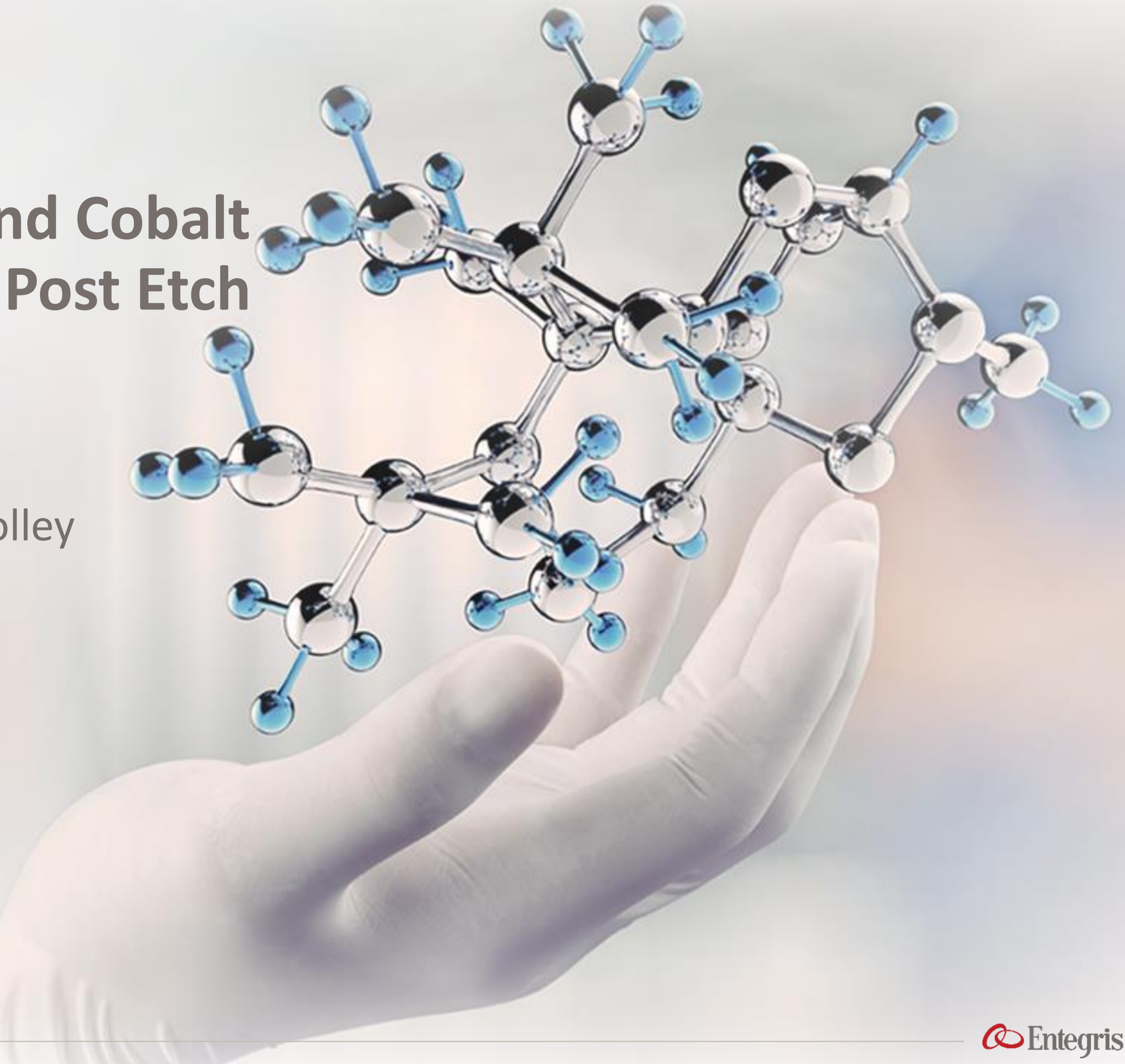
50 YEARS OF PURE ADVANTAGE

JULY 12 2017

Challenges in Cleaning Tungsten and Cobalt for Advanced Node Post CMP and Post Etch Residue Removal Applications

Michael White. Daniela White, Thomas Parson, Elizabeth Thomas, Shining Jeng, Ruben Lieten, Volley Wang, Sean Kim, Wisma Hsu and Steve Lippy



AGENDA

01 Cleaning requirements for Co and W at the advanced Node

02 Co cleaning mechanisms

03 Controlling corrosion on Co

04 Cobalt defectivity improvements

05 Cobalt wet etch & cleaning

06 W Cleaning mechanisms

07 Cleaning Si_3N_4 after W polishing

08 W wet etch & cleaning

09 Conclusions

CLEANING CHALLENGES FOR BULK COBALT AND TUNGSTEN

Post CMP Bulk Co Cleaners

- **Replace more traditional copper cleaners with rationally designed Co cleaners**
- Low/No Cobalt corrosion
    - Low/no galvanic corrosion
    - Low/no dendritic CoOx growth
    - Low/no Co pitting
- Low/no organic residues
- Low/no silica particles or clusters
- No increased roughness
- Green chemistry (TMAH free)

Post CMP W Cleaners

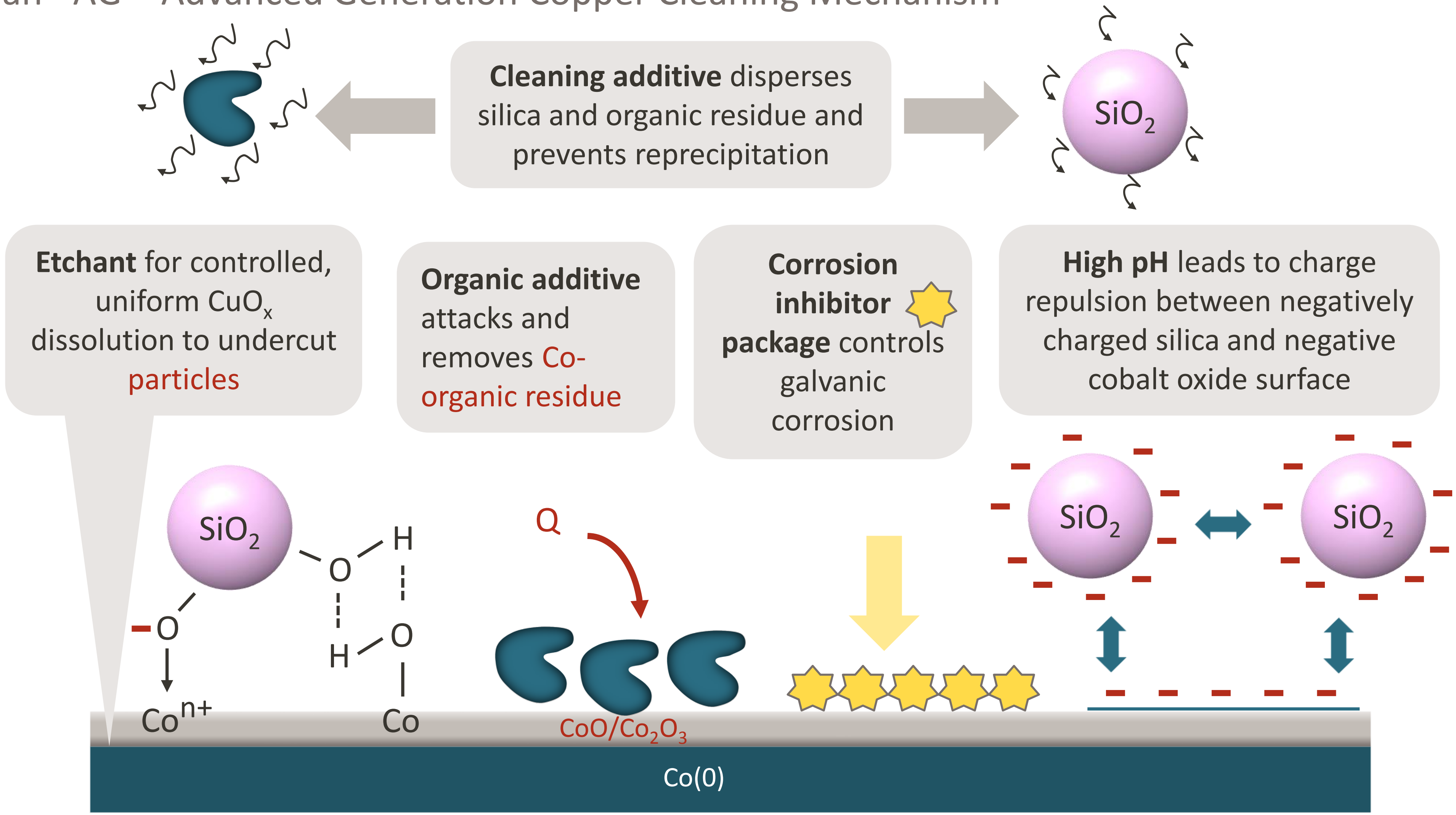
- **Market increasing challenged by W recess**
    - High pH commodities (SC1, dil NH_3)
    - Traditional low pH cleaners
- Low W etch rates (<2 Å/min)
- Low/no Organic Residue
    - Nitride cleaning is particularly problematic
- Low no silica particles or clusters
- No increased roughness
- Green chemistry.(TMAH free)

Post Etch Residue Remover

- **Post Etch Residue Remover.- Cu, W, Co**
- Multi Function Cleaner - Clean + Etch etc…
- PERR for advanced FEOL application (Ge and SiGe)
- Green chemistry (TMAH free)

THE RATIONAL DESIGN OF A POST CMP CLEANER PLANARCLEAN® AG COPPER CLEANING

PlanarClean® AG – Advanced Generation Copper Cleaning Mechanism



Cleaning additive disperses silica and organic residue and prevents reprecipitation

Etchant for controlled, uniform CuO_x dissolution to undercut particles

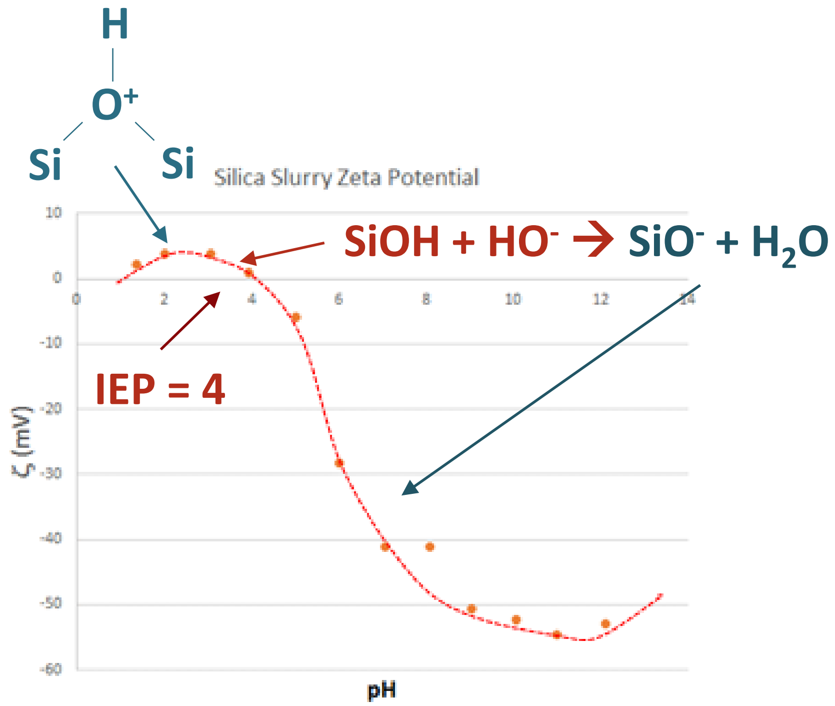
Organic additive attacks and removes Co-organic residue

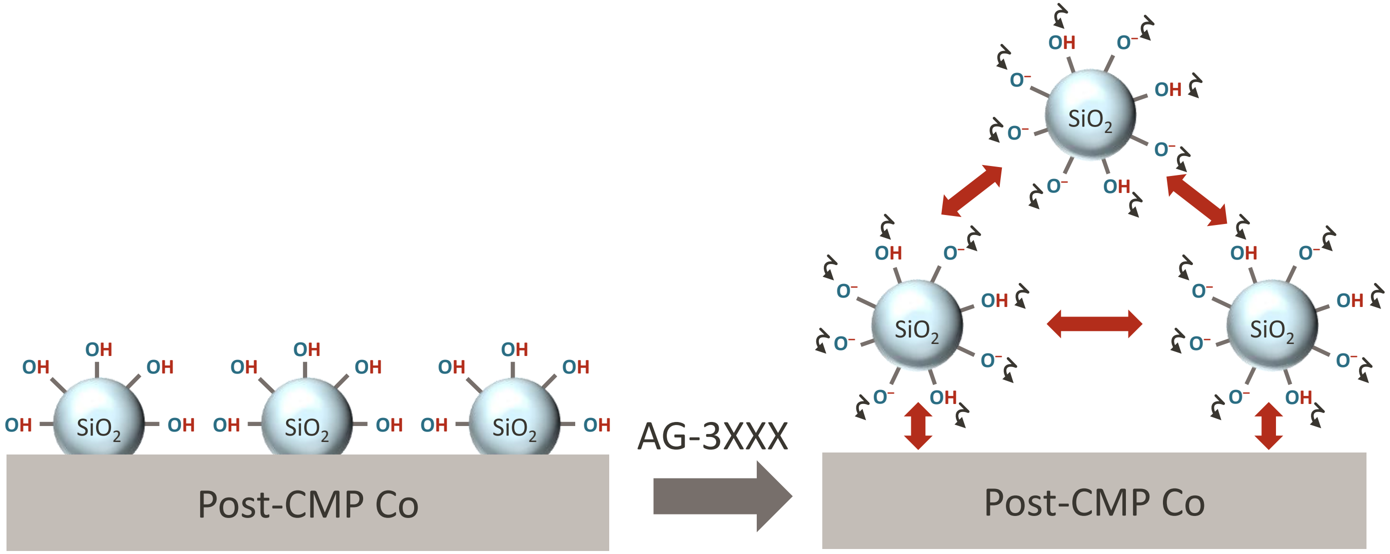
Corrosion inhibitor package controls galvanic corrosion

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

PLANARCLEAN AG PREVENTS SILICA AGGREGATION

- Particle adhesion mechanisms
  - **Physisorption** (van der Waals attraction – increases with PS)
  - **Electrostatic** attraction or repulsion (zeta potential)
  - **Chemisorption** (chemical reaction particle-surface)
  - **Capillary condensation**

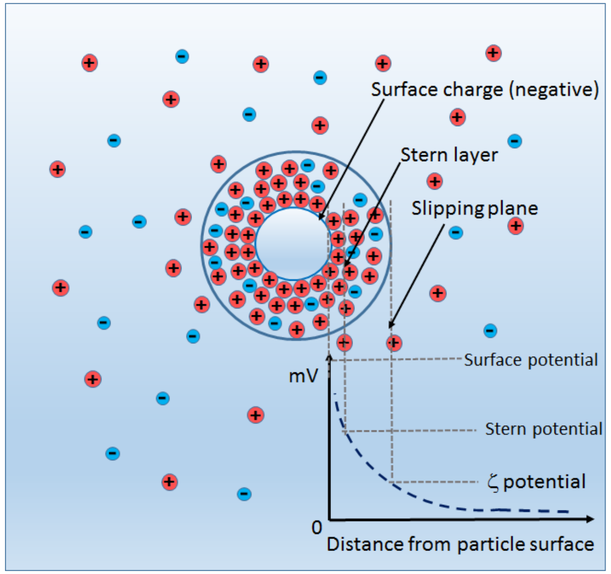




Dispersed particles
Highly negatively charged
No particles agglomeration

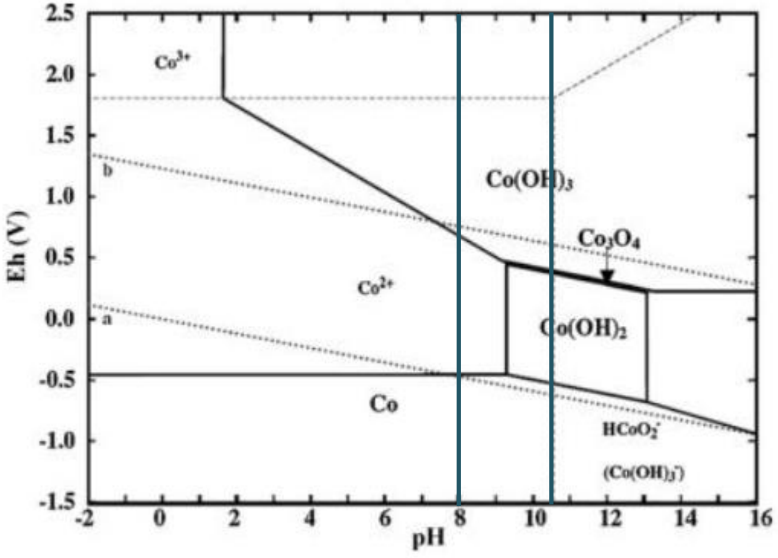
Zeta Potential

$$\zeta = 4\pi\gamma(\nu/E)/\varepsilon$$

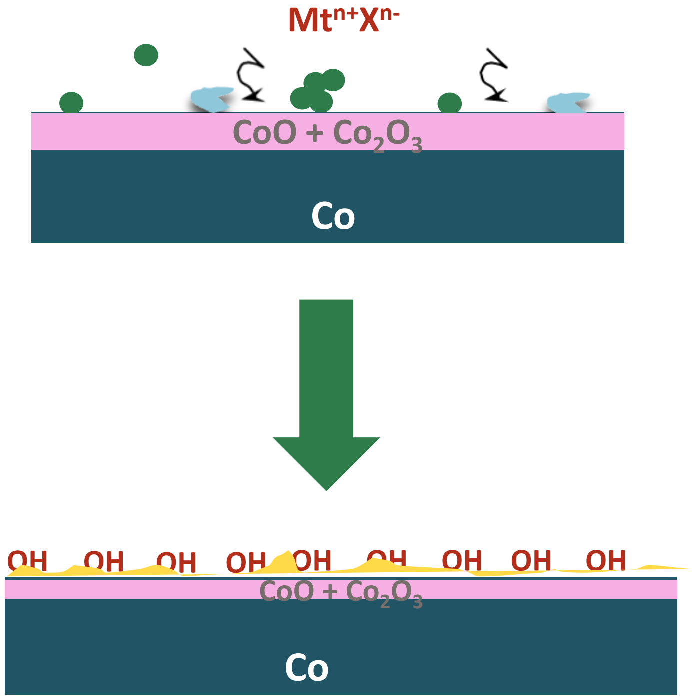


SOME CHALLENGES ASSOCIATED WITH CO CLEANER DEVELOPMENT

Co Pourbaix Diagram

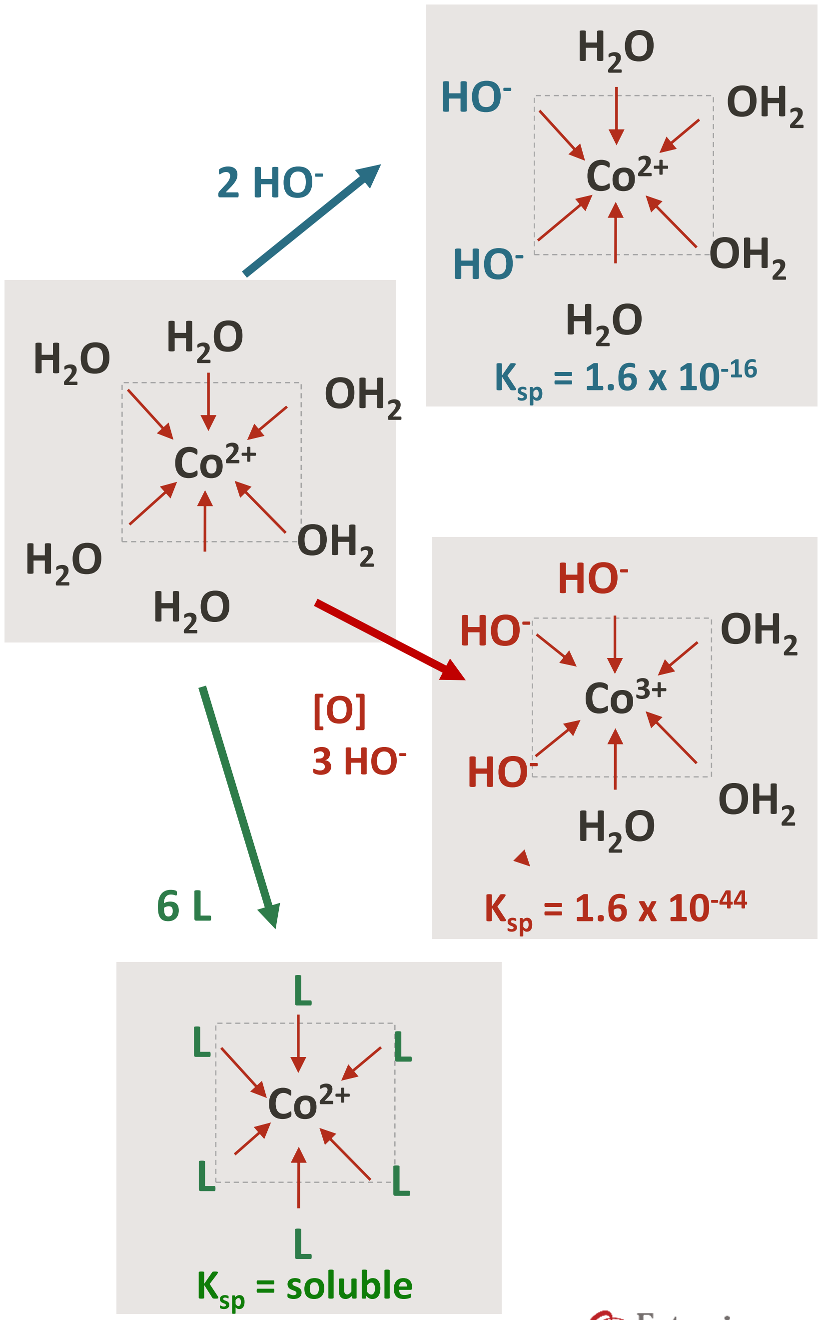


- Ideal pH range for Silica slurry removal to prevent hydroxide precipitation

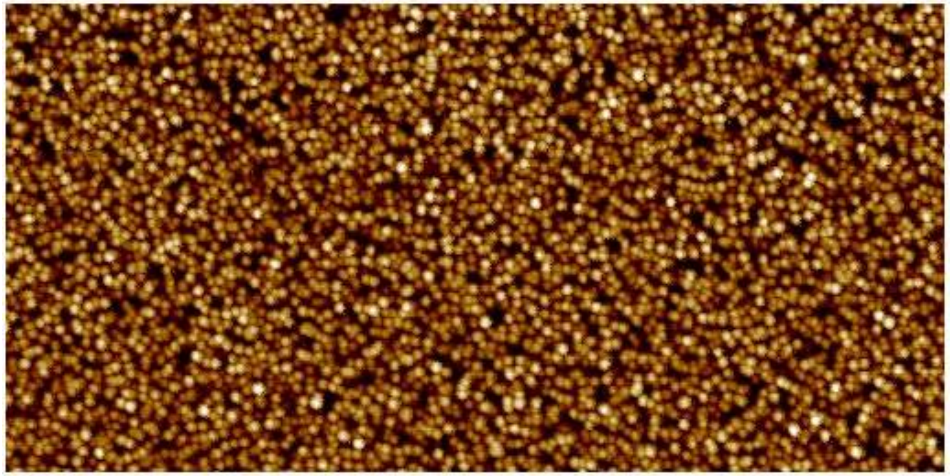


Surface passivation

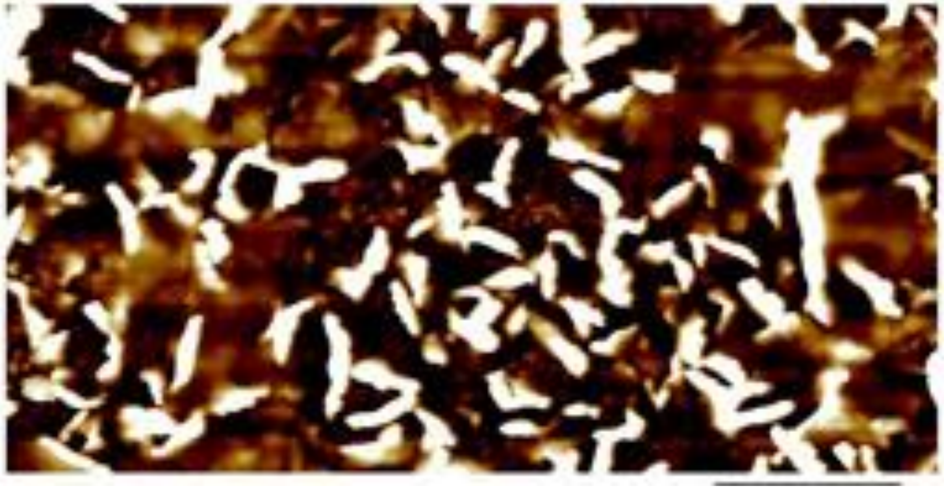
- Co passivation by both cobalt oxide/hydroxide and/or corrosion inhibitor
- Can result in $CoO_x(OH)_y$ growth without the proper complexing agent



SOME CHALLENGES ASSOCIATED WITH CO CLEANER DEVELOPMENT



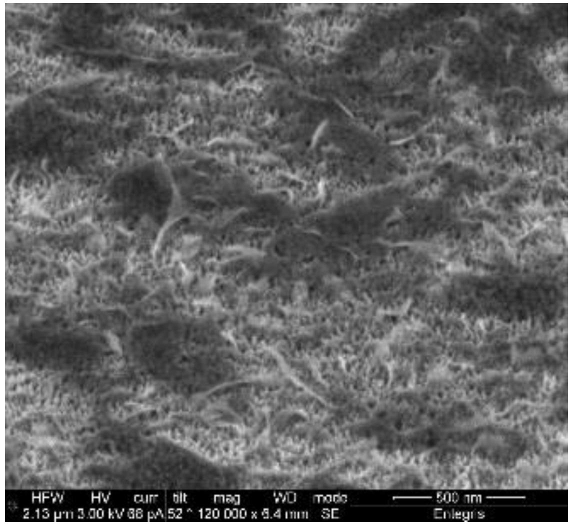
AFM



- **Well-passivated Co surface**

AFM, SEM – no CoOx surface precipitates, low surface roughness (R_a = 5 nm)

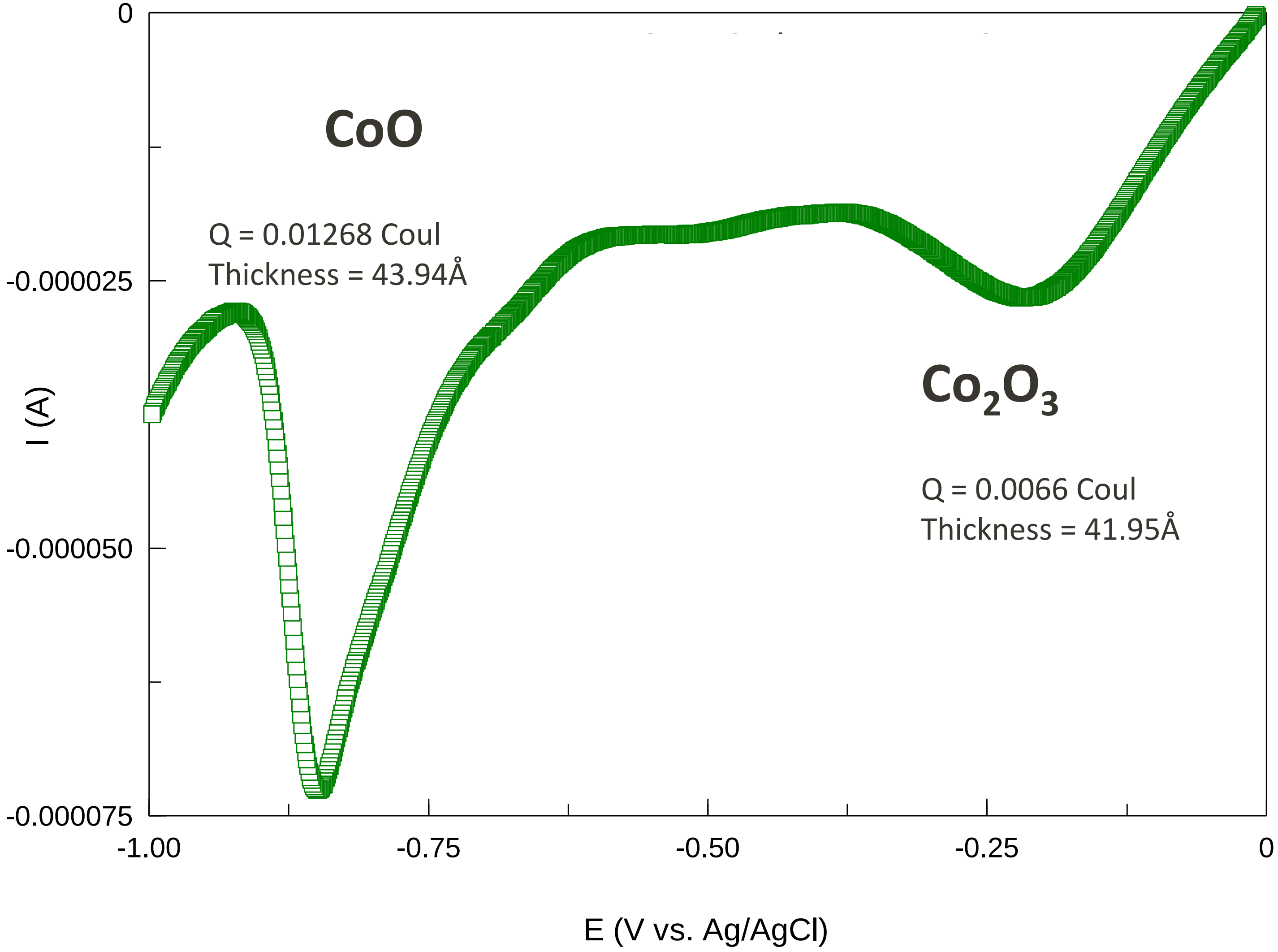
- **Uniform, smooth etching (no pitting)**



- Poorly passivated surface or insufficuent complexation
- Dendritic CoOx growth

SEM

POTENTIODYNAMIC REDUCTION OF CO OXIDE LAYERS CAN MEASURE THE RELATIVE CONCENTRATIONS OF CO(II) AND CO(III) OXIDE/HYDROXIDES



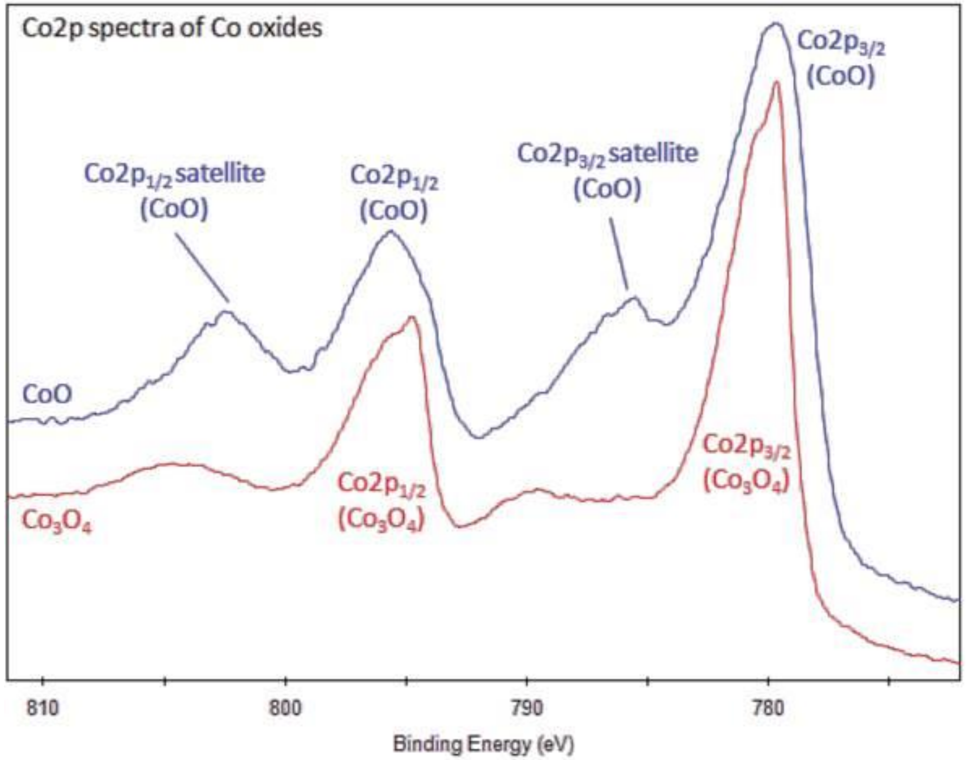
CoO

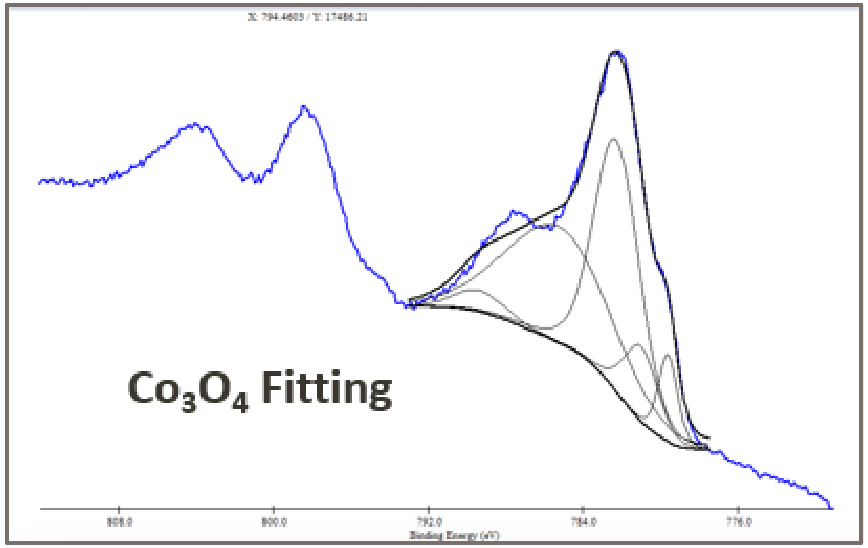
Q = 0.01268 Coul
Thickness = 43.94Å

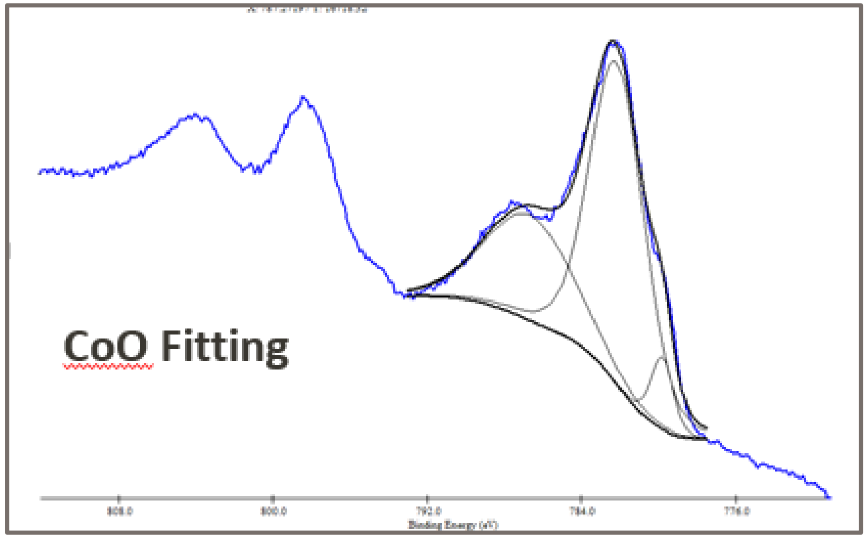
Co_2O_3

Q = 0.0066 Coul
Thickness = 41.95Å

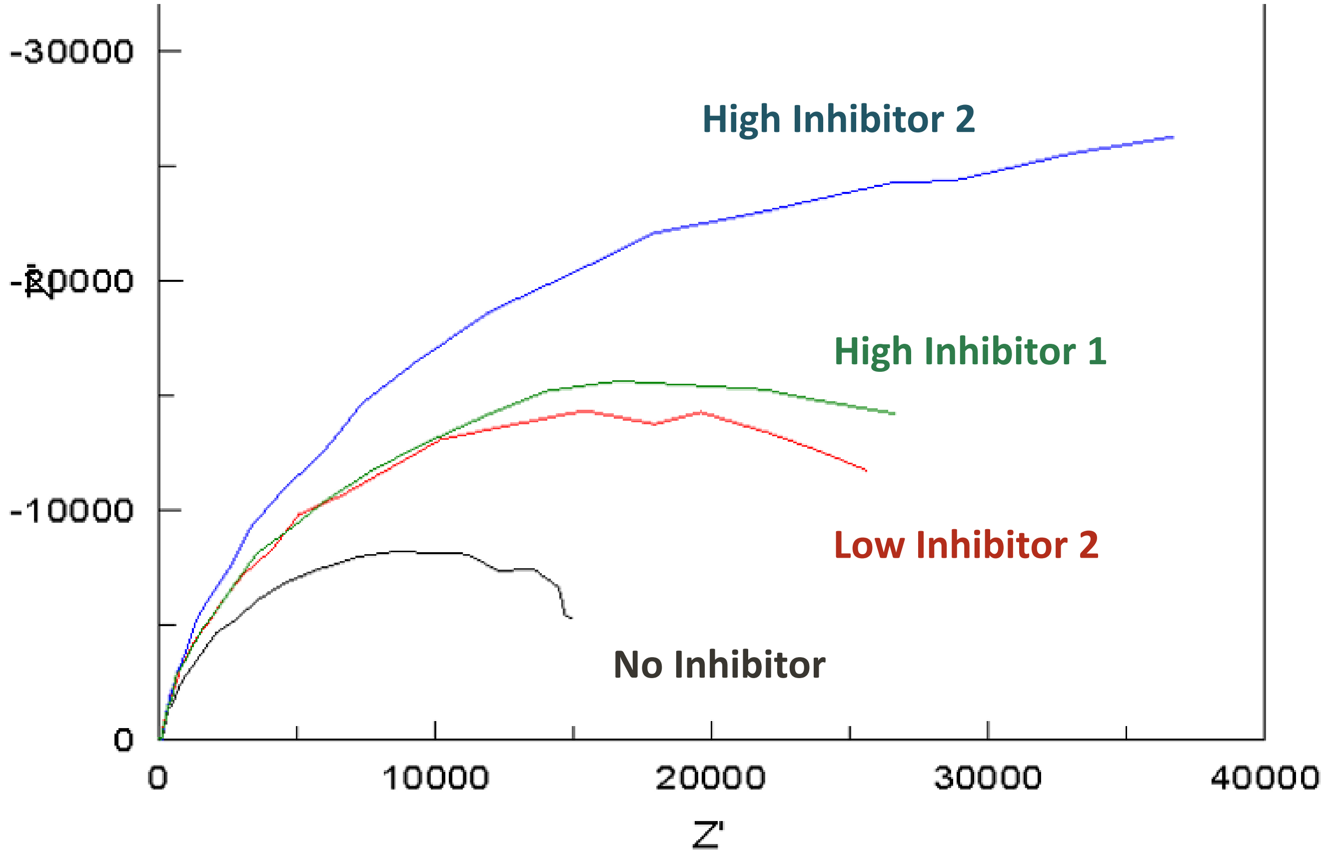
XPS FITTING SHOWS COBALT(II) AND COBALT(III) CAN BOTH BE PRESENT







NYQUIST PLOTS SHOW INFLUENCE OF PROPER INHIBITOR SELECTION AND CONCENTRATION ON COBALT PASSIVATION



Higher impedance storage and loss components→ higher film integrity

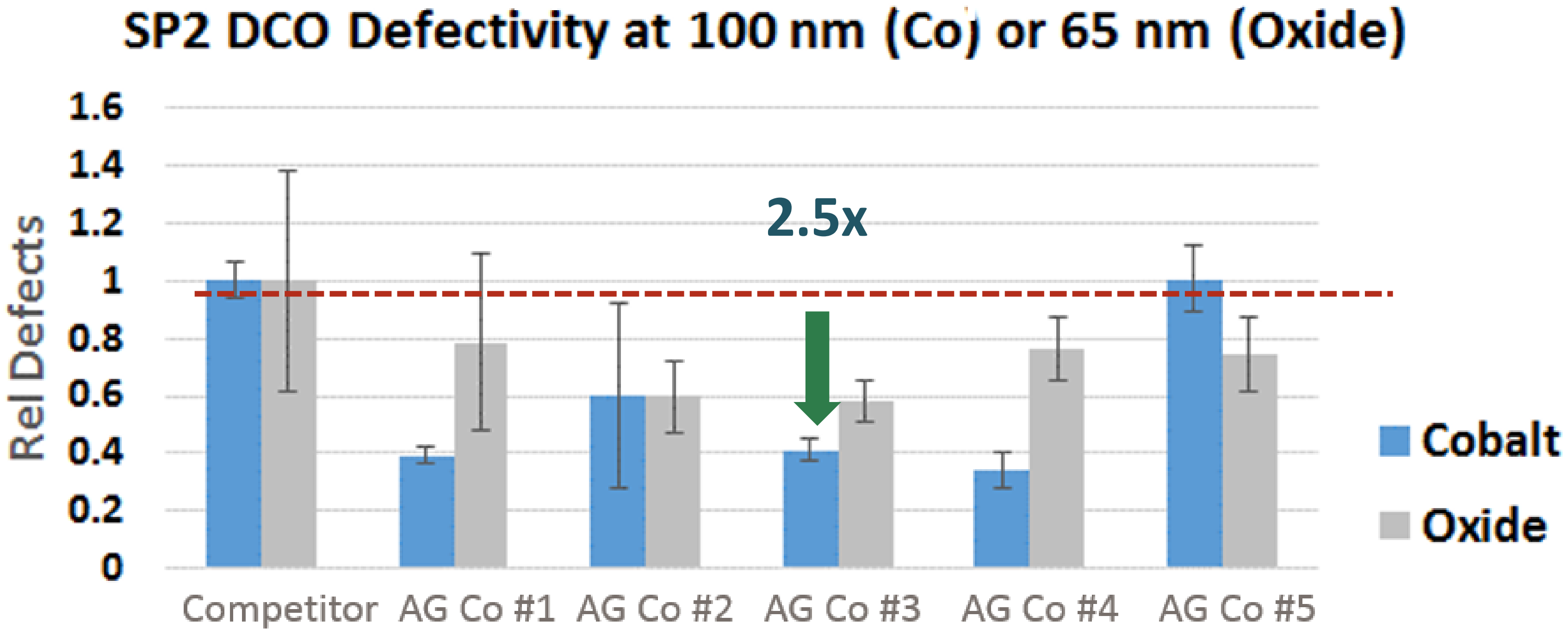
When ω -> 0

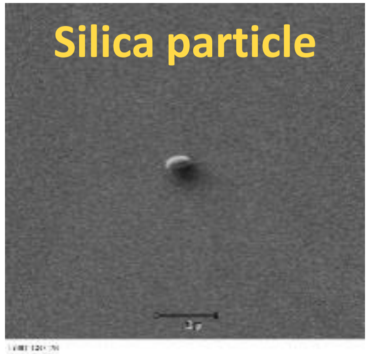
$$Z' = R_{\Omega} + \frac{R_{ct} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma\omega^{-1/2})^2}$$

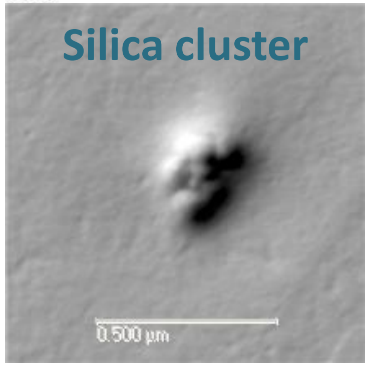
$$Z'' = -\frac{\omega C_{dl}(R_{ct} + \sigma\omega^{-1/2})^2 + \sigma^2 C_{dl} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma\omega^{-1/2})^2} a$$

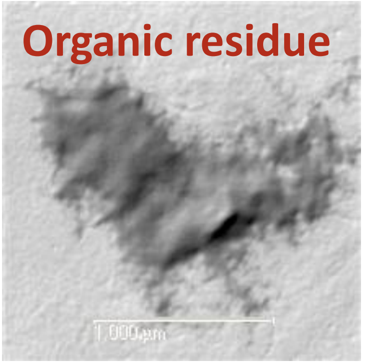
Ref:
1. Wang, et al. SPIE Beijing 2016 Conf. Proc.
2. Bard, A. J. Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications; Wiley and Sons 2001

AG- CO FORMULATIONS SHOW UP TO A 2X IMPROVEMENT IN DEFECTIVITY OVER COMPETITOR



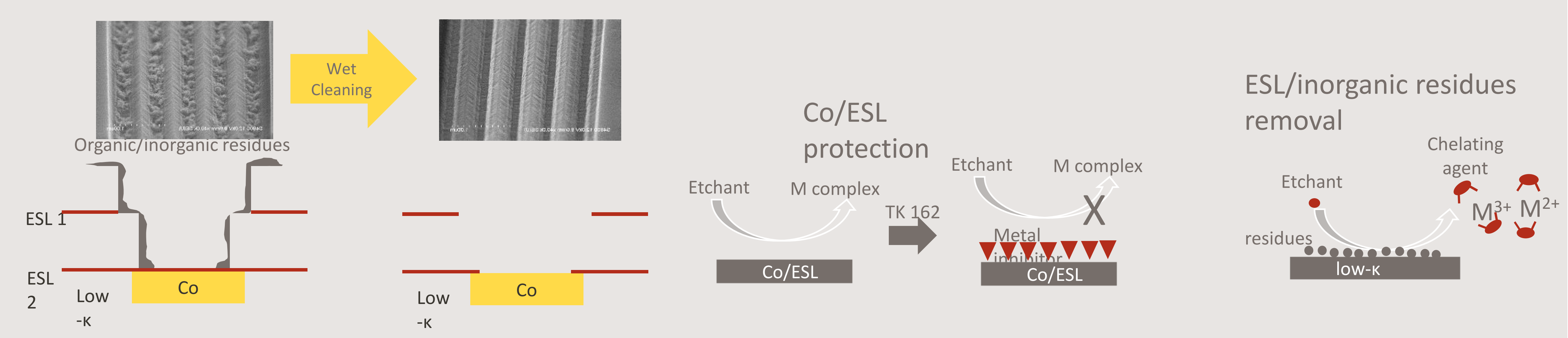






Judicious selection of cleaning additives leads to lower defectivity

TITANKLEAN MECHANISM FOR REMOVING DRY ETCH RESIDUES WHILE PROTECTING COBALT



Wet Cleaning

Organic/inorganic residues

ESL 1

ESL 2

Low -κ

Co

Low -κ

Co

Co/ESL protection

Etchant

M complex

Co/ESL

TK 162

Etchant

M complex

X

Metal inhibitor

Co/ESL

ESL/inorganic residues removal

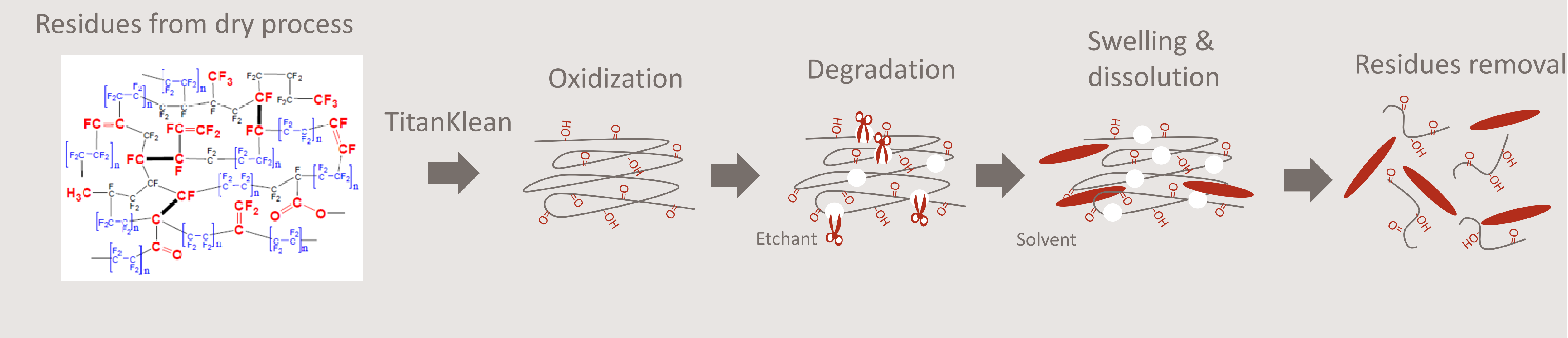
Etchant

Chelating agent

residues

M^{3+} M^{2+}

low-κ



Residues from dry process

TitanKlean

Oxidization

Degradation

Swelling & dissolution

Residues removal

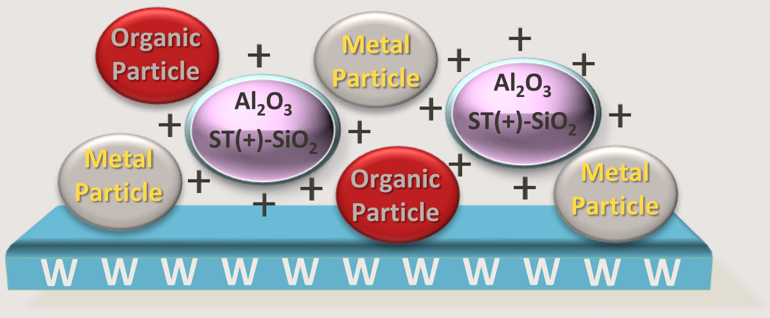
Etchant

Solvent

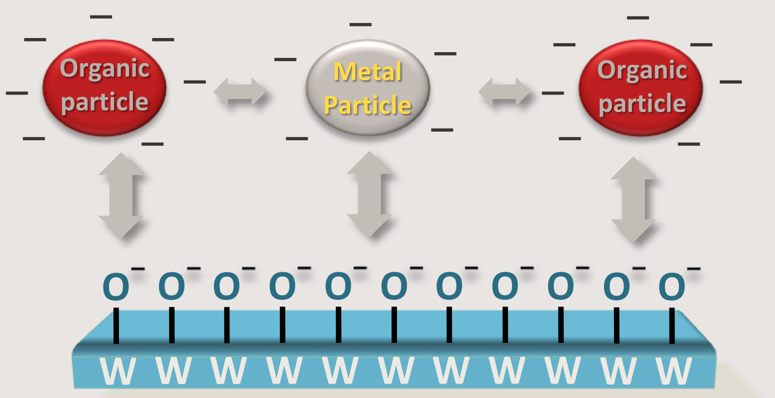
Mukherjee, T. Thesis N. Texas U., 2016

PLANARCLEAN AG-W CLEAN MECHANISM FOR ALUMINA OR SURFACE TREATED SILICA (ST-SiO_2)-Based CMP Slurries

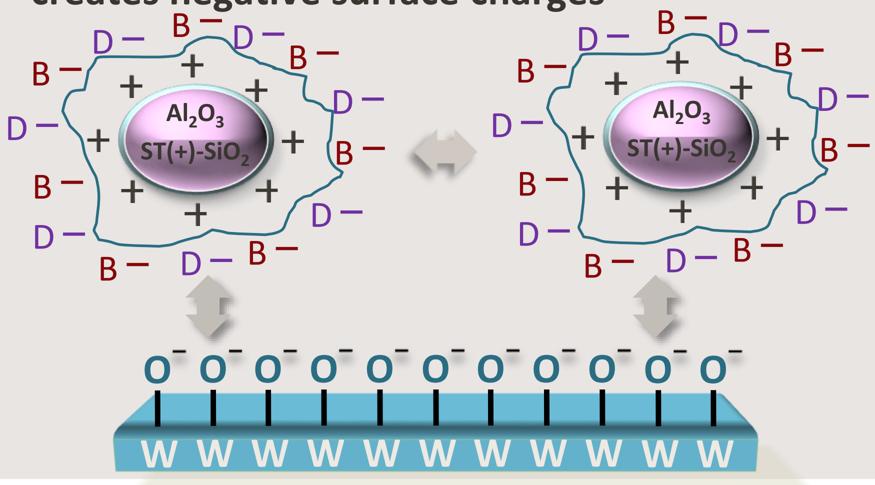
Polishing produces many particles (slurry, metal, and organics)

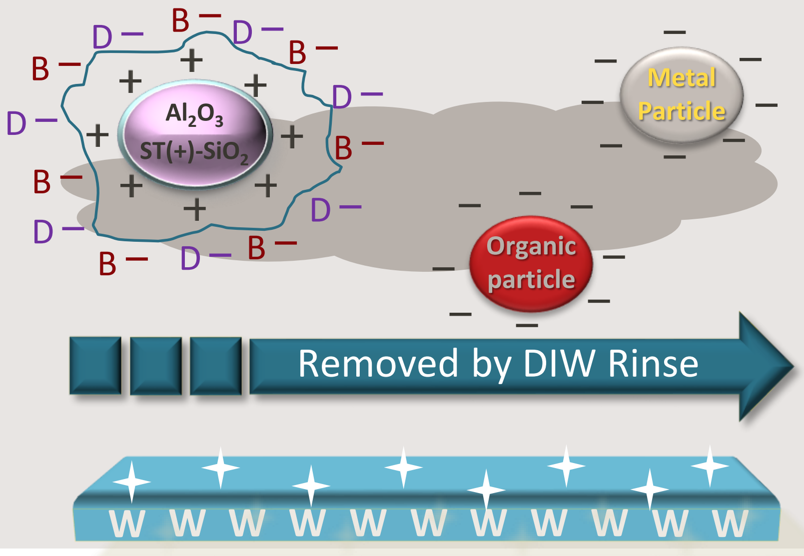


Component A – Insures negative charges on W surface and organic particles.



Comp B & D – modifies particles surface and creates negative surface charges



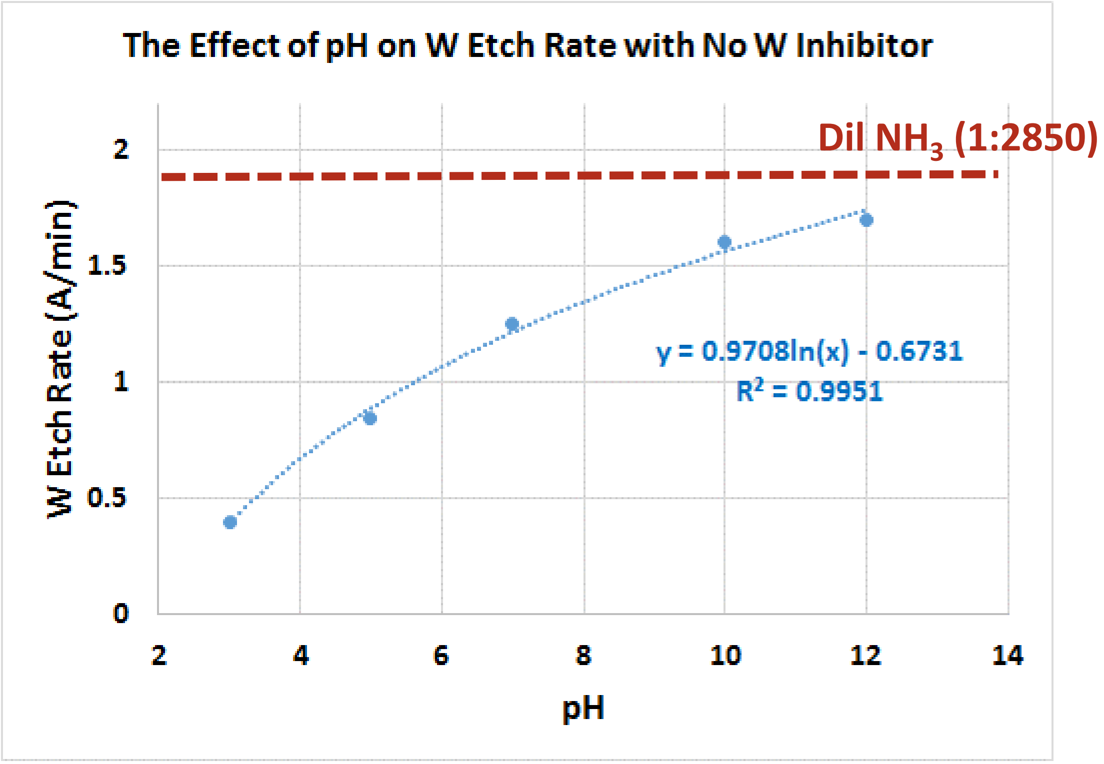


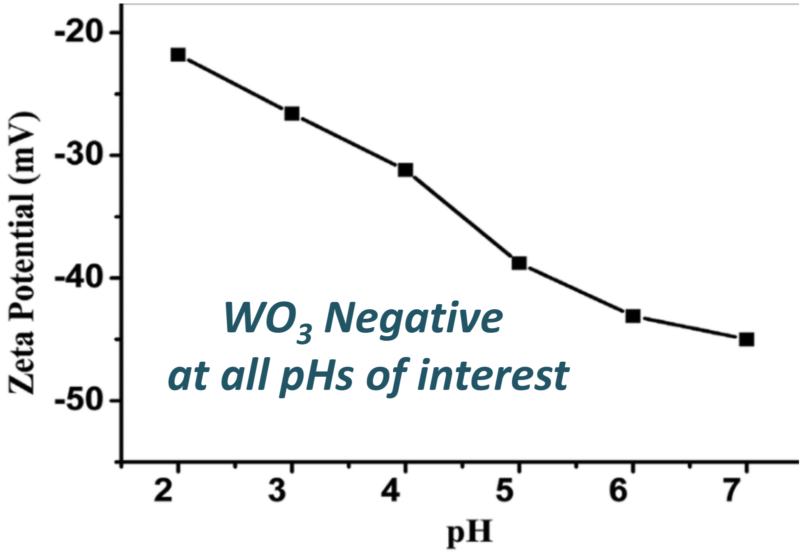
PC AG-W formulations:

- Inhibits W corrosion
- Controls the W etch rate
- Particle and surface modification
- Dielectric compatibility
- Non-TMAH additives for organic residue removal

HIGHER TUNGSTEN ETCH RATES WITH INCREASING pH DUE TO DISSOLUTION AS POLYOXOTUNGSTATE KEGGIN IONS

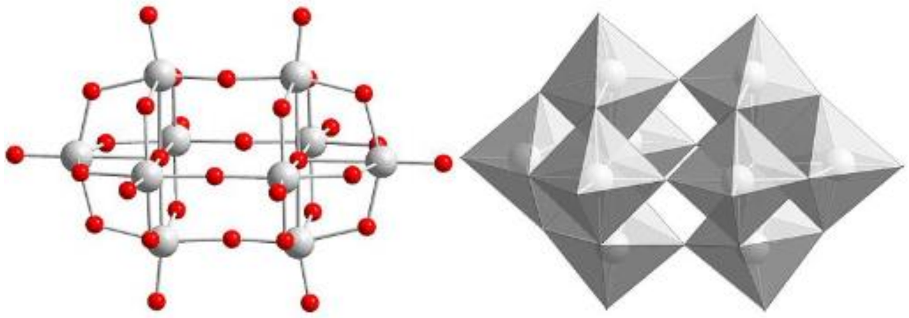
SC1: 1:50 > 6 A/min





WO$_3$ Negative
at all pHs of interest

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

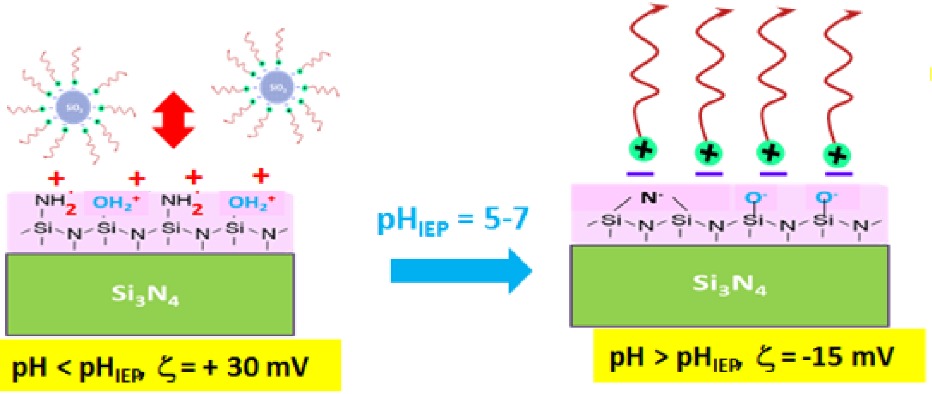


Decatungstate ($[W_{10}O_{32}]^{4-}$)

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

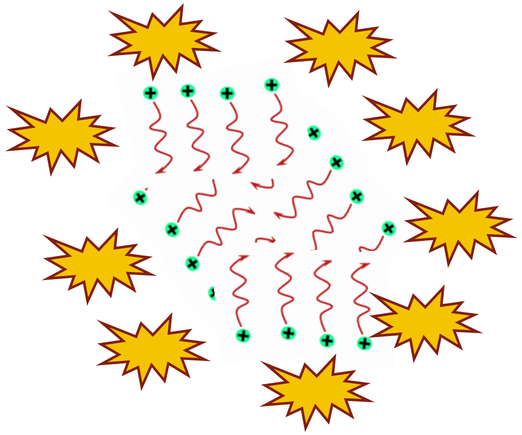
MECHANISMS FOR IMPROVING ORGANIC RESIDUE REMOVAL FROM SI$_3$N$_4$ STUDIED BY CONTACT ANGLE AND FTIR

Electrostatic Repulsion during CMP



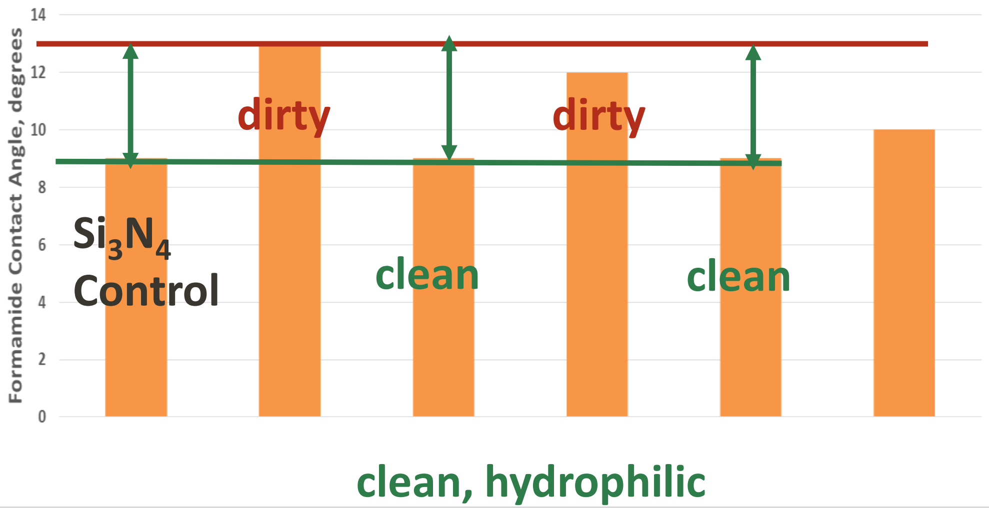
AG- W Cleaner

Si$_3$N$_4$ surface typically Highly contaminated by cationic dishing and erosion control agents

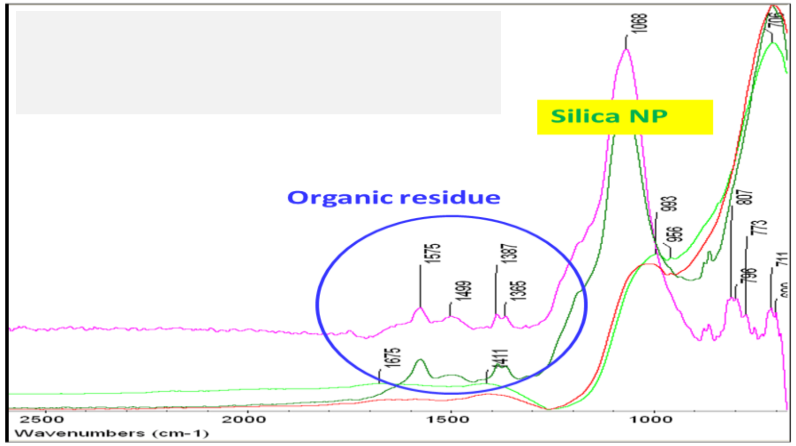


Cleaning additive removes cationic Contamination form dielectric surface and disperses

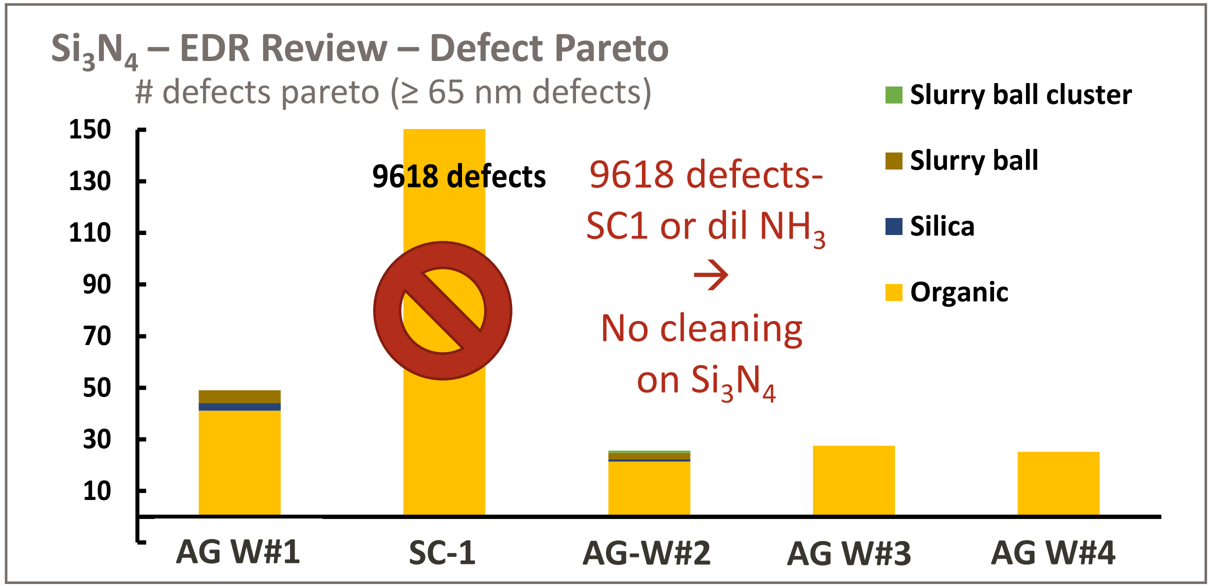
Contact Angle



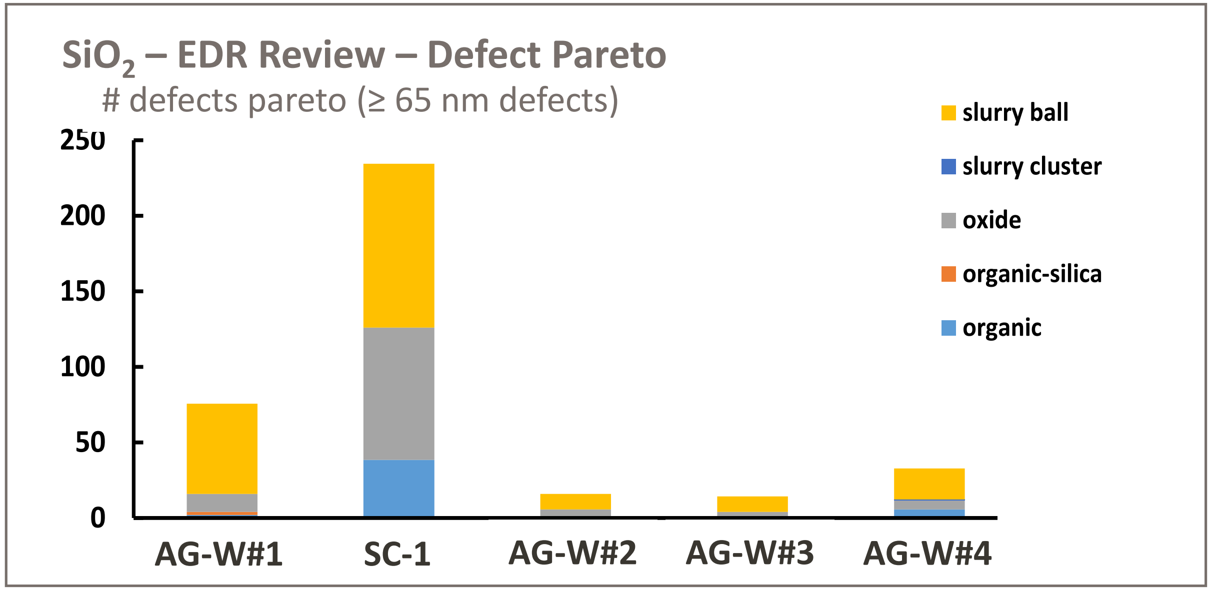
FTIR



PLANARCLEAN AG-W FORMULATIONS EXHIBIT LOWER DEFECTS AND ORGANIC RESIDUES OVER TRADITIONAL CLEANS

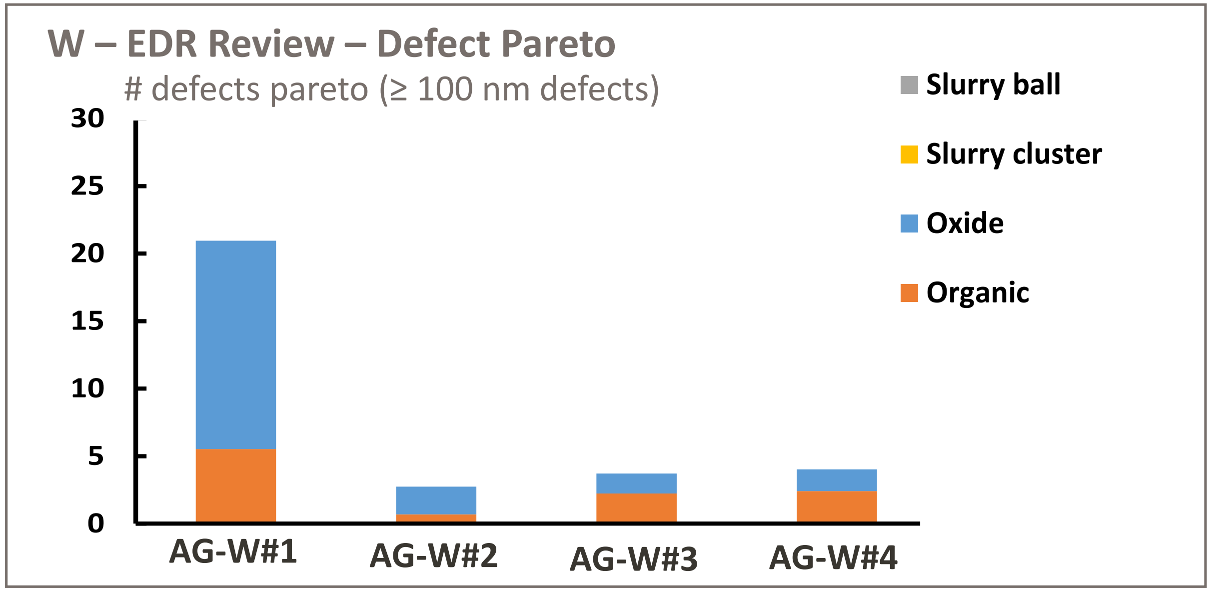

Si_3N_4 – EDR Review – Defect Pareto

defects pareto (≥ 65 nm defects)


SiO_2 – EDR Review – Defect Pareto

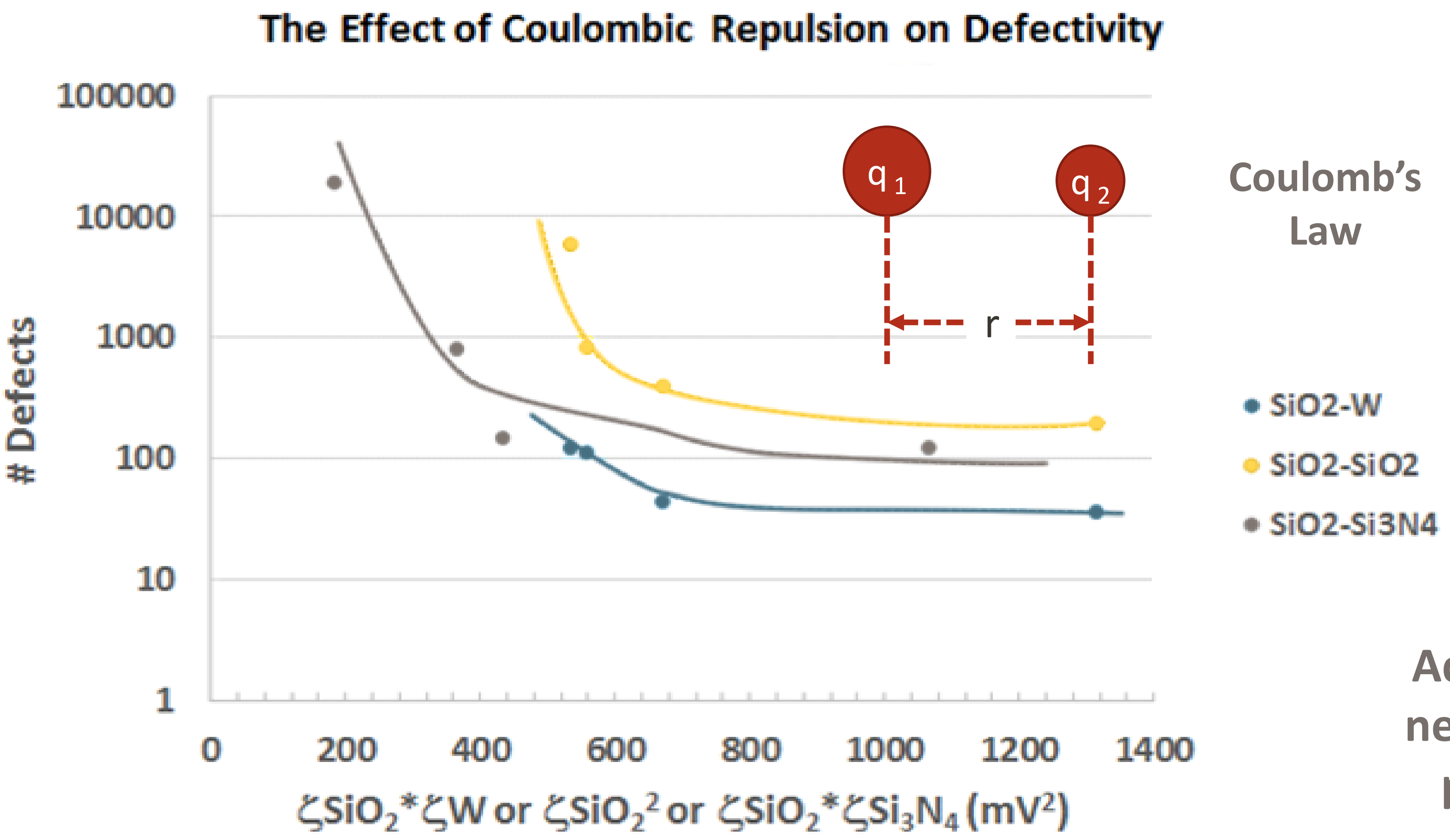
defects pareto (≥ 65 nm defects)

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


W – EDR Review – Defect Pareto

defects pareto (≥ 100 nm defects)

DEFECTIVITY CORRELATED TO CHARGE REPULSION BETWEEN SILICA PARTICLES



Coulomb's Law

$$F = kq_1 * q_2/r^2$$

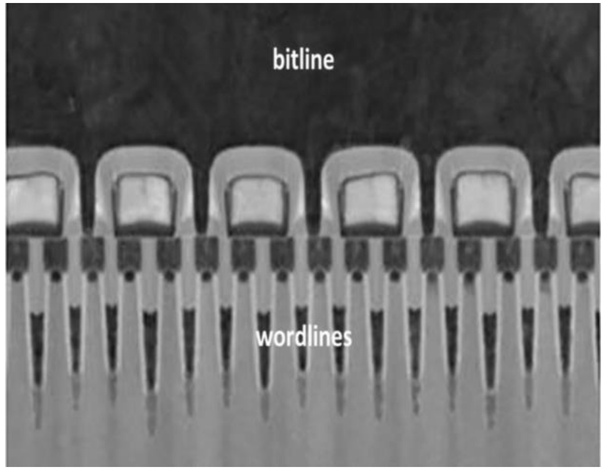
Additive increases negative charge on particle surface

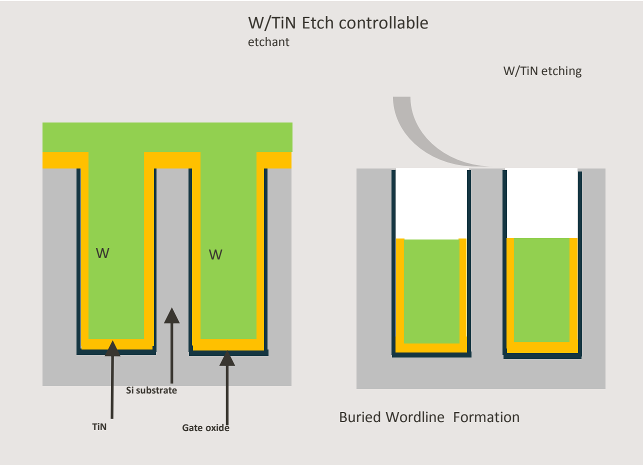
1. White, M. L. et al, *Materials Research Society Symposium Proceedings* Volume 991Issue Advances and Challenges in Chemical Mechanical Planarization Pages 207-212Journal 2007

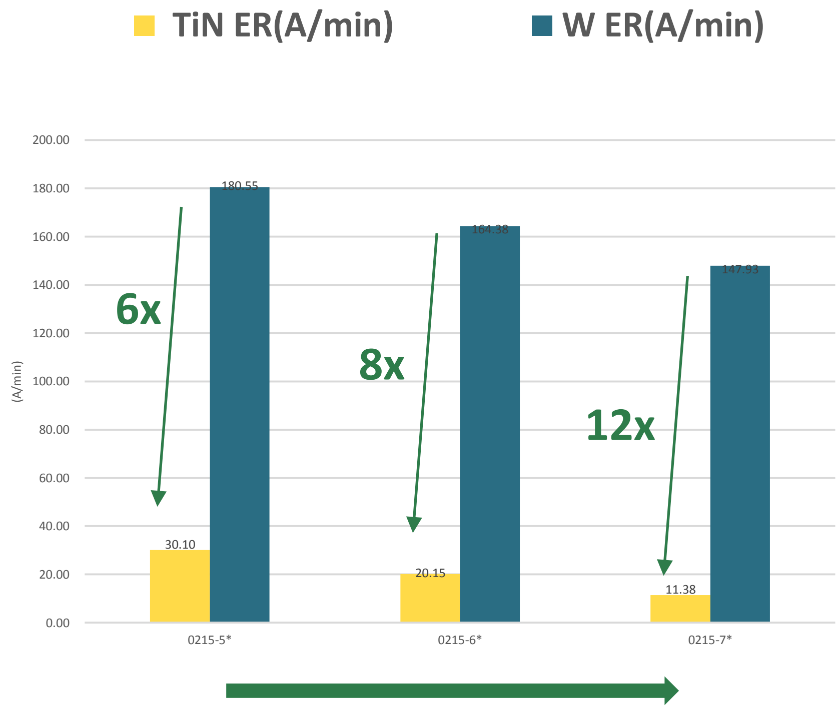
2. Hegde, Sharath; Babu, S. V. Electrochemical and Solid-State Letters (2004), **7**(12), G316-G3183. White , M. L. et al. Mat. Sc. For. 1249 E04-07 (2010).

TITANKLEAN® PERR AND SELECTIVE ETCH APPLICATIONS

Application: W vs. TiN selective etching







Better W Inhibitors

- Challenge and Requirements: **Control selectivity of TiN/W; compatible with various dielectric materials**
- W Etch rate controlled through selective W Inhibitors

CONCLUSIONS

- Proper selection of Cobalt inhibitors and complexers can virtually eliminate cobalt corrosion
- Certain cobalt cleaning additives improve defectivity on cobalt
- Additives have been found that remove and disperse organic residue from silicon nitride after W CMP
- Tungsten etch rate and corrosion can be controlled through the proper selection of W inhibitors

50 YEARS OF
PURE ADVANTAGE