Understanding Interfacial Surface Interactions

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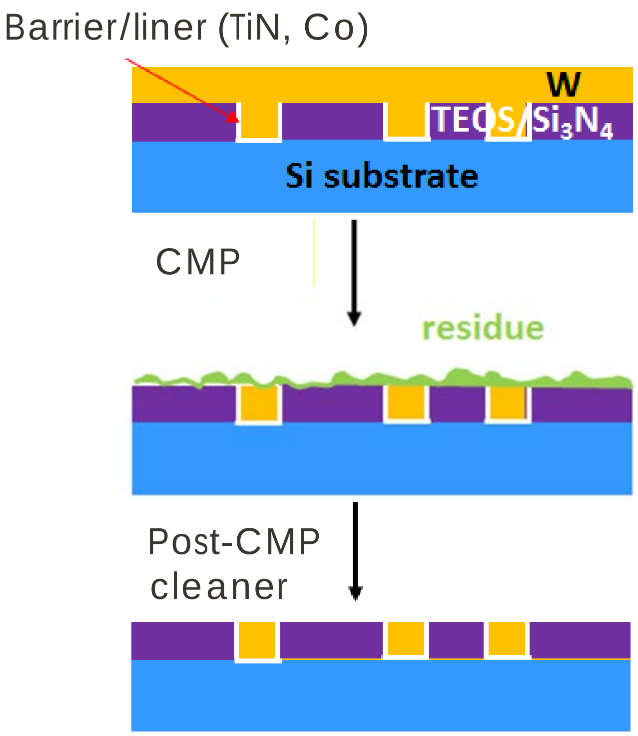
Challenges for W Post-CMP Cleaners

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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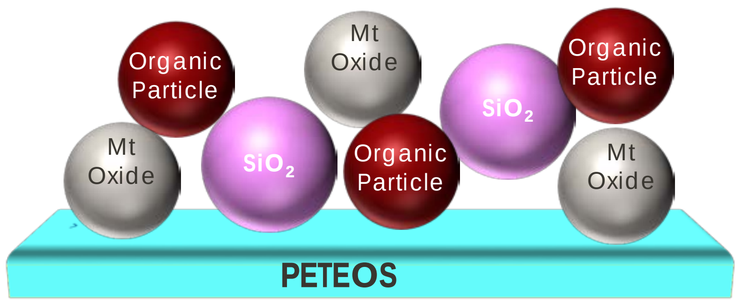
Post-CMP W Cleaning Mechanisms vs. pH

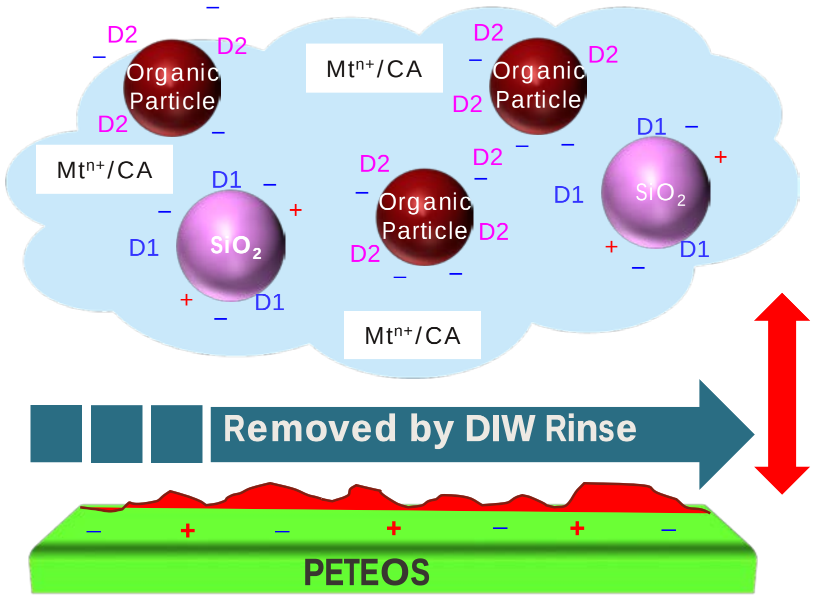


Low pH

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

High pH

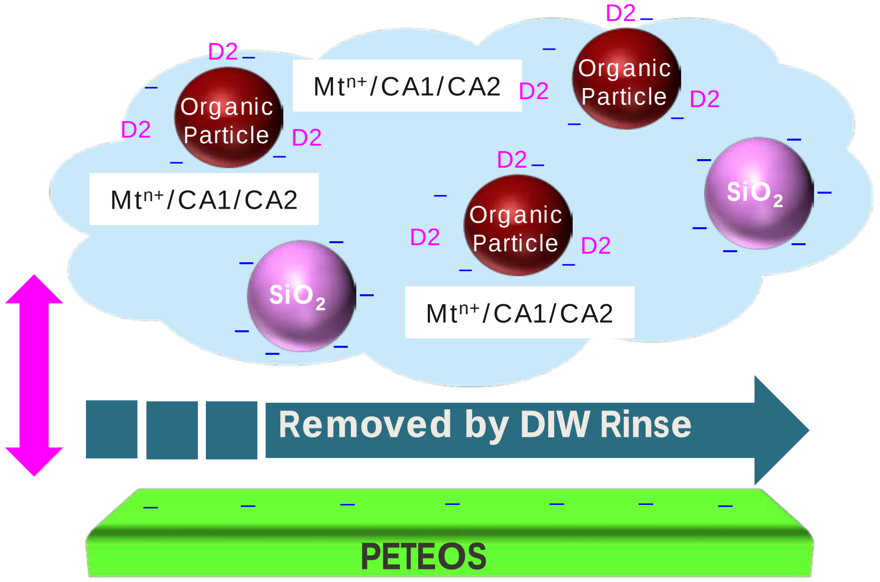
- No Silica brush imprints
- Poor Mt removal (4-6 X10^{10} atoms/cm^2)



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

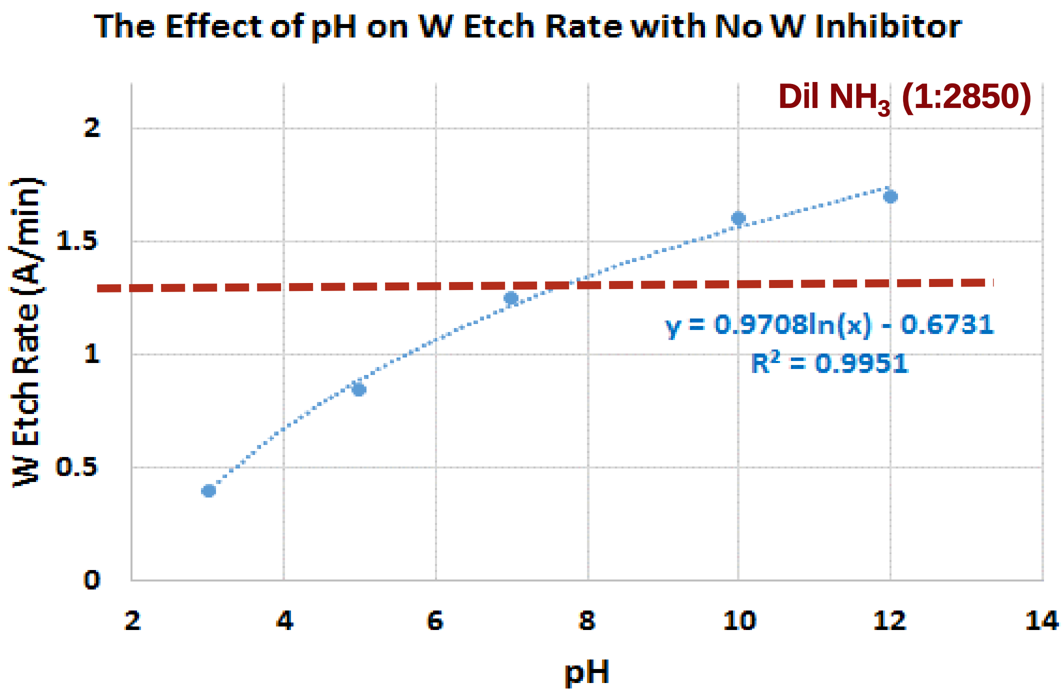
steric repulsion

electrostatic repulsion



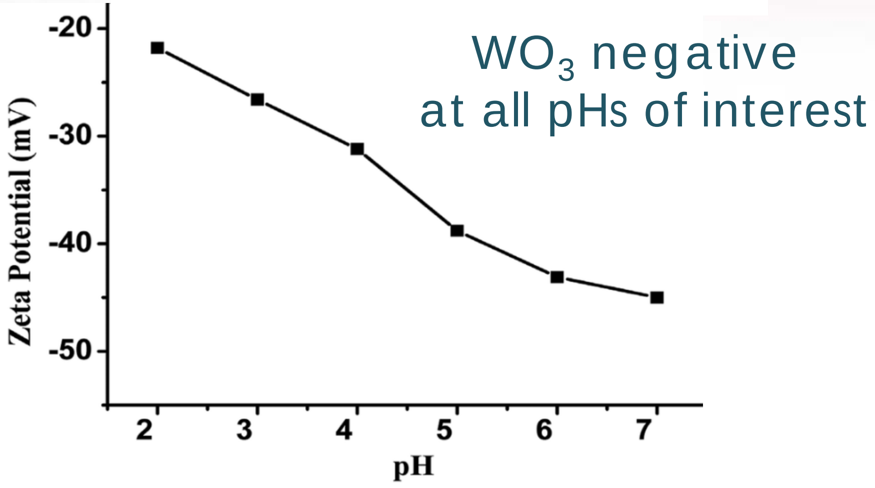
Higher Tungsten Etch Rates Observed

Increasing pH due to dissolution as Polyoxotungstate Keggin ions

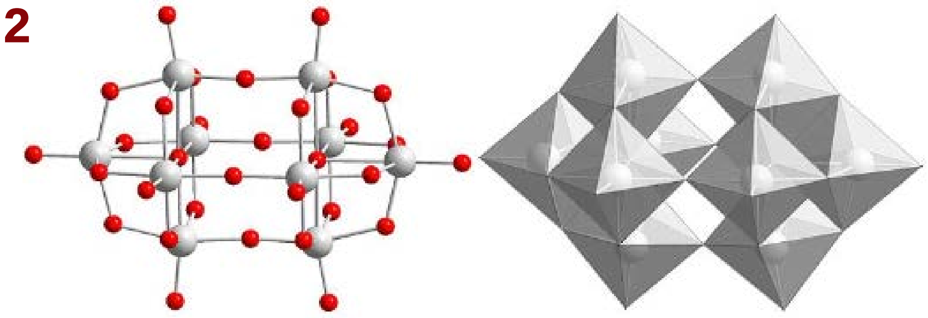


SC1: 1:50 > 6 A/min

1



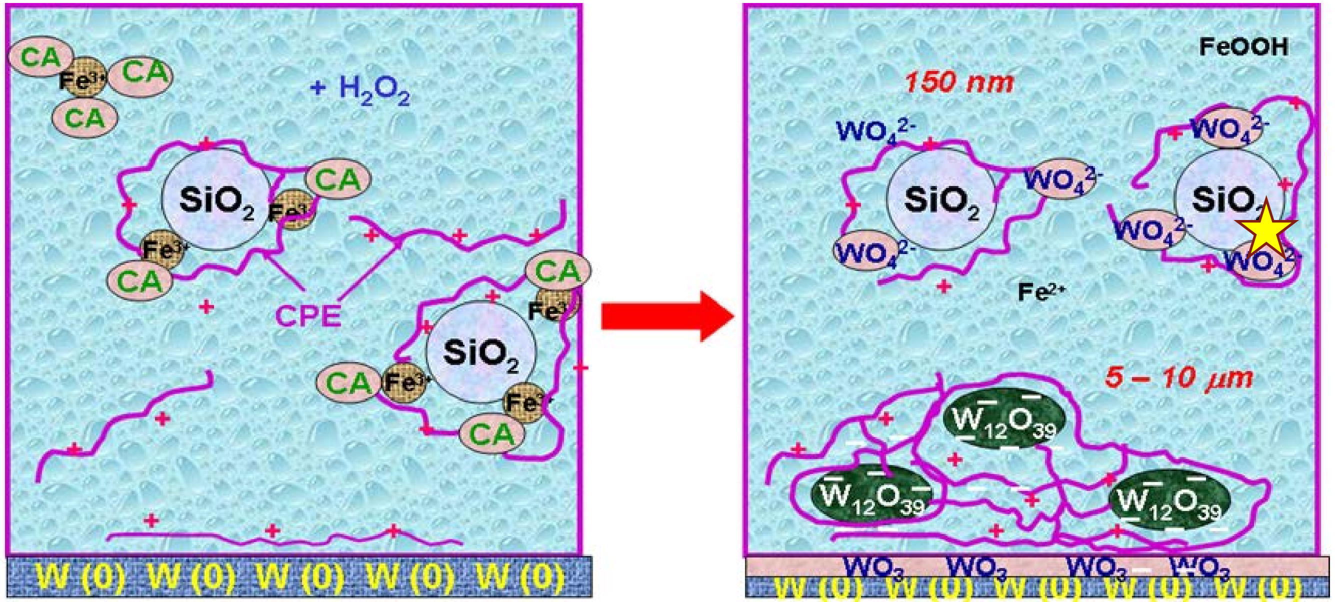
2



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.

Surface Residue PCMP Cleaning with W Slurries[1]



Nanodispersion before polishing **Dispersion during/after polishing**

- **W(0) is oxidized to W(VI)O_3 (pp) and W(VI)O_4^{2-} (s);**
- **WO_4^{2-} (s) is adsorbed on the surface of the Fe^{3+}/CPE coated, positively charged Si particles;**
- **WO_4^{2-} precipitates @ pH < 3 as $(N^+R_4)_n(H_xW_qO_y)^{n-}$/silica aggregates that act as *additional abrasive* during polishing.**

W CMP slurry – 15-32 ppm Fe

- Fe^{2+} /CA (complexing agent) on the silica surface and in the CMP slurry at pH = 2.5;
- End of polishing, soluble Fe^{2+} complexes on the wafer surface;
- DI water rinse and high pH post-CMP W cleaners **precipitate Fe^{3+} as insoluble $Fe(OH)_3$** on the PETEOS/SiN surface

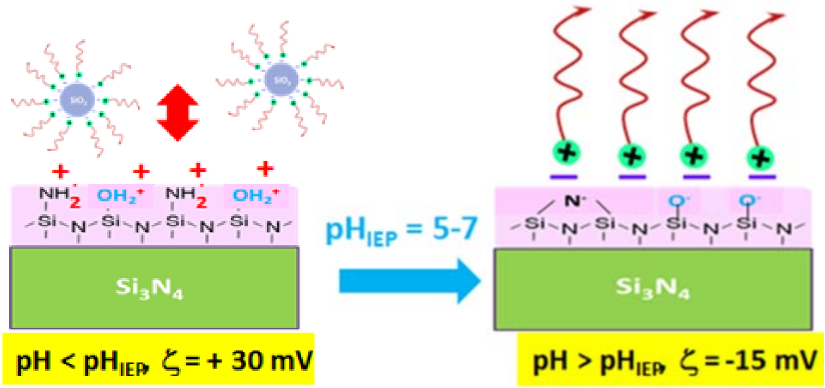
FeOx Very difficult to remove

1 - D. White et al, Materials Research Society Symposium Proceedings (2007), 991(Advances and Challenges in Chemical Mechanical Planarization), 145-150

Improving Organic Residue Removal

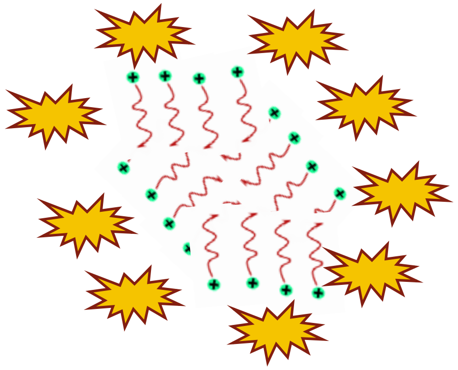
from Si_3N_4 Contact Angle and FTIR

Electrostatic Repulsion during CMP



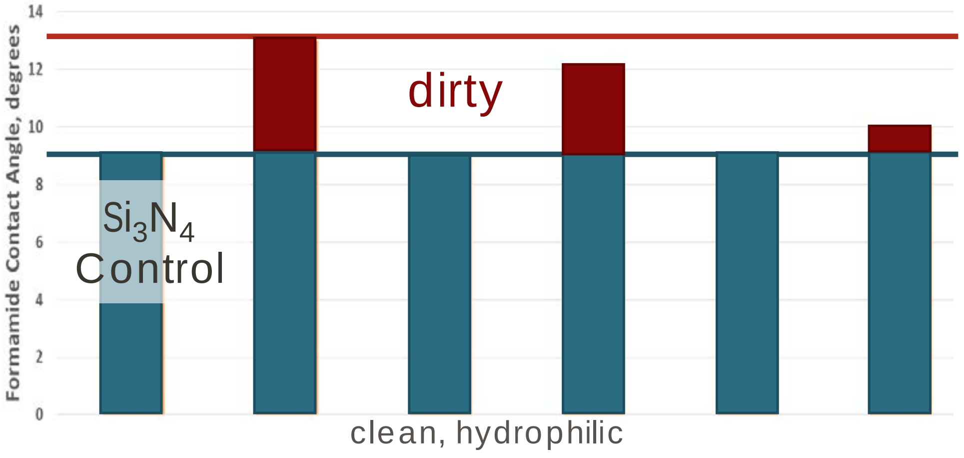
W Post-CMP Cleaner

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

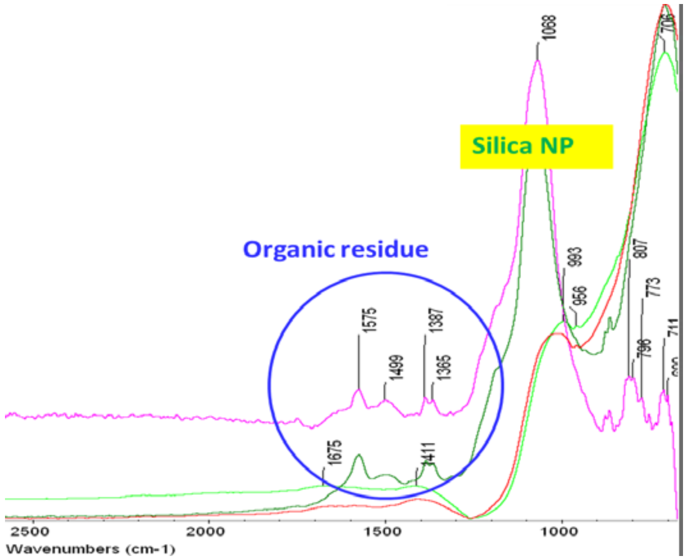


Cleaning additive removes cationic contamination from dielectric surface and disperses

Contact Angle

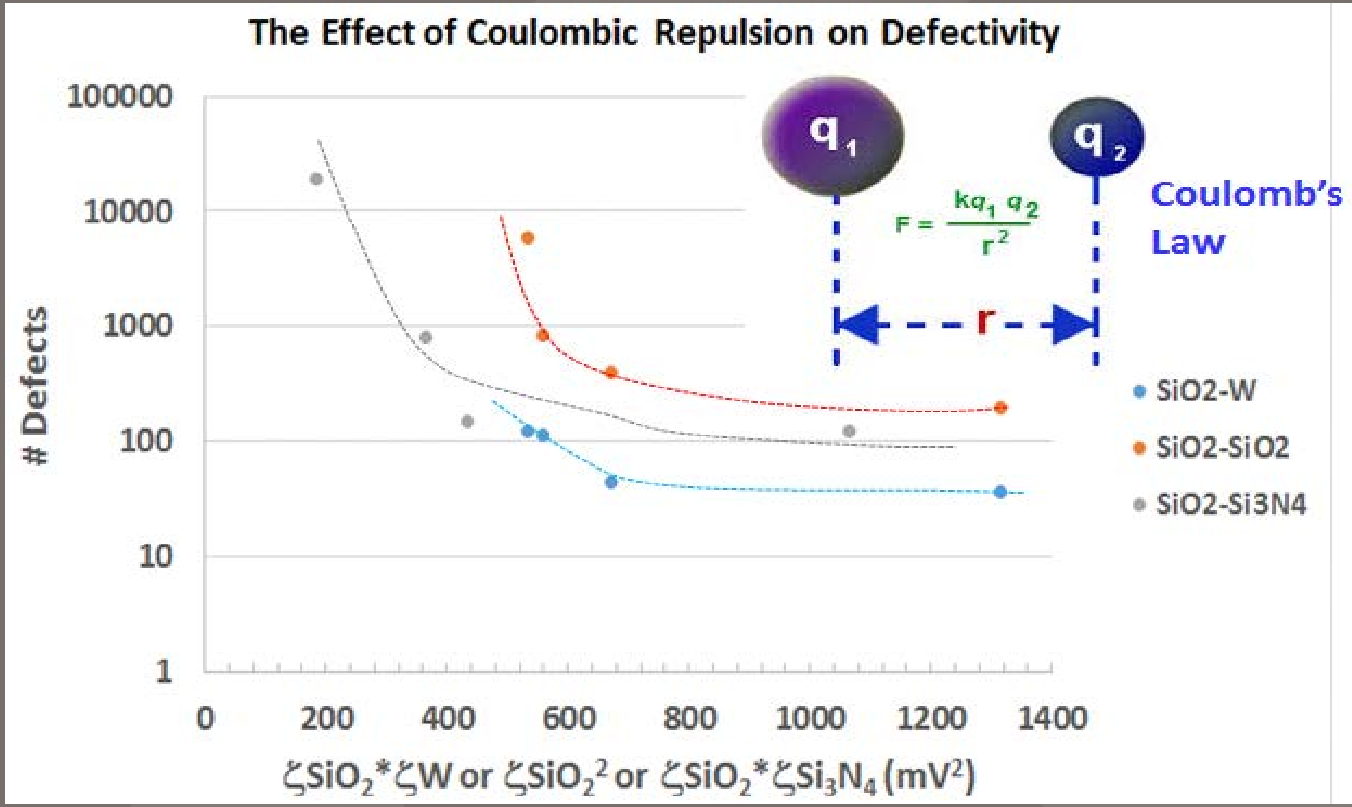


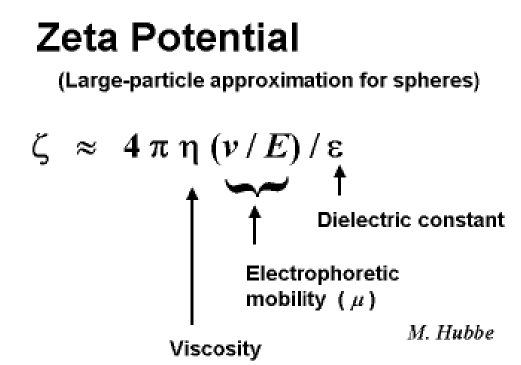
FTIR



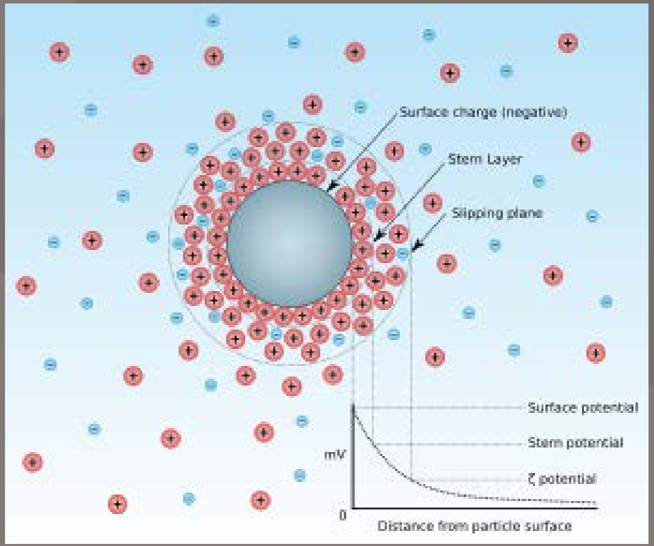
Defectivity Correlated to Charge Repulsion

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)

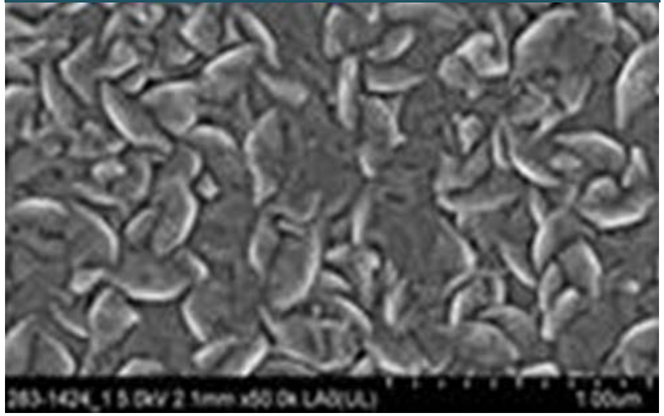
2 - Hedge, S. and Babu, *H. V. 2Eelectrochem. Soc. St. Lett*. V7, pp. 316-318 (2008)

3 - White , M. L. et al. *Mat. Sc. For*. 1249 E04-07 (2010).

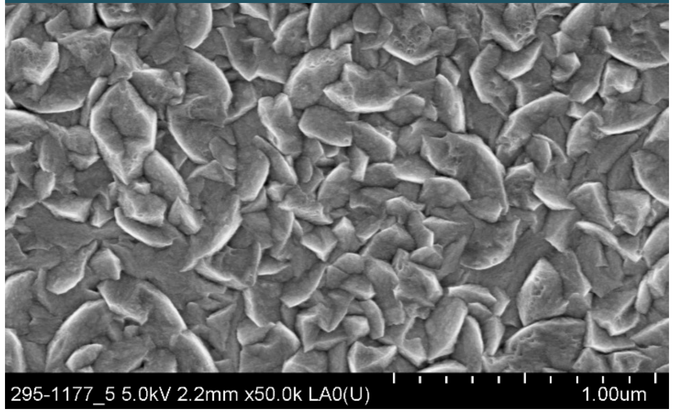
PlanarClean® AG-WXXX Exhibits

No bulk corrosion and no OCP gap between W and TiN

W Control

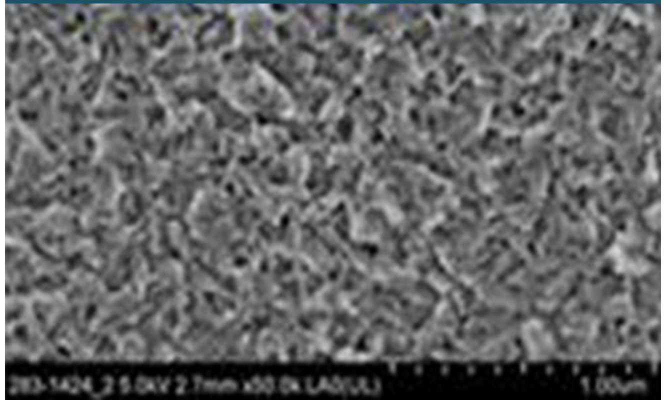


Post PC AG-WXXX

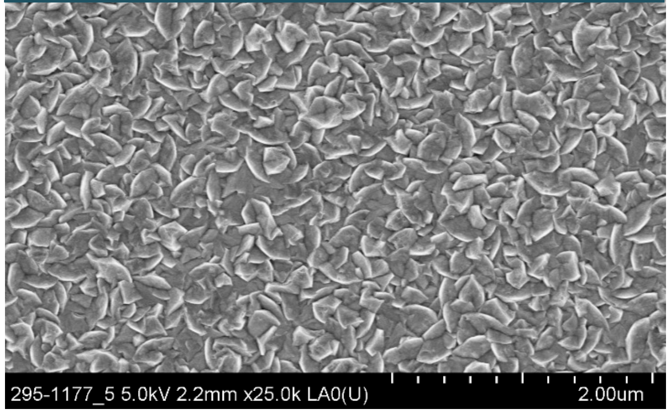


No Visible Etching of Tungsten

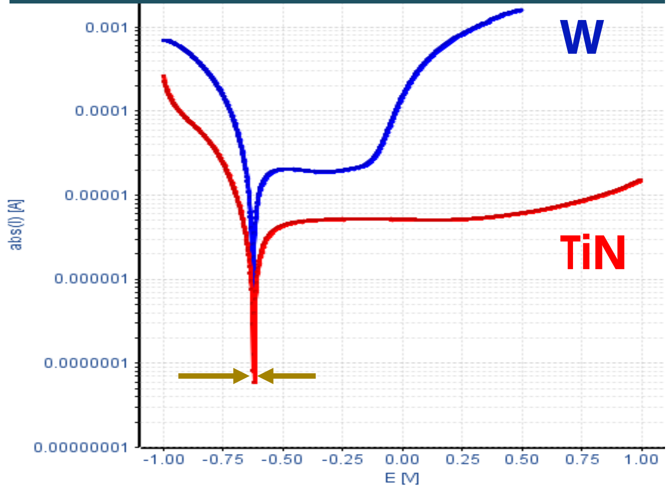
Etched W Surface



Post PC AG-WXXX



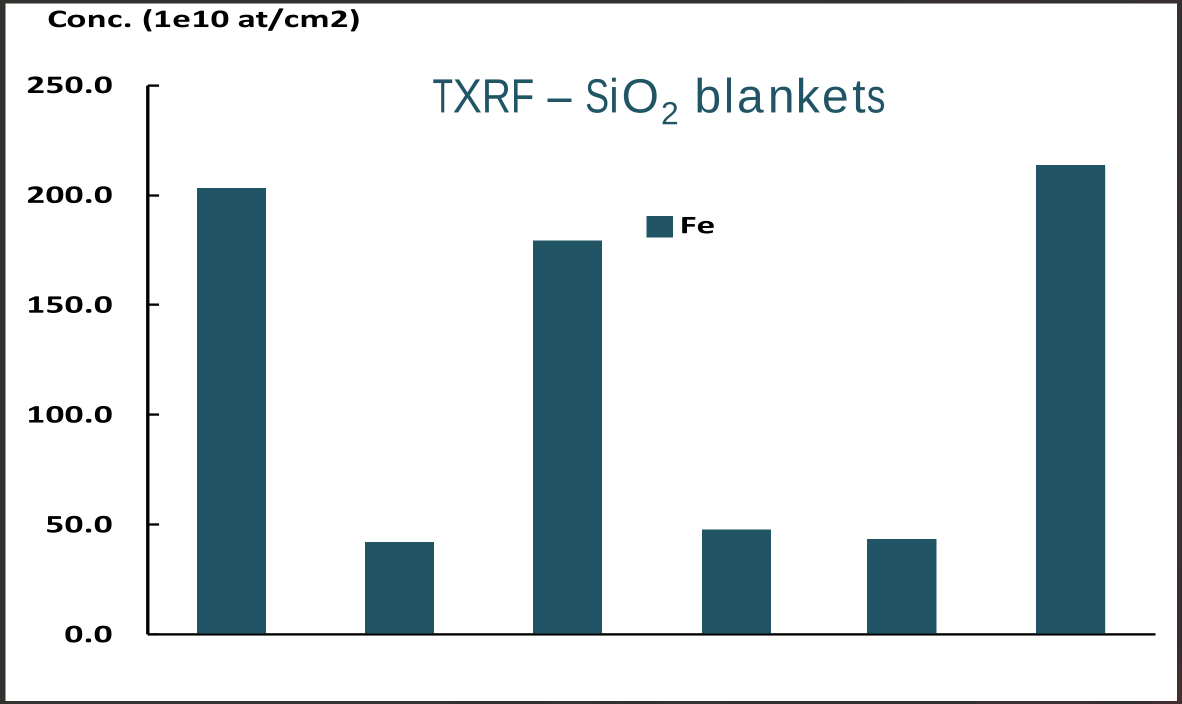
WXXX



	TiN	Galvanic Corrosion	W
	Cathode		Anode
Corrosion Potential (V)	-0.622	-0.626	-0.625
Corrosion Current (A)	1.76×10^{-06}	2.35×10^{-07}	1.13×10^{-05}
Corrosion Rate (Å/min.)	0.167	0.013	0.642
Galvanic Corrosion (Å/min.)	0.013		

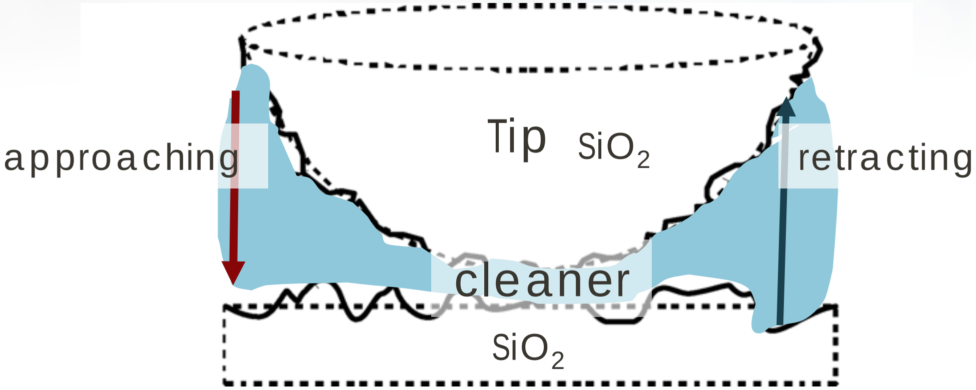
Low pH PCMP W Cleaners

Further reduce metal defects after CMP



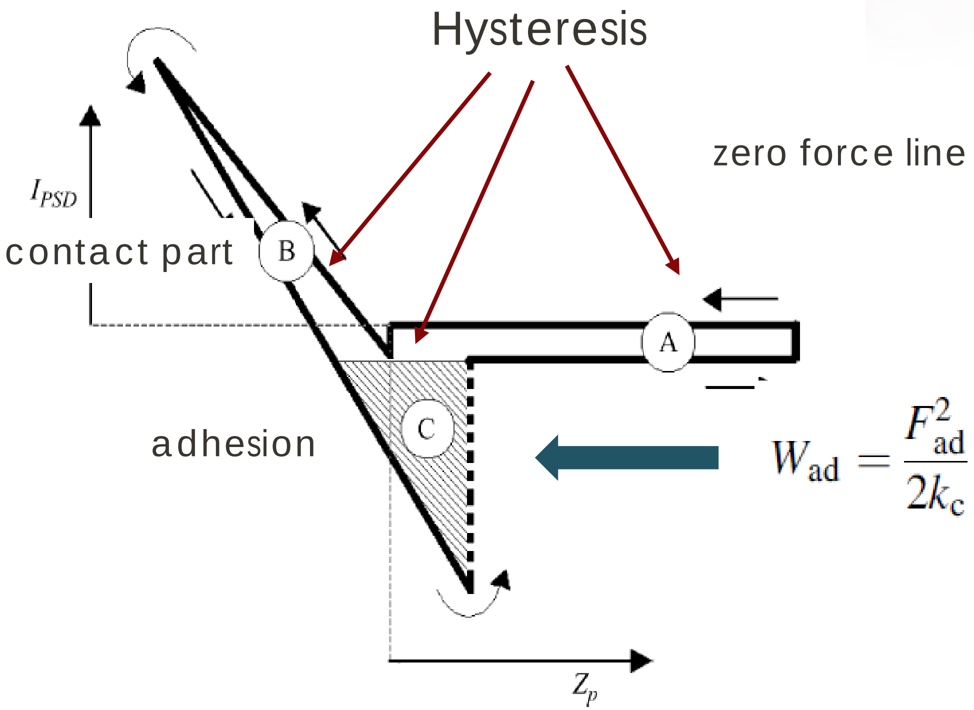
- Complexing reagents: to keep in solution soluble Fe^{2+} species
- Cleaning additives: able to eliminate silica brush marks at pH = 2

Force of Adhesion – AFM Measurements



$$dF = k_c\, dZ_c + \frac{dF_{surf}}{dD}\, dD = \left(k_c - \frac{dF_{surf}}{dD}\right) dZ_c$$

F **= force of adhesion**
k$_c$ **= spring constant of the cantilever**
Z$_c$ **= cantilever deflection**
F$_{surf}$ **= distance-dependent surface force**
D **= separation distance**



Types of hysteresis[3]

I_{PSD} = detector current signal
Z_p = height position of the piezoelectric translator

3. Hans-Jurgen Butt, Brunero Cappella*, Michael Kappl, Surface Science Reports 59 (2005) 1–152

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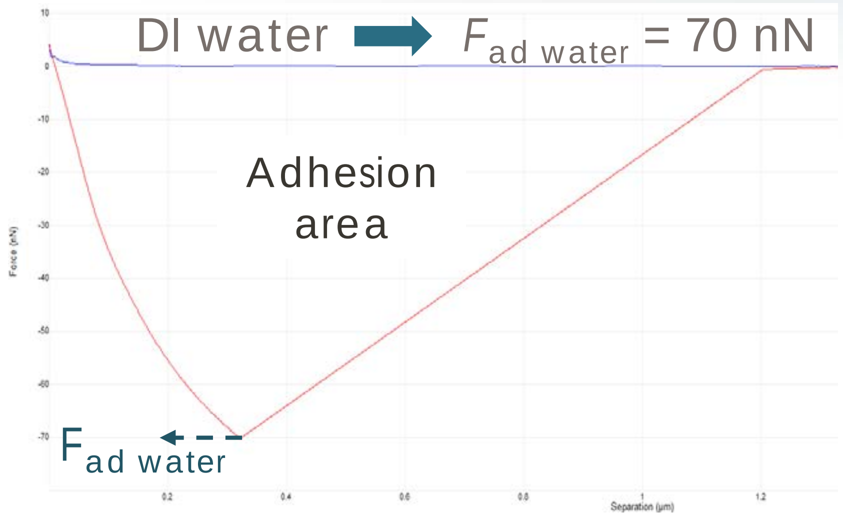
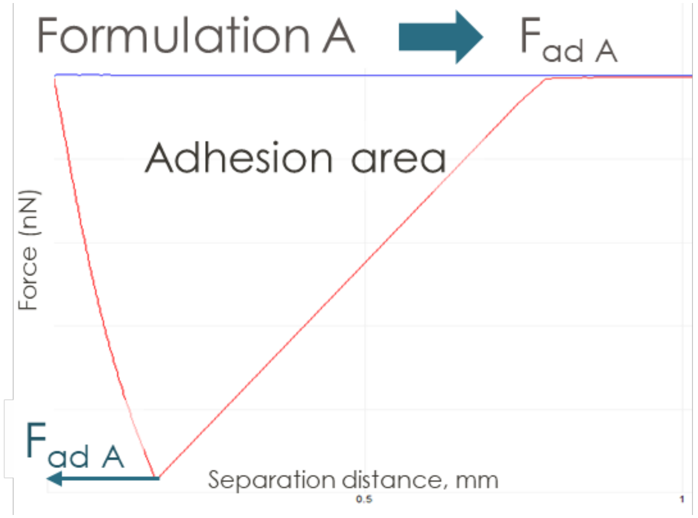
Example of Cleaning Performance Prediction
via AFM force of adhesion measurements

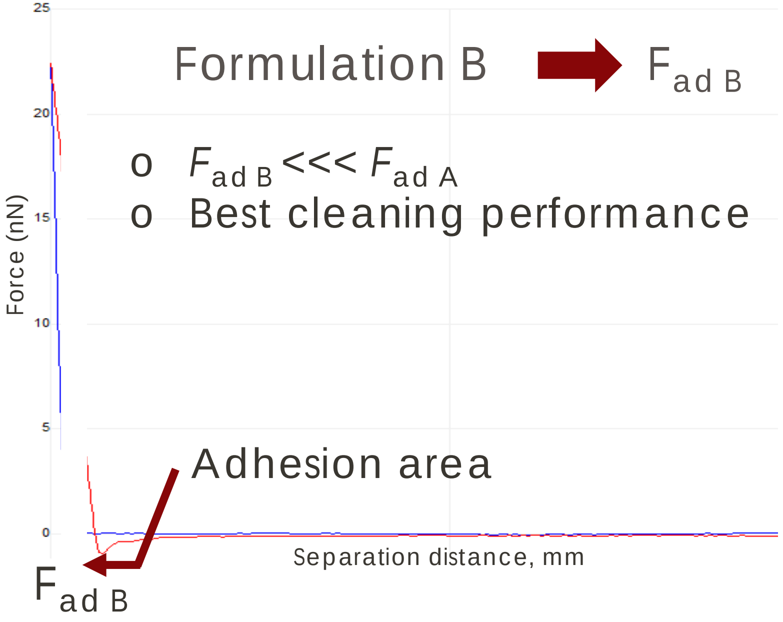


Main adhesion forces:
- Van der Waals
- Electrostatic double layer
- Hydration repulsion
- Hydrophobic attraction



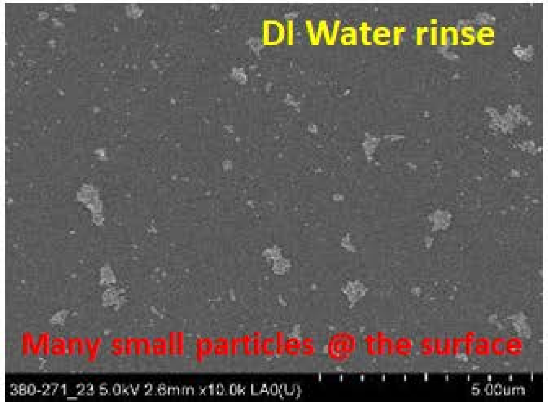
+ additive X →

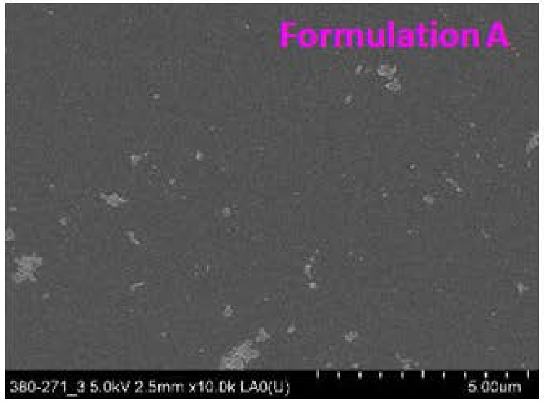
Formulations A & B, pH = 2

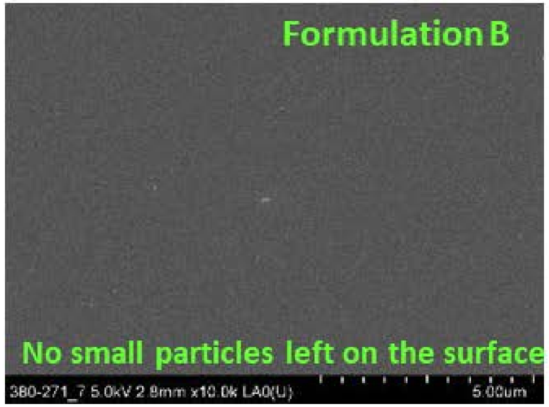


SEM Images of PETEOS Coupons

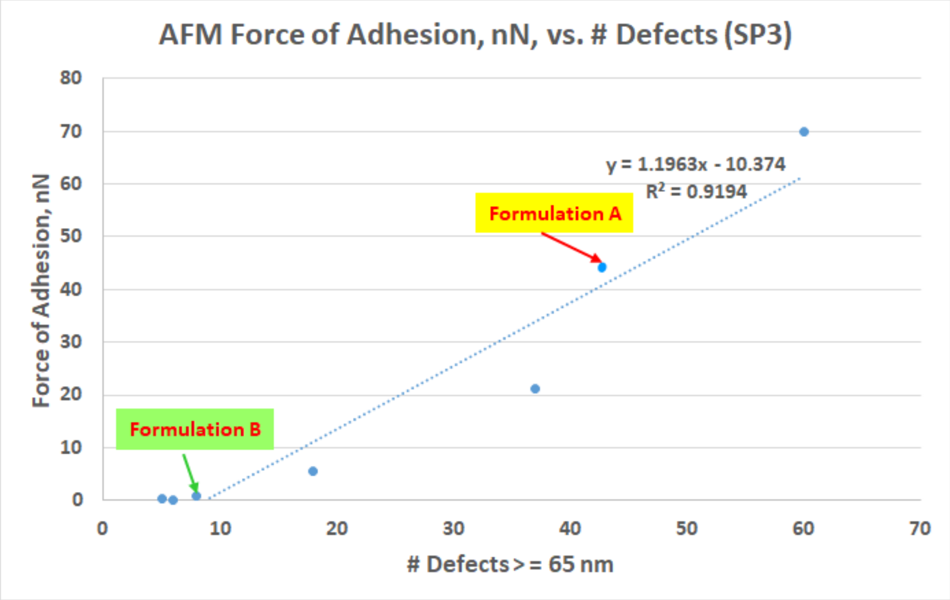
Polished with W CMP slurry and cleaned with Formulations A and B





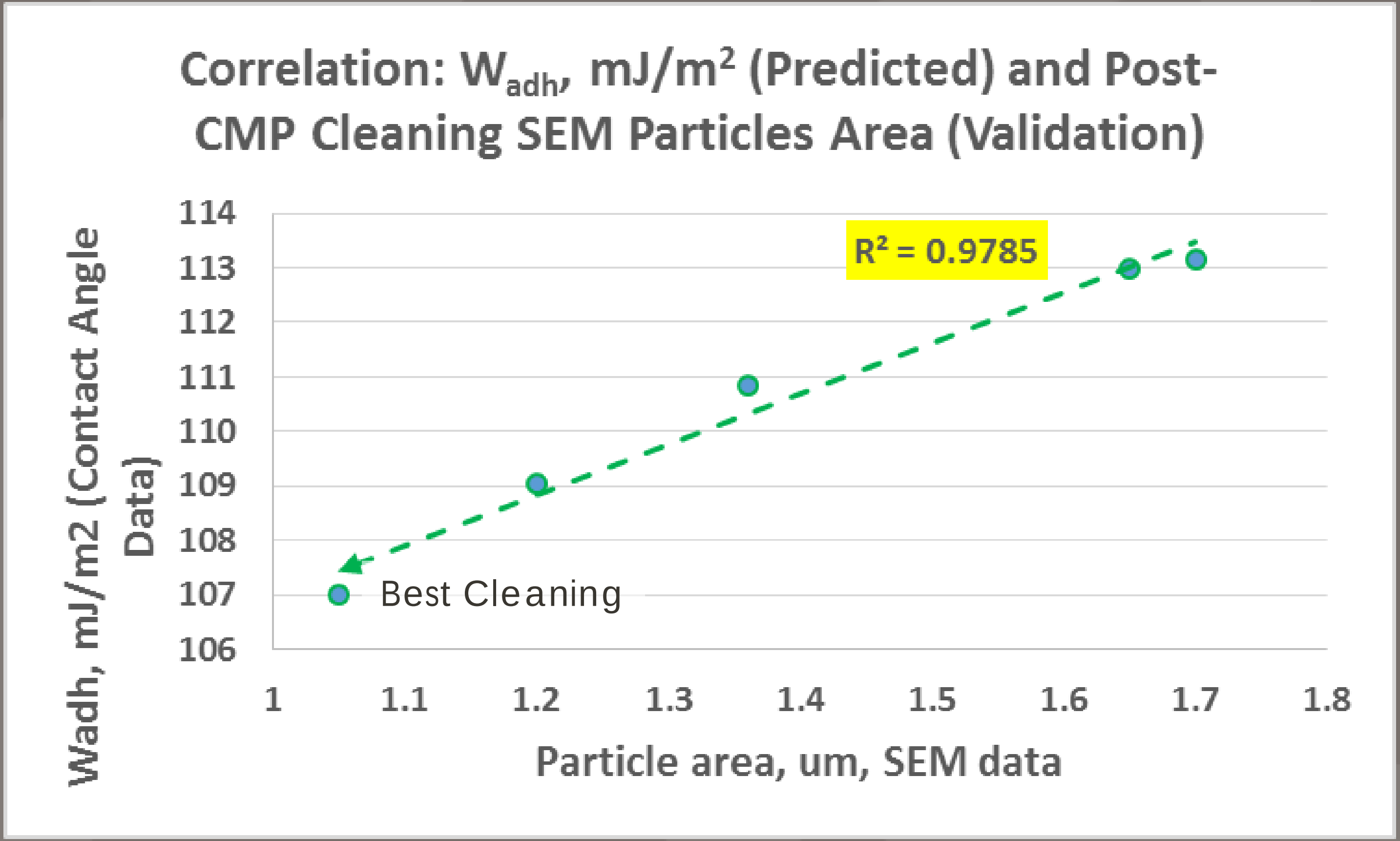


- Tabletop polishing
- Colloidal silica Ludox, PS = 20-30 nm
- pH = 2.3



Correlation SEM vs. Calculated Adhesion

Based on contact angle measurements

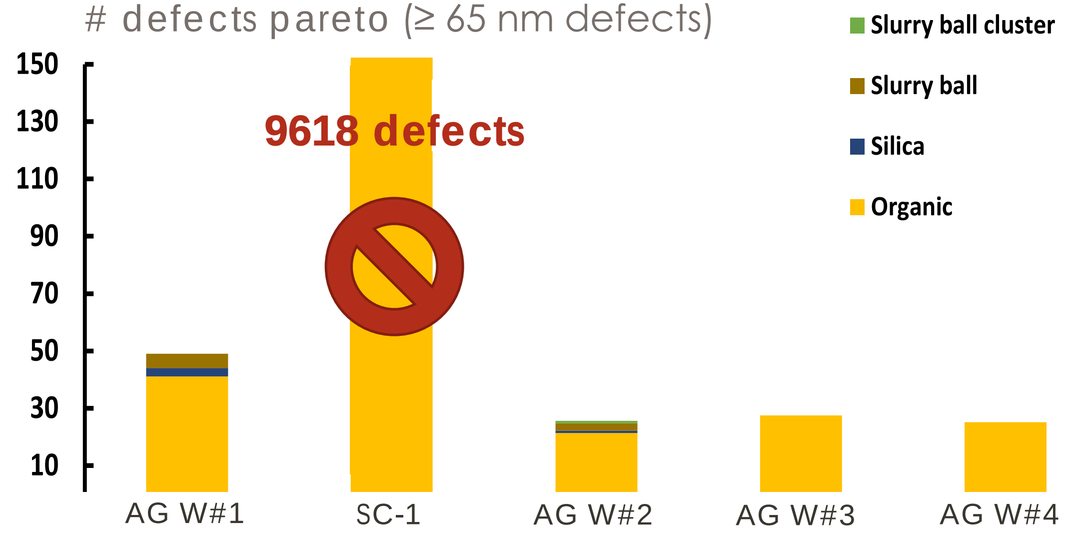


PlanarClean AG-W formulations

exhibit lower defects and organic residues over traditional cleans

Si_3N_4 – EDR Review – Defect Pareto

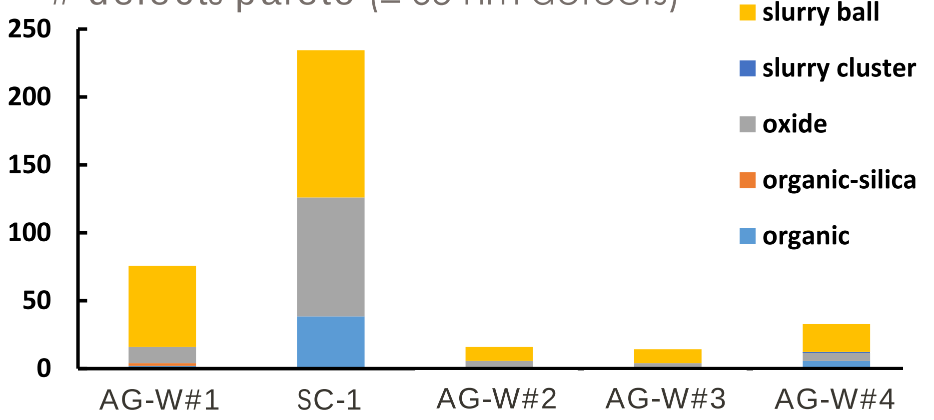
defects pareto (≥ 65 nm defects)



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

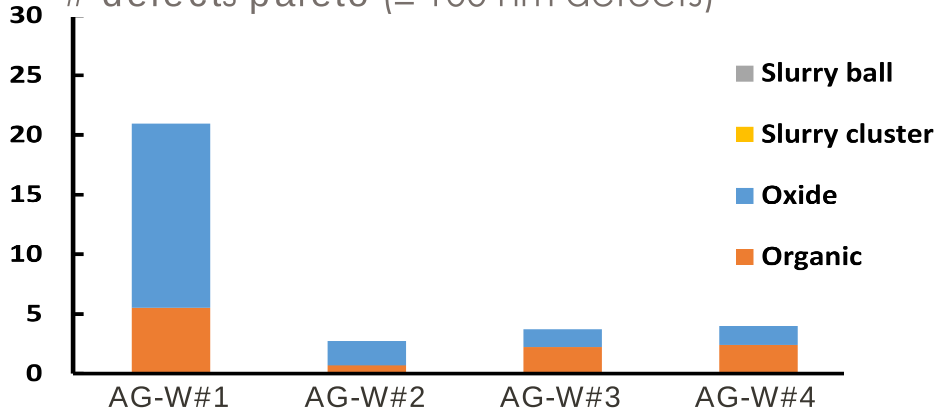
SiO_2 – EDR Review – Defect Pareto

defects pareto (≥ 65 nm defects)



W – EDR Review – Defect Pareto

defects pareto (≥ 100 nm defects)



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Summary

Organic contamination reduction studied by FTIR and contact angle

Work of adhesion and AFM force of adhesion show that less energy is needed to remove silica slurry particles in the presence of the cleaner

Entegris AG-W Formulations show significantly lower defects on Si_3N_4, TEOS and W wafers compared to commodity cleans

Thank you!

Q&A

Appendix