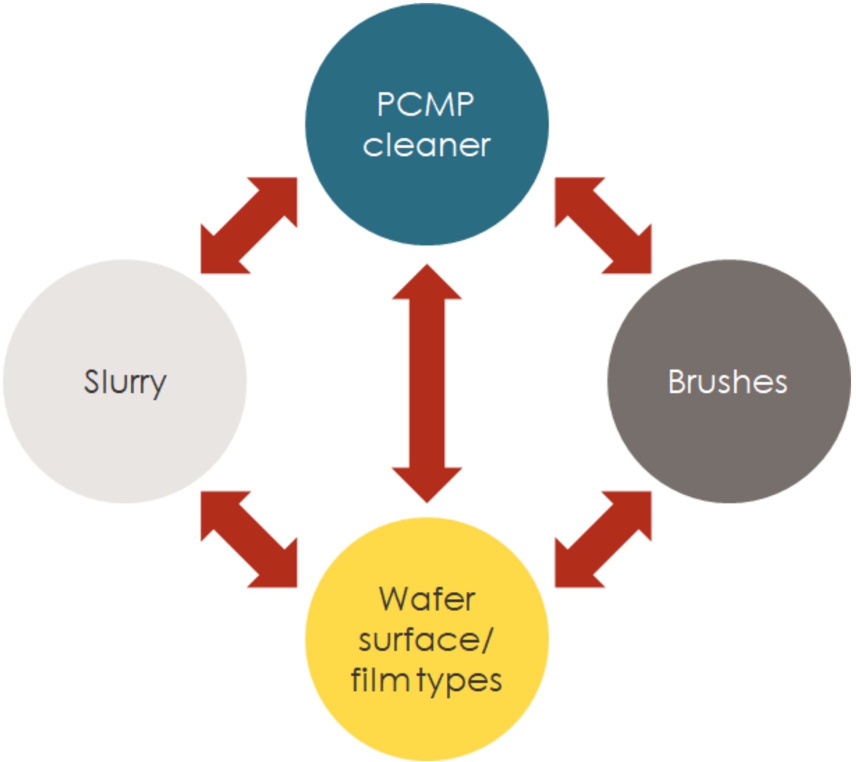
Zeta potential $\zeta = 4\pi\gamma(v/E)/\varepsilon$



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



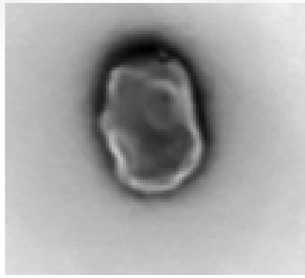
More predictive simulation/models needed

Challenges in Cu PCMP

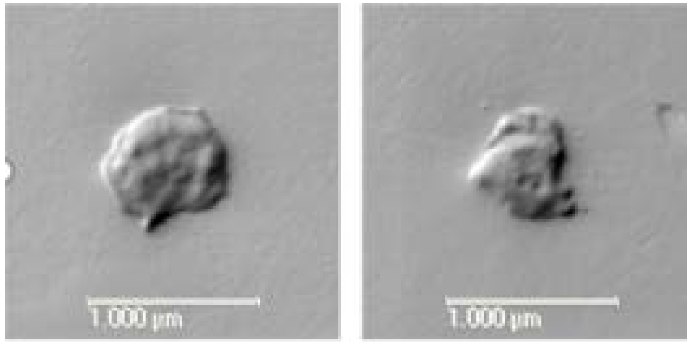
- Advanced generations requiring very low or no defects
  - Organic residue
  - Silica particles
  - Metal particles
- Minimal/zero corrosion to exposed metals (Cu, TaN, Co, Ru)
  - No galvanic corrosion or barrier attack
  - Low Cu recess/etch rates → 3–10 nm technology
- Minimal Cu surface roughness
- 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

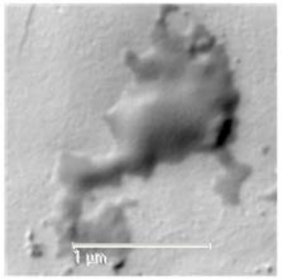
- Corrosion-inhibitor – metal complexes (i.e., Cu-BTA)
- Surfactant residues
- Interactions between slurry additives and cleaning additives
- Pad debris (polyurethane – hydrophobic or hydrophilic)
- Brush debris (crosslinked PVA – hydrophilic)
- Plating additives
- Filter or tubing shedding/residues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



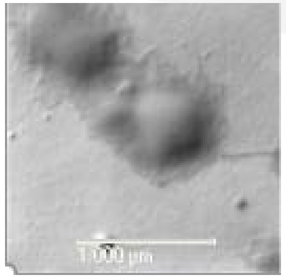
Pad or brush debris
EDX = C, N, O → polyurethane pad
EDX C, O only → brush



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



Soluble organic
or
surfactant residue



Advanced defect metrology has enabled detection of smaller defect sizes

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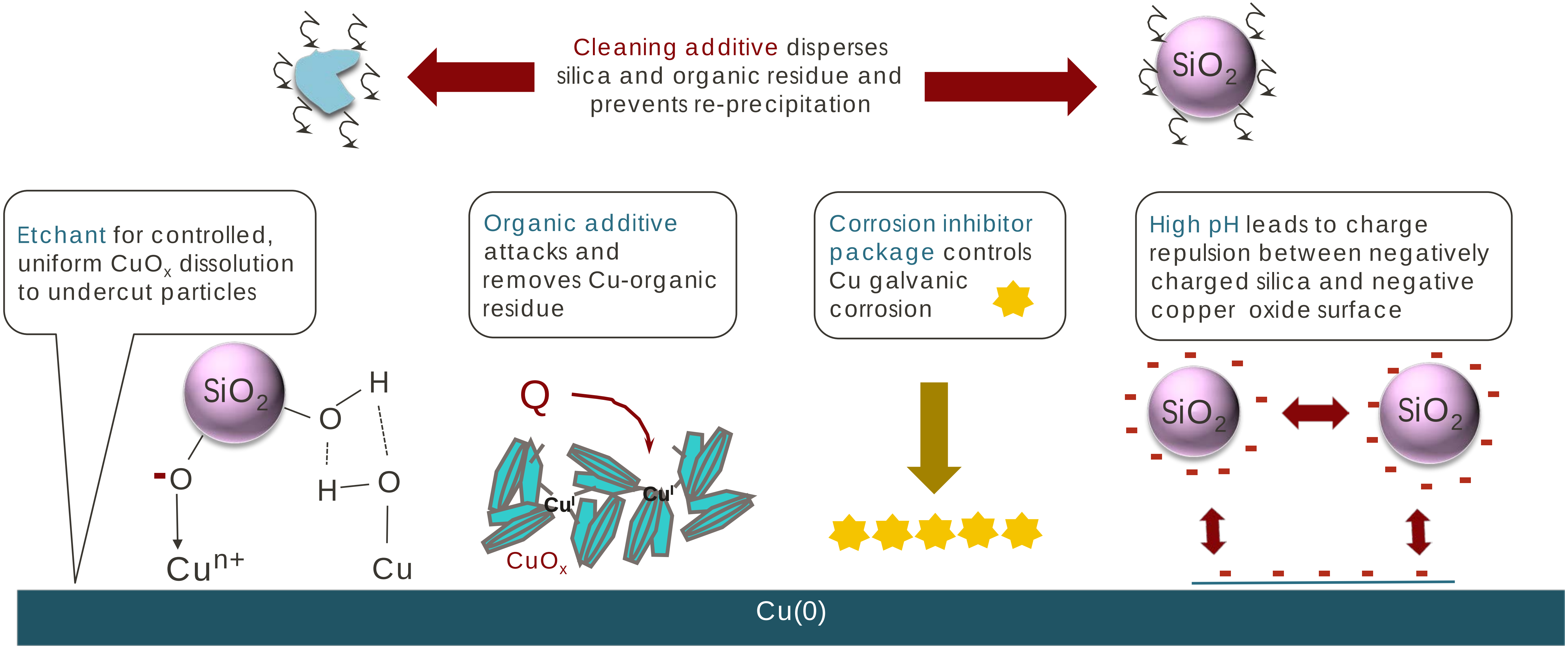
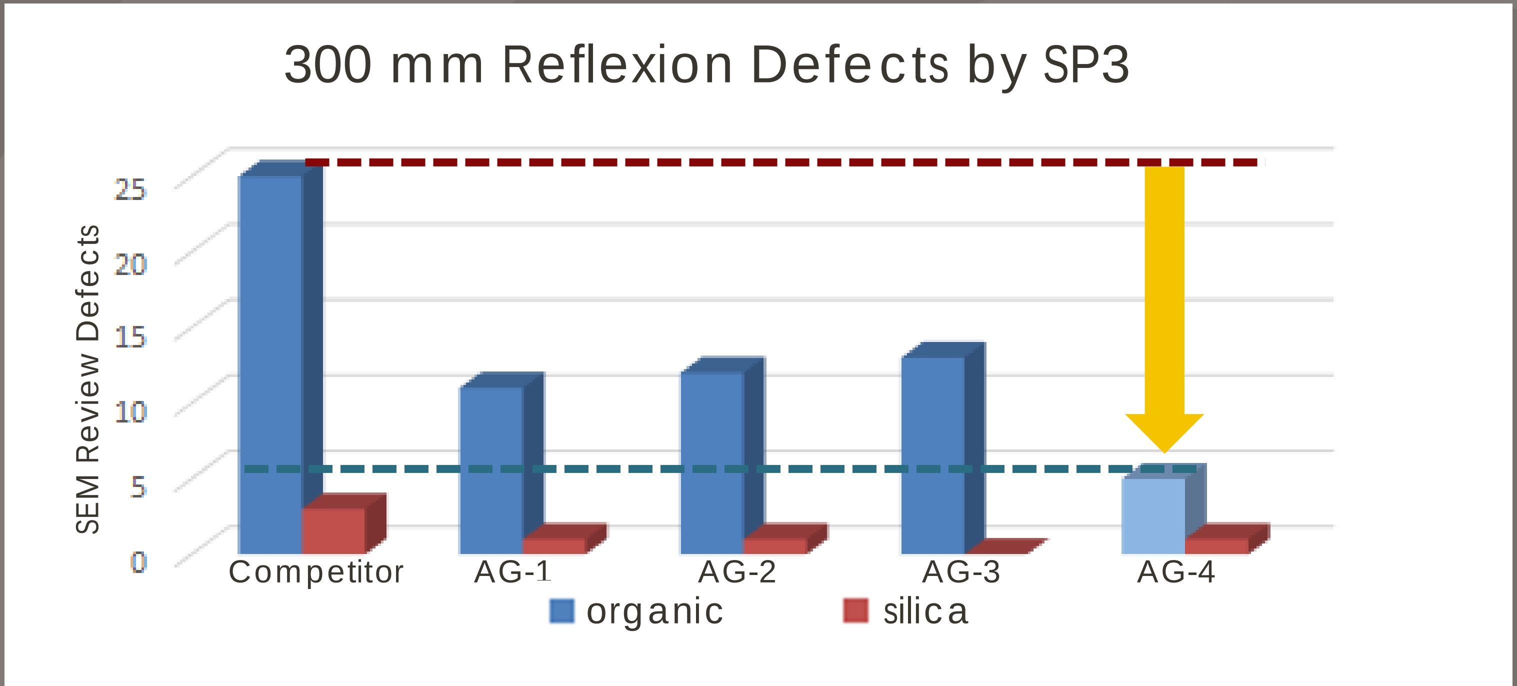
PlanarClean® AG - Advanced Generation Copper Cleaning Mechanism



IMEC Reflexion Data

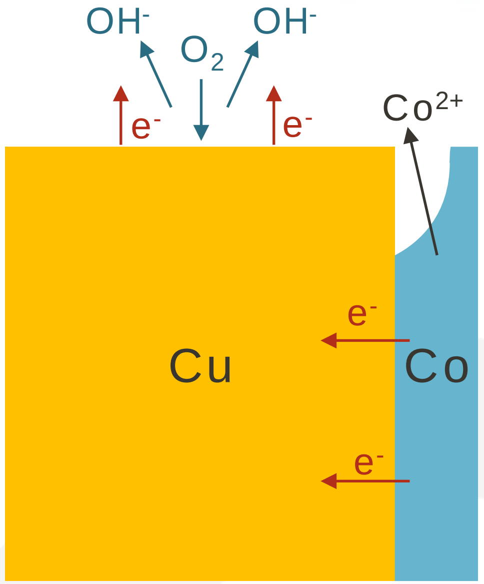
Shows lower organic and silica defects compared to the competitor



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

Copper Wafers

PlanarClean® AG Formulations
show improved galvanic corrosion

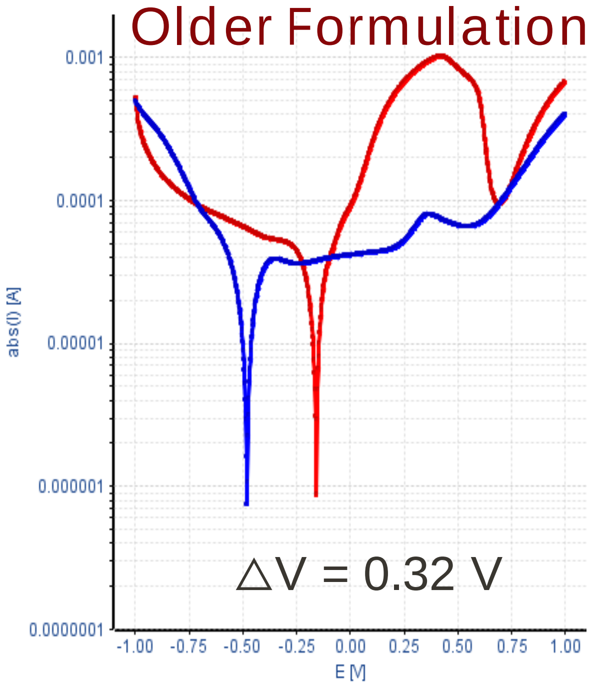


$$Co \rightarrow Co^{2+} + 2e^-$$

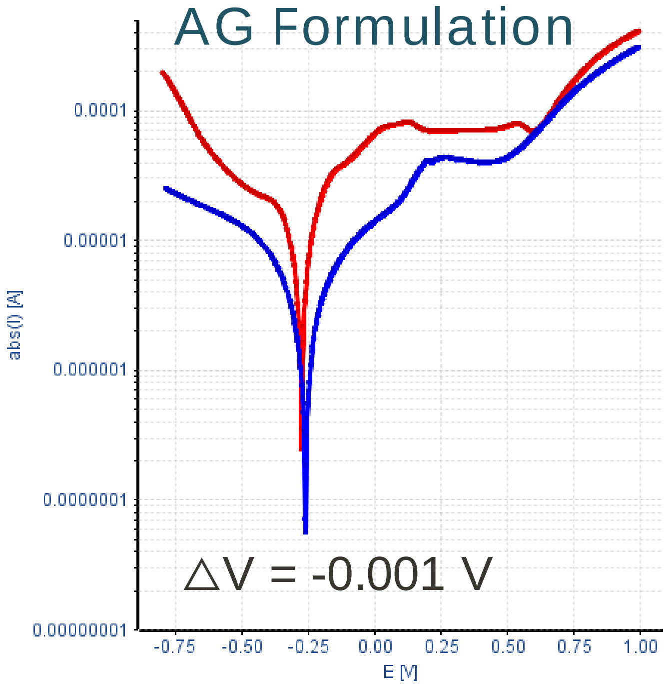
$$0.5O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

Controlled Electrochemical Properties

- Ligands to control OCP gap
- Passivation to modify resistivity



Anodic Co corrosion



Nearly zero galvanic corrosion

Copper **Cobalt**

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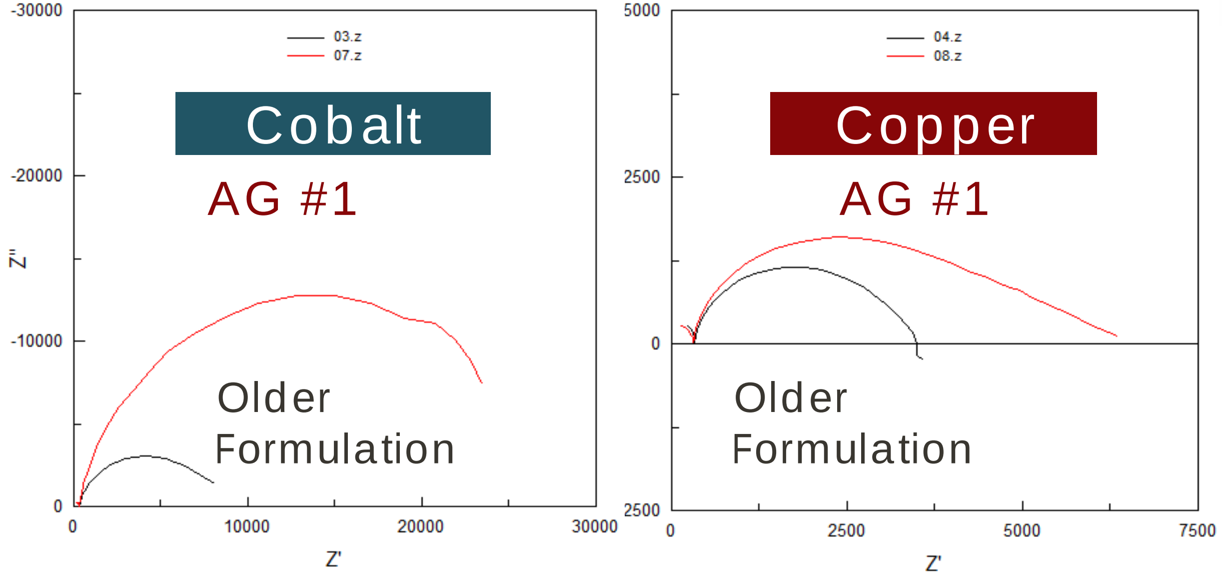
PlanarClean® AG Formulations

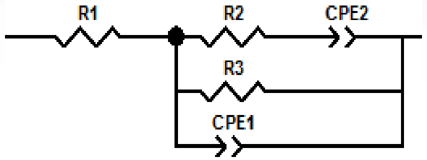
maintain higher film integrity on both Cu and Co

Impedance Spectroscopy



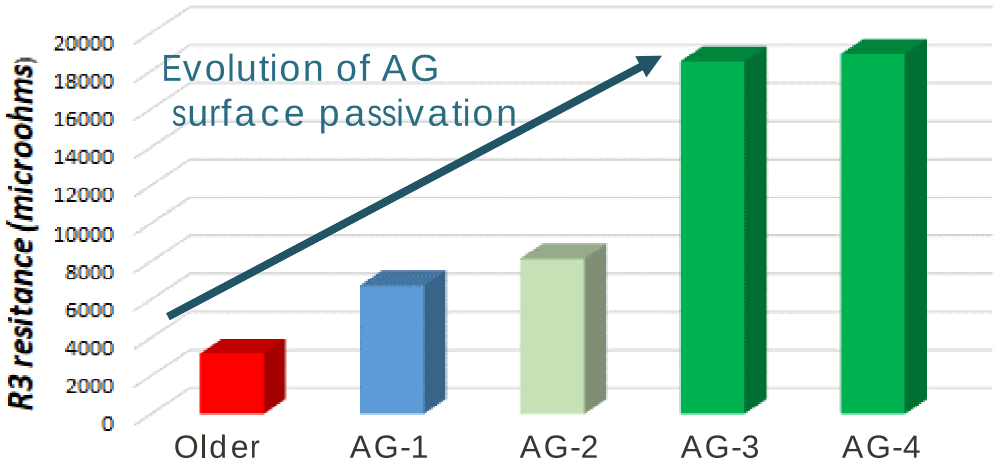
Higher impedance storage and loss components → higher film integrity

Additional novel Cu inhibitor in AG Formulations improves Cu passivation



Fitting model

Calculated Cu Film Resistance for Various PCMP Formulations



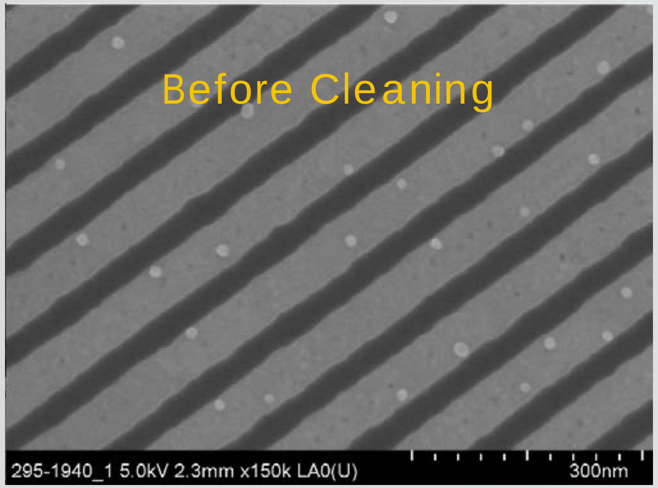
When w -> 0

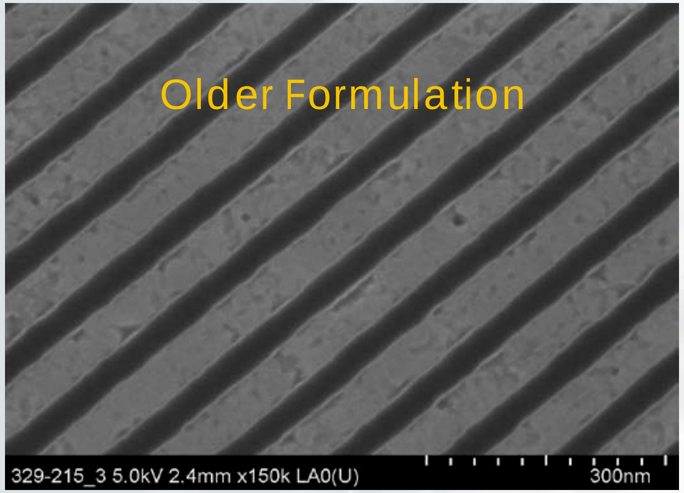
$$Z' = R_{\Omega} + \frac{R_{ct} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl}+1)^2 + \omega^2 C_{dl}^2 (R_{ct}+\sigma\omega^{-1/2})^2}$$

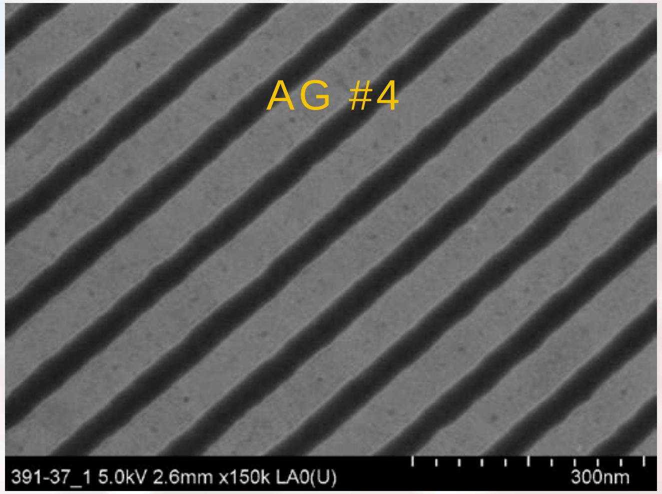
$$Z'' = -\frac{\omega C_{dl}(R_{ct}+\sigma\omega^{-1/2})^2 + \sigma^2 C_{dl} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl}+1)^2 + \omega^2 C_{dl}^2 (R_{ct}+\sigma\omega^{-1/2})^2} a$$

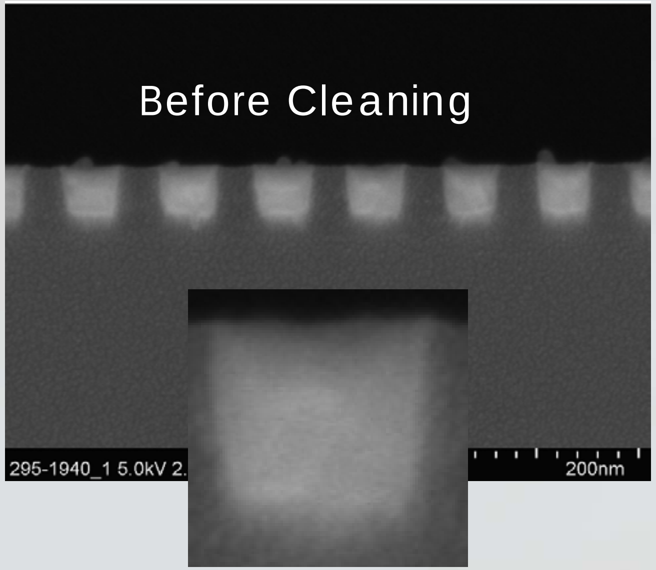
SEM Cross-Section Analysis

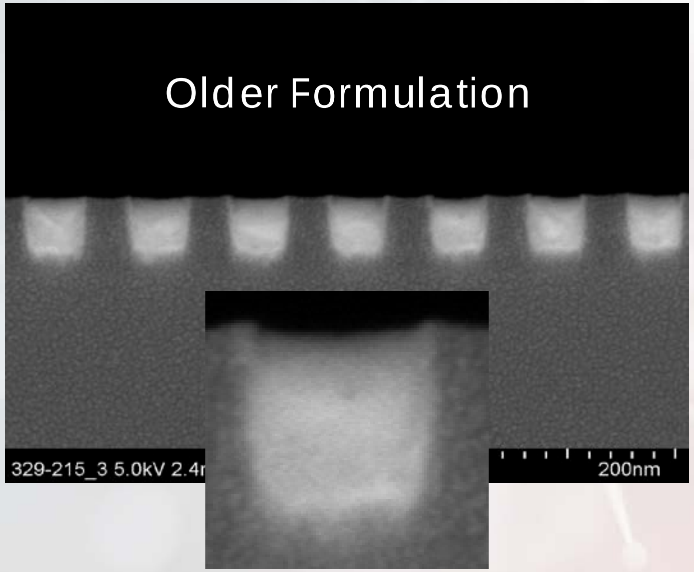
IMEC 45nm Cu/Co patterned wafers show no evidence for corrosion

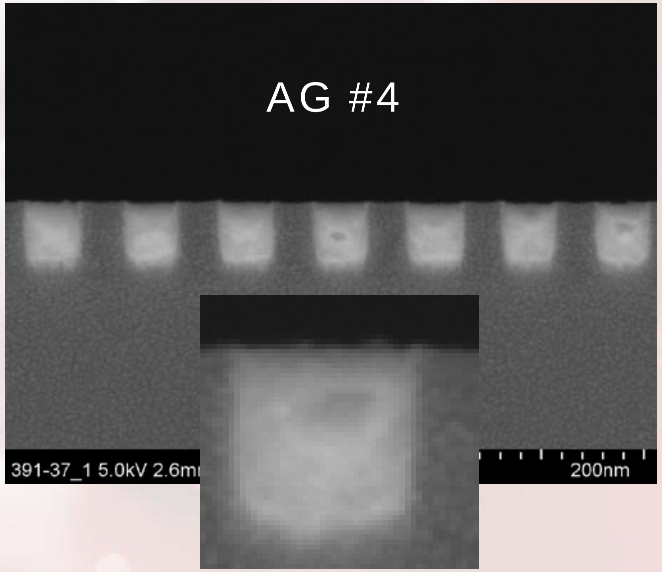










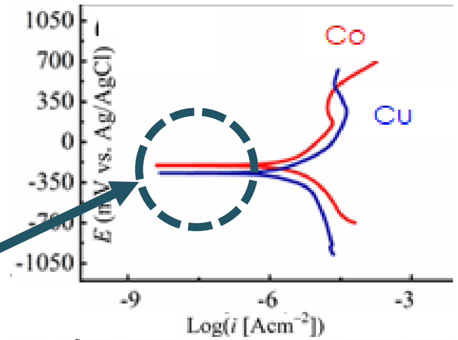


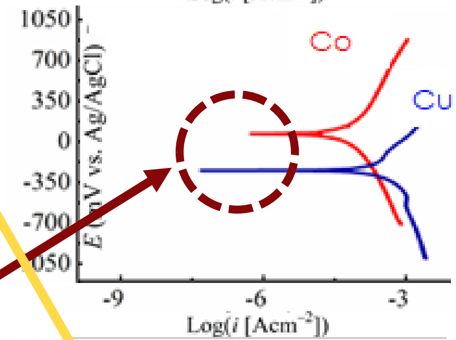
In-Situ Electrochemistry

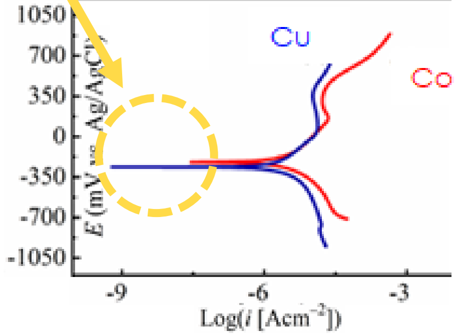
shows OCP shift under brushing conditions

Nearly Matched OCP for Cupper and Cobalt
No corrosion indicated

Galvanic corrosion

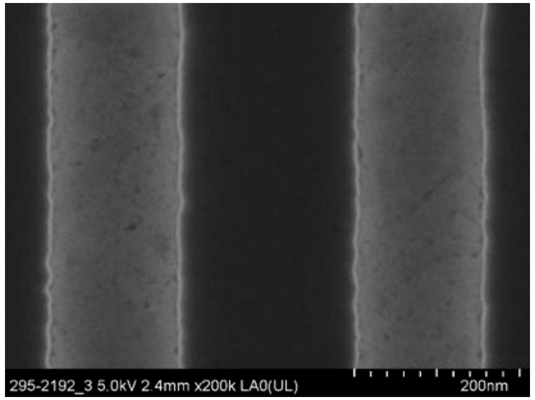




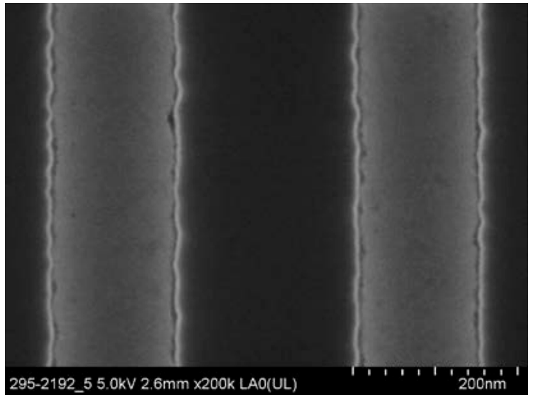


Data indicates the kinetics of the inhibitor reacting with cobalt is critical

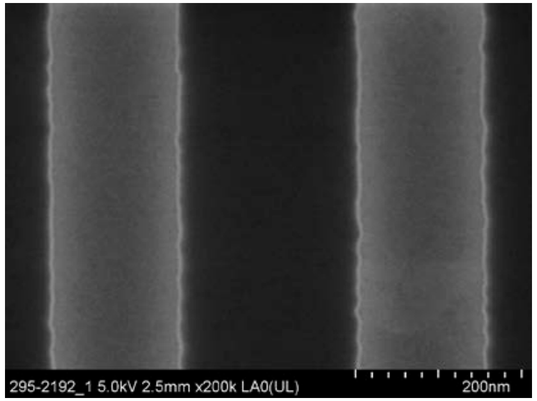
Old formulation - no brush



Old formulation dynamic with 60 RPM brush



Good formulation with 60 RPM brush

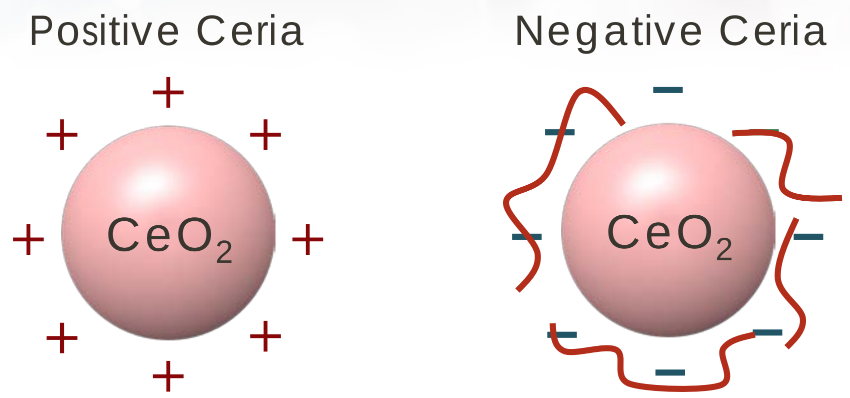


Developed in conjunction with Prof. D. Roy and C. Johnson at Clarkson University

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 (H_2O_2 + H_2SO_4)
- TMAH + SC-1

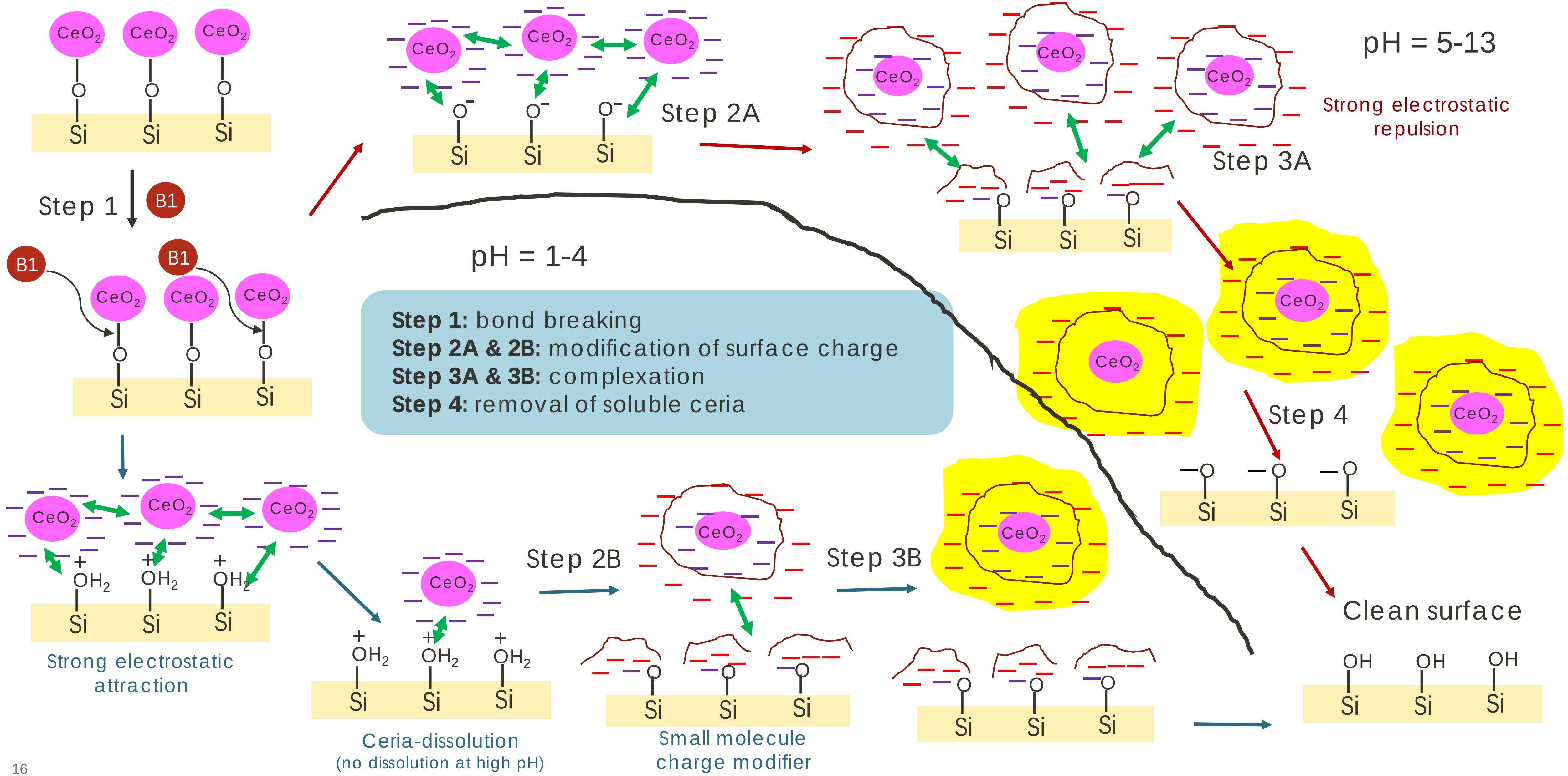
- Highly toxic
- Unformulated
- Environmentally unfriendly
- Damage to dielectric

Entegris AG Ce-XXXX formulations

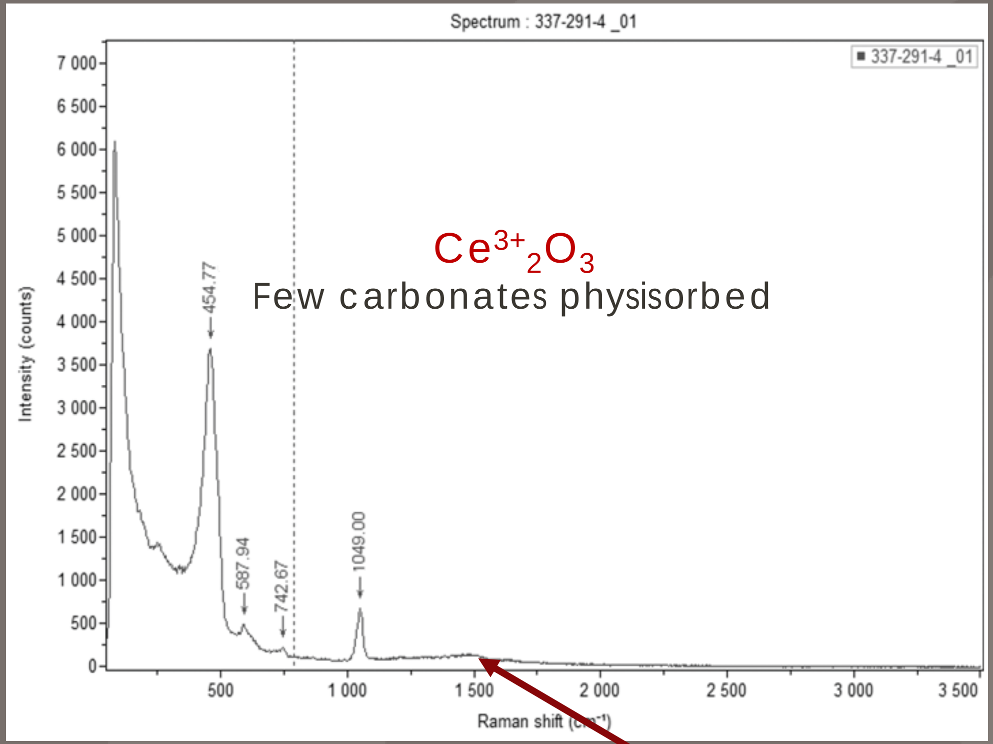
- Improved particle and metal removal
- Replace toxic commodity cleaners
- Environmentally friendly
- No damage to dielectric surfaces
- Ce residue post-CMP cleaning < 10^{10} atoms/cm^2

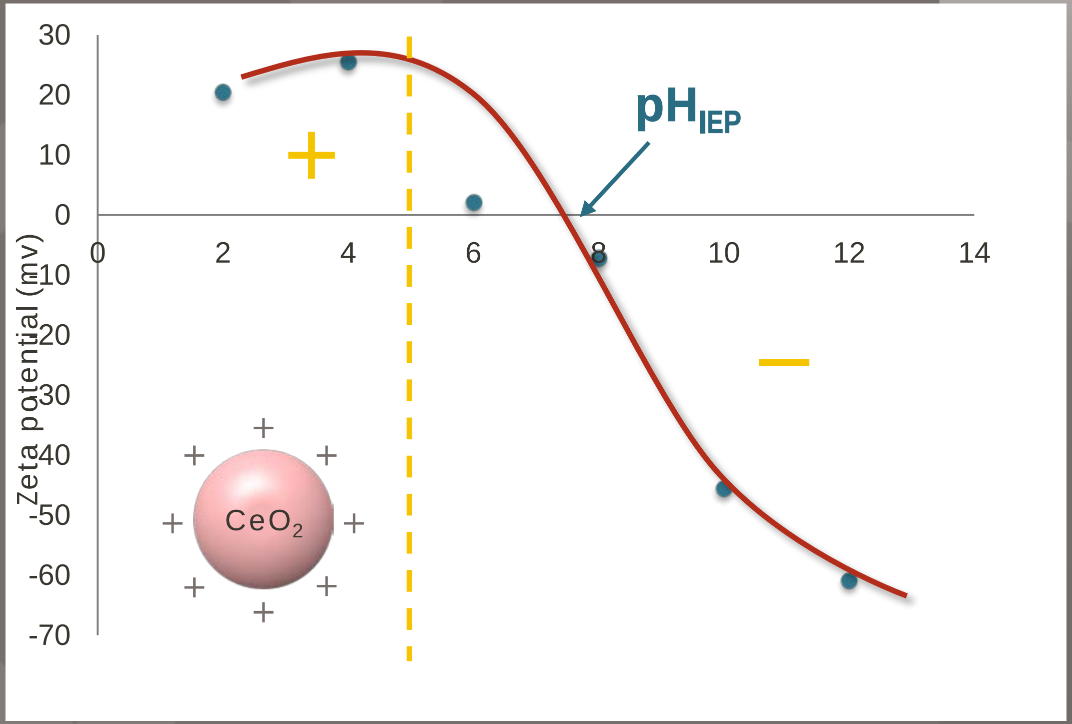
Entegris

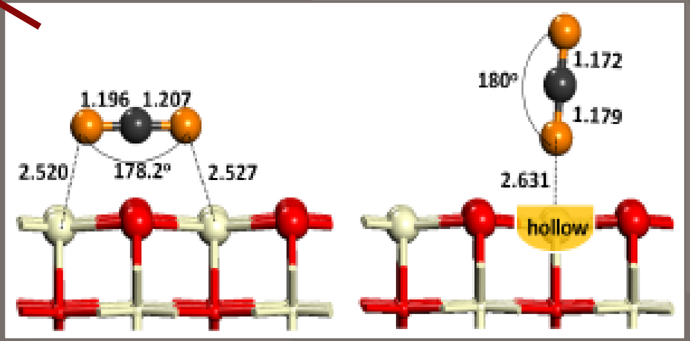
Higher pH vs. low pH Cleaning Mechanism of Negative Ceria



Ceria Particle Surface Chemistry Enables the Design of Efficient Ceria Cleaners



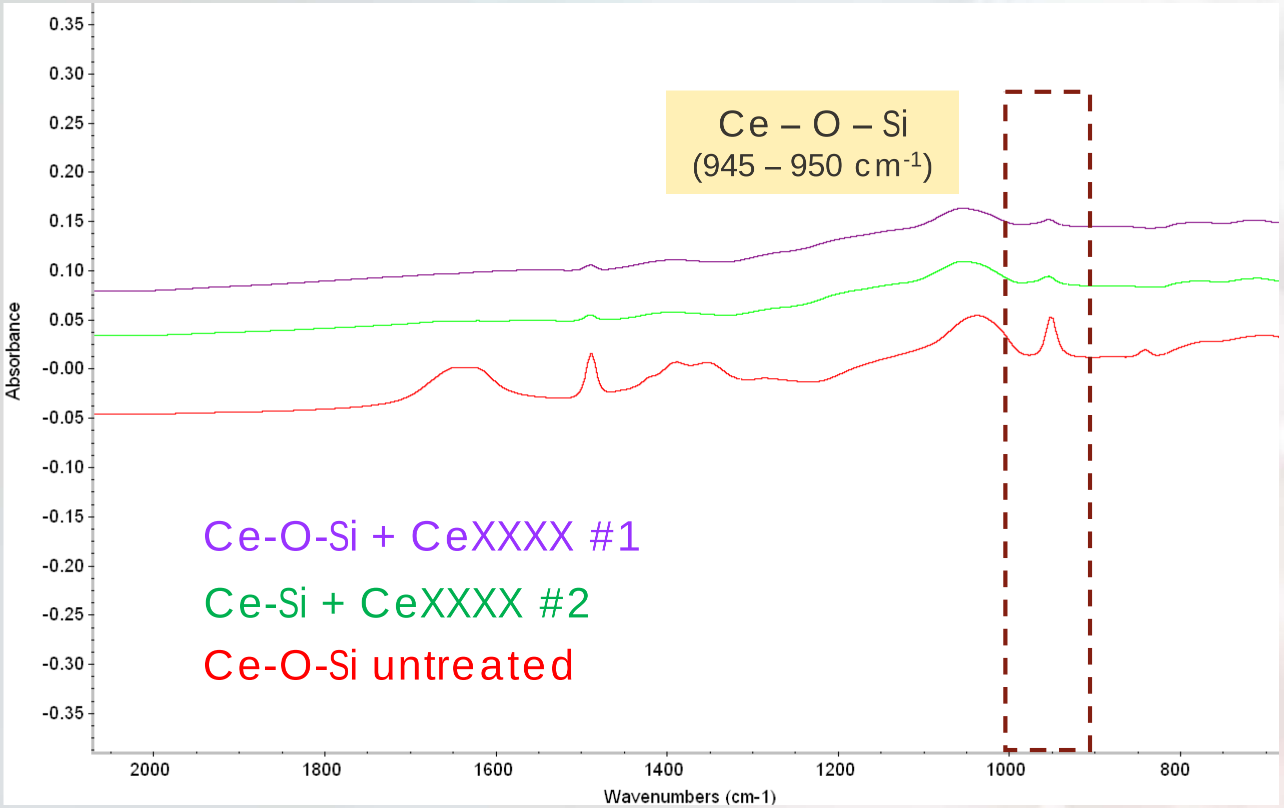


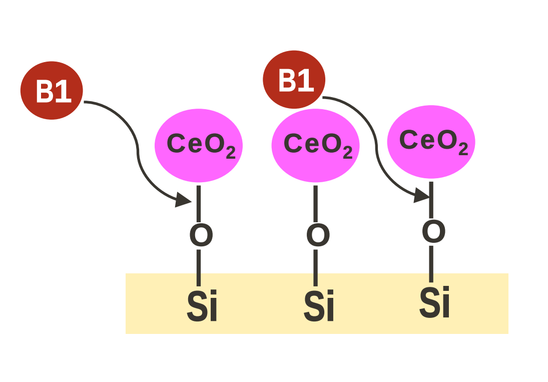


FTIR IR Spectra of Cerium Silicate Shows the Effectiveness Bond Breaking Agent

Si – O – Ce solid sample + CeXXXX sample → Solid material isolated + filtrate isolated

IR of sample before and after treatment

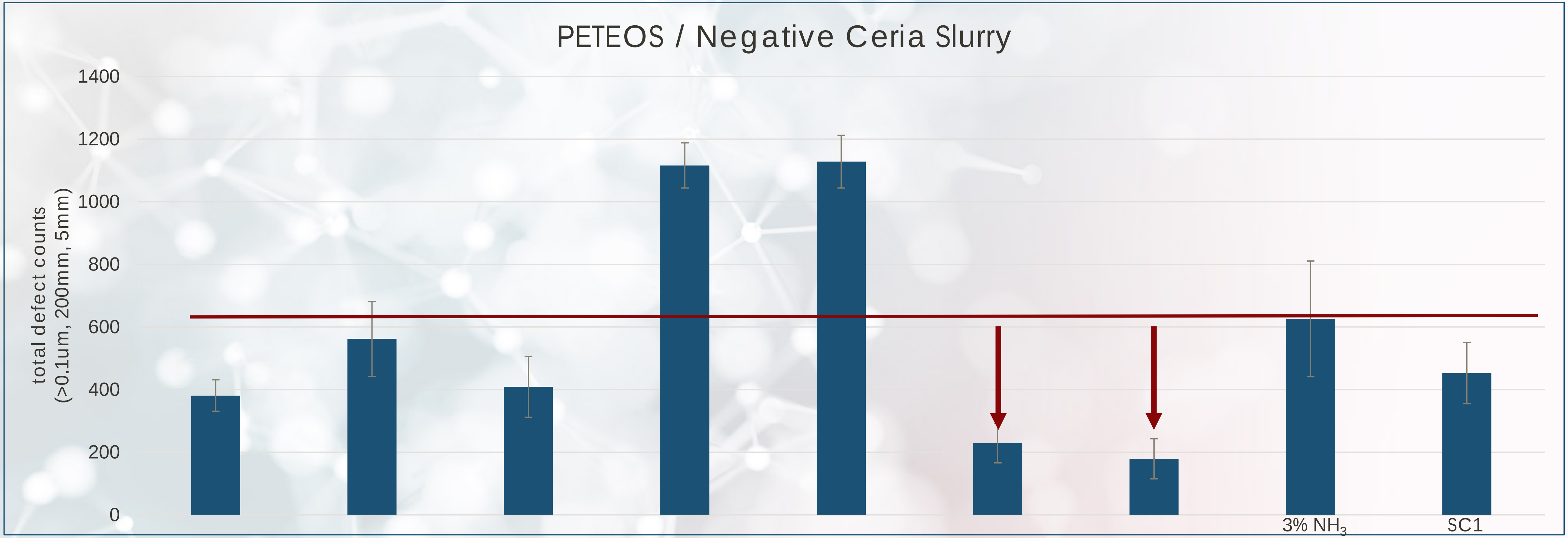




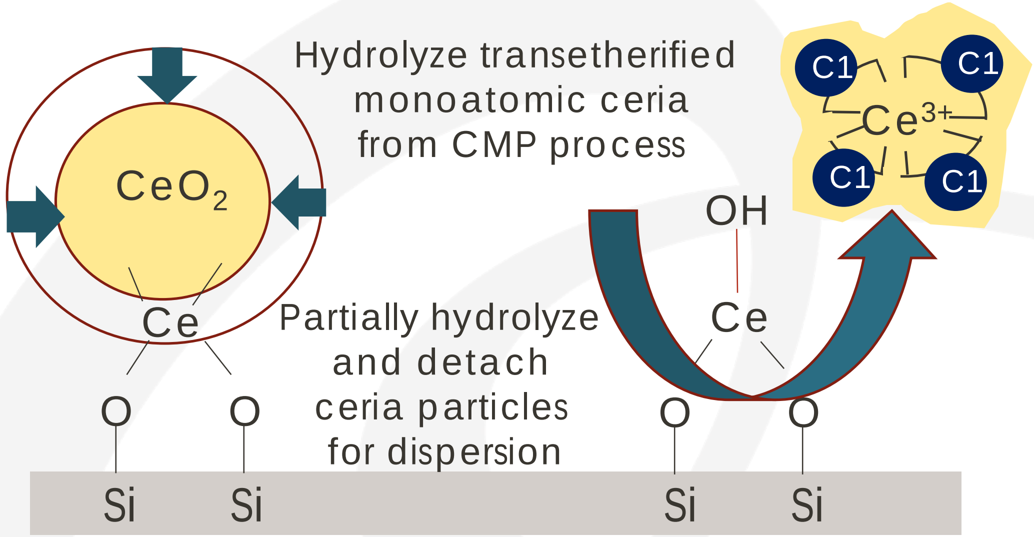
Relative Ce – O – Si intensity is greatly reduced with CeXXXX

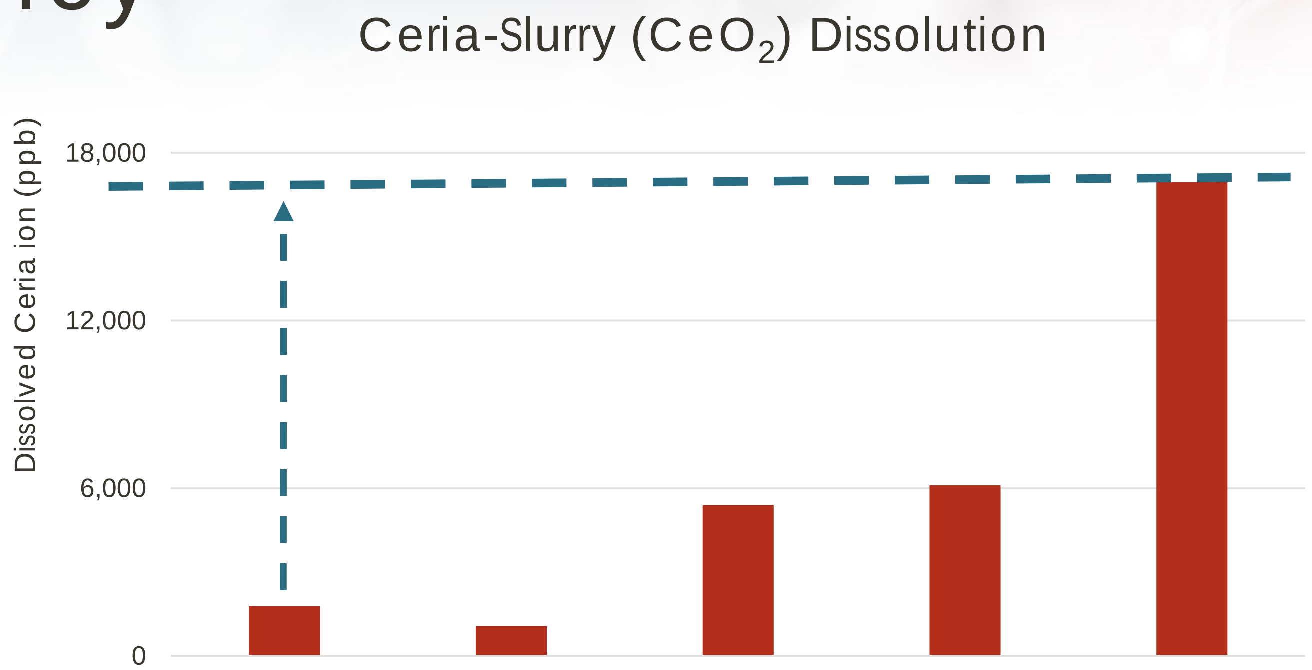
Full Wafer Cleaning Data

shows significant cleaning improvements



Advanced Products Have Higher CeO_2 Dissolution Efficiency



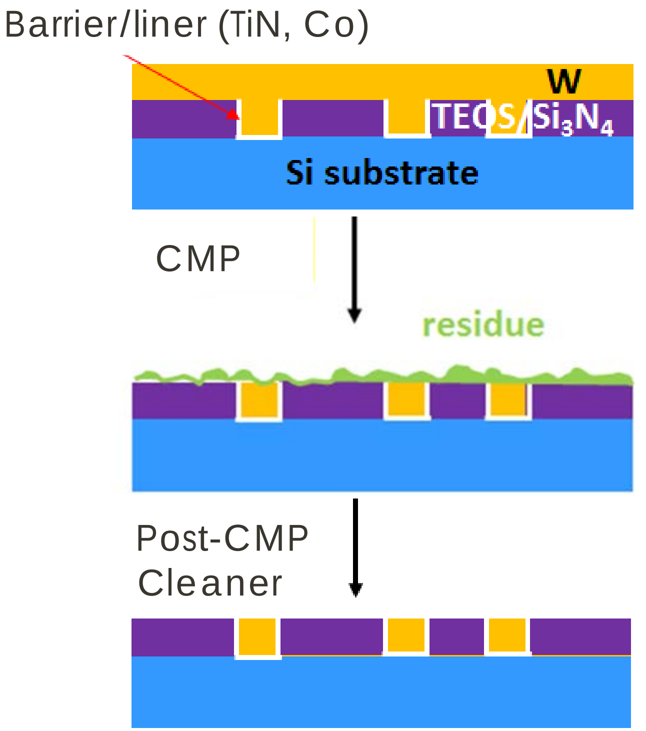


Why is increased ceria dissolution desirable?

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: Si_3N_4, TEOS, SiC, etc.
- Defect counts DDC ≥ 0.065 mm lower than commodities: dAmmonia, SC-1
- Low W/TiN galvanic corrosion
- Mt atoms < 10^{10} Mt/cm^2

- No increased roughness
- Market increasingly challenged by W recess
  - High pH commodities (SC1, dil NH_3)
  - 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)

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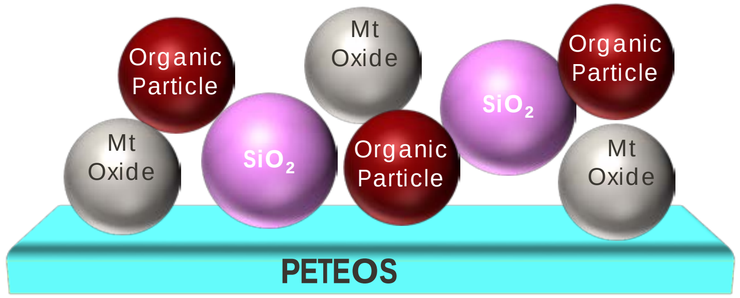
Post-CMP W Cleaning Mechanisms vs. pH

W CMP residue: silica, Mt oxide, organics

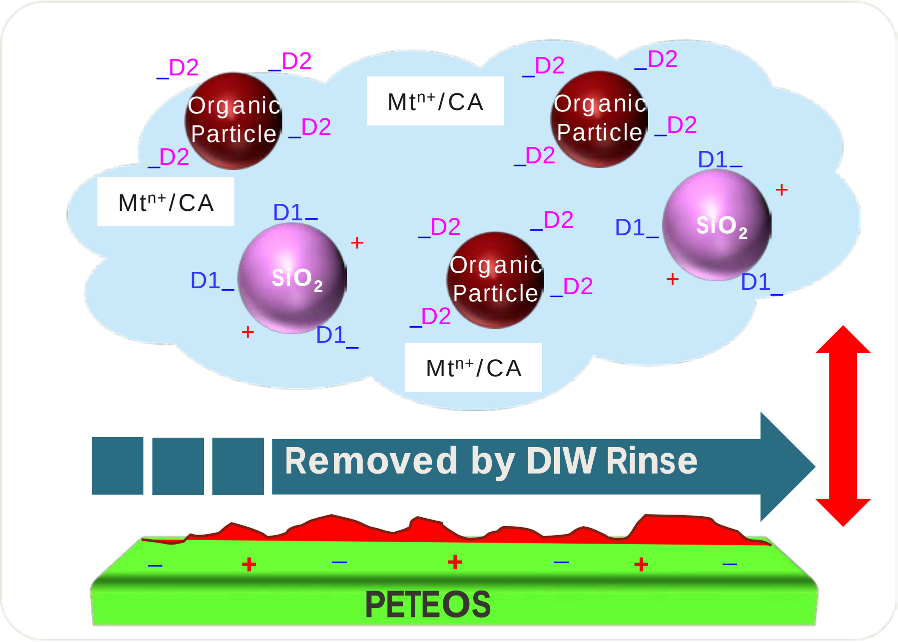


Low pH

- Silica brush imprints
- Good Mt removal (~10^{10} atoms/cm^2)

High pH

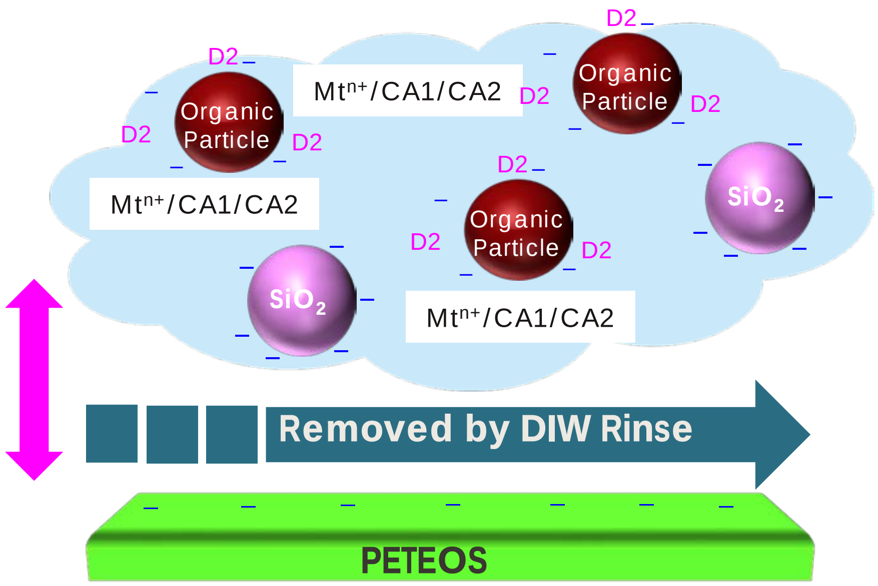
- No Silica brush imprints
- Poor Mt removal (4-6 X10^{10} atoms/cm^2)



CA = Mt complexing agent
D1 = SiO_2 dispersant
D2 = organic residue dispersant

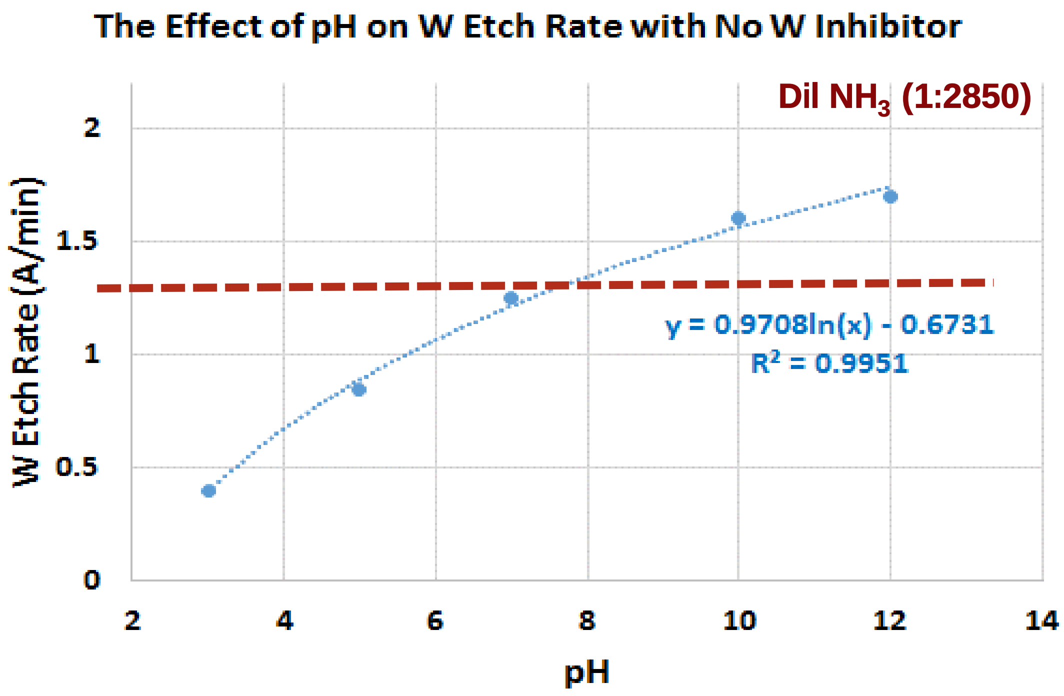
steric repulsion

electrostatic repulsion



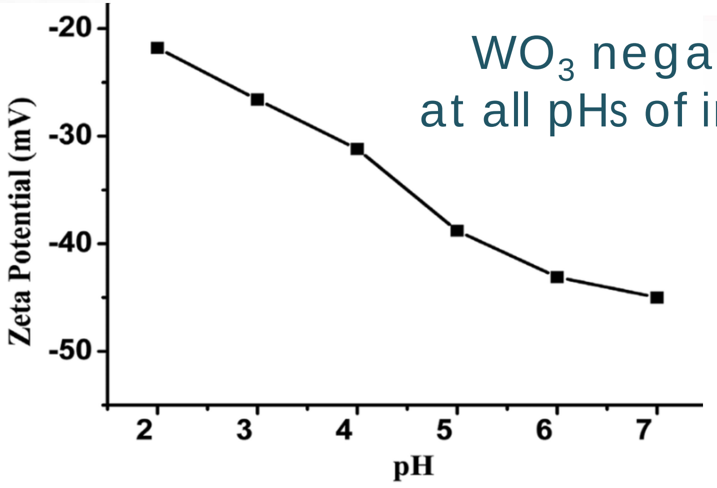
Higher Tungsten Etch Rates Observed

Increasing pH due to dissolution as Polyoxotungstate Keggin ions



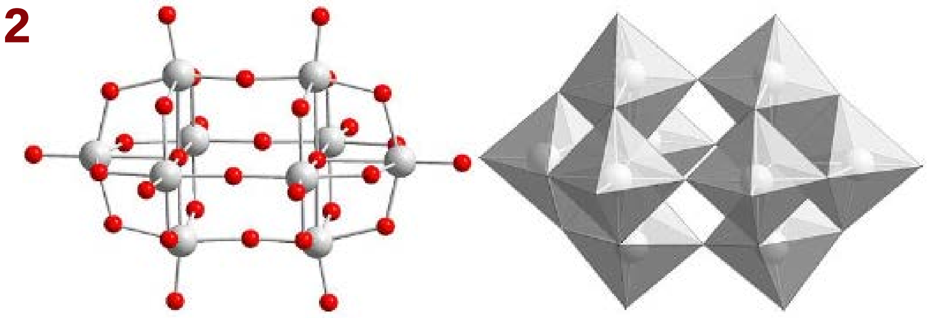
SC1: 1:50 > 6 A/min

1



WO_3 negative at all pHs of interest

2

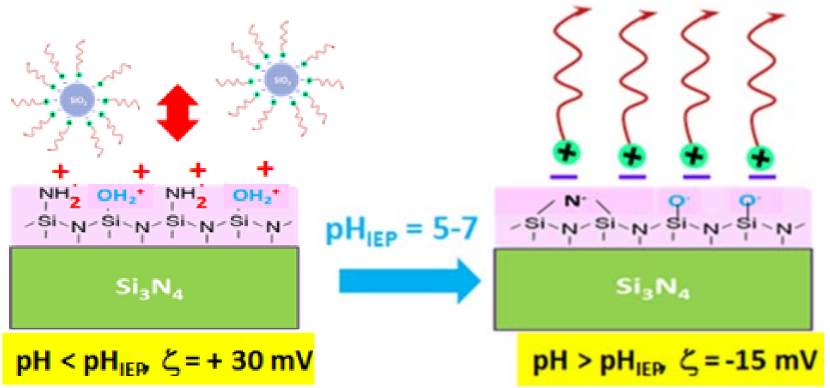


Decatungstate ($[W_{10}O_{32}]^{4-}$)

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.

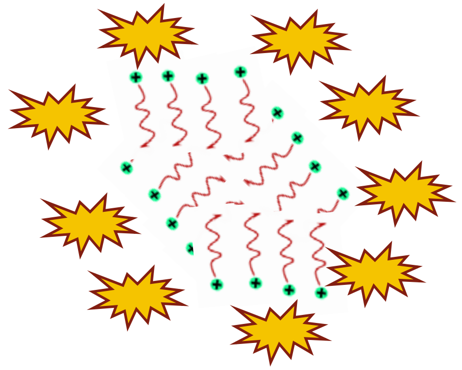
Improving Organic Residue Removal
from Si_3N_4 Contact Angle and FTIR

Electrostatic Repulsion during CMP



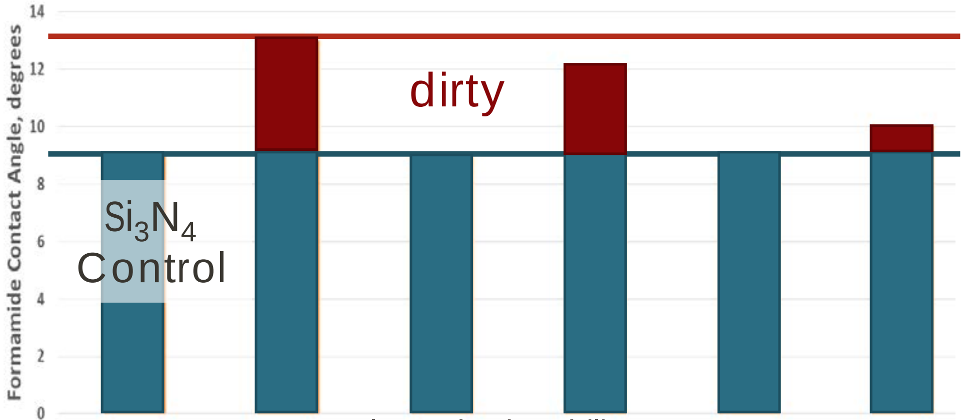
W Post-CMP Cleaner

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

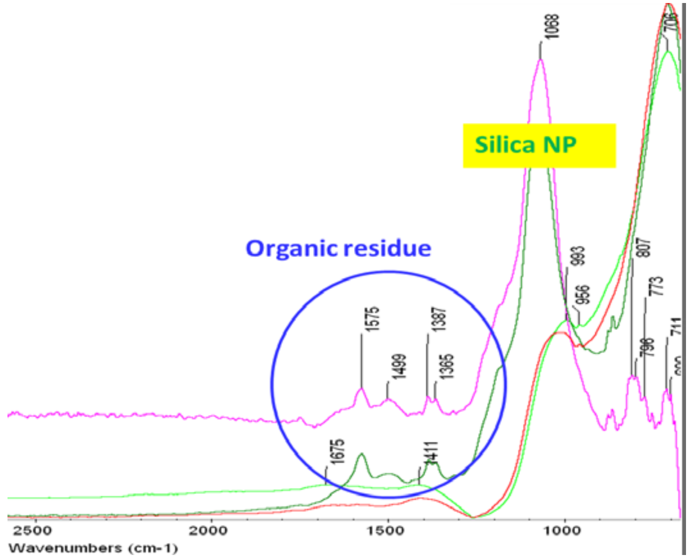


Cleaning additive removes cationic contamination from dielectric surface and disperses

Contact Angle

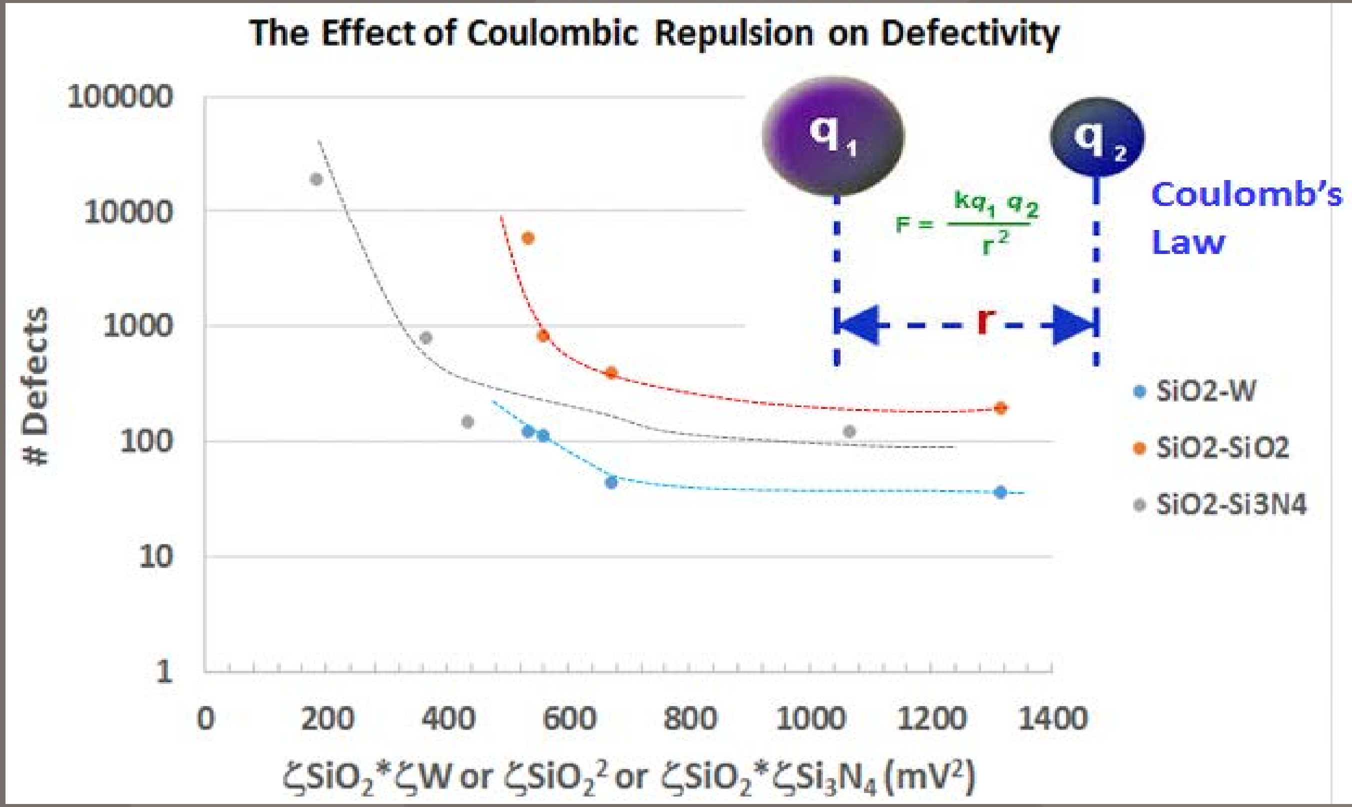


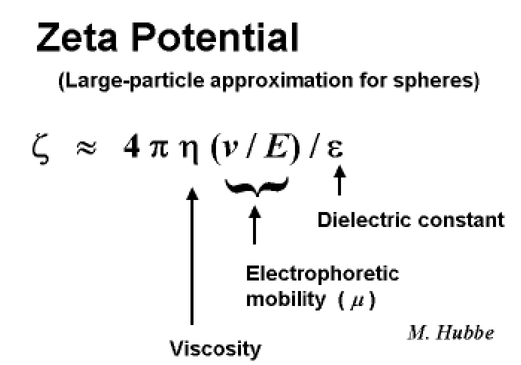
FTIR



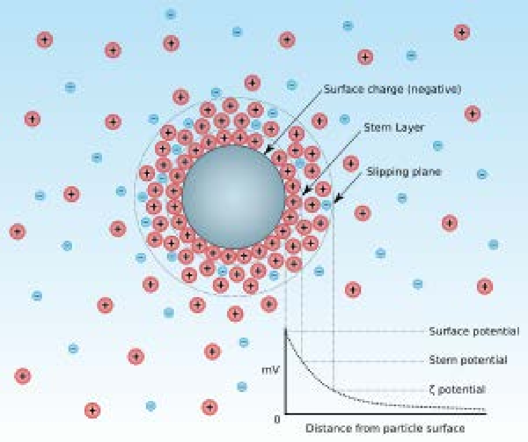
Defectivity Correlated to Charge Repulsion

between silica particles and various surfaces (W, SiO_2, Si_3N_4)





Additive increases negative charge on silica surface

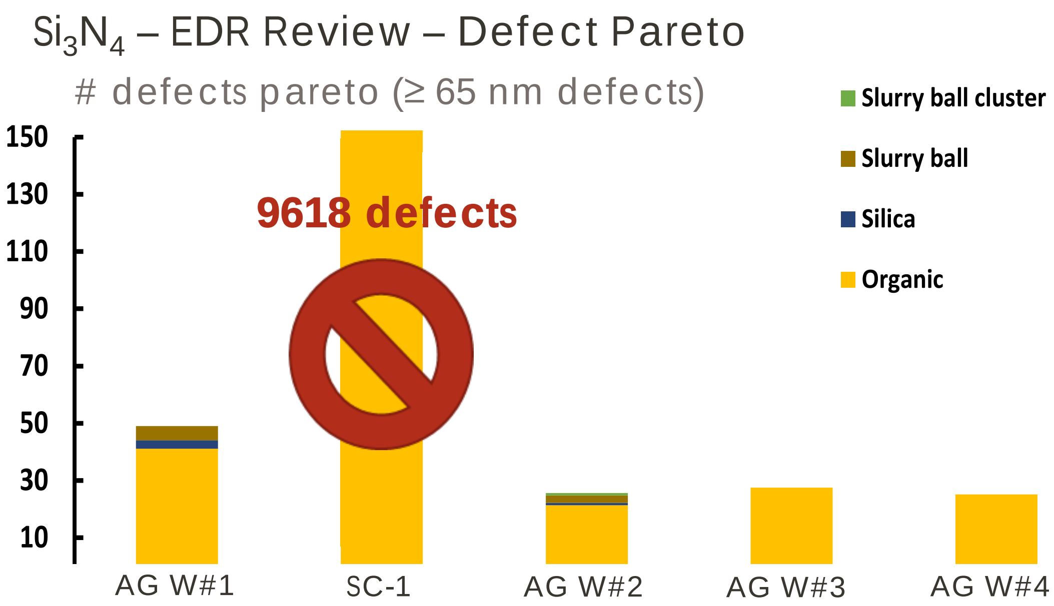


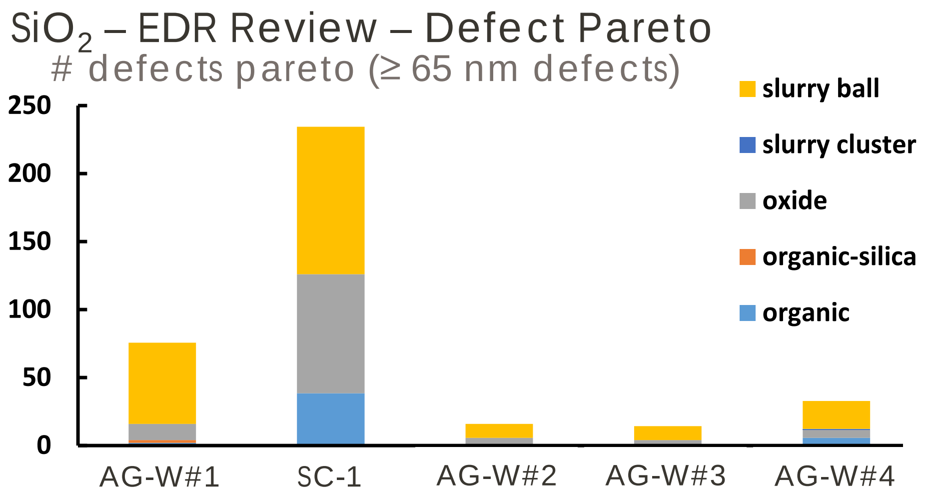
1- White, M. L. et al, *Mater. Res. Soc. Symp. Proc.* 991, 0991-C07-02 (2007)
2- Hedge, S. and Babu, *H. V. 2Eelectrochem. Soc. St. Lett*. V7, pp. 316-318 (2008)
3- White , M. L. et al. *Mat. Sc. For*. 1249 E04-07 (2010).

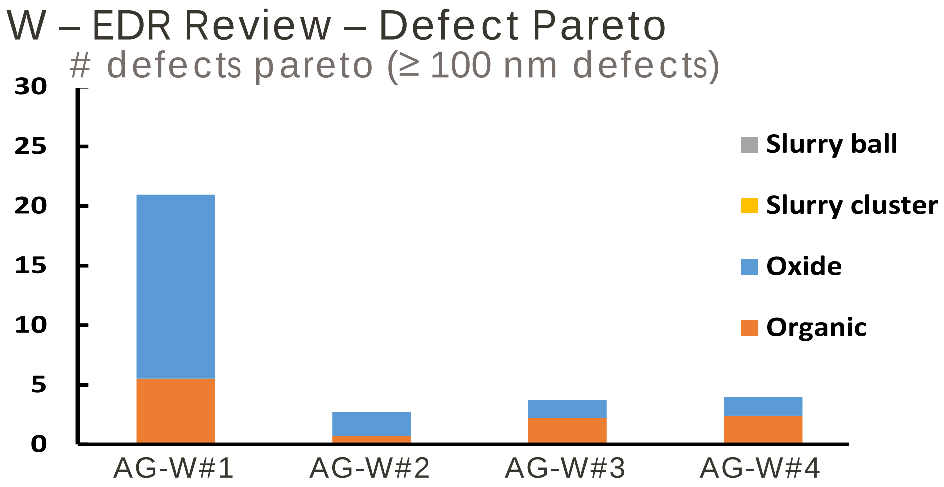
Acknowledgements:
Thomas Parson, Daniela White, Michael Owens

PlanarClean AG-W formulations

exhibit lower defects and organic residues over traditional cleans



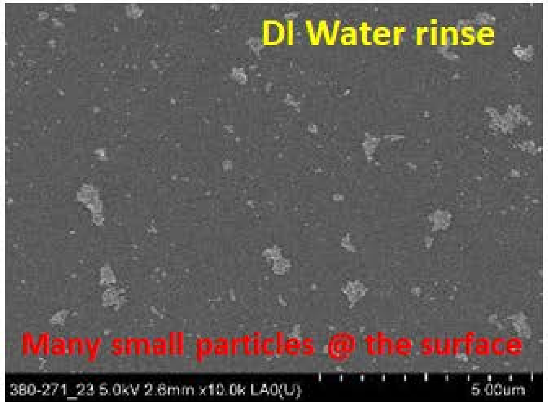


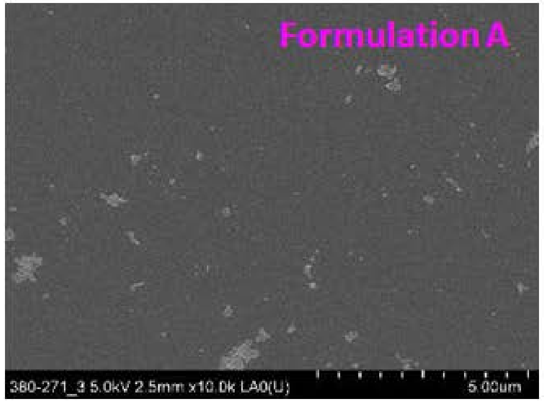


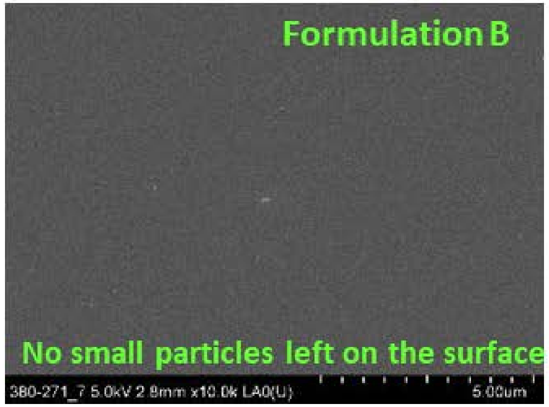
PC AG-W Series show improved performance over SC-1 on all substrates

SEM Images of PETEOS Coupons

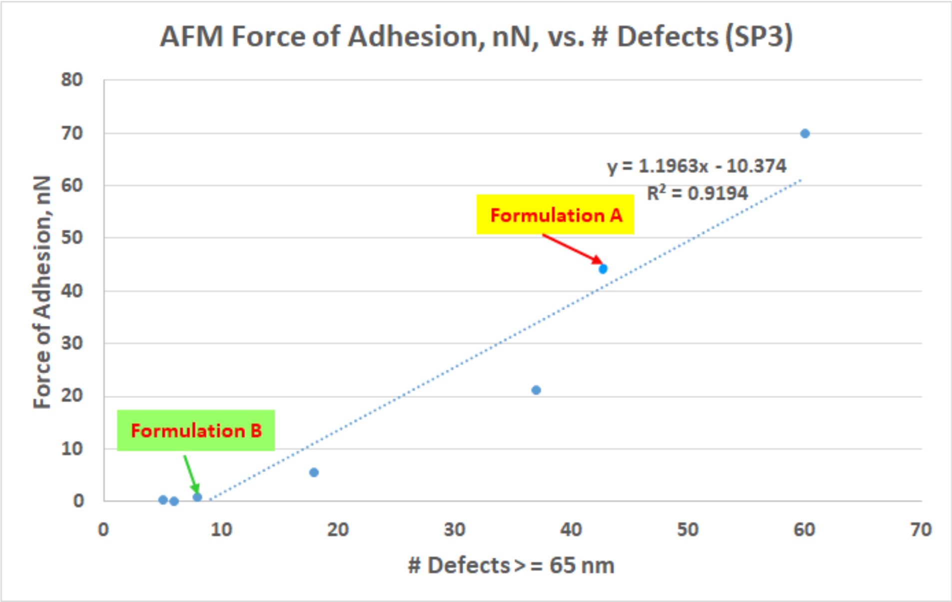
Polished with W CMP slurry and cleaned with Formulations A and B







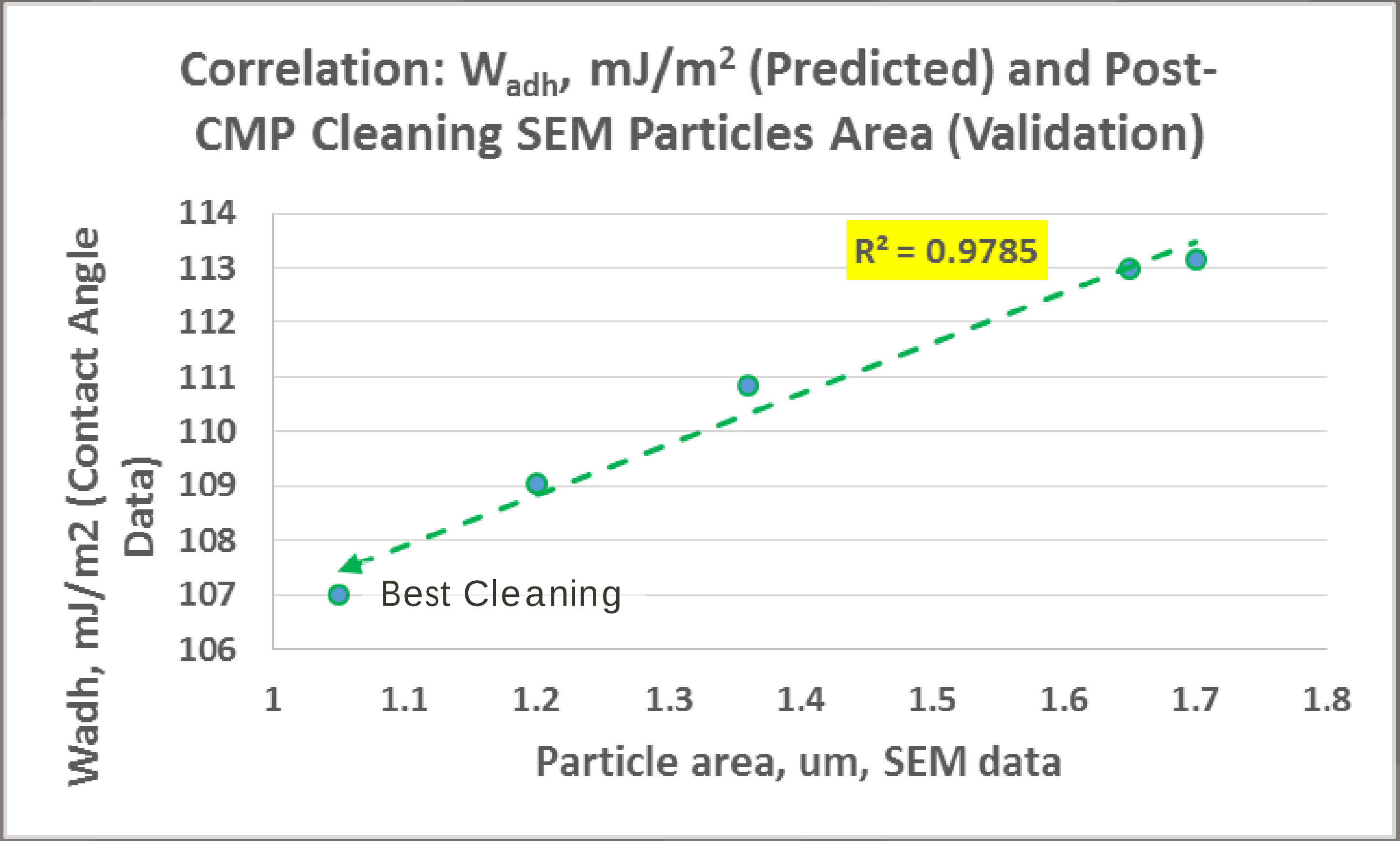
- Tabletop polishing
- Colloidal silica Ludox, PS = 20-30 nm
- pH = 2.3



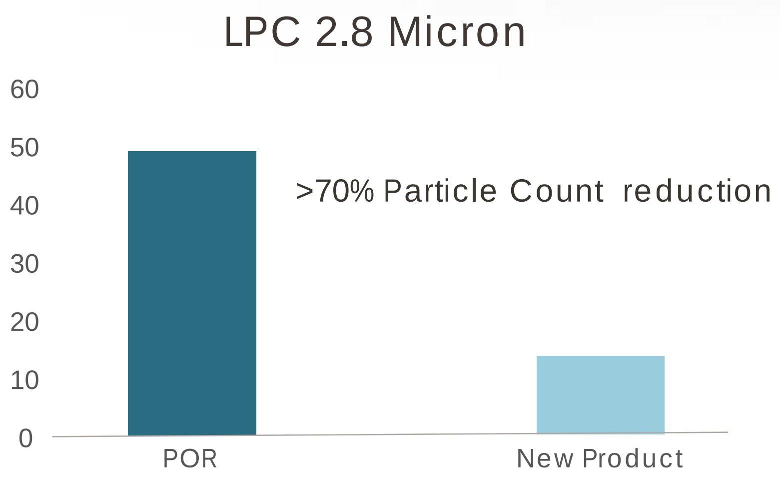
Entegris

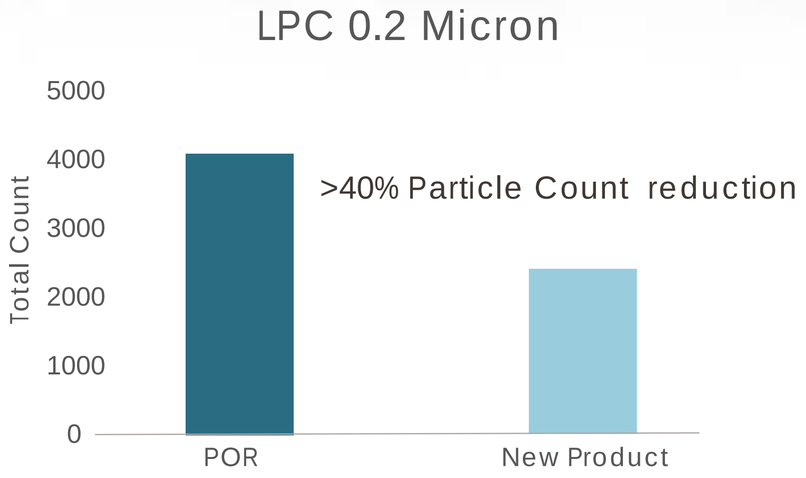
Correlation SEM vs. Calculated Adhesion

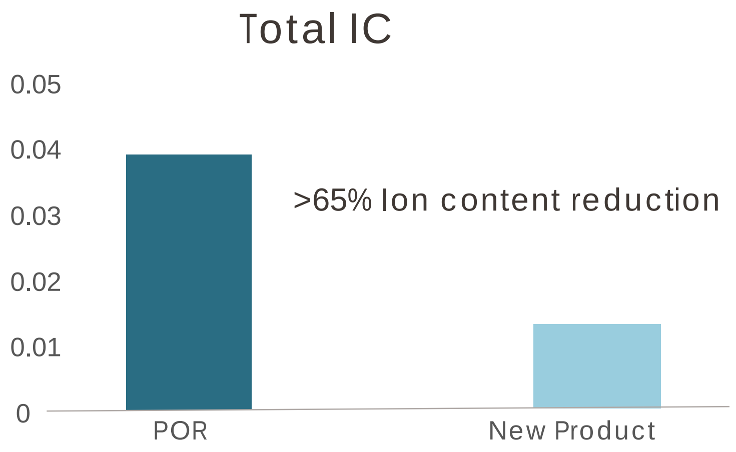
Based on contact angle measurements



Planarcore® Improved Manufacturing for Reduced Particles



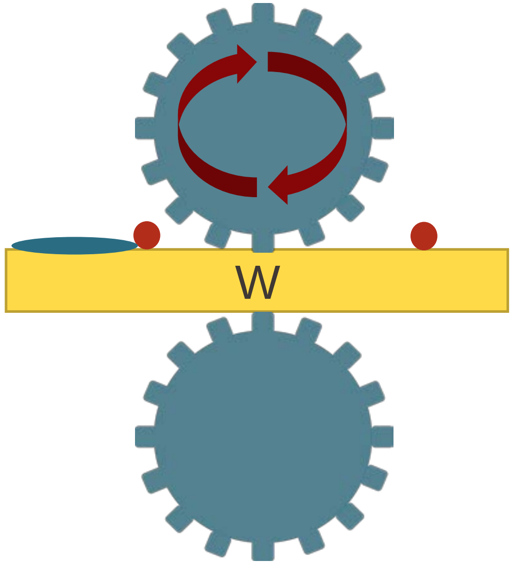


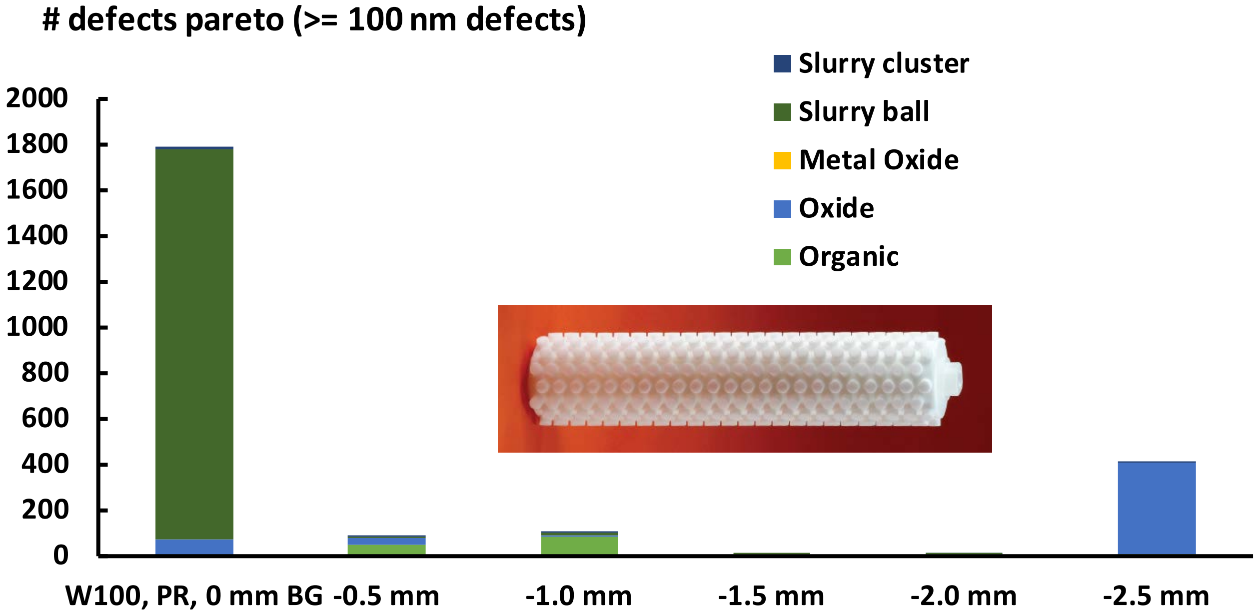


Process Can Often Play a Large Role

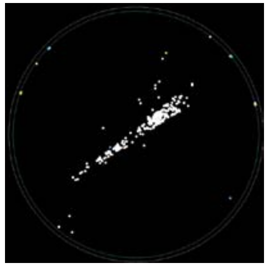
Impact of the Brush Gap

Brush cleaning:
physical + chemical cleaning

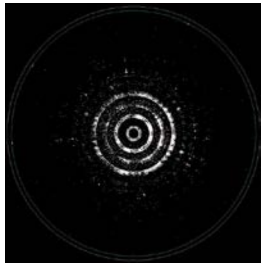




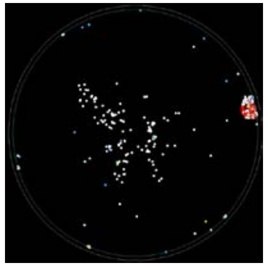
-2.5 mm



0 mm



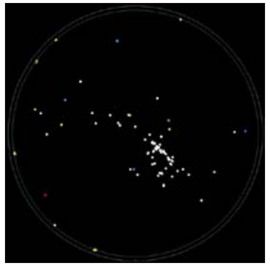
-0.5 mm



-1.0 mm

-1.5 mm

-2.0 mm



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, 1H/13C/multinuclear NMR)

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

Thank you!

Q&A

Appendix