Entegris
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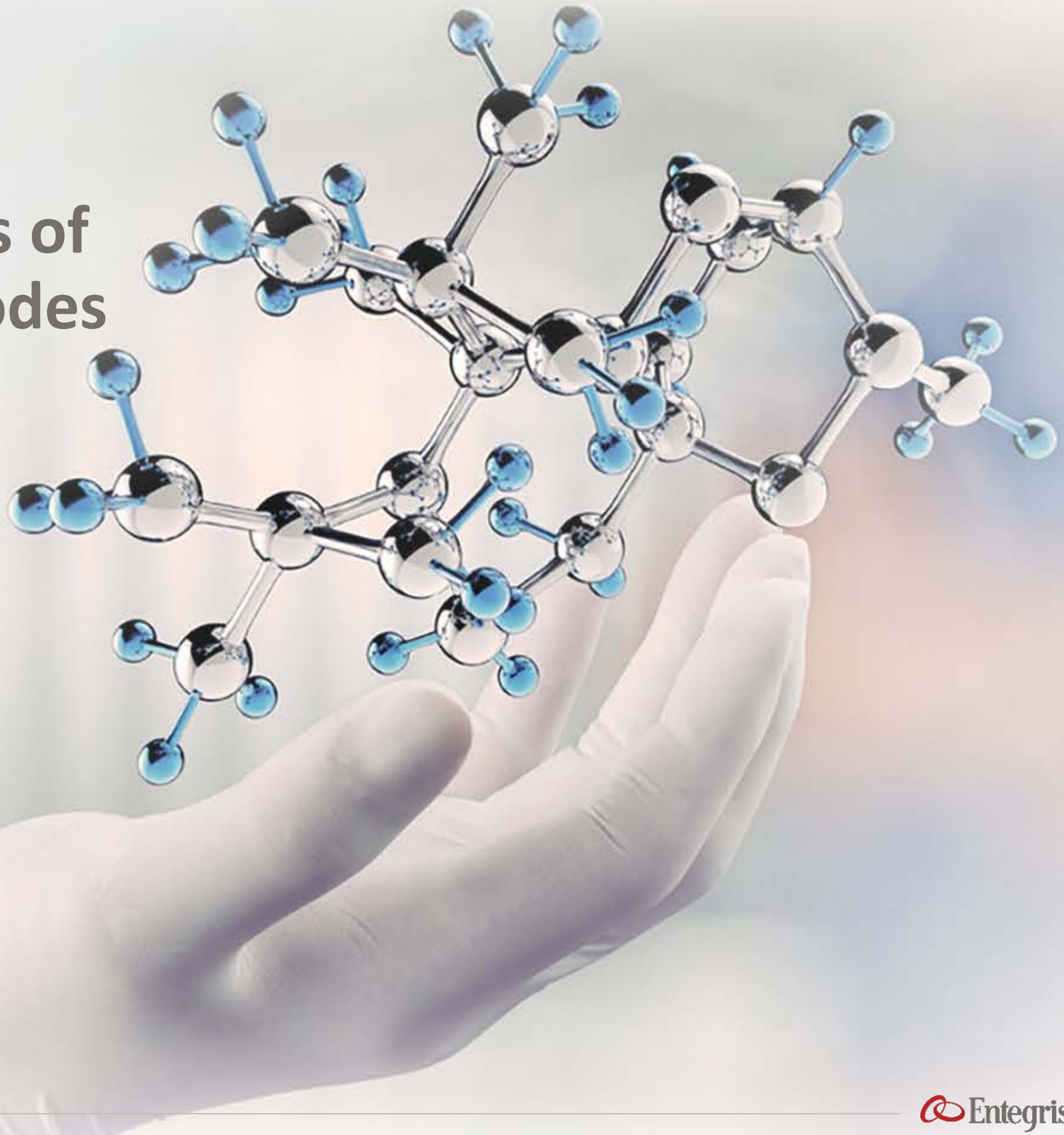
Mechanistic and Electrochemical Aspects of Copper Post CMP Cleaners for 5-7 nm Nodes



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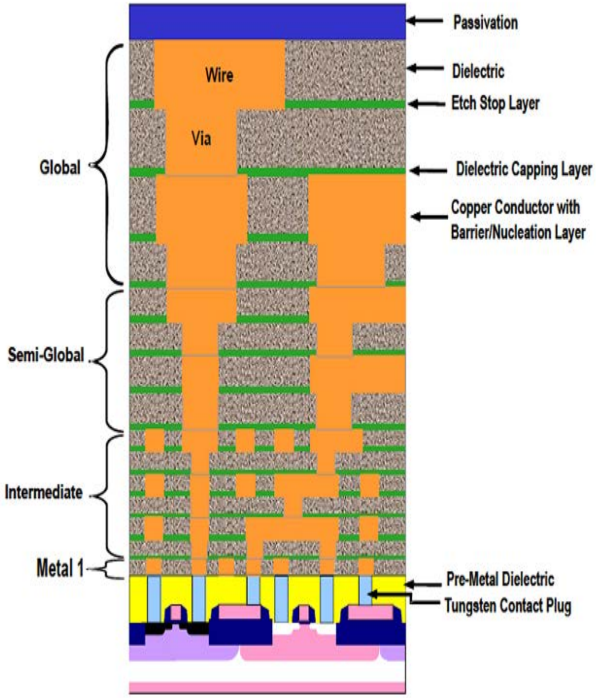
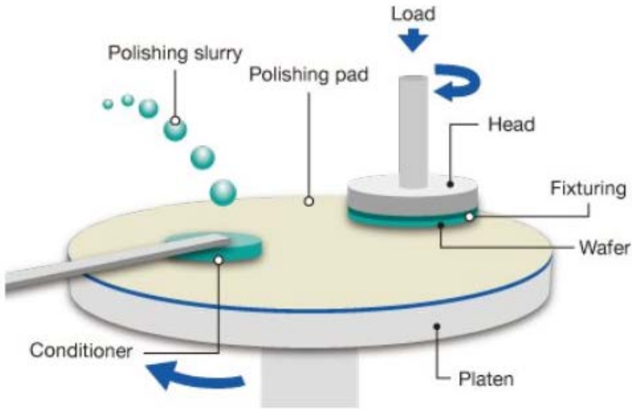
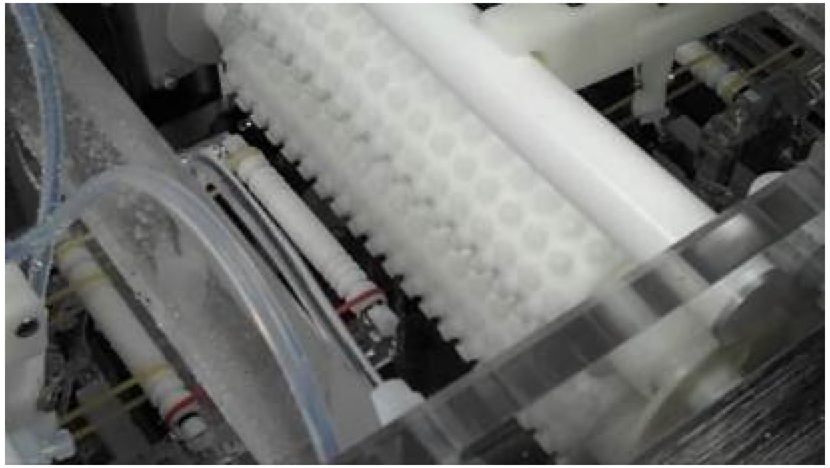
WHAT IS CMP (CHEMICAL MECHANICAL PLANARIZATION)?



Source: International Roadmap for Semiconductors ITRS press conference, Dec 2004, 25.



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



Layers/Materials that need to be Cleaned

1. Copper/barrier
   Ta, TaN, TiN, Co, Ru, Mn
2. Tungsten
3. Cobalt (bulk)
4. Aluminum
5. Dielectrics (including CeO_2 polishing)
   - TEOS, Si_3N_4, Low-k dielectric, SiC (SiOC, SiON, …), Polysilicon, Single crystal silicon (wafer, various doping)

Challenges in Post CMP Cleaning

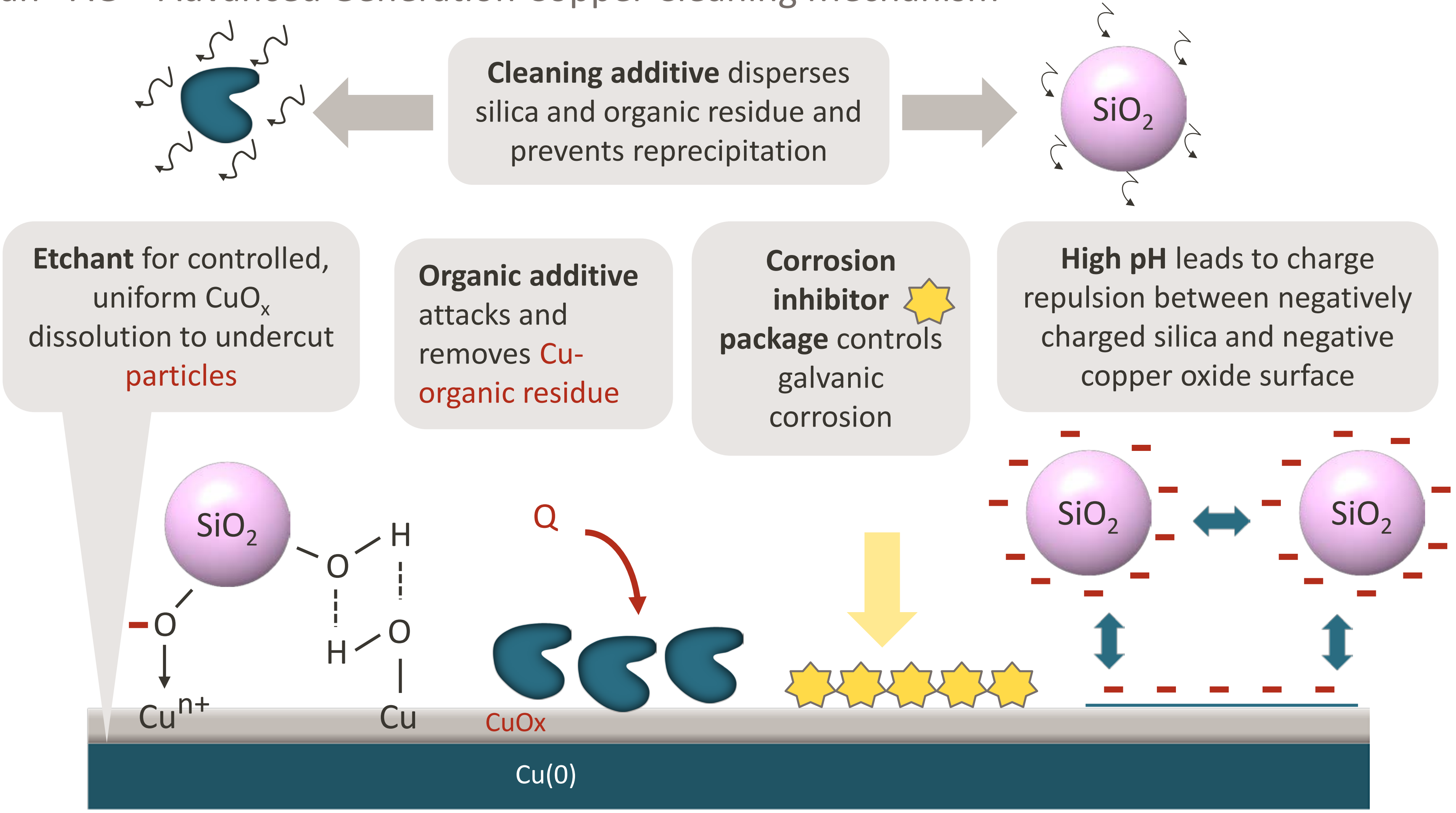
1. Variety of CMP slurry particle types
   - Silica (native, surface treated + or -)
   - Al_2O_3, CeO_2, TiO_2, ZrO_2, SiC, diamonds
2. Organic residue
   1. Corrosion inhibitors (BTA, …)
   2. Dishing/erosion/selectivity additives (polymers, surfactants, small molecules)
   3. Rate additives
3. Pad debris
4. Plating additives

PERFORMANCE GOALS FOR POST-CMP CLEANERS

1. Best in class defectivity
   1. Very low particle defects (silica, ceria, alumina, …)
   2. Greater challenges arising as particle sizes decrease
   3. Low organic residue (Cu-BTA or other thick film formers,
      W or other metal inhibitors, pad debris, plating additives, …)
2. Very low or no interfacial or surface metal/barrier corrosion or recess
   1. Advanced nodes <10 nm
   2. Low galvanic corrosion
3. Uniform, smooth etching with low roughness
   1. Affects thresholds for defectivity measurements
   2. No attack on low-k dielectric/dielectric loss
4. Low metallic impurities on wafer ($<10^{10}$ atoms/cm^2) on dielectrics
5. Good buffering/no brush interactions to avoid ring scratches

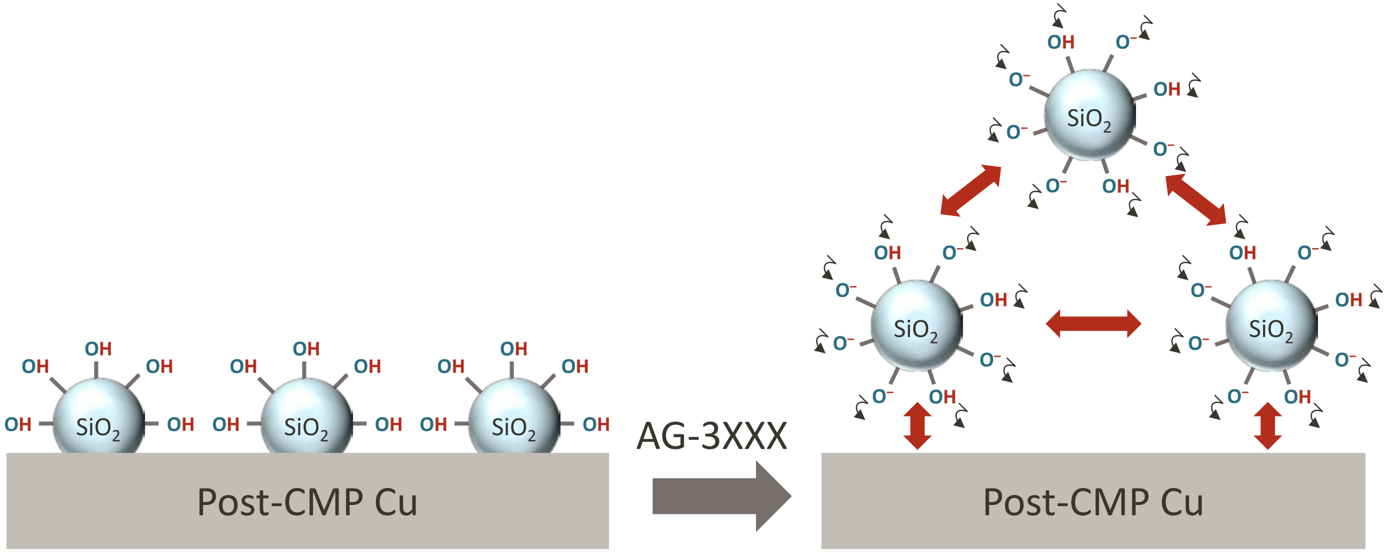
THE RATIONAL DESIGN OF A POST CMP CLEANER PLANARCLEAN® AG COPPER CLEANING

PlanarClean® AG – Advanced Generation Copper Cleaning Mechanism

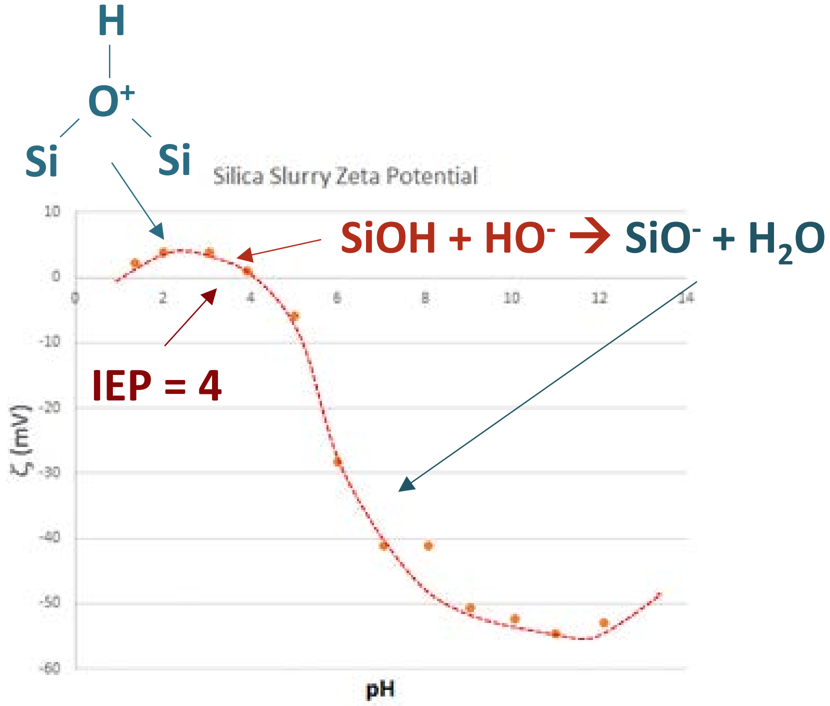


PLANARCLEAN® AG PREVENTS SILICA AGGREGATION

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

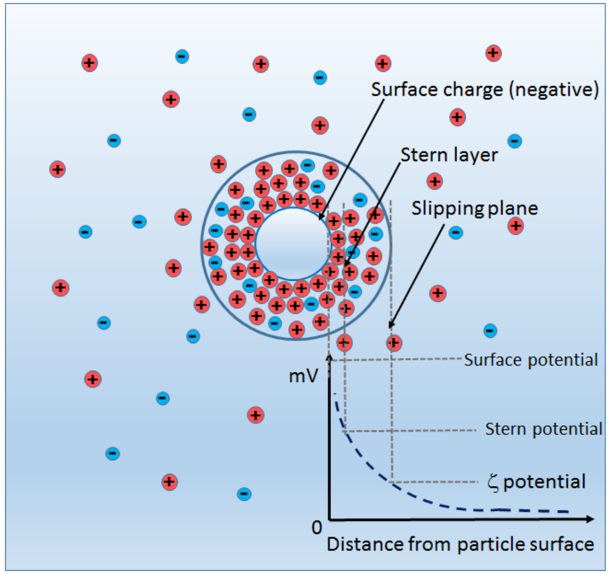


Dispersed particles
Highly negatively charged
No particles agglomeration

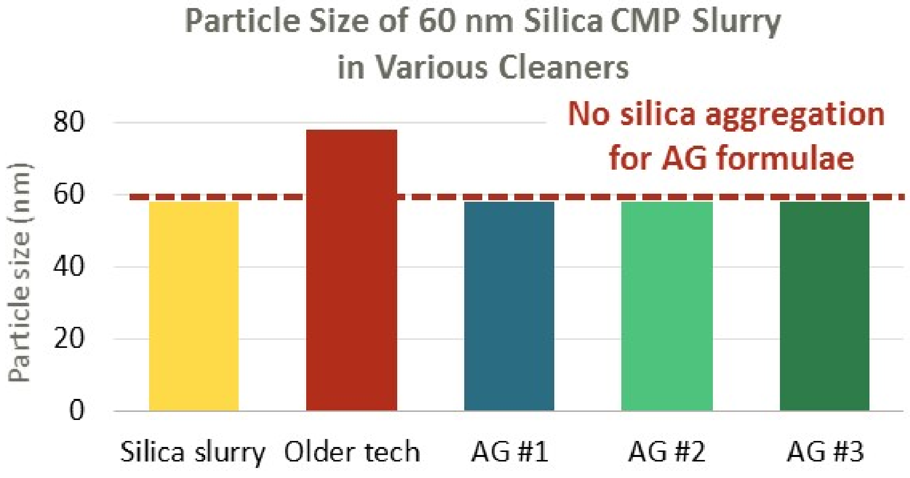


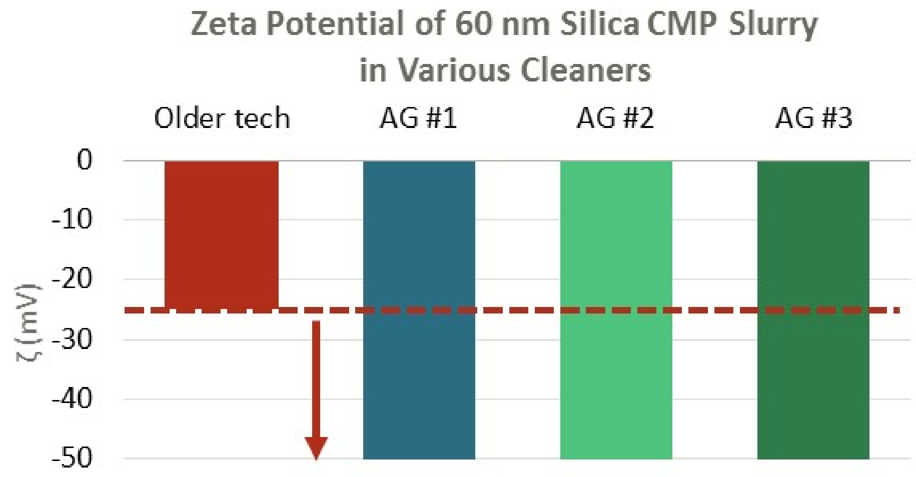
Zeta Potential

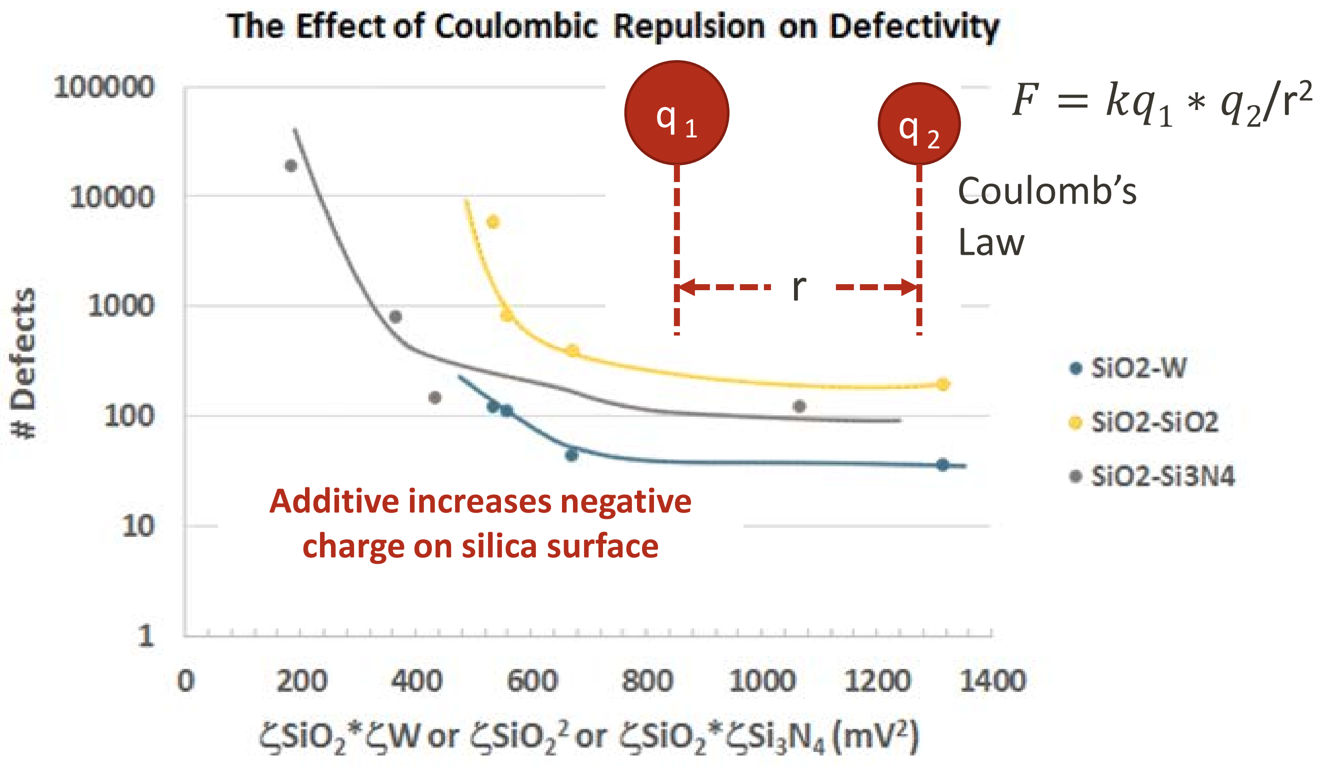
$$\zeta = 4\pi\gamma(\nu/E)/\varepsilon$$



DEFECTIVITY CORRELATED TO CHARGE REPULSION BETWEEN SILICA PARTICLES



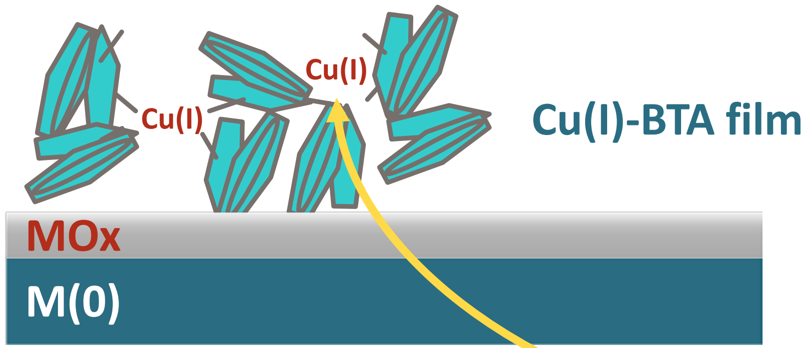


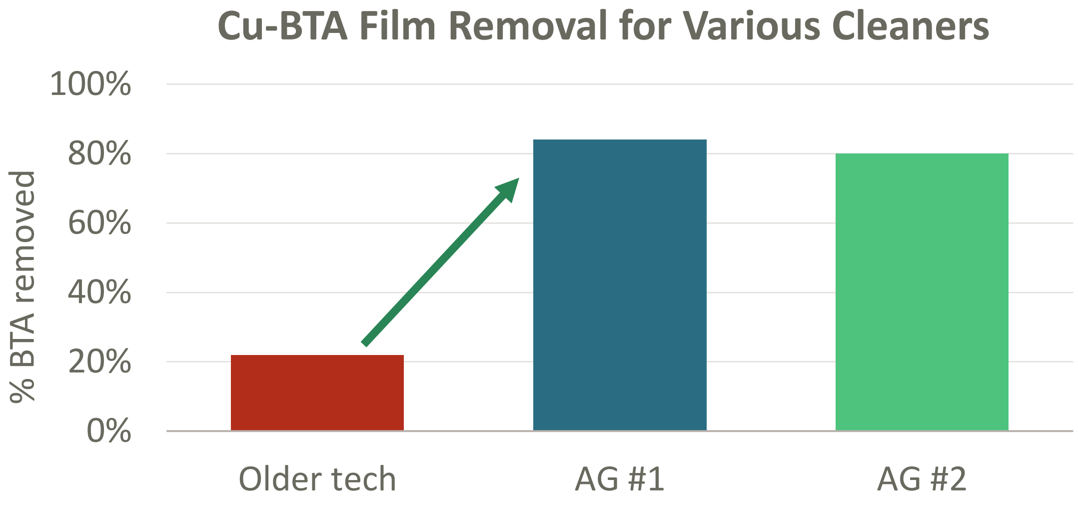


Zeta potential of all AG formulations is highly negative

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).

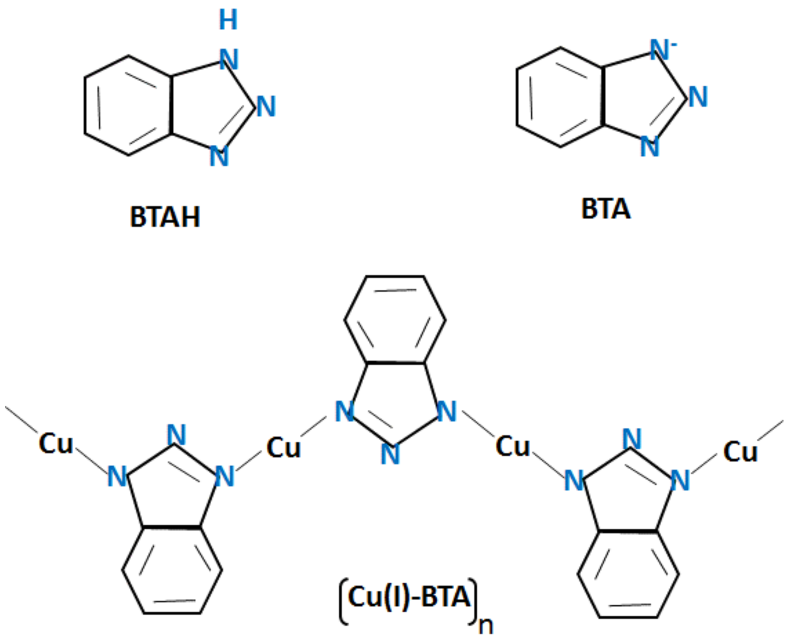
BREAK-UP AND DISPERSION OF Cu(I)-BTA COMPLEXES

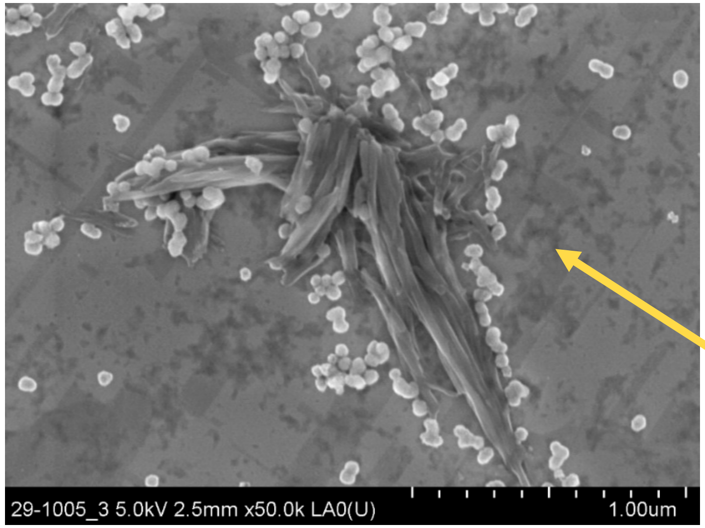




Additive tailored to attack Cu(I)BTA and similar films

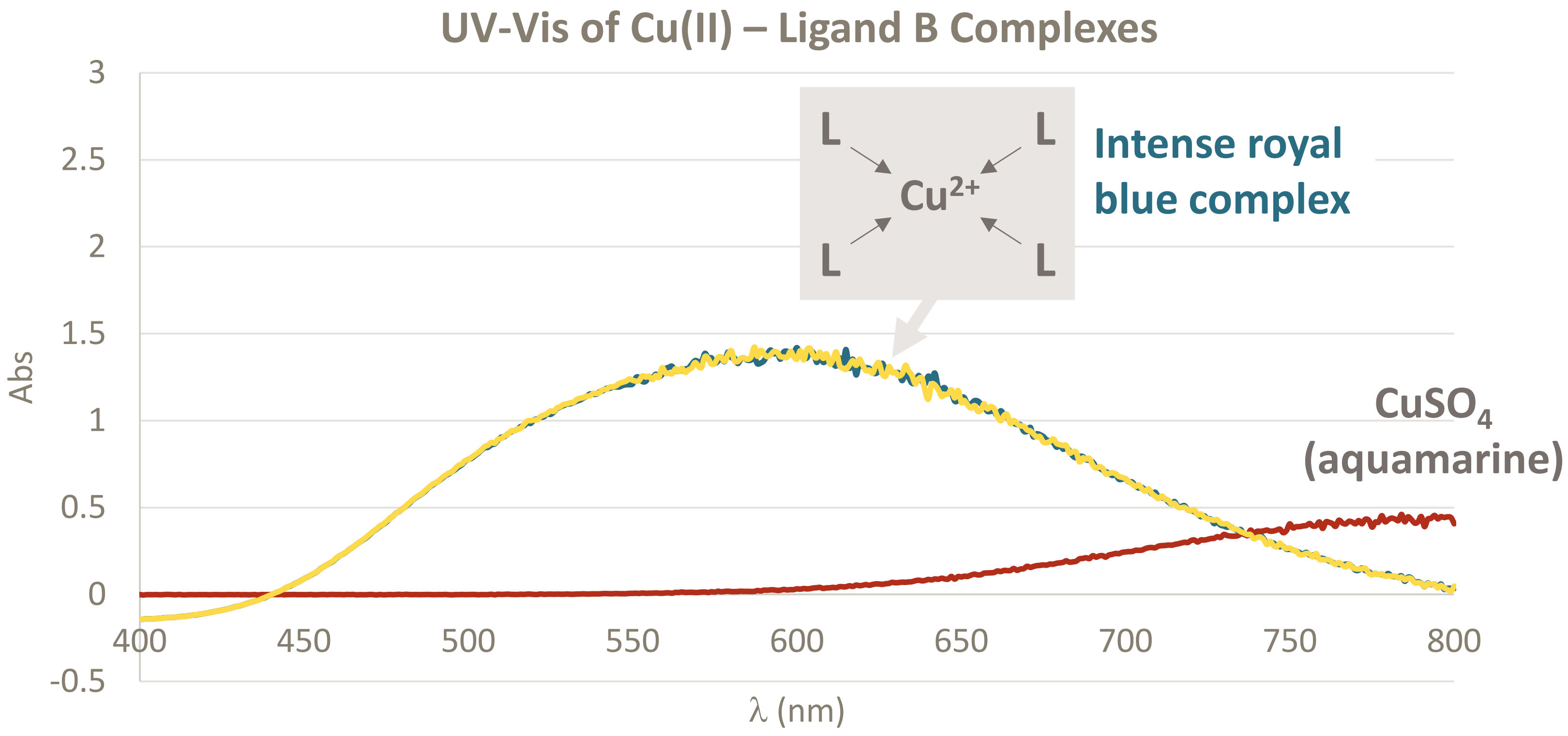
- Fast kinetics
- Thermodynamically favored
- (Higher Cu binding constant than BTA)





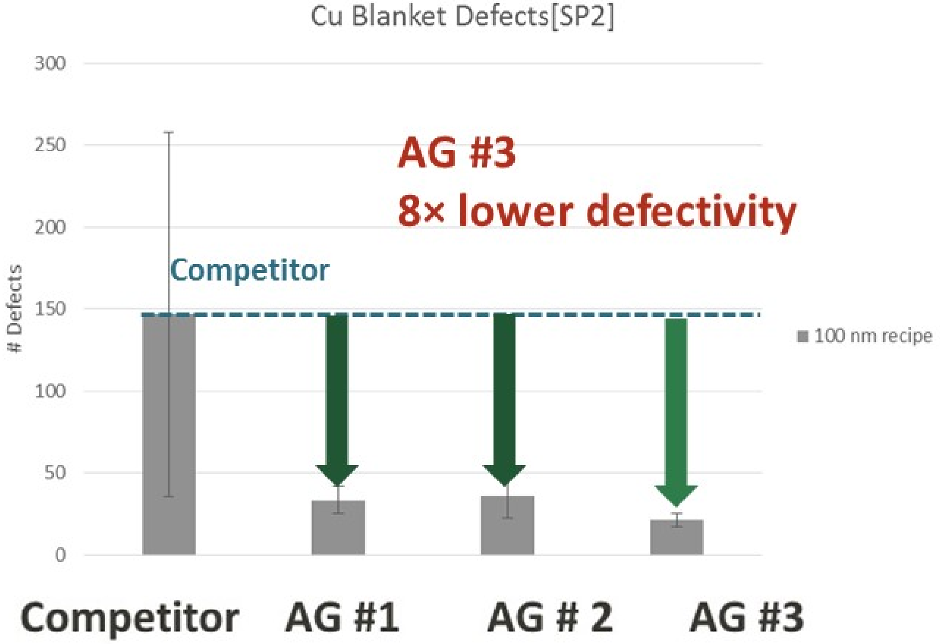
Cu(I)-BTA can redeposit if Cu is not properly complexed or dispersed

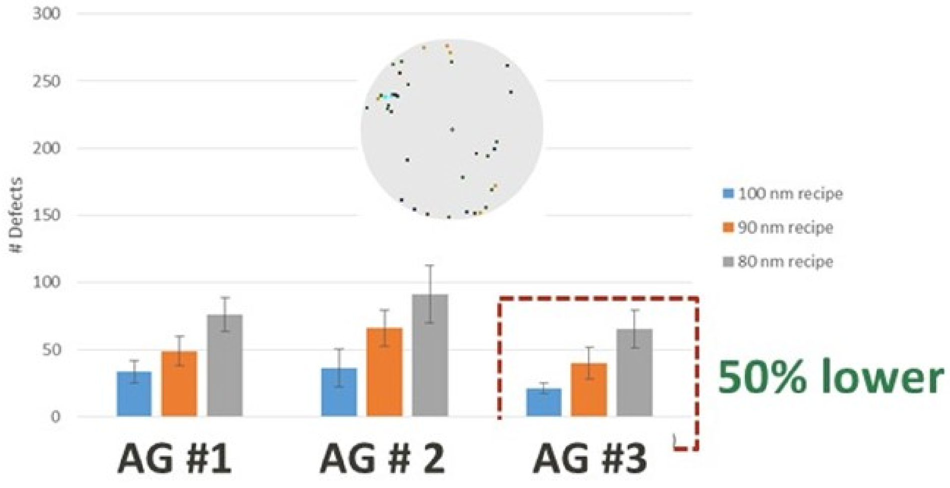
UV-VIS USED TO PREDICT OPTIMUM COMPLEXANT AND LIGAND CONCENTRATION

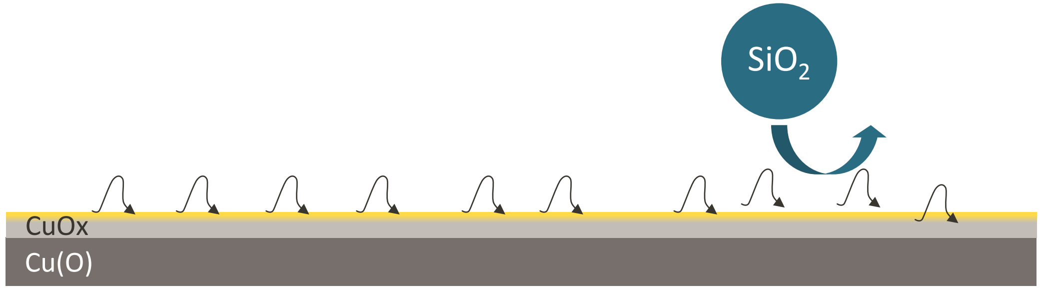


Ligands complex copper as soluble Cu(II) and prevent redeposition as CuOx defects or reprecipitating BTA

PLANARCLEAN AG: LOWER DEFECTS THAN COMPETITORS

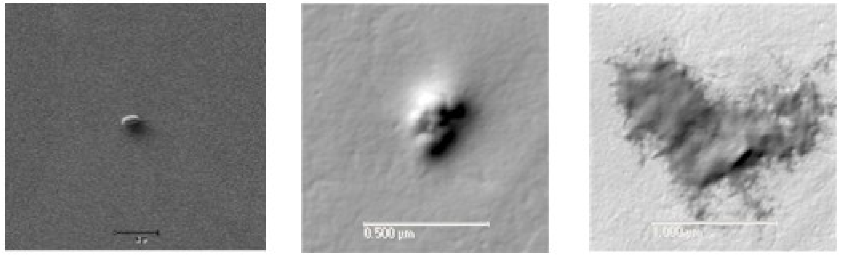


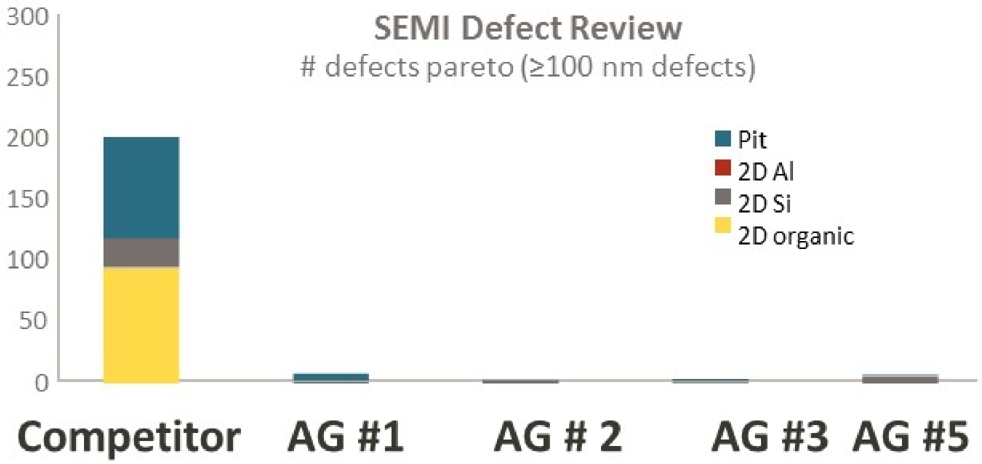




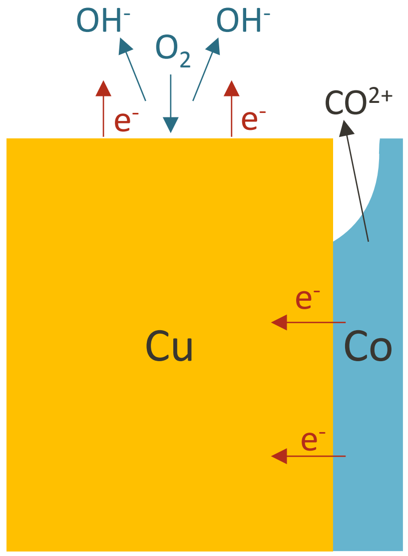
Additive forms weakly interacting film that prevents silica (re)attachment

Silica | Silica cluster | Organic residue





ELECTROCHEMISTRY REVEALS PLANARCLEAN® AG EXHIBITS IMPROVED CORROSION PERFORMANCE



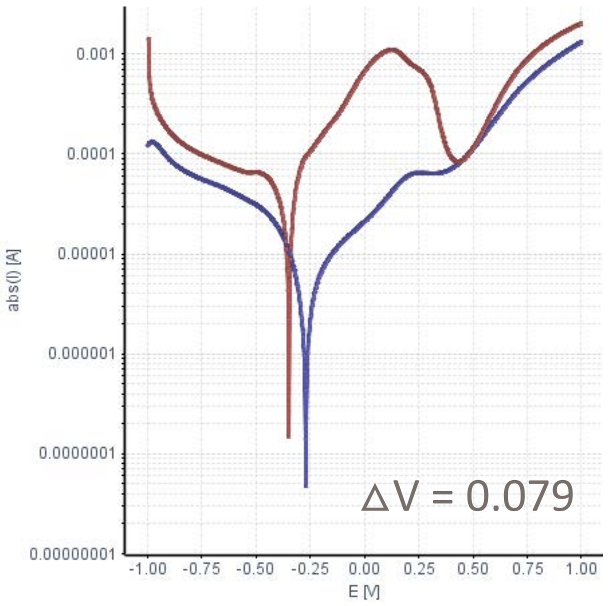
$$Co \rightarrow Co^{2+} + 2e^{-}$$

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

Co OCP < Cu OCP-:
Co not protected

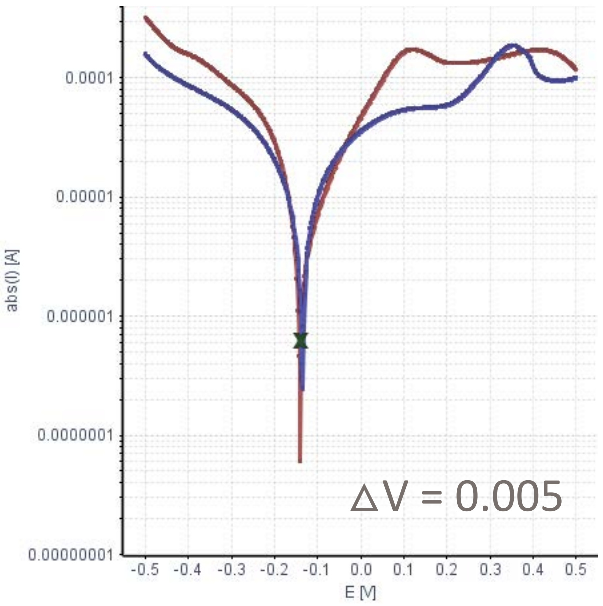
Copper — Cobalt

AG #1



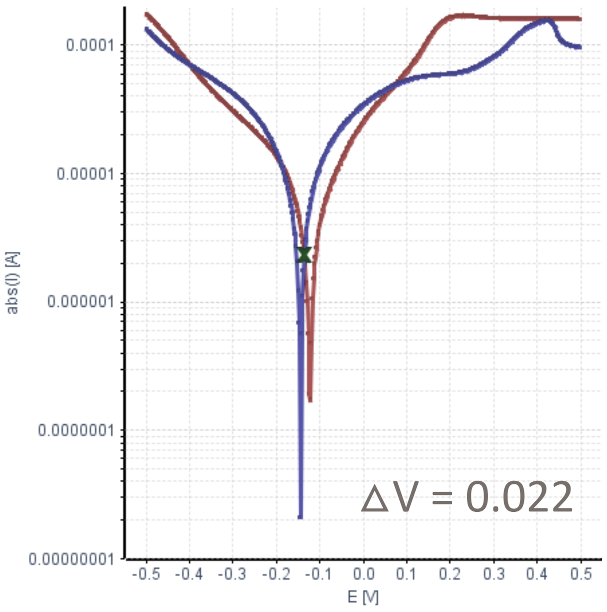
Co protected
(Cu 1.210 Ǻ/min)

AG #2



Nearly zero
galvanic corrosion
(Cu 0.078 Ǻ/min)

AG #3



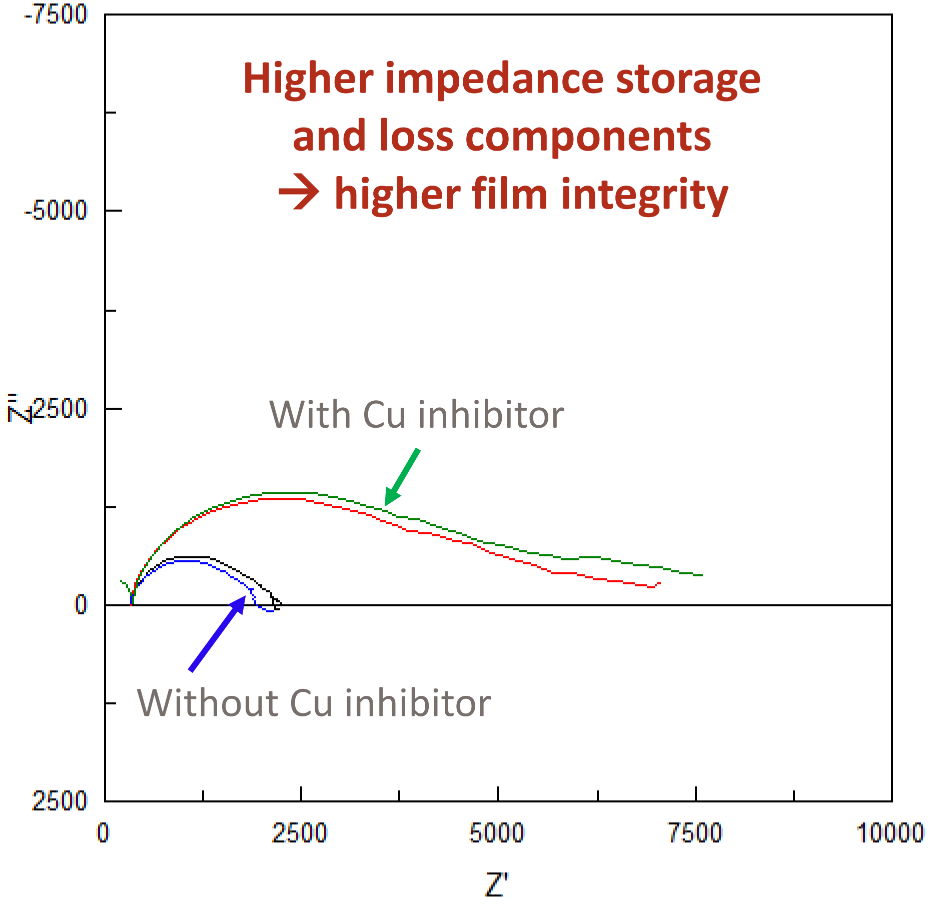
Very low galvanic
corrosion
(Co 0.270 Ǻ/min)

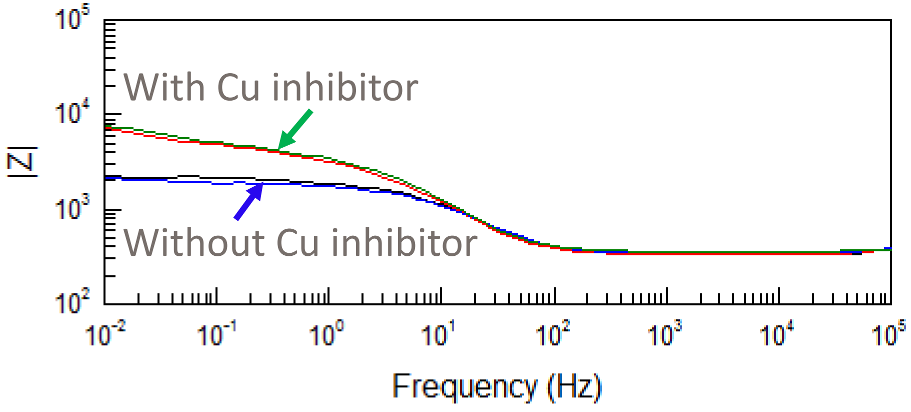
Controlled Electrochemical properties

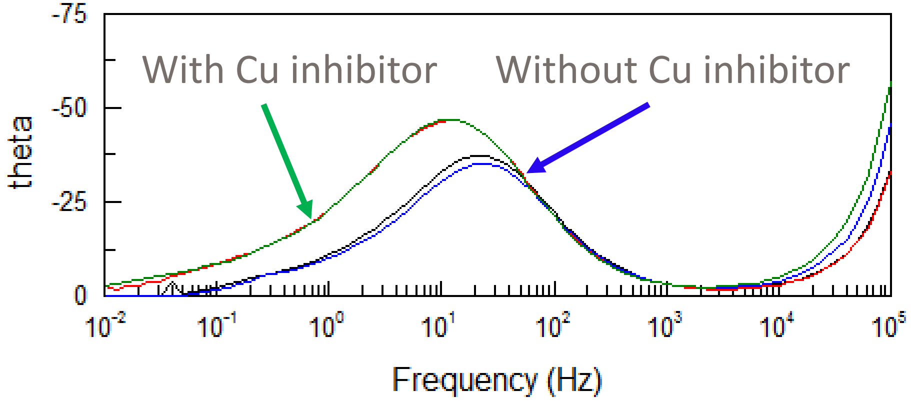
✓ **Ligands to control potential gap**

✓ **Passivation to modify resistivity**

IMPEDANCE SPECTROSCOPY SHOWS THAT AG COPPER INHIBITOR IMPROVES Cu PASSIVATION

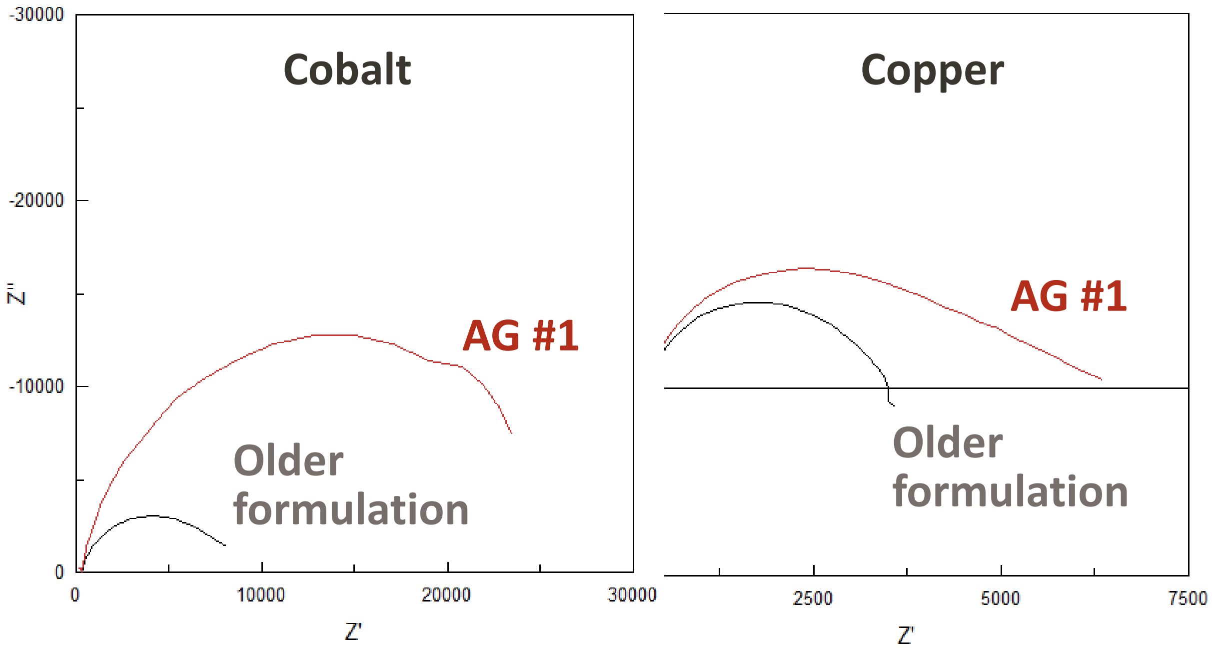




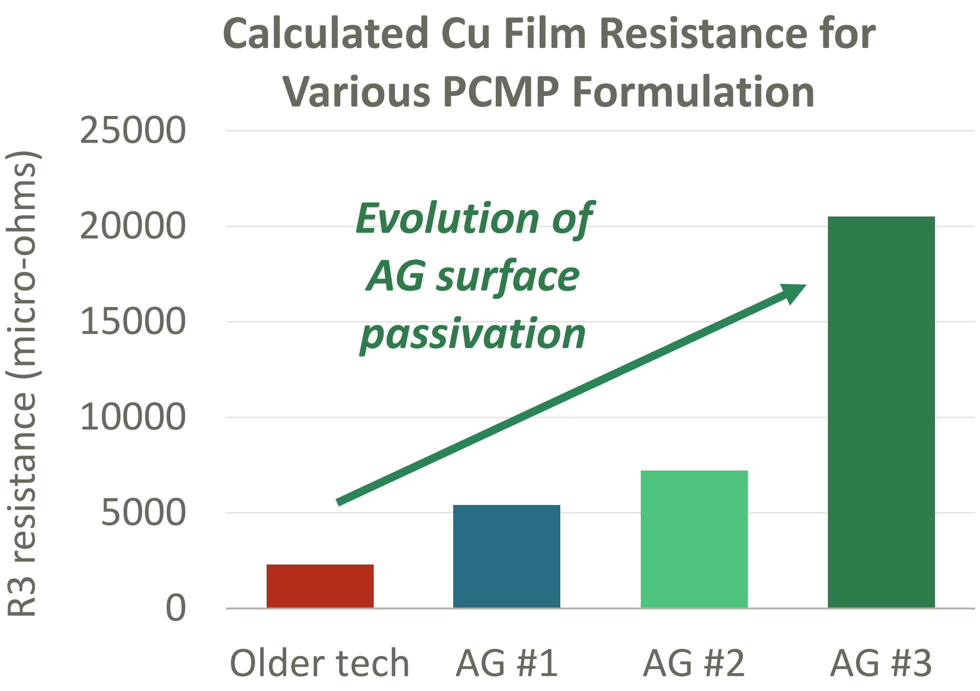


PLANARCLEAN® AG FORMULATIONS PROVIDE BETTER PASSIVATION ON BOTH Cu AND Co

Impedance Spectroscopy



Additional Novel Cu Inhibitor Improves Cu Passivation



When ω -> 0

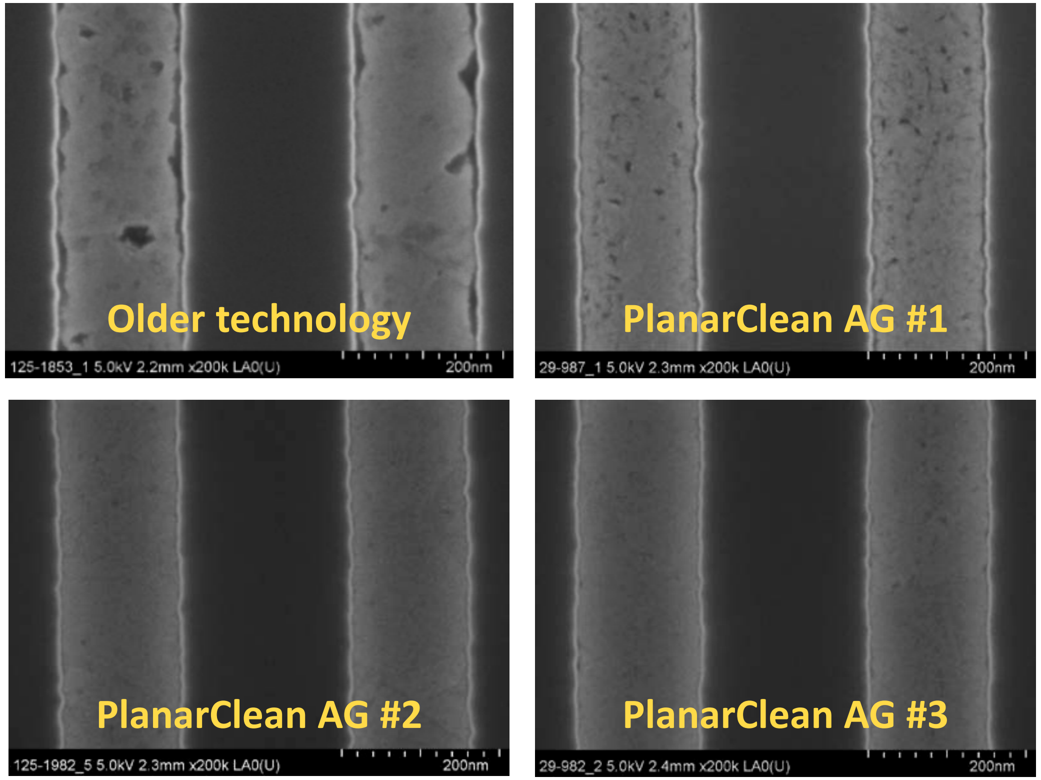
$$Z' = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/2}}{(\sigma\omega^{1/2}C_{dl}+1)^2 + \omega^2 C_{dl}^2 (R_{ct}+\sigma\omega^{-1/2})^2}$$

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

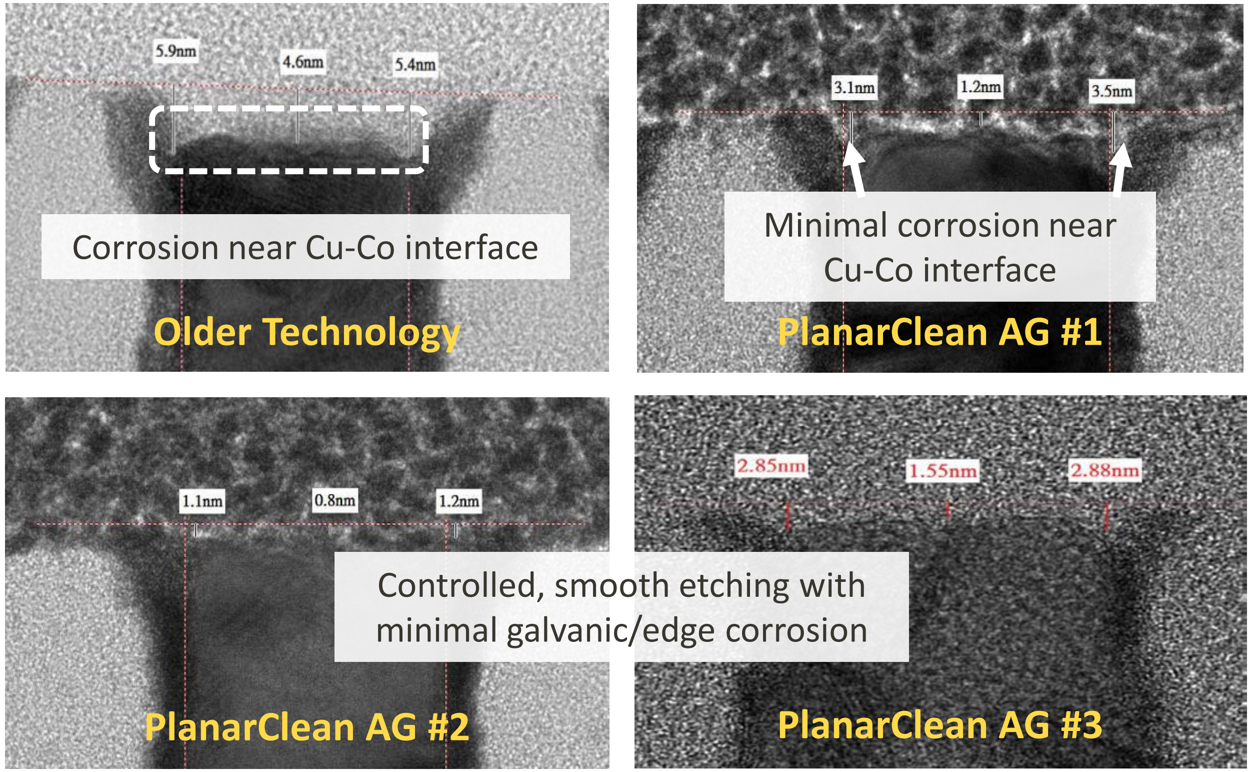
Ref:
1. Wang, et al. SPIE Beijing 2016 Conf. Proc.
2. Bard, A. J. Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications; Wiley and Sons 2001

ELECTRON MICROSCOPY SHOWS SIGNIFICANTLY IMPROVED Cu/Co CORROSION PERFORMANCE FOR PLANARCLEAN® AG

SEM on Sematech® 754 Wafers



TEM on 45 nm Cu/Co Wafers



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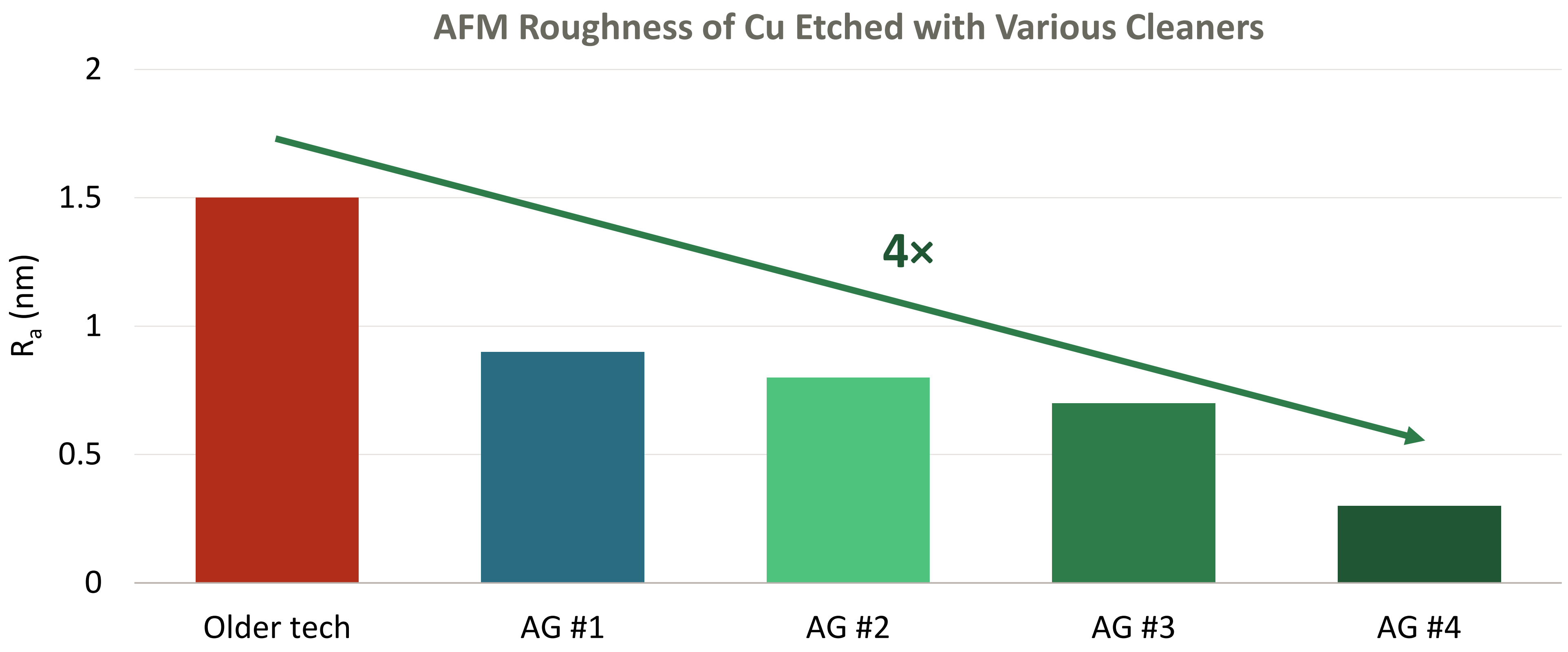
IMPROVED CORROSION ADDITIVES REDUCE SURFACE ROUGHNESS BY 2-4×



CONCLUSIONS

- Charge repulsion shown to be a key driver towards cleaning performance
- Rate of attack on Cu(I)-BTA polymer, dispersion and complexation important for removal and preventing re-deposition of organic residues and particles
- OCP gap must be minimized by optimal ligand selection to minimize galvanic corrosion
- Impedance spectroscopy and Tafel plots have been used to Optimize corrosion inhibiting package
- Very low Cu roughnesses can be obtained with the correct inhibitor (4 Å)