Mechanistic Aspects of Wafer Cleaning After Chemical Mechanical Planarization

Michael White*[*1], Daniela White[1], Atanu Das[1], Don Frye[1], Shining Jeng[2], Ruben Lieten[3], Jun Liu[1], Roger Luo[2], Thomas Parson[1], Elizabeth Thomas[1], Volley Wang[2], John Clement[1] and Michael Owens[1]

[1] Entegris, Inc. 7 Commerce Dr., Danbury, CT 06810, USA;

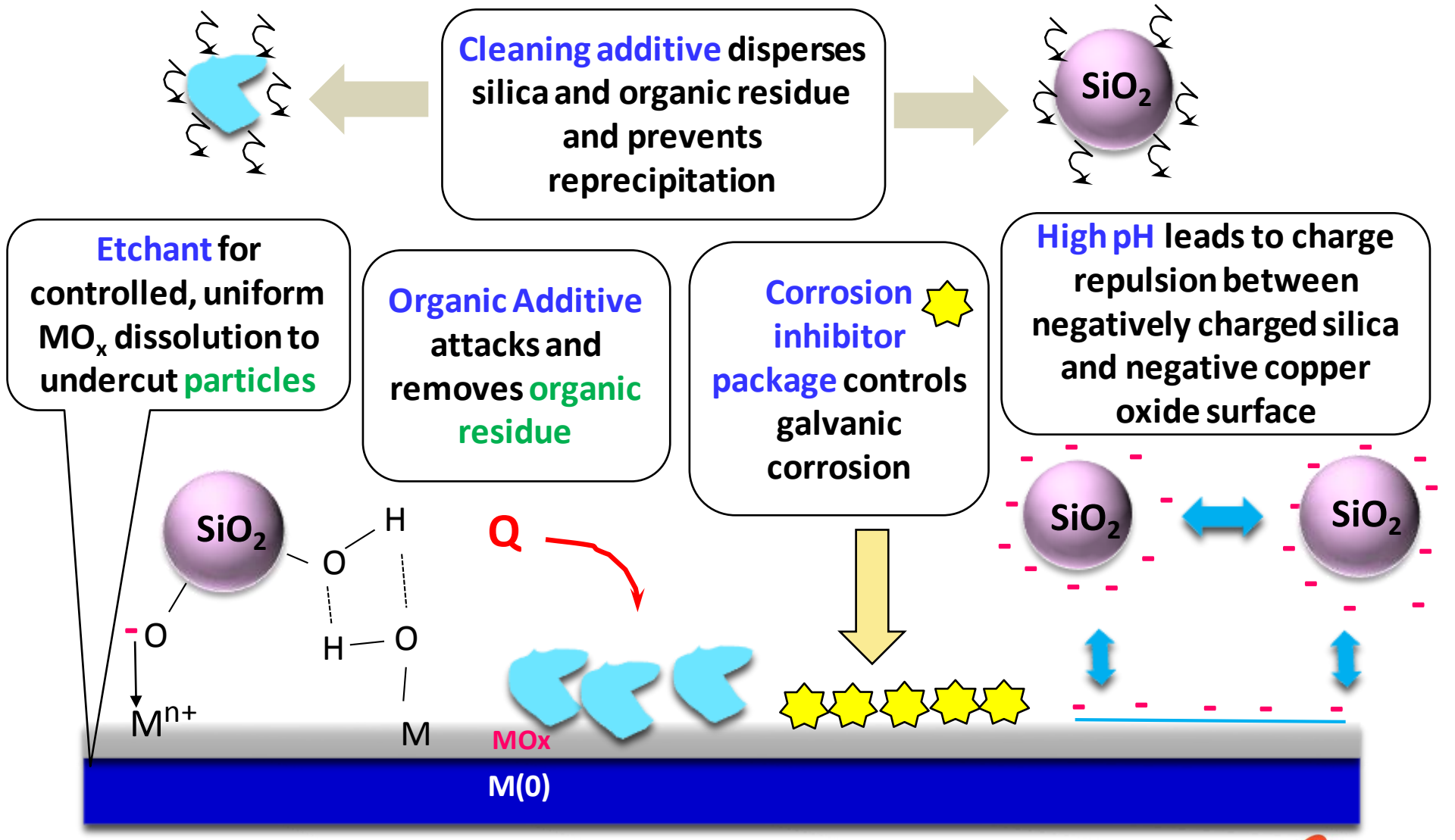
[2] Entegris, Inc. 1F, No. 669, Section 4, Chung-Hsin Rd., Chutung Town, 31061, Taiwan

[3] Entegris, Gmbh, Hugo-Junkers-Ring 5, Gebaud 107/W, 01109 Dresden, Germany

Performance Goals for Post CMP Cleaners

- 1. Best in class defectivity
  - Very low particle defects (silica, ceria, alumina, …)
    - Greater challenges arising as particle sizes decrease
  - 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
  - Advanced nodes <10 nm
  - Low galvanic corrosion
- 3. Uniform, smooth etching with low roughness
  - Affects thresholds for defectivity measurements
  - No attack on low k dielectric/dielectric loss
- 4. Low metallic Impurities on wafer (<10^{10} atoms/cm^2) on dielectrics
- 5. Good buffering/minimal brush interactions to avoid ring scratches

Rational Design of a Post CMP Cleaner



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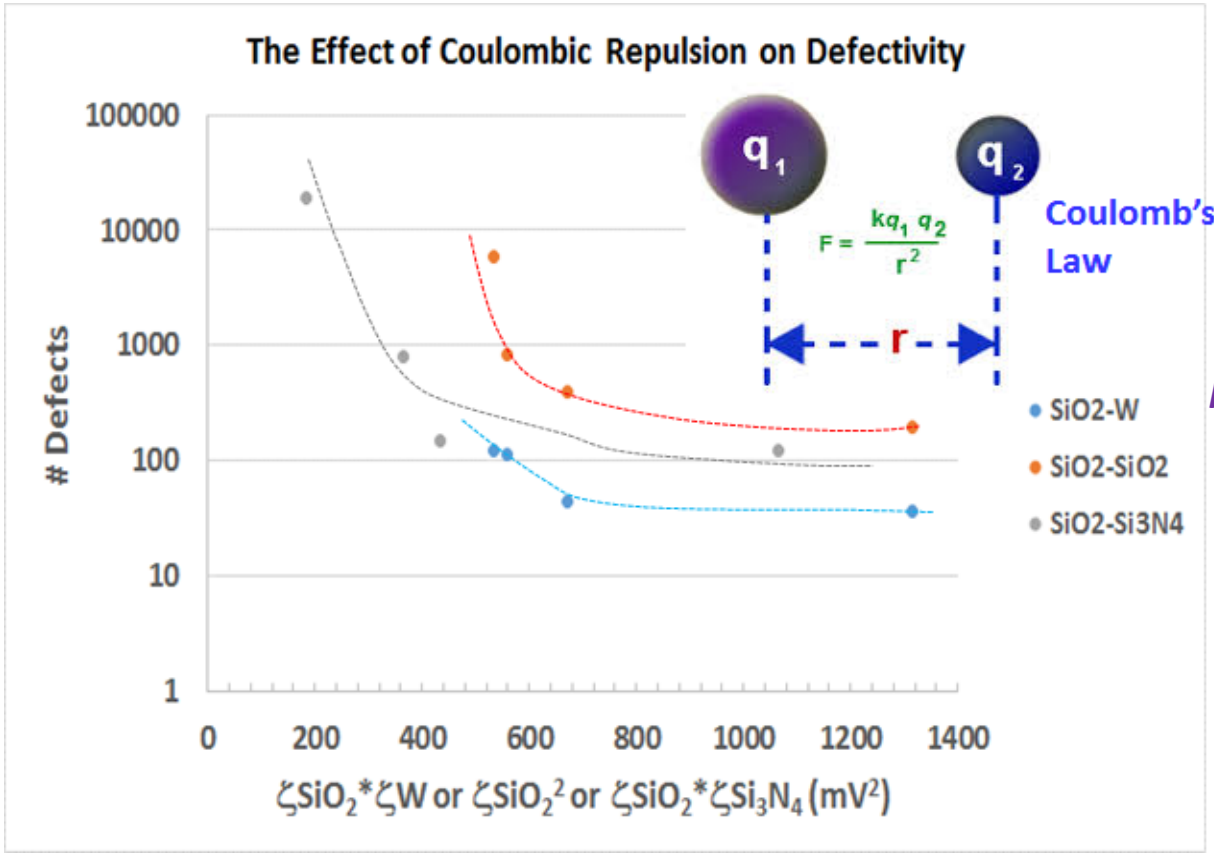
Defectivity Correlated to Charge Repulsion Between Silica Particles and Various Surfaces (W, SiO_2, Si_3N_4)



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).

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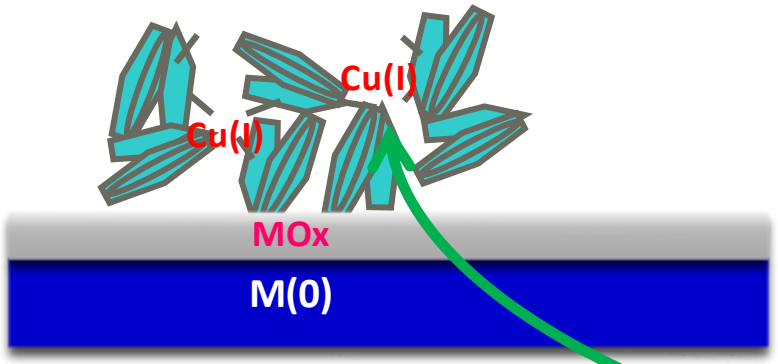
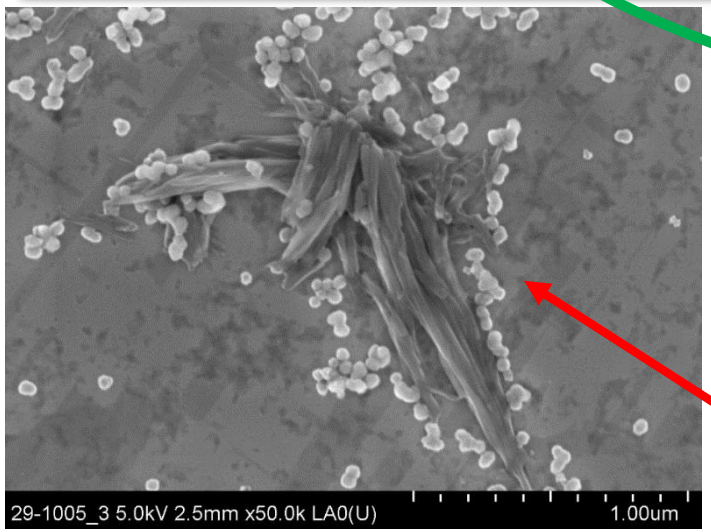
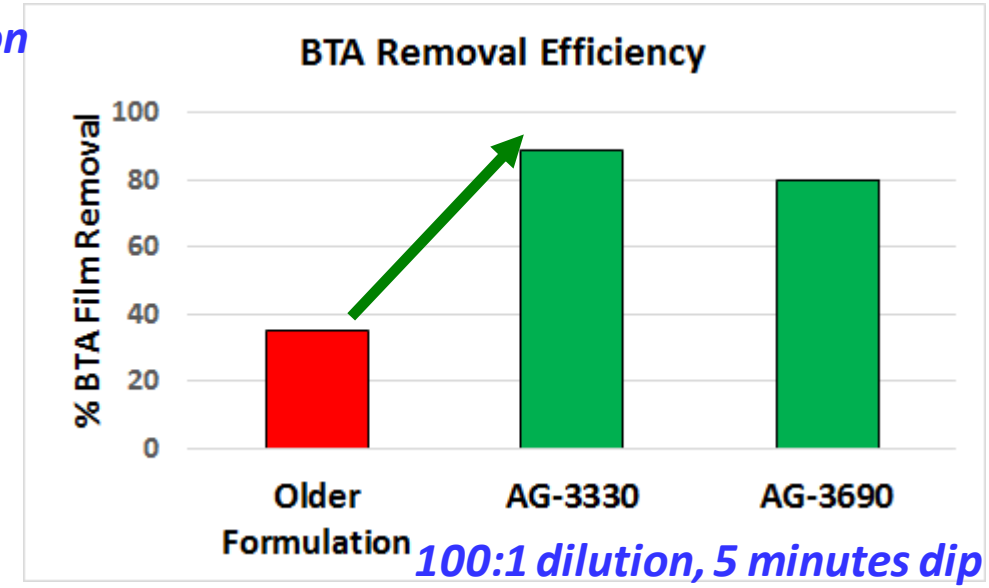
Break-up and Disperion of Cu(I)-BTA Complexes

80 nm Cu(I)-BTA film formed by Immersion of Cu coupons in 1% BTA solution → Measured by ellipsometry







100:1 dilution, 5 minutes dip

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

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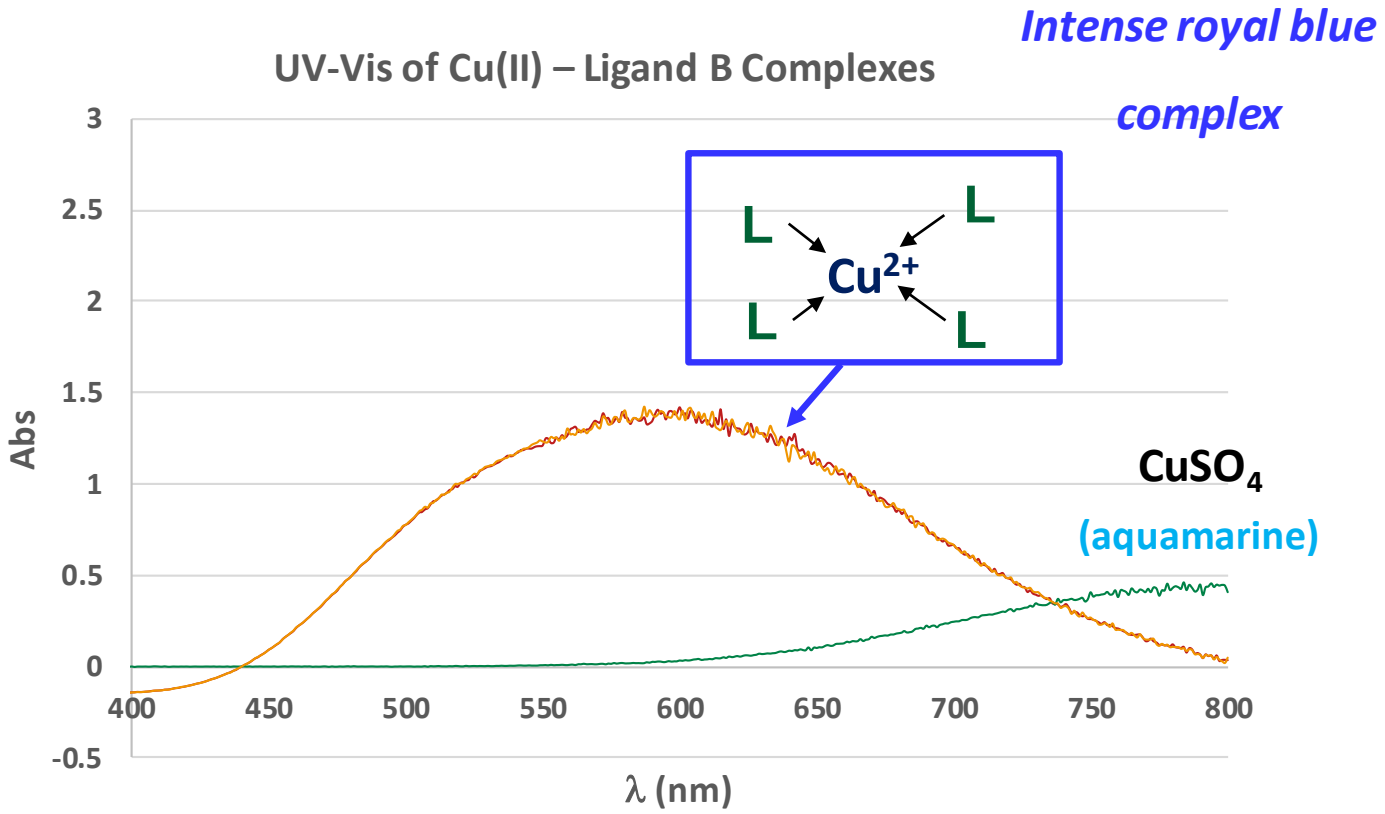
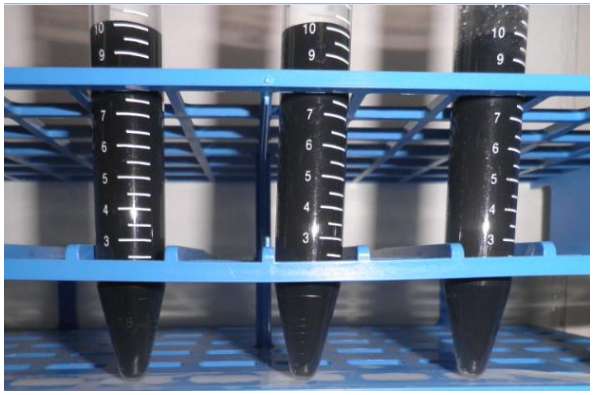
UV-Vis Used to Predict Optimium Complexant and Ligand Concentration



Sedimentation of Metal Oxides Used to Determine Effective Dispersant and Concentration

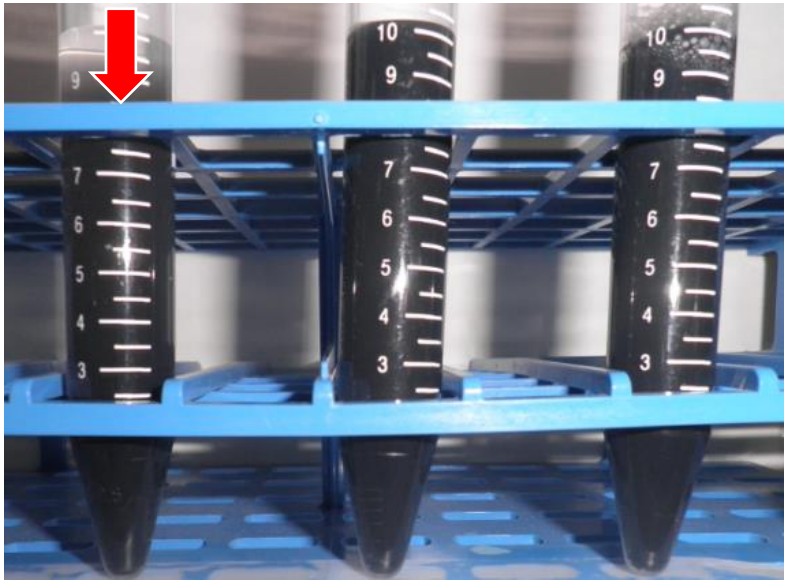
Start (t = 0)

DIW **A** **B**



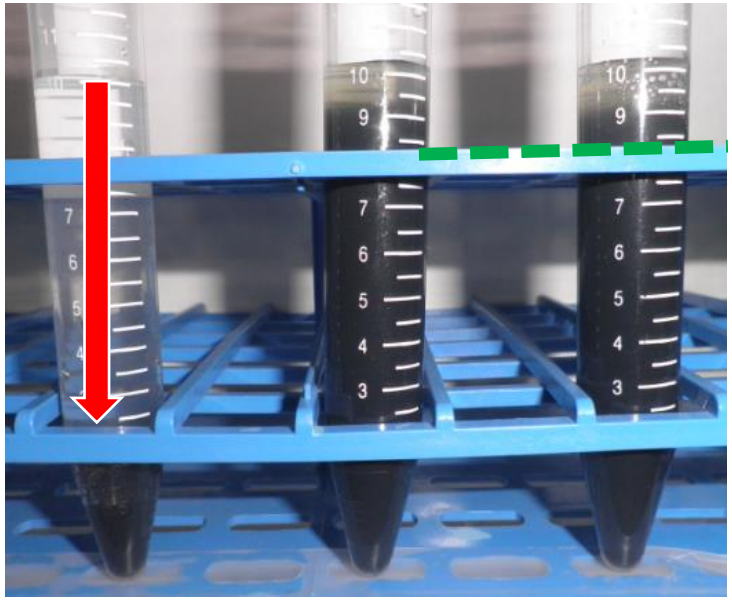
60 mins

DIW **A** **B**



18hrs

DIW **A** **B**



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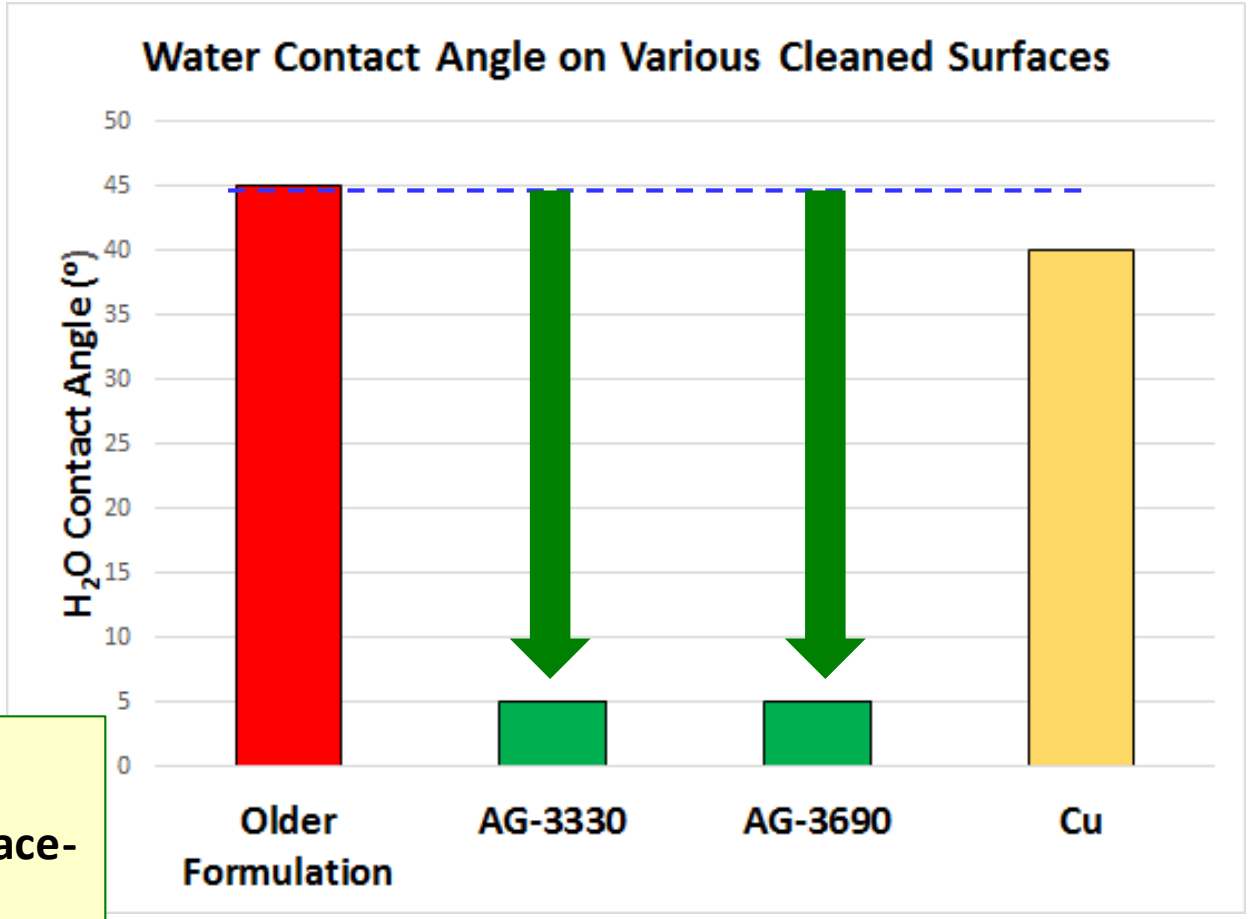
Additives Enable Hydrophilic Surface with Low Forces of Adhesion for Maximum Cleanability



- **Highly hydrophilic surfaces**
- **Lowest adhesion forces: surface-particles**
- **Best cleaning**
- **Lowest defects**

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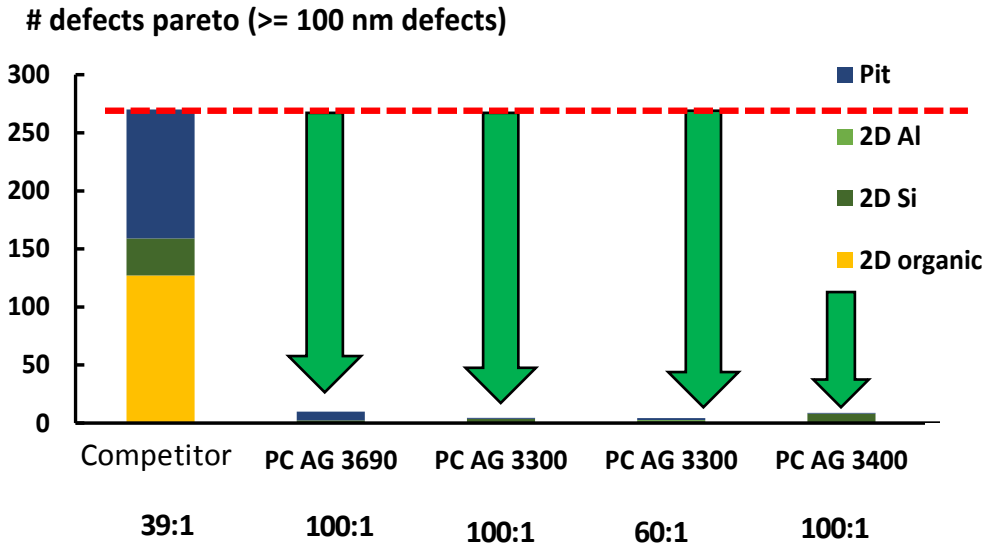
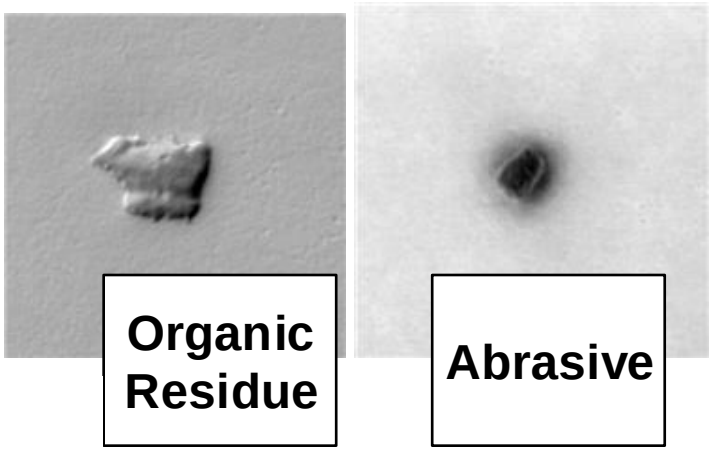
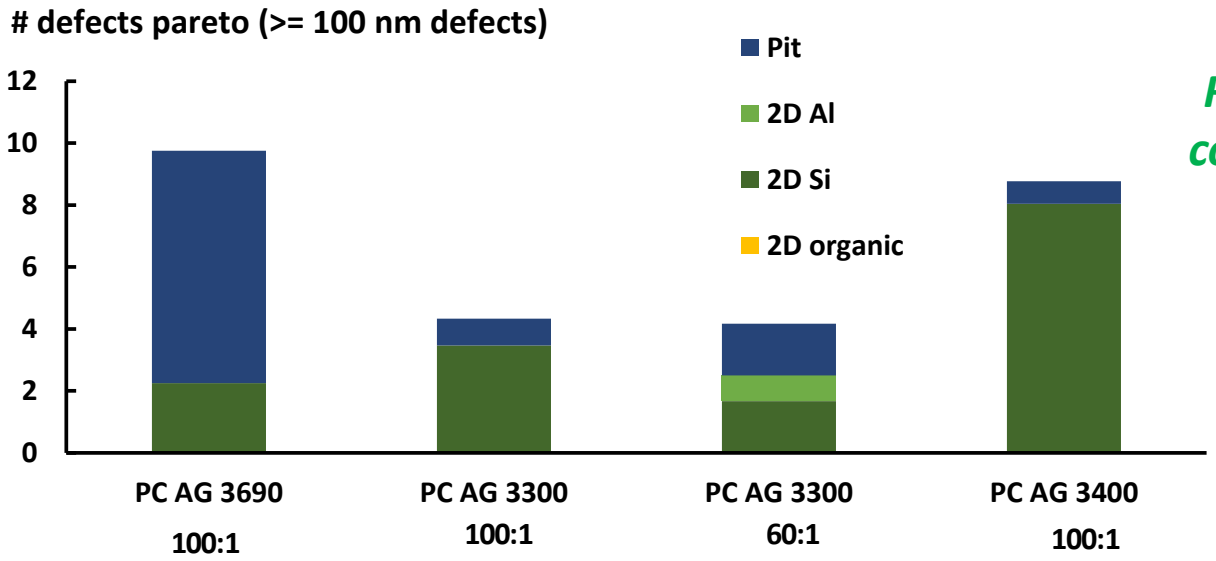
SEM Defect Review Shows AG-3300 and AG-3690 Have Excellent Silica Removal and No Detectable Organic Residue







No Organic Residue- silica counts very low

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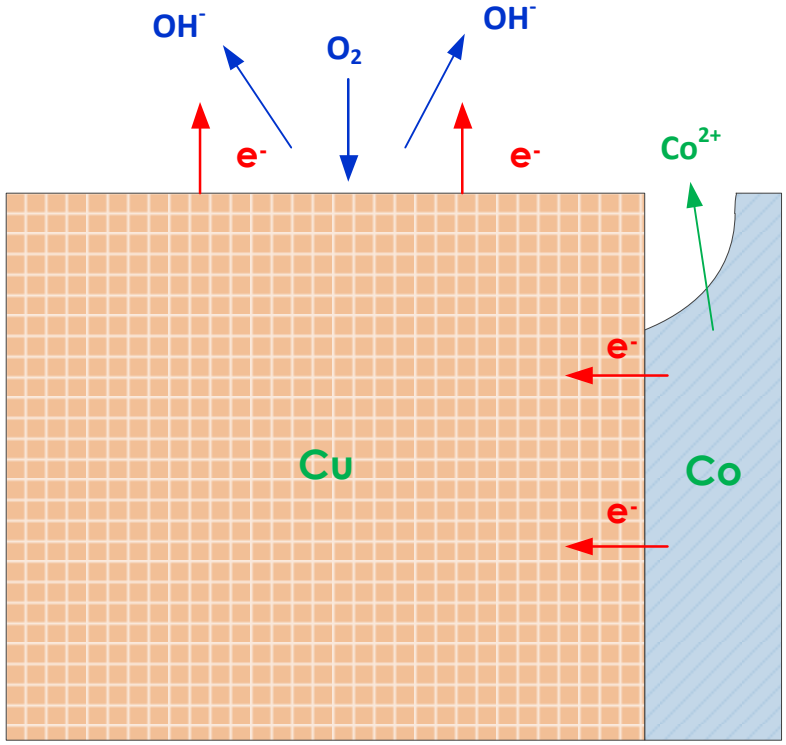
Co/Cu Galvanic Corrosion Mechanisms

Co OCP < Cu OCP: Co not protected



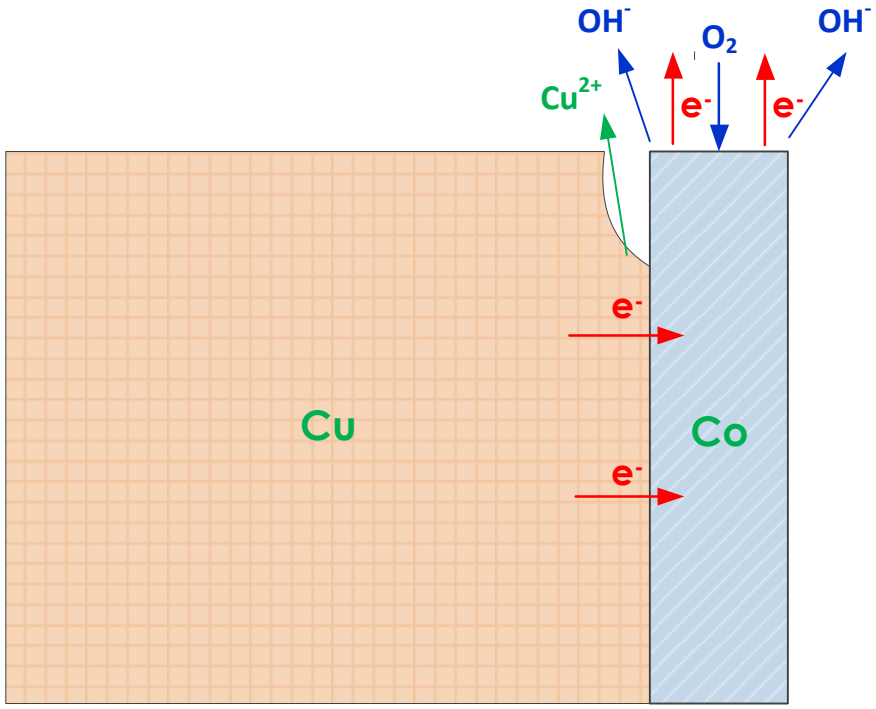
- anodic reaction on Co:

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

- cathodic reaction on Cu:

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

Co OCP > Cu OCP: Co cathodically protected



- anodic reaction on Cu:

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

- cathodic reaction on Co:

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

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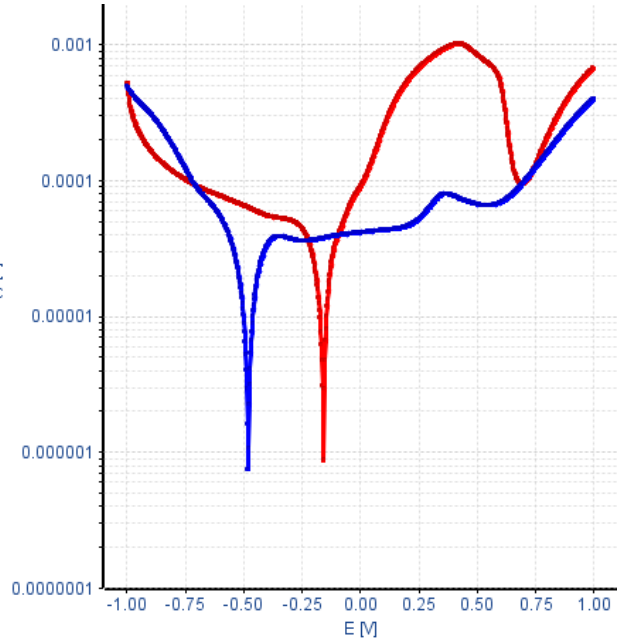
Electrochemistry Reveals PlanarClean® AG Exhibits Improved Corrosion Performance

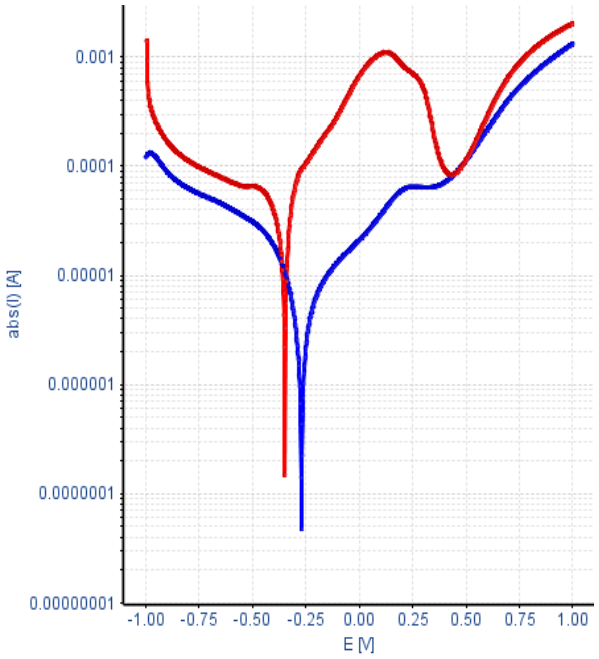
Older Technology



△V = - 0.37

Anodic Co Corrosion

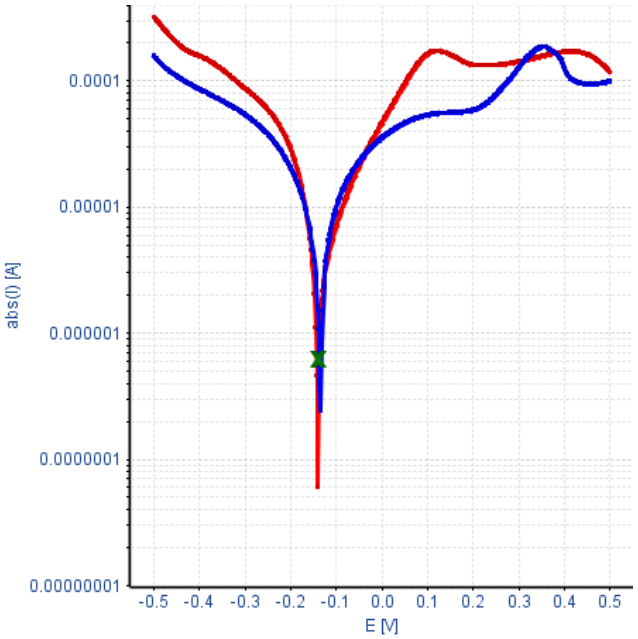
AG-3300



△V = 0.079

Co Protected

AG-3690



△V = 0.005

Nearly Zero Galvanic Corrosion (0.063 Å/min)

Controlled Electrochemical properties

- ✓ ***Ligands to control OCP gap***
- ✓ ***Passivation to modify resistivity***

Copper **Cobalt**

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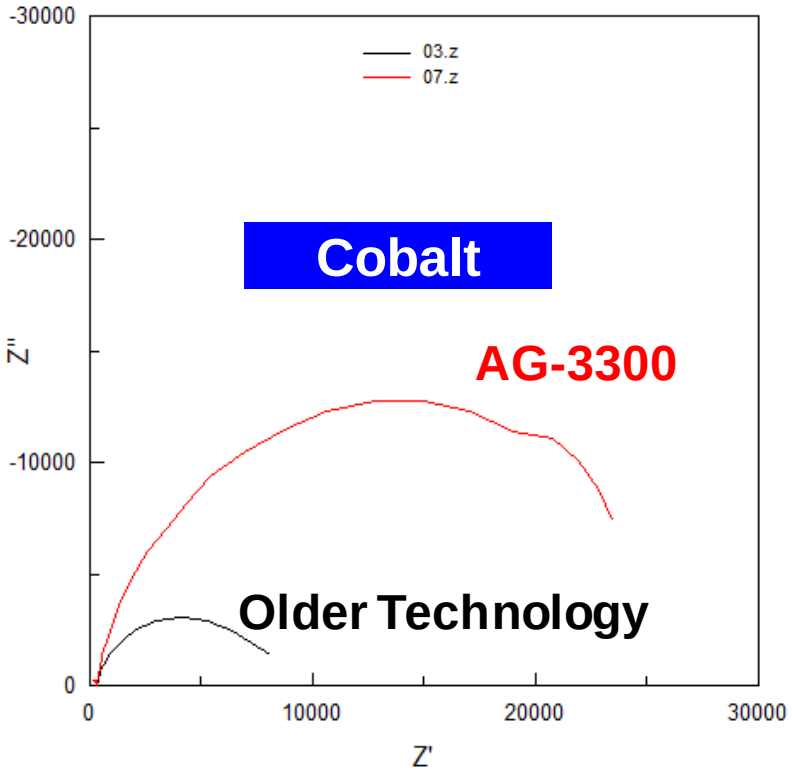
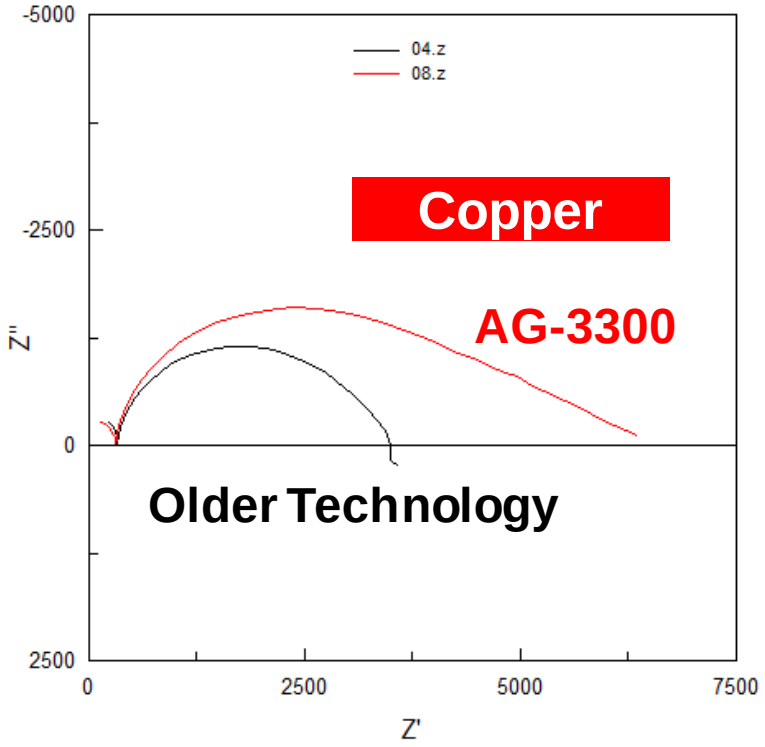
Nyquist Plots Show that AG-3300 Has Significantly Higher Film Impedance on Both Cu and Co than Older Technology





Higher impedance storage and loss components → higher film integrity

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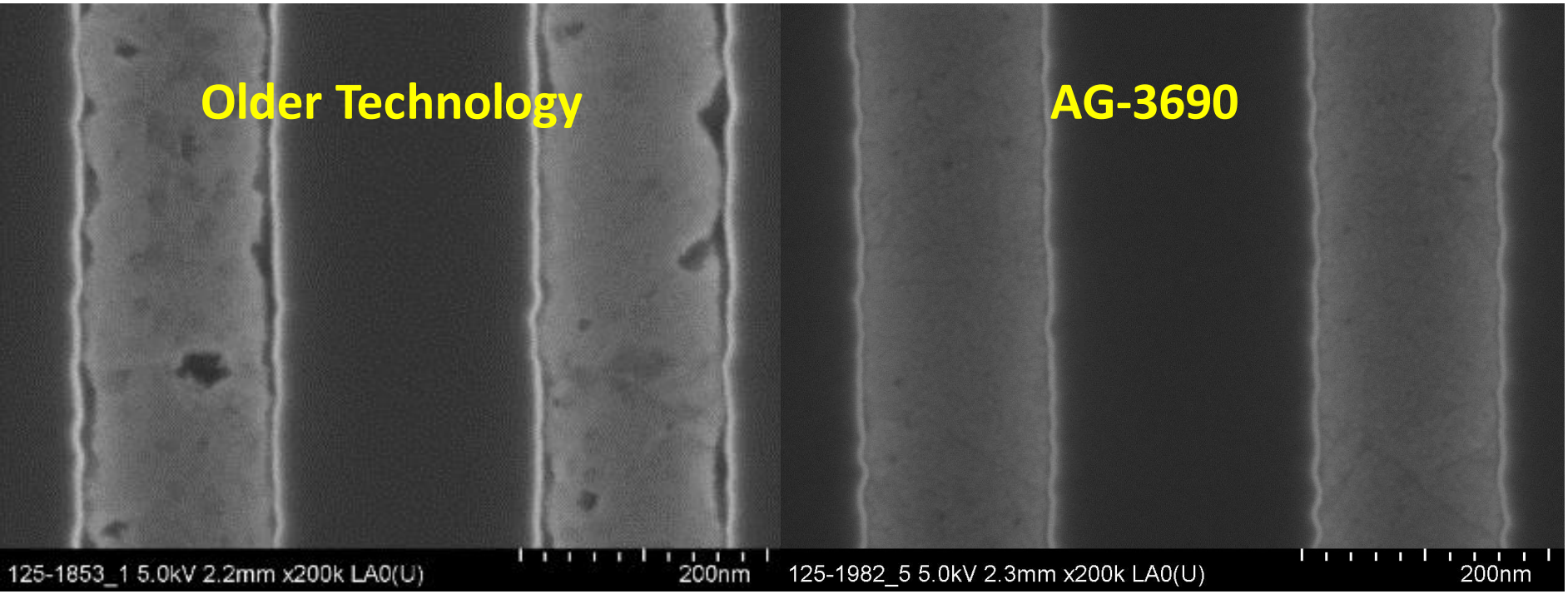
SEM Analysis Shows Significantly Improved Cu/Co Corrosion Performance for PlanarClean® AG



All AG dilutions: 100:1, 20 minute room temperature static etch

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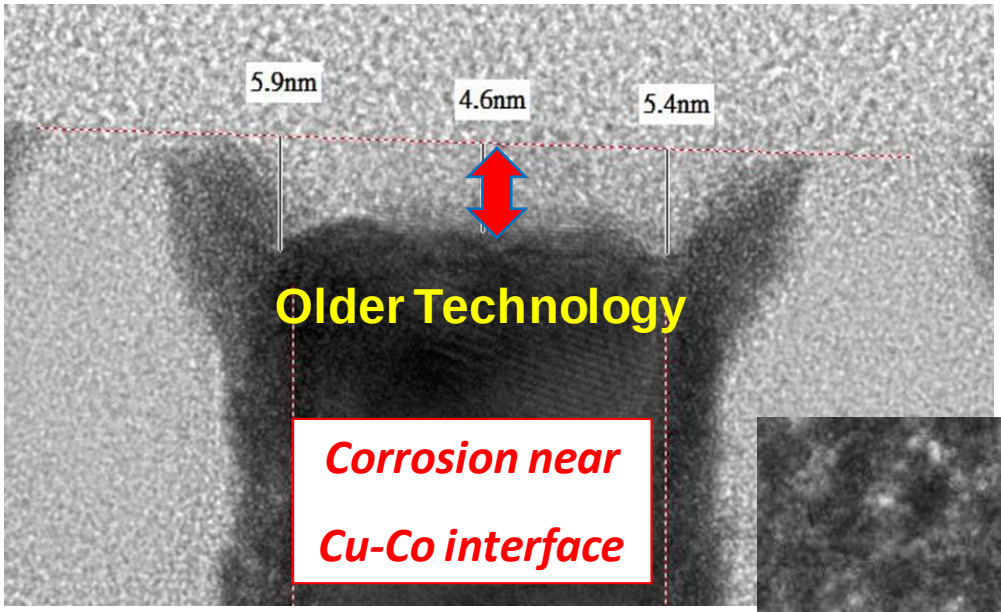
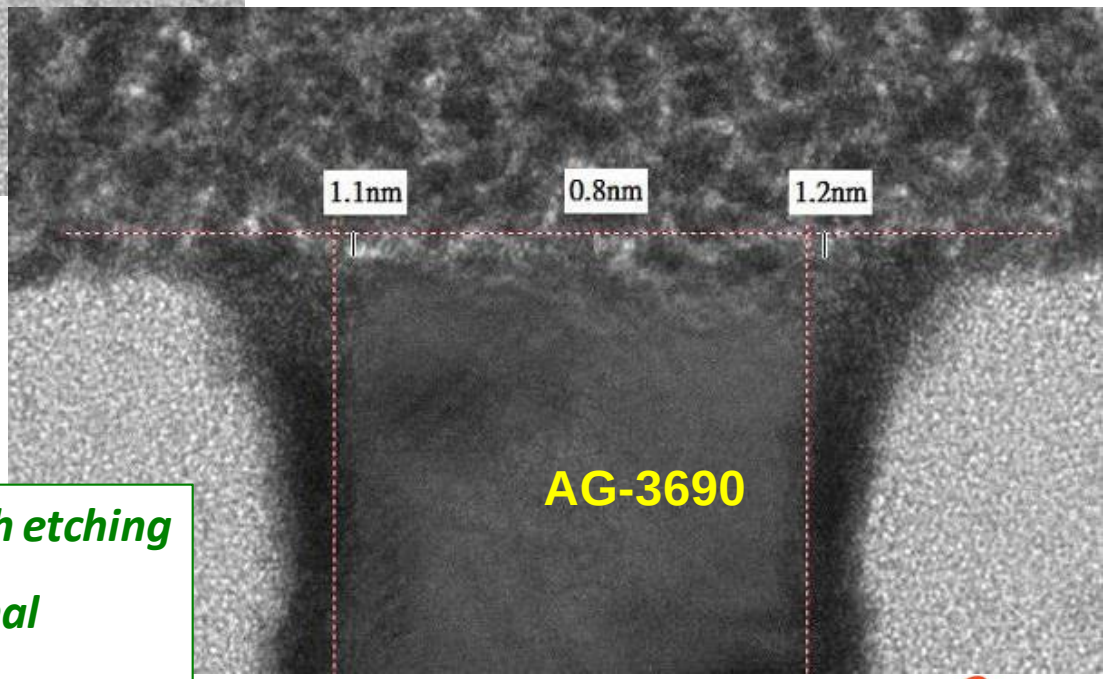
TEM Images on 45 nm IMEC Cu/Co Wafers Show that PlanarClean® AG Series Has Excellent Corrosion





Controlled, smooth etching with minimal Galvanic/edge corrosion

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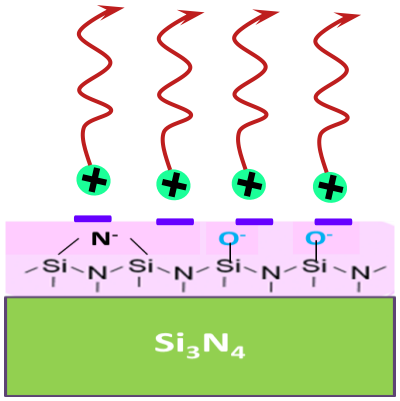
Mechanisms for Improving Organic Residue Removal from Si_3N_4

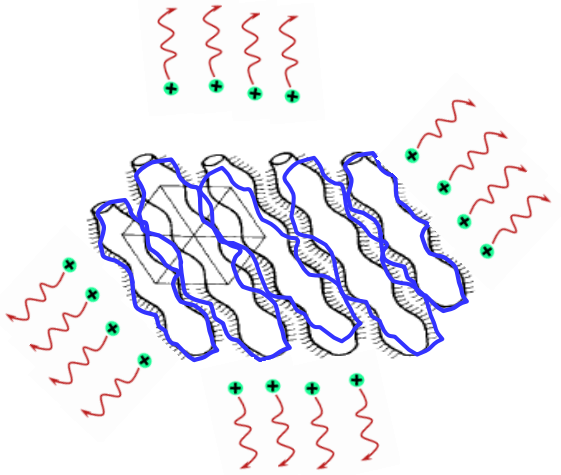
Market drivers for formulated W cleaners

- *Minimize W recess inherent ion commodity cleaners*

- *Improved cleaning performance*



(Defect Reduction Additive)



+ Other surfactants, dispersing agents and solvents also being studied

- **Aggregates with the organic residue**
- **Removes it from Si_3N_4 surface**

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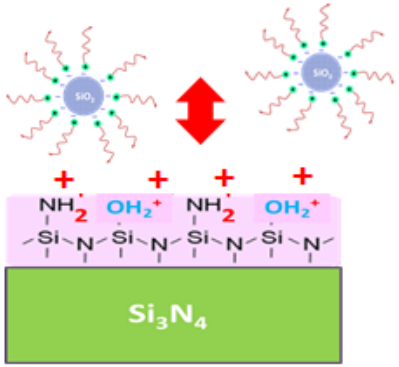
Contact Angle and FTIR Show that Organic Residue on Si_3N_4 is Removed

1. Contact Angle – Acid-Base Van Oss Theory

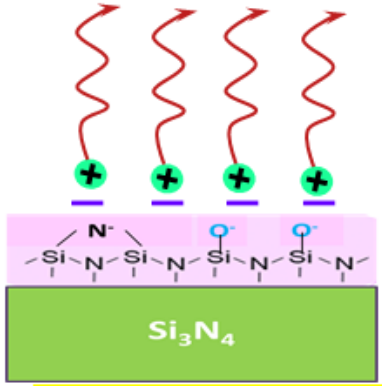
Electrostatic Repulsion During CMP



pH < pH_{IEP}, ζ = + 30 mV

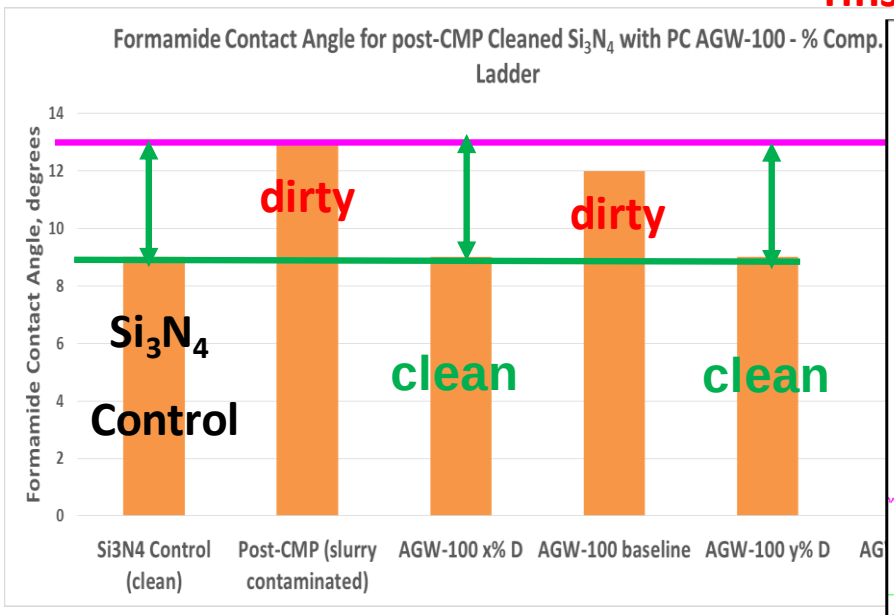
pH_{IEP} = 5-7

DI Water rinse

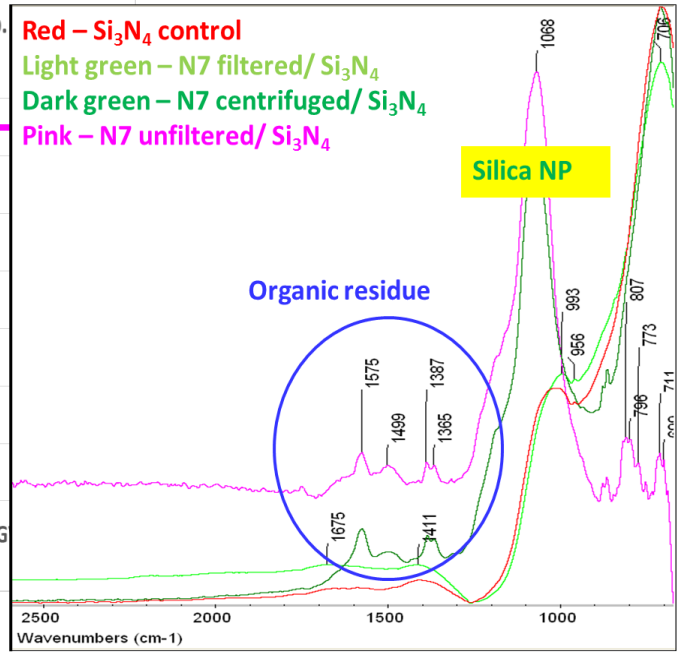


pH > pH_{IEP}, ζ = -15 mV

Electrostatic adsorption or precipitation Post-CMP rinse



clean, hydrophilic



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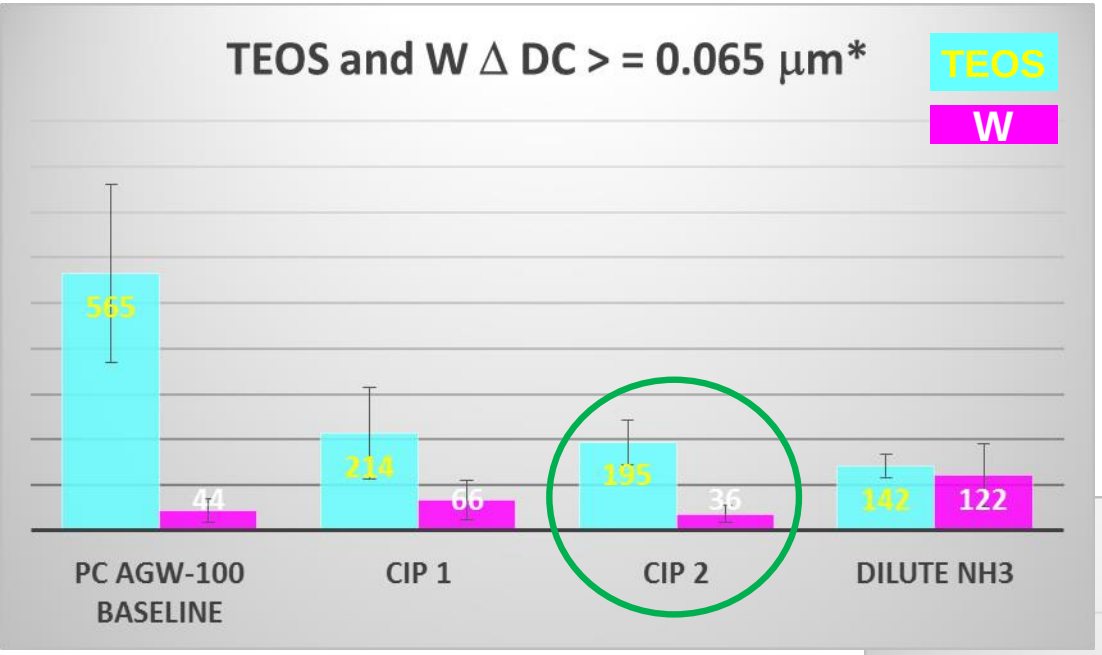
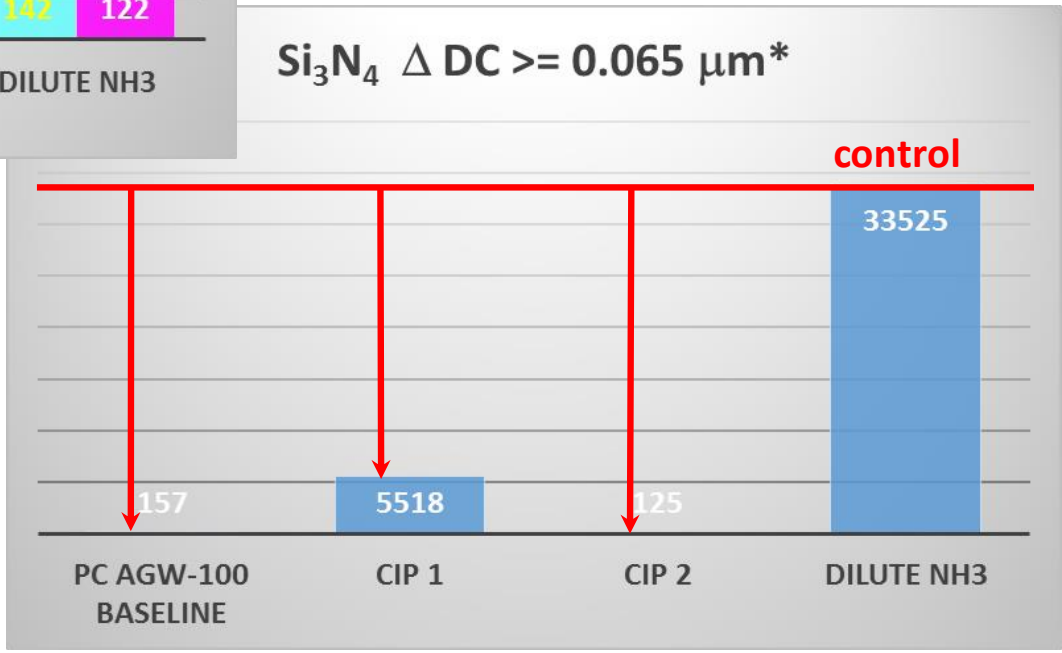
AG W-100 and W-210 Show Improved Cleaning Performance Over Dilute Ammonia

Experiment done in collaboration with IMEC, Leuven, Belgium



- AMAT Reflexion LK polishing tool

- KLA SP-3 defect inspection tool



- **Si_3N_4 – 250x less defects than dNH_3**
- **W ~ 3.5x less defects than dNH_3**
- **TEOS – comparable with dNH_3**

Conclusions

- ***Charge repulsion shown to be a key driver towards cleaning performance***
- ***Dispersion and complexation important for removal and preventing redeposition of organic residues and particles***
- ***OCP gap must be minimized by optimal ligand selection to minimize galvanic corrosion***
- ***Optimal corrosion inhibitors can studied by Impedance spectroscopy and Tafel plots***

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