Tungsten Post-CMP Cleaning Formulations for Advanced Nodes: 10 nm and 7 nm

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Outline

- Development of an efficient W post-CMP cleaner for 10 nm and 7 nm nodes, compatible with barrier liners (TiN) and dielectrics (TEOS, Si_3N_4, SiC, polysilicon);
- Mechanistic considerations and AG-W100 formulation design;
- Particle defect count results on W and dielectric surfaces using AG-W100 formulation;
- W/TiN galvanic corrosion data and knobs to control it;
- SEM on W/TiN 45 nm pattern wafers cleaned with AG-W100;
- Understanding and cleaning organic residue post-CMP on dielectric substrates: contact angle and XPS metrology;
- New AG-W100 CIP formulations with tunable and improved performance.

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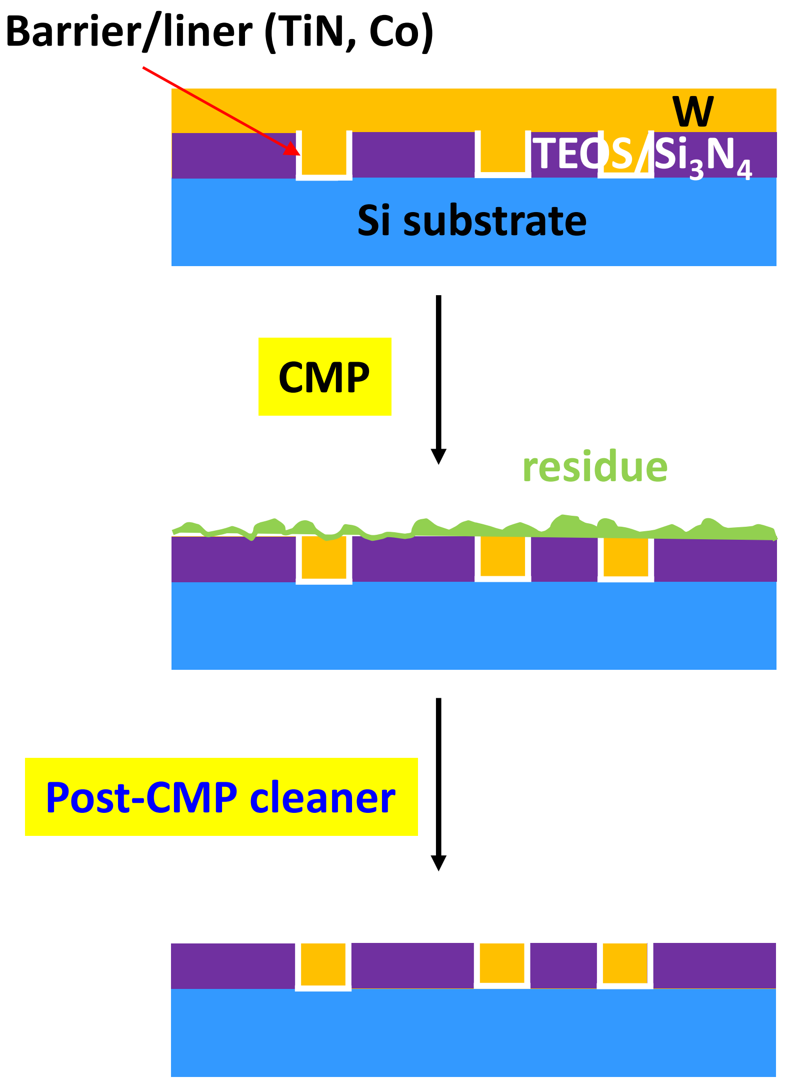
W/Liner Compatibility, Electrochemical and Cleaning Requirements



Traditional W cleaning with SC-1 or dAmmonia causes bad W etching, recess, galvanic corrosion and poor Si_3N_4 cleaning (particles, organics)!

Need to design a new W post-CMP cleaner with very low W ER, as well as good barrier(liner)/dielectrics compatibility.

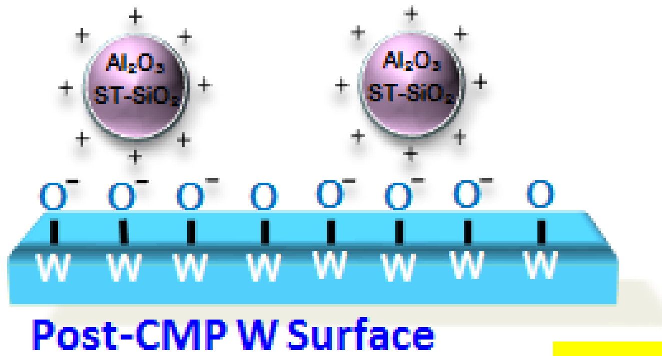
Cleaning Requirements:

- W ER < 2 Å/min
- TiN ER < 1 Å/min
- Dielectrics ER < 1 Å/min
- Dielectrics: Si_3N_4, TEOS, SiC, etc.
- Defect counts ΔDC $\geq$ 0.065 μm lower than commodities: dAmmonia, SC-1
- No/Low W/TiN galvanic corrosion

W Post-CMP Cleaning Formulation – Mechanistic Design Concepts

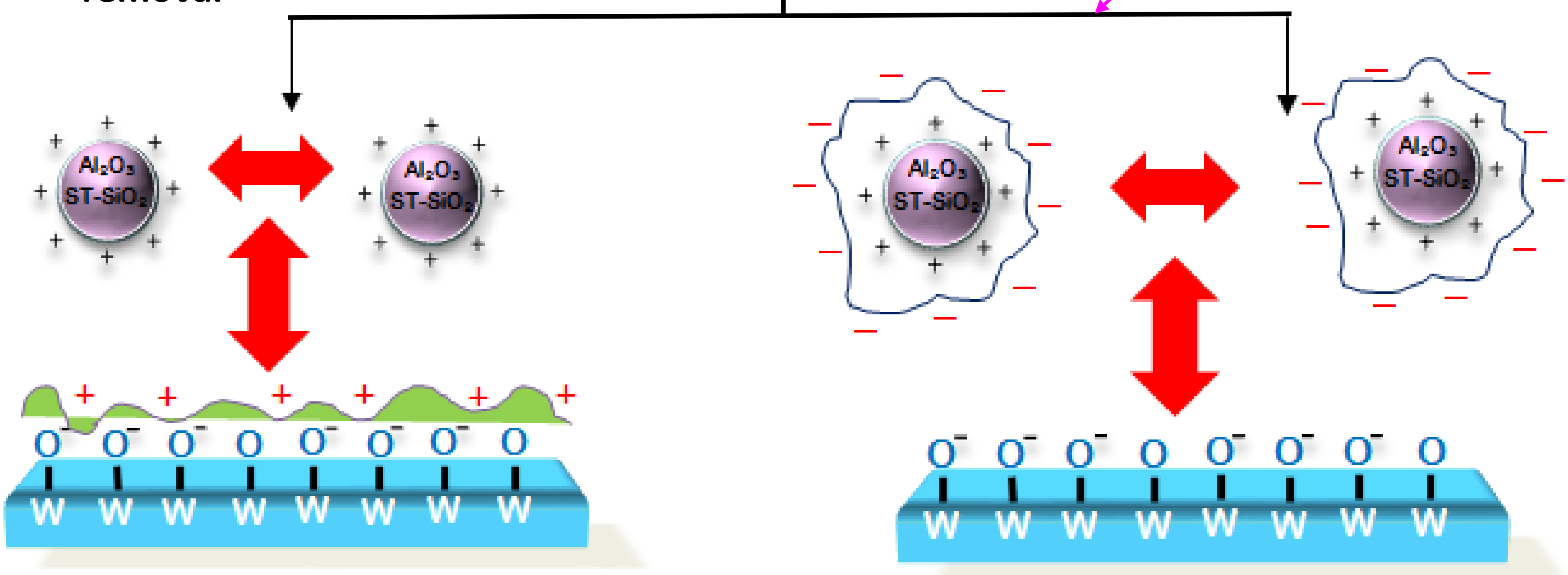
CMP Slurry abrasive:

- Al_2O_3 $\zeta > 0$ mV;
- Surface-Treated silica ($ST\text{-}SiO_2$) – $\zeta > 0$ mV;
- Silica ($\zeta < 0$ mV).



- W ζ reversal
- non-TMAH additive for organic residue removal

Primary Approach (next slide)



PlanarClean® AG-W100 Formulation Additives List – Function and Mechanism

Component	Function	Mechanism
A	non-TMAH pH Adjustor	• Provides the hydroxyl anions and adjust pH needed for W surface hydroxylation and good wetting • Ensures negative surface charge on both wafer and contamination, by being adsorbed on inorganic and organic residues.
B & C	Complexing Agents	• Surface Modification (ST-SiO_2 and Al_2O_3 complexants) • Stabilization of particle with electrostatic repulsion (prevent agglomeration and re-precipitation)
D	Dispersing Agent	• Interacts with particles and wafer surfaces to prevent aggregation and control etch rate.

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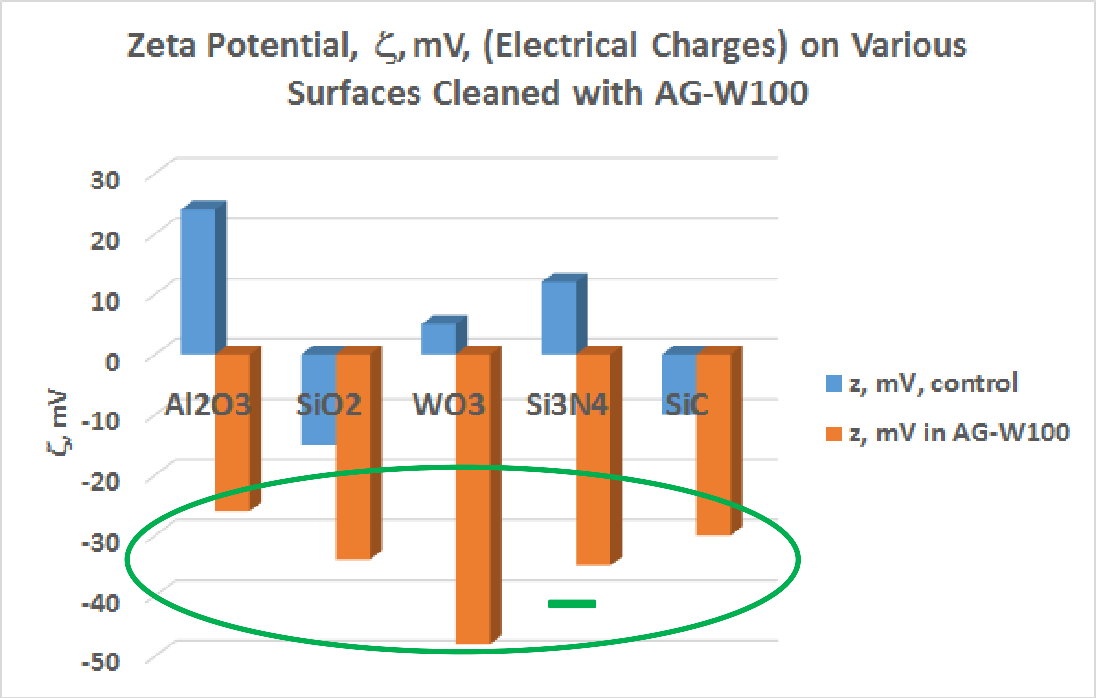
Zeta Potential for Slurry NP (Alumina, Silica), W and Dielectrics Surfaces in Contact with AG-W100 Formulation



- Control dispersions, pH ~ 3-4;
- **All surfaces are strongly negatively charged in AG-W100;**
- Charge reversal for alumina, silicon nitride and silicon carbide;
- pH_{IEP}TiN ~ 4-5, TiN surfaces negatively charged in AG-W100;
- **Strong repulsion-type interactions** between all surfaces to be cleaned (W/WO_3, TiN, TEOS, Si_3N_4, SiC) and CMP slurry particles (alumina, silica).

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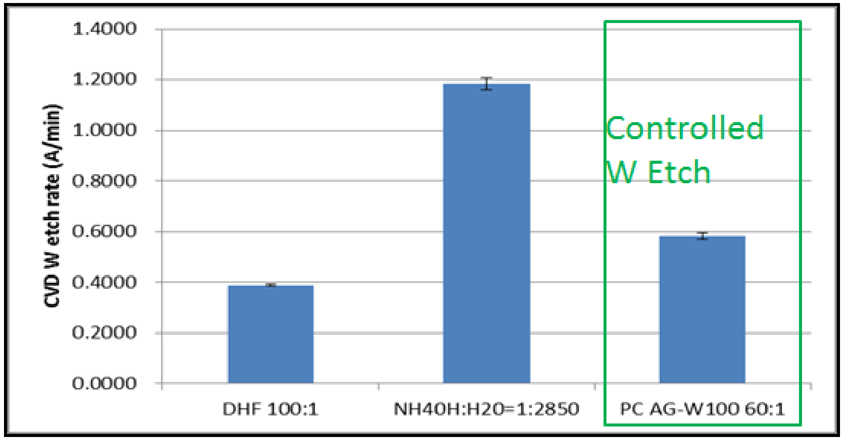
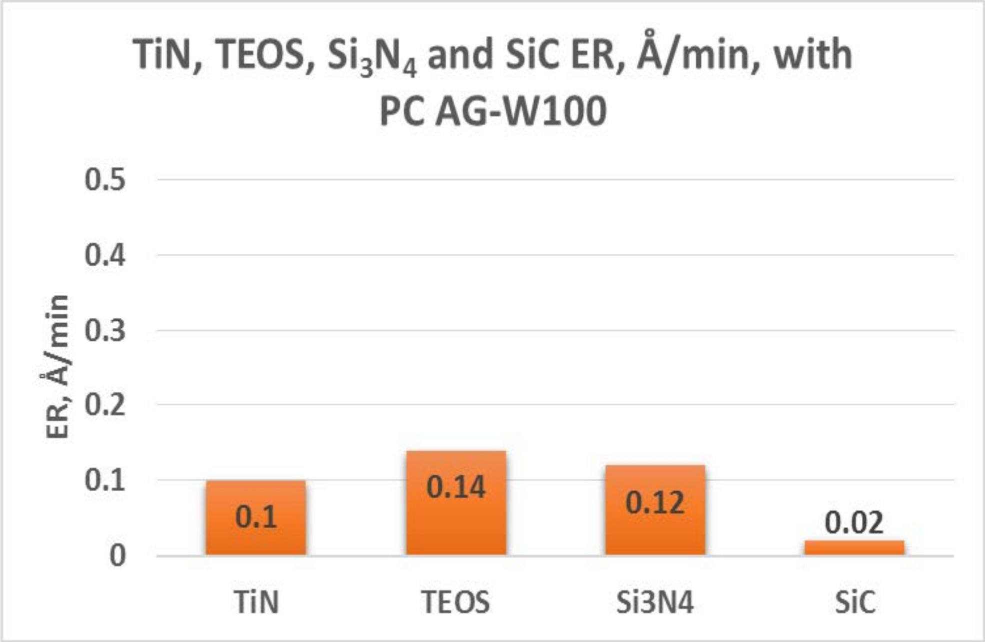
Etch Rates of CVD W, TiN, TEOS, Si_3N_4 and SiC with PlanarClean® AG-W100

Formulation	Avg. ER(Å/min)	Std. Dev.
DHF 100:1	0.3889	0.0038
$NH_4OH:H_2O$ = 1:2850	1.1844	0.0234
PC AG-W100 60:1	0.5822	0.0139



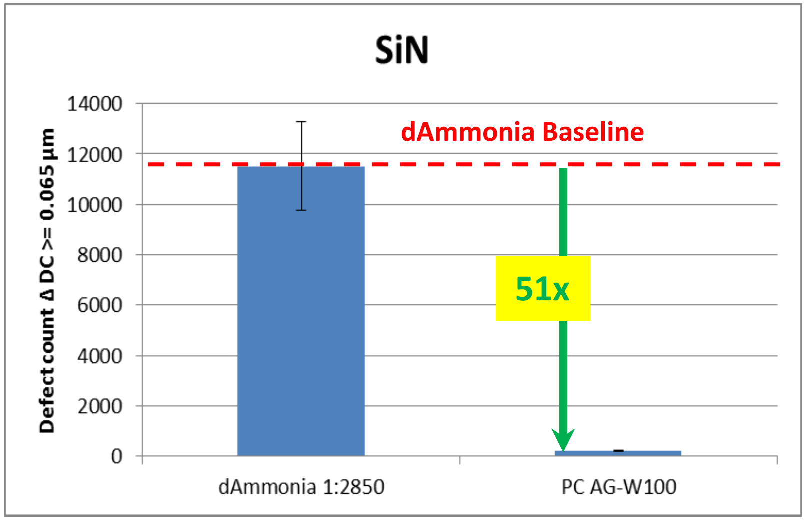


- **PlanarClean® AG-W100 has W etch rate < 0.6 Å/min.**
- **PlanarClean® AG-W100 has lower (controlled) W etch rate than $NH_4OH:H_2O$ = 1:2850.**
- **TiN, TEOS, Si_3N_4 and SiC have ERs < 0.2Å/min**

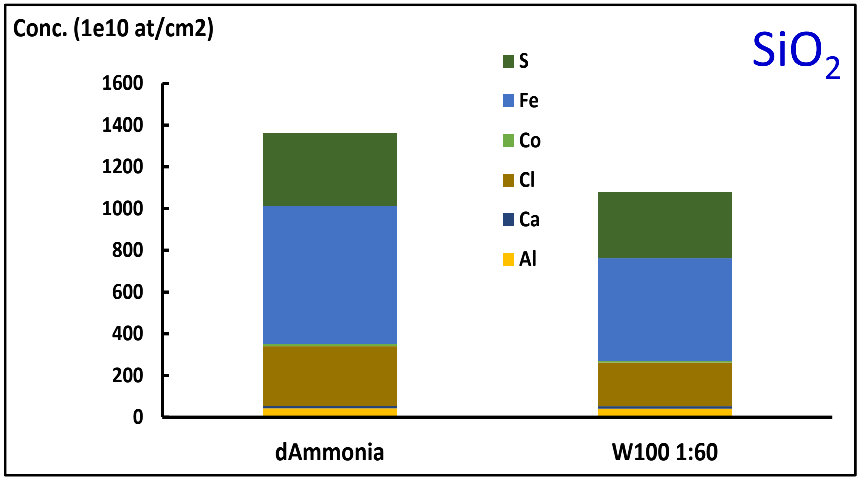
PC AG-W100 vs. dAmmonia Cleaning Data

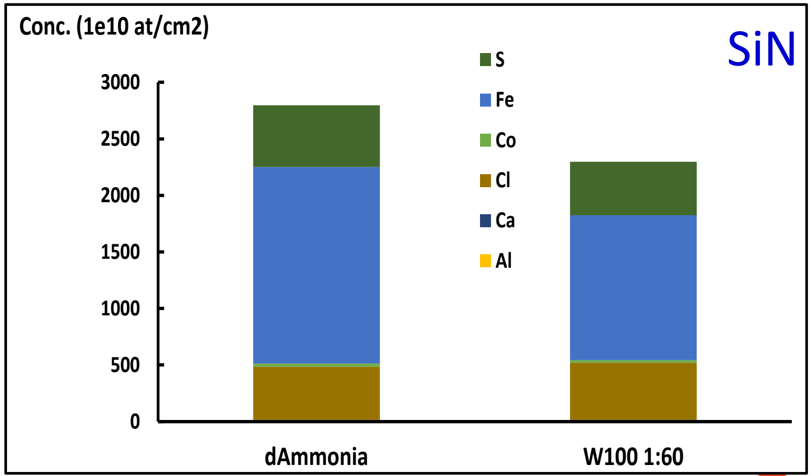
Experiment done in collaboration with IMEC - Leuven, Belgium

- AMAT Reflexion LK polishing tool
- KLA SP-3 defect inspection tool



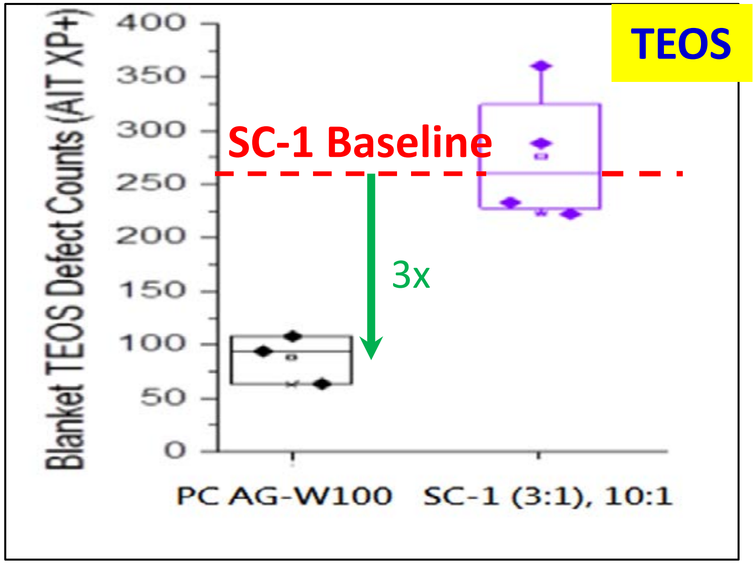
- Si_3N_4 – 51X less defects than dAmmonia;
- SiO_2 defects – comparable to dAmmonia;
- W defects – very low;
- Metal impurities on W wafers – much lower.

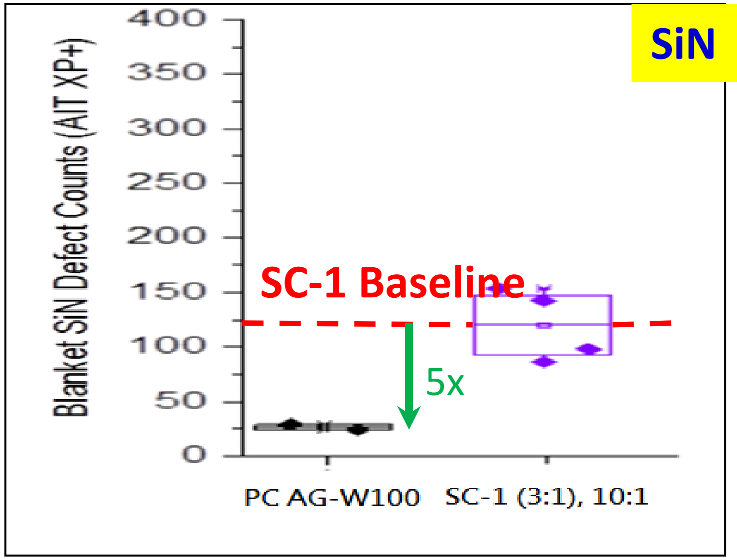




Defect Counts on 8" TEOS & Si_3N_4 Wafers After Cleaning : PlanarClean® AG-W100 vs. SC-1 – 3X-5X Less Defects

Experiment done in collaboration with AXUS - AZ





The defect counts on TEOS with PC AG-W100 are 3X better than SC-1

The defect on SiN with PC AG-W100 is 5X better than SC-1

- Detection limit: 150 nm

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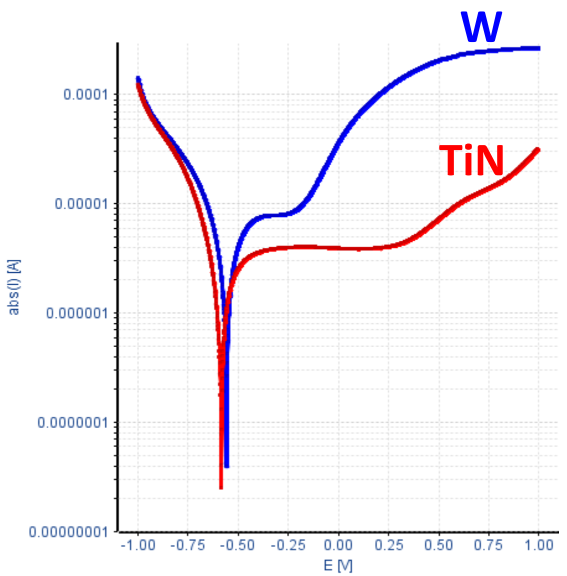
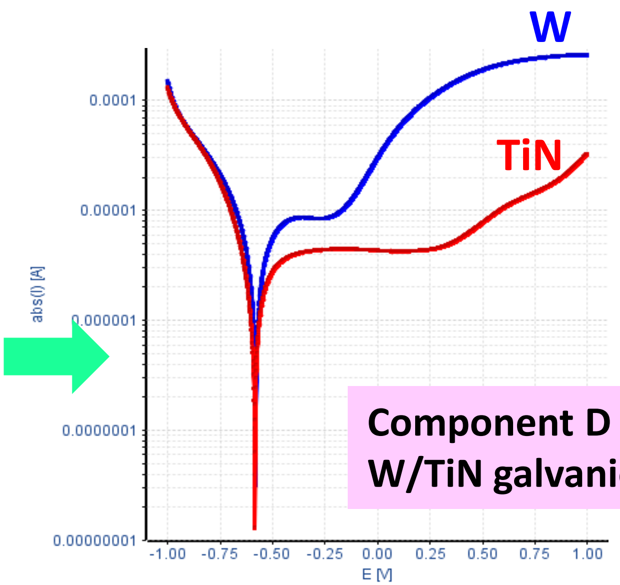
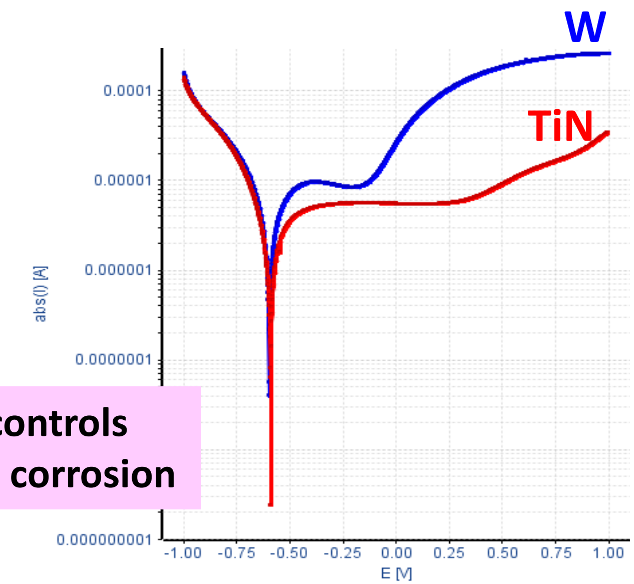
PC AG-W100 W/TiN Galvanic Corrosion Tafel Plots



PC AGW-100 baseline





Component D controls W/TiN galvanic corrosion

PC AGW-100 baseline + different % [Component D]

	TiN	Galvanic Corrosion	W
Galvanic Corrosion of TiN (Å/min)	**0.069**		
Material	Anode: TiN		Cathode: W
Corrosion Potential (V)	-0.584	-0.566	-0.557
Corrosion Current (A)	9.85E-07	7.24E-07	1.78E-06
Corrosion Rate (Å/min)	0.093	0.069	0.101
Slope	4.48E-05		8.09E-05

	TiN	Galvanic Corrosion	W
Galvanic Corrosion of TiN (Å/min)	**0.013**		
Material	Anode: TiN		Cathode: W
Corrosion Potential (V)	-0.584	-0.581	-0.579
Corrosion Current (A)	1.08E-06	1.37E-07	1.90E-06
Corrosion Rate (Å/min)	0.102	0.013	0.108
Slope	4.89E-05		8.64E-05

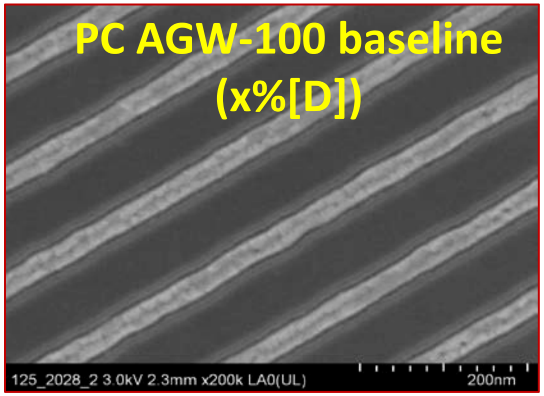
	TiN	Galvanic Corrosion	W
Galvanic Corrosion of W (Å/min)			**0.013**
Material	Cathode: TiN		Anode: W
Corrosion Potential (V)	-0.59	-0.594	-0.596
Corrosion Current (A)	1.26E-06	2.26E-07	2.10E-06
Corrosion Rate (Å/min)	0.119	0.013	0.119
Slope	5.72E-05		9.54E-05

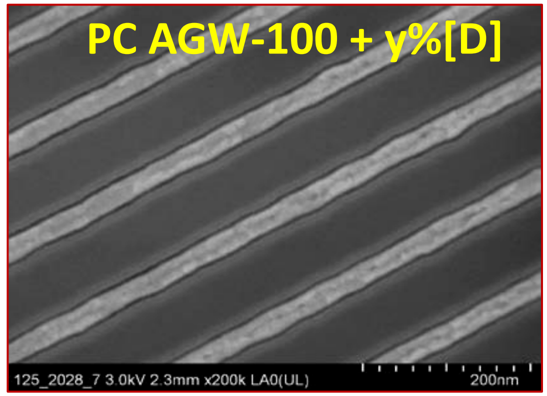
W (cathode) protected
TiN (anode) low corrosion

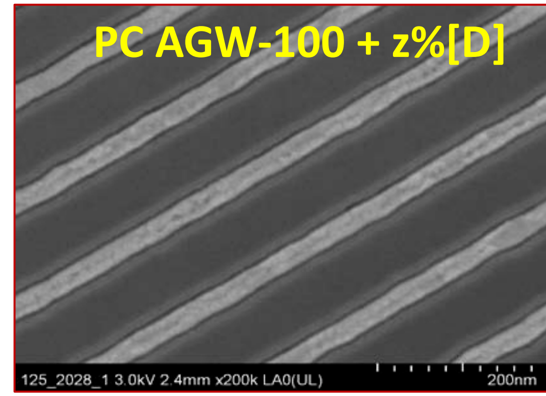
Good overlay
W (cathode) protected
Minimal galvanic corrosion

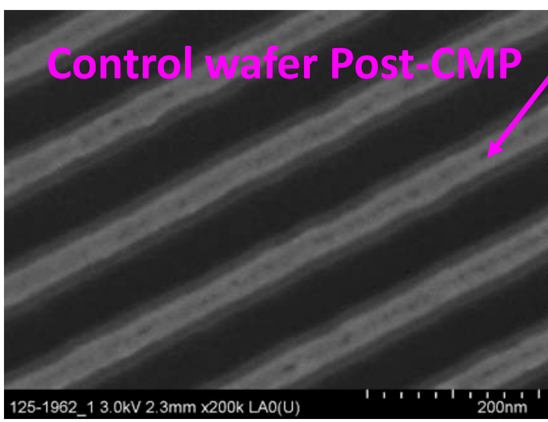
TiN (cathode) protected
Minimal galvanic corrosion

PC AGW-300 - 45nm W/TiN Pattern SEM Characterization



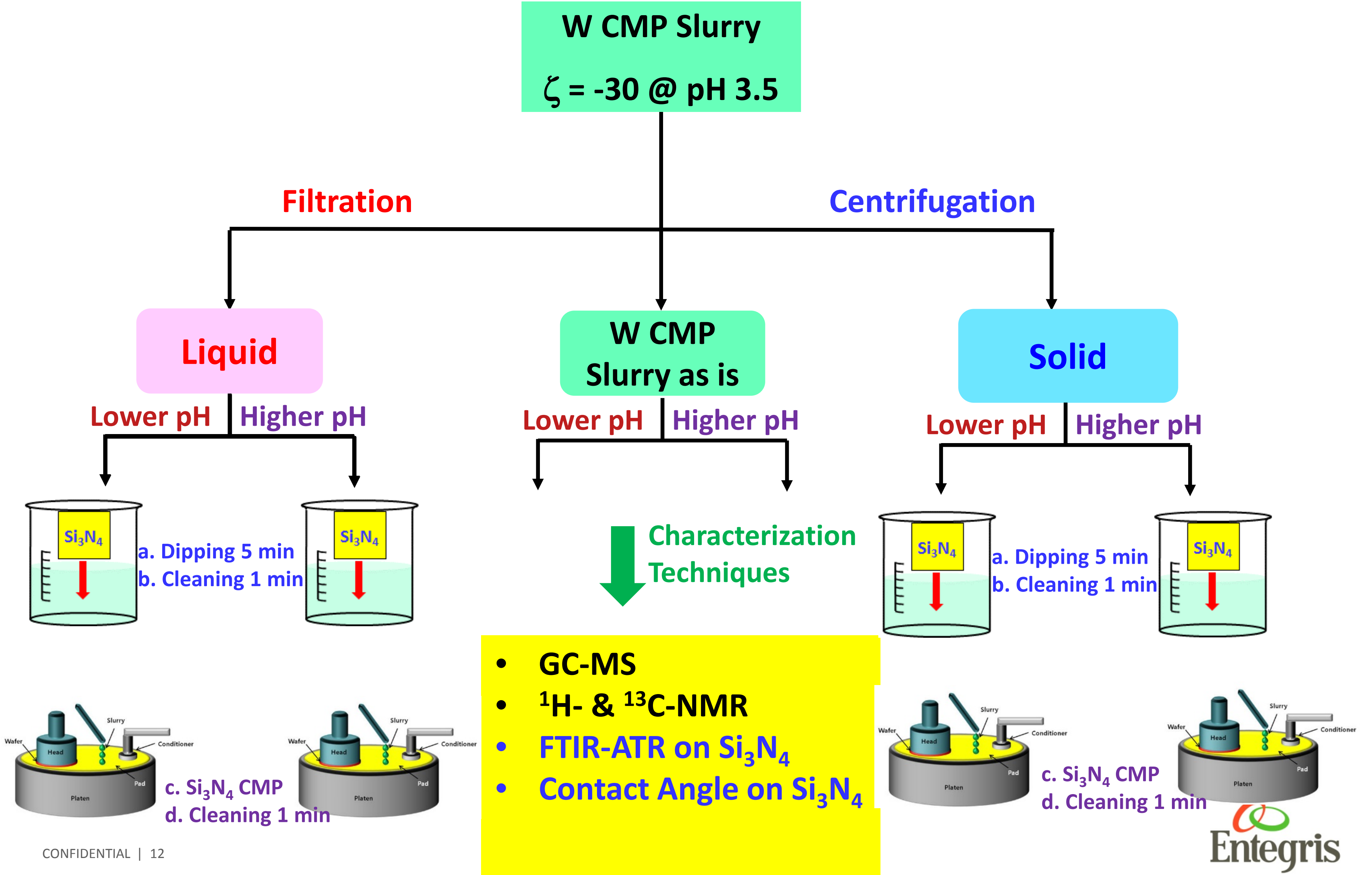




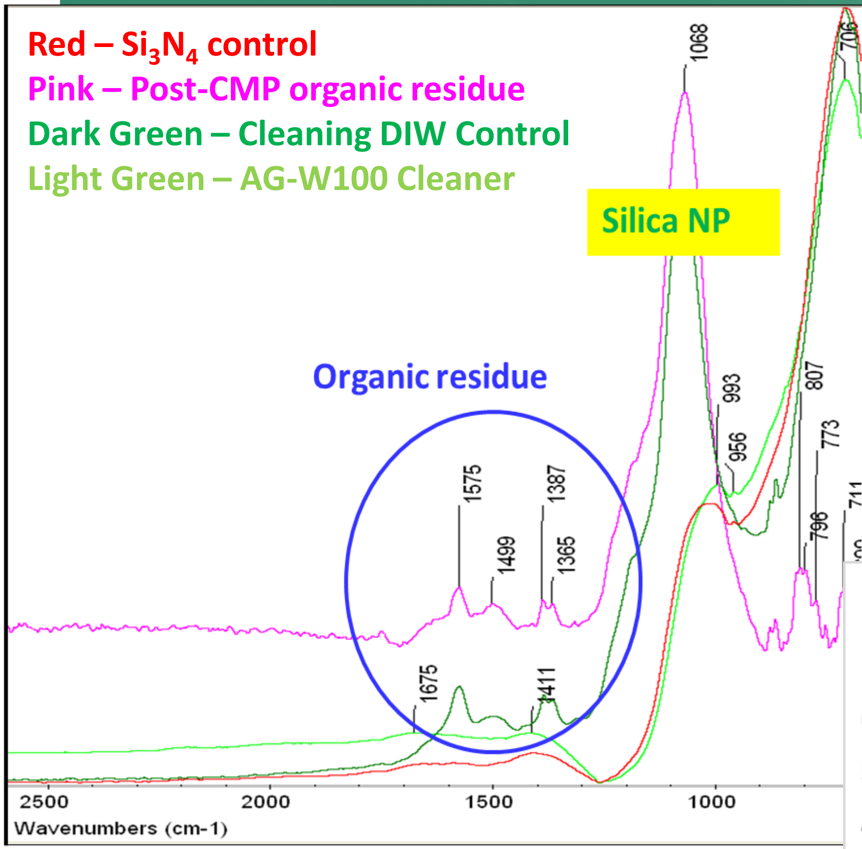


- W lines (control) already etched in the center by the CMP process
- Dirty control generates fuzzy SEM images;
- AG-W100 cleaned controls have **sharper lines @ W/TiN interfaces and generate clear SEM pictures**

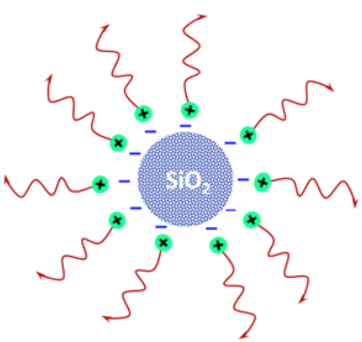
Silicon Nitride Contamination Study with W CMP Slurry Additives: Organic Contaminants



Organic Contaminants Precipitated During Post-CMP DIW Rinse

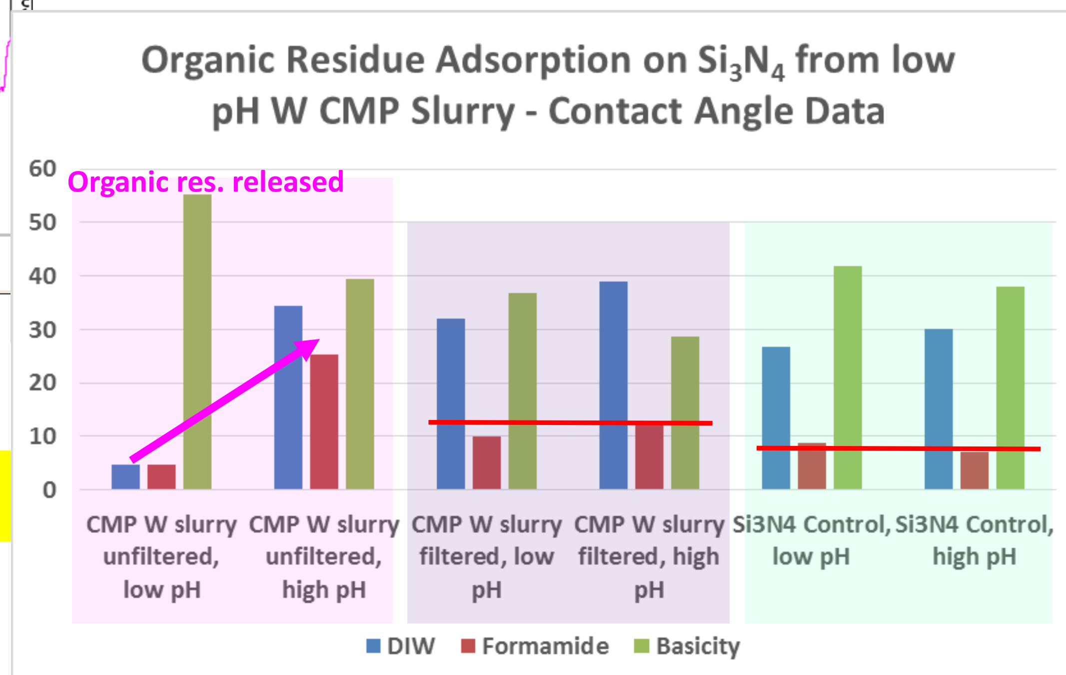


FTIR-ATR spectrum



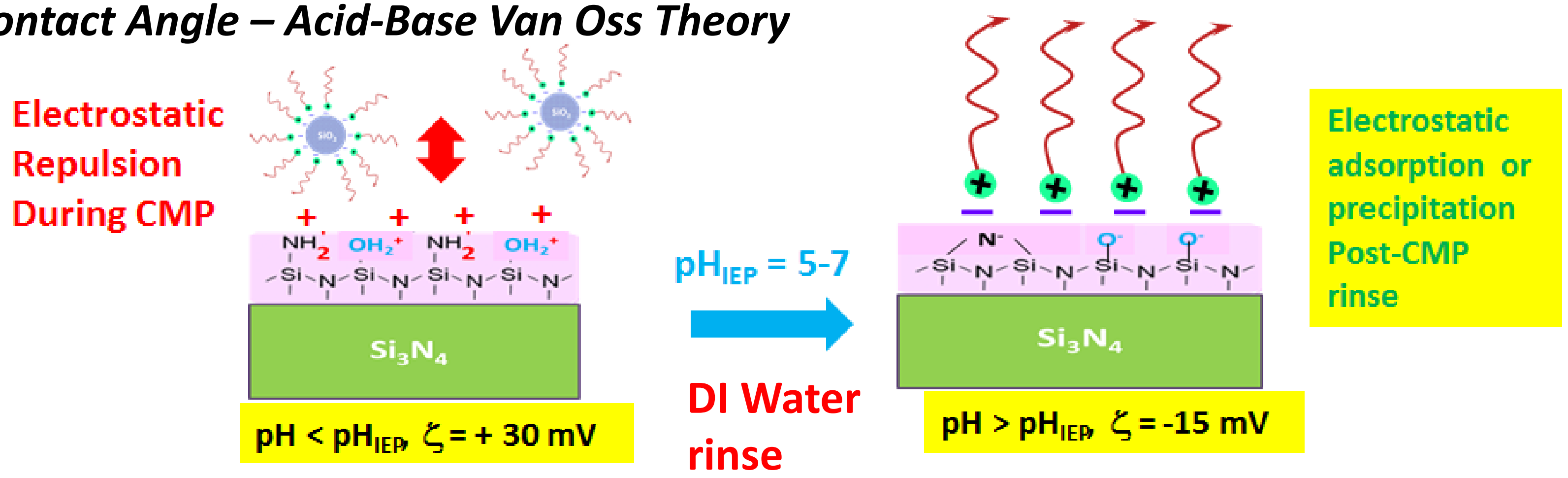
Organic contaminant (W inhibitor) adsorbed on silica particles @ pH 3

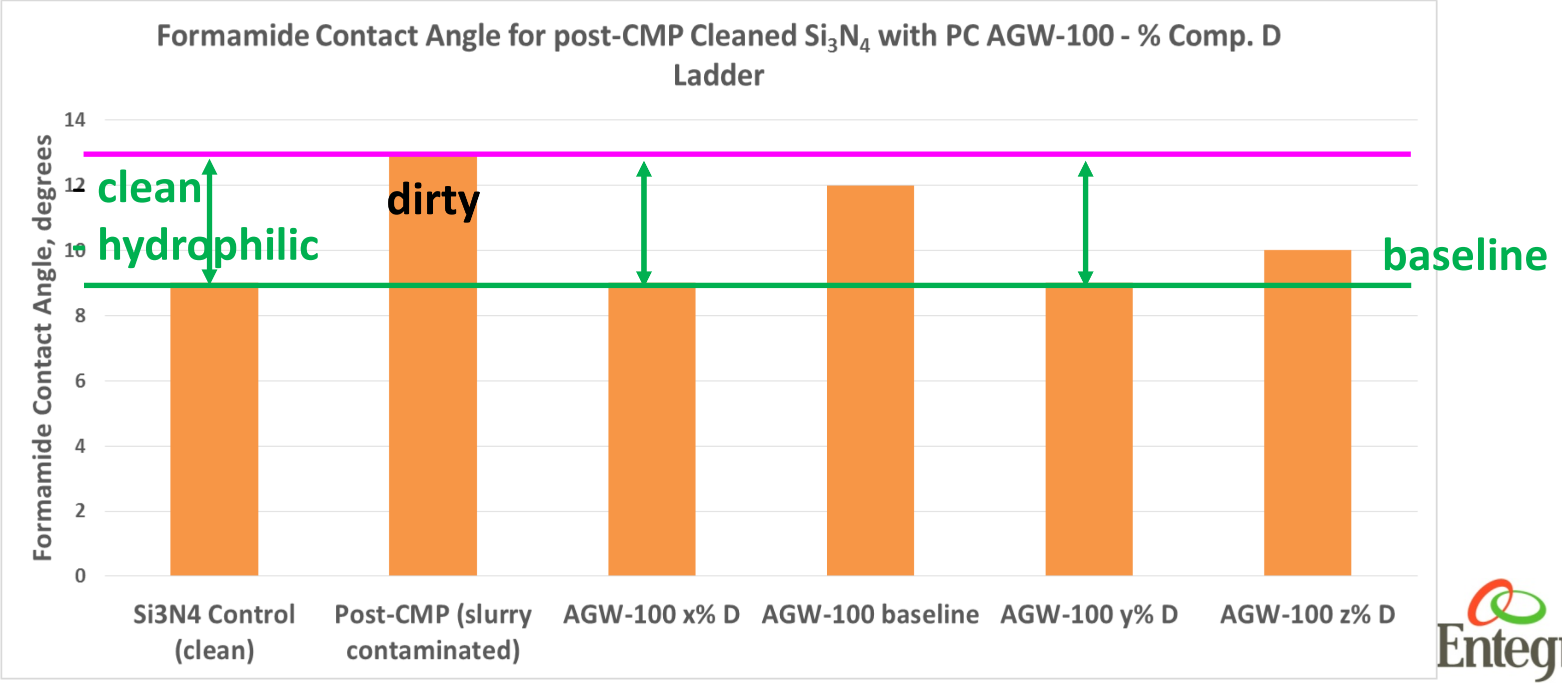
- No/minimal changes for slurry filtrate with pH
- CMP slurry releases organic residue during post-CMP rinse;
- Most sensitive: Formamide values variation



Cleaning Organic Residue on Si_3N_4 with PC AGW-100 - Metrology

1. Contact Angle – Acid-Base Van Oss Theory





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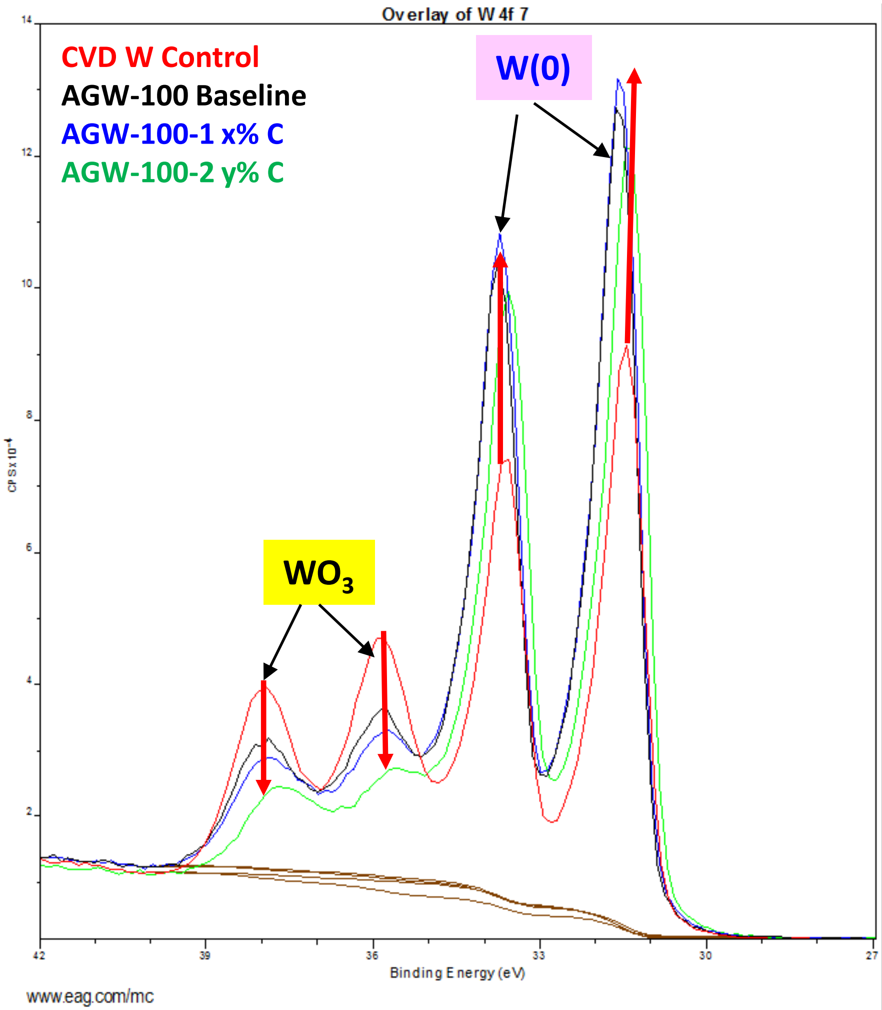
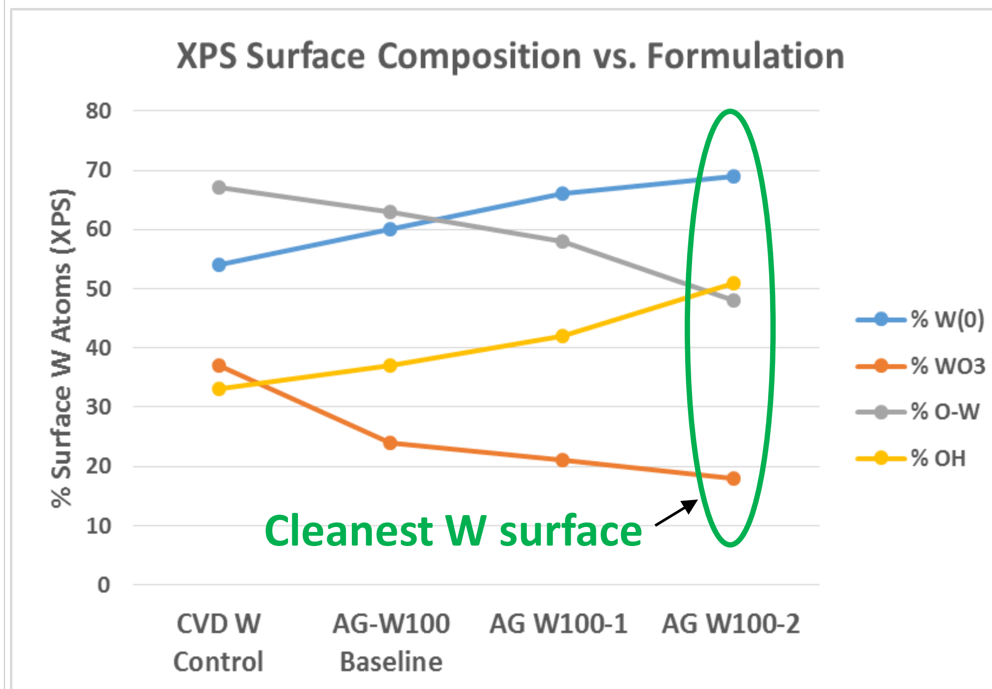
Cleaning Organic Residue on Si_3N_4 with PC AG-W100 - Metrology

2. X-Ray Photoelectron Spectroscopy (XPS)





Best cleaner generates:
- **the thinnest WO_3 surface layer;**
- **lowest % surface atoms: C, N, O, etc.**

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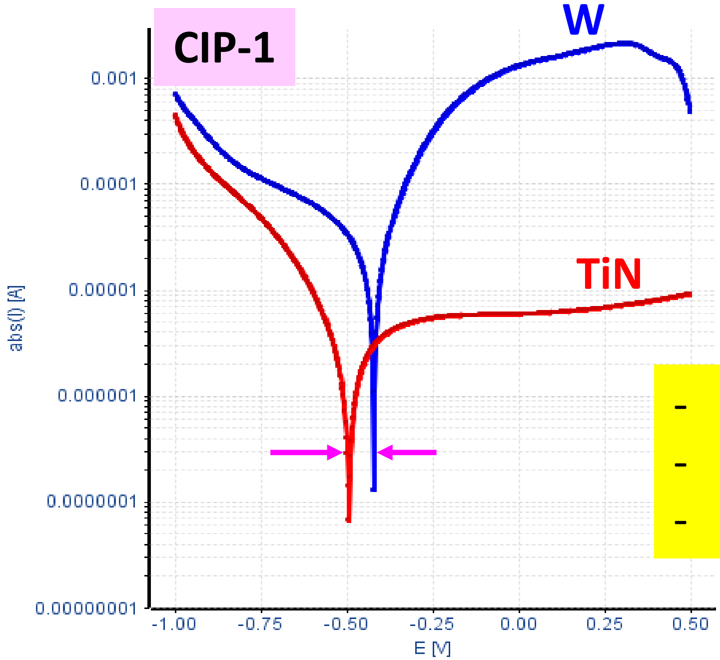
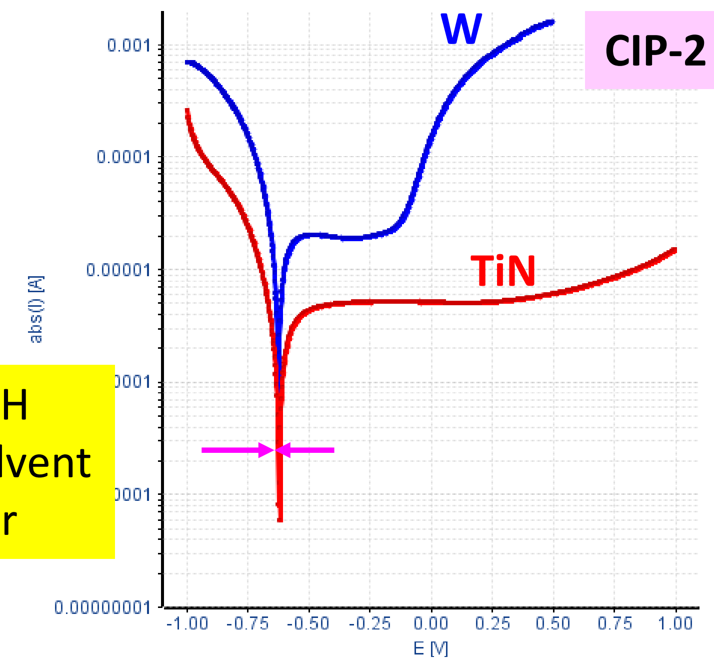
PC AG-W100 CIP Formulations





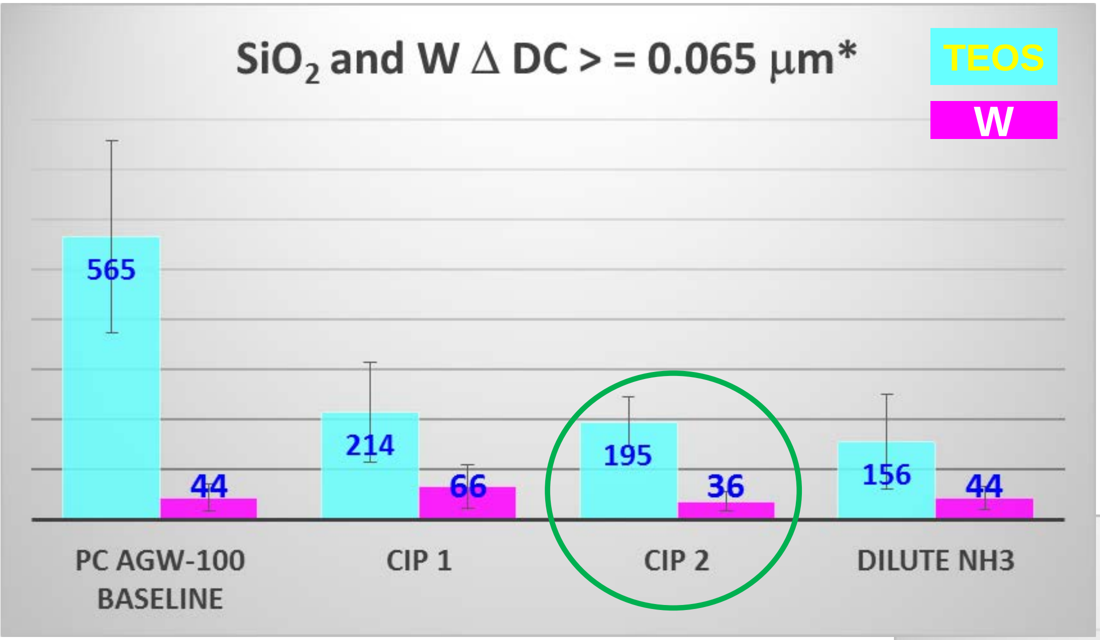
- Different pH
- Organic solvent
- pH adjustor

	TiN	Galvanic Corrosion	W
Galvanic Corrosion of TiN (Å/min)	**0.268**		
Material	Anode: TiN		Cathode: W
Corrosion Potential (V)	-0.494	-0.426	-0.422
Corrosion Current (A)	1.22E-06	2.83E-06	1.31E-05
Corrosion Rate (Å/min)	0.115	0.268	0.744
Slope	5.53E-05		5.97E-04

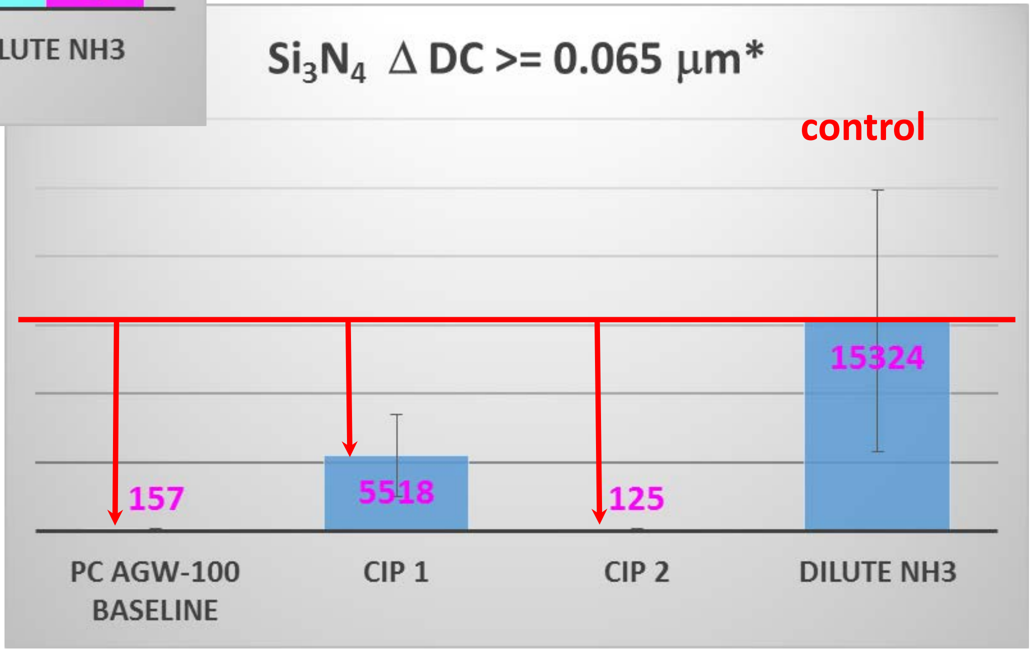
	TiN	Galvanic Corrosion	W
Galvanic Corrosion of W (Å/min)	**0.013**		
Material	Cathode: TiN		Anode: W
Corrosion Potential (V)	-0.622	-0.626	-0.625
Corrosion Current (A)	1.76E-06	2.35E-07	1.13E-05
Corrosion Rate (Å/min)	0.167	0.013	0.642
Slope	8.02E-05		5.16E-04

Cleaning Performance for PC AG-W100 CIP 1 and CIP 2 Formulations

Experiment done in collaboration with IMEC, Leuven, Belgium



- AMAT Reflexion LK polishing tool
- KLA SP-3 defect inspection tool



- **Si_3N_4 – ~125x less defects than dNH_3**
- **W - ~ 3.5x less defects than dNH_3**
- **SiO_2 – comparable with dNH_3**

Conclusions

- W/TiN/Dielectrics post-CMP cleaning formulation PlanarClean® AG-W100, was successfully developed and tested for performance:

- Low particle count defects (on SP3) – big improvement over the commodities like dAmmonia and SC-1;

- Low/no W/TiN galvanic corrosion (Tafel plots) – tunable by varying components;

- Low/no W/TiN interfacial corrosion on 45 nm pattern wafers (SEM);

- Low/no post-CMP organic residue on dielectric substrates (FTIR-ATR, contact angle, XPS);

- CIP versions with tunable and improved performance in development.

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