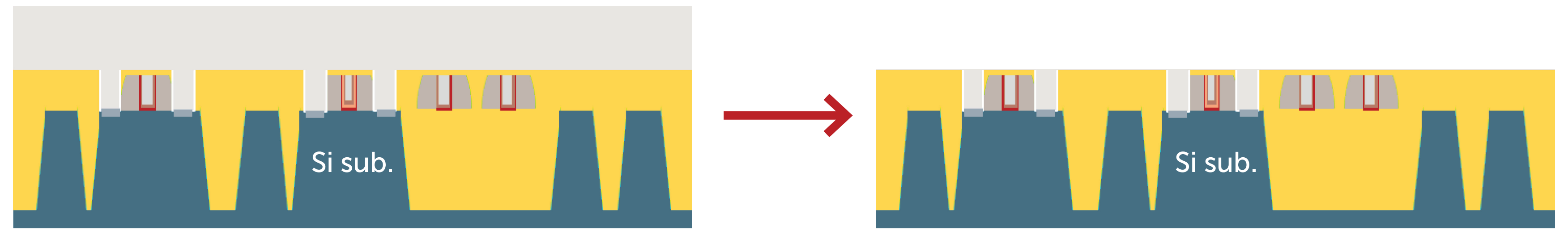


Post-CMP cleaners for tungsten at advanced nodes

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SCOPE OF WORK

- Design of formulated post-CMP cleaners for W plugs with TiN as barrier liner, dielectrics SiO_2 and Si_3N_4 , for use at 10 nm technology node (40 nm metal pitch)



INTRODUCTION

- W bulk and barrier CMP slurries consist of:
 - (a) abrasive particles (fumed alumina or silica: fumed or colloidal)
 - (b) oxidizer (usually H_2O_2): $\text{W} \rightarrow \text{W(VI)O}_3$ for removal by slurry abrasive
 - (c) H_2O_2 decomposition accelerator
 - (d) W corrosion protection additive
- Particle charge in low pH W CMP slurries are usually positive (isoelectric point, $\text{pH}_{\text{IEP Al}_2\text{O}_3} = 6-8$ and $\text{pH}_{\text{IEP SiO}_2} = 2-4$).
- W surface is always negatively charged at $\text{pH} > 3$ ($\text{pH}_{\text{IEP W}} = 2-3$,) $\rightarrow$ strong electrostatic attraction W surface and residual particles during PCMP cleaning.

Significant surface contamination after CMP: abrasive particles, organic residue, pad debris, metal cations.

TABLE 1: PLANARCLEAN® AG-W100 FORMULATION ADDITIVES LIST – FUNCTION AND MECHANISM

Component	Function	Mechanism
A	Non-TMAH pH adjustor	W surface hydroxylation and good wetting Negative surface charge surface of wafer and contamination
B & C	Complexing agents	Surface modification of particles to prevent agglomeration and re-precipitation
D	Dispersing agents	Prevent aggregation and control etch rate

RESULTS AND DISCUSSION

- Corrosion: Minimized Galvanic corrosion by using new and specific ligands that adsorb on metal or barrier liner $\rightarrow$ additional passivation less noble material
- Particle cleaning: Upon mixing with AG-W100, all nanoparticle dispersions reversed charges from positive to negative (Al_2O_3 , WO_3 , SiN) or became more negatively charged (SiO_2 , SiC) $\rightarrow$ strong repulsion (from Zeta Potential)
- Organic residue cleaning:
 - Contamination takes place during post-CMP rinsing with DI water
 - Organics disappeared after 1' cleaning of SiN with AG-W100 (FTIR-ATR)
- Defectivity: 300 mm CMP + brush cleaning
 - AMAT Reflexion® LK polishing tool with integrated brush cleaner (Desica)
 - IC1010 pad, silica abrasive slurry (100 nm particle size), PVA brushes
 - Defect inspection by laser light scattering (SP3, KLA-Tencor Corp.)
 - dAmmonia as reference (W and other metals are significantly etched)
 - dAmmonia dissolves some of the SiO_2 surface and particles
 - Significant progress in removal of organic residues
 - AG W-100 represents a significant improvement in cleaning
 - CIP2: unique cleaning additive designed to disperse silica and prevent reattachment to SiO_2 surface

Number of defects pareto (≥ 60 nm defects)

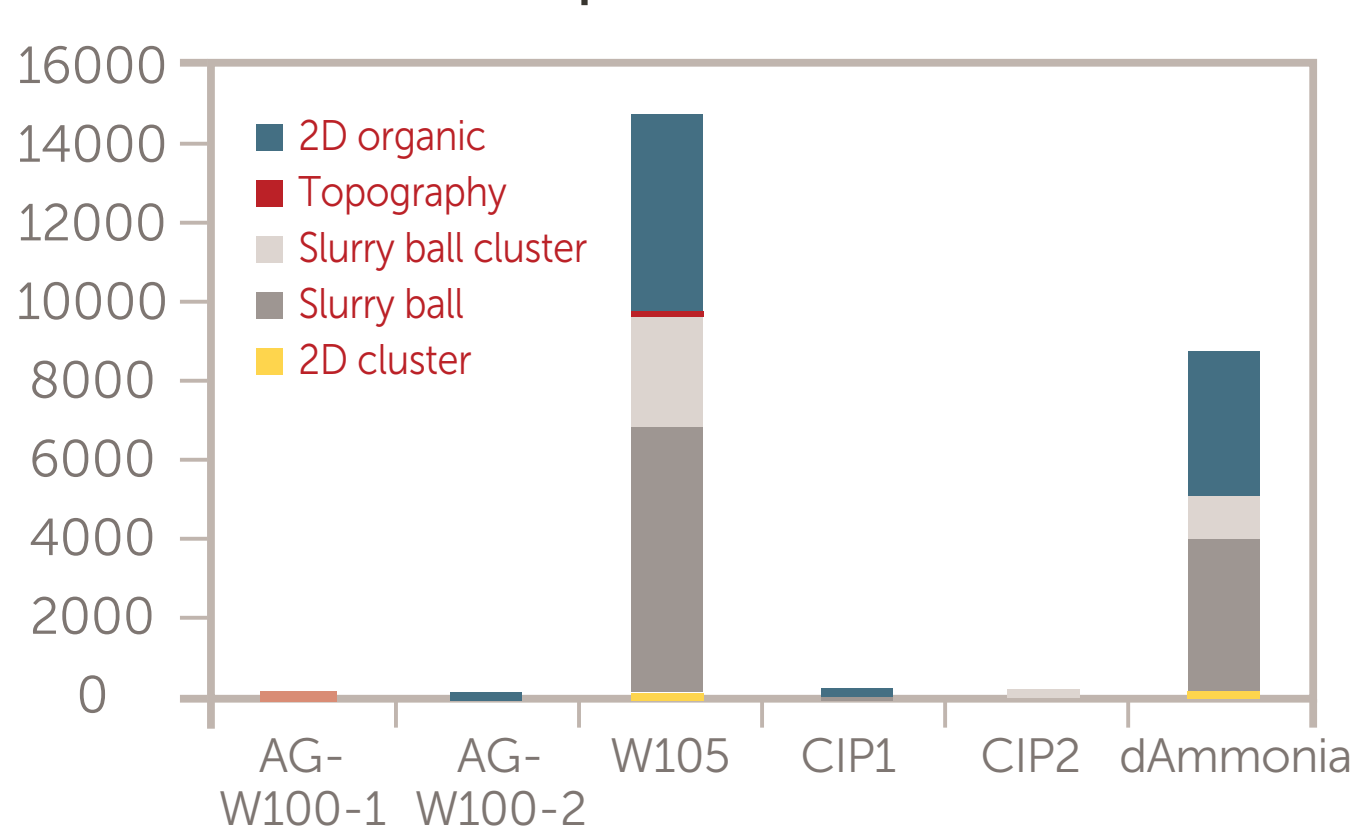


Figure 1: Number of defects (particles and organic residue) pareto on silicon-nitride blanket wafers (boborn figure is a zoom in of top figure).

Number of defects pareto (≥ 100 nm defects)

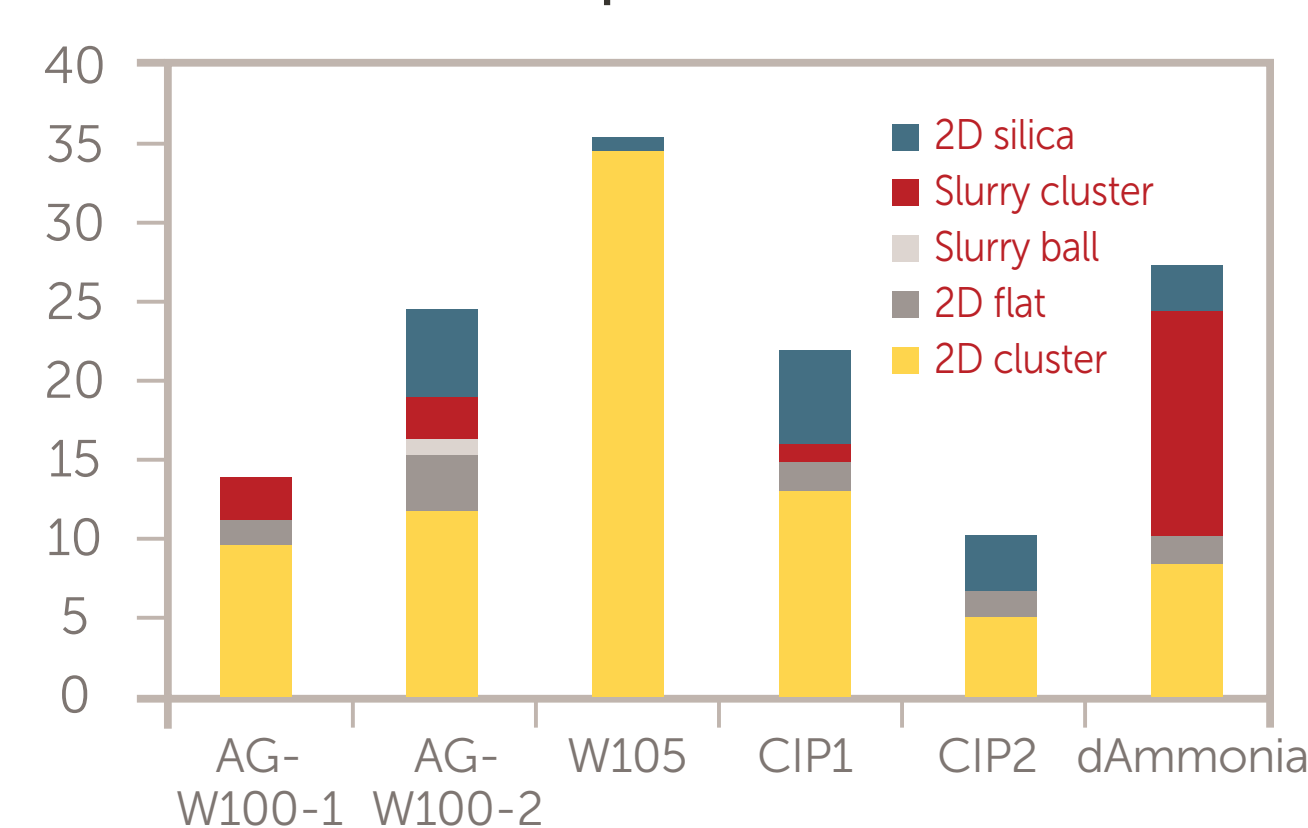
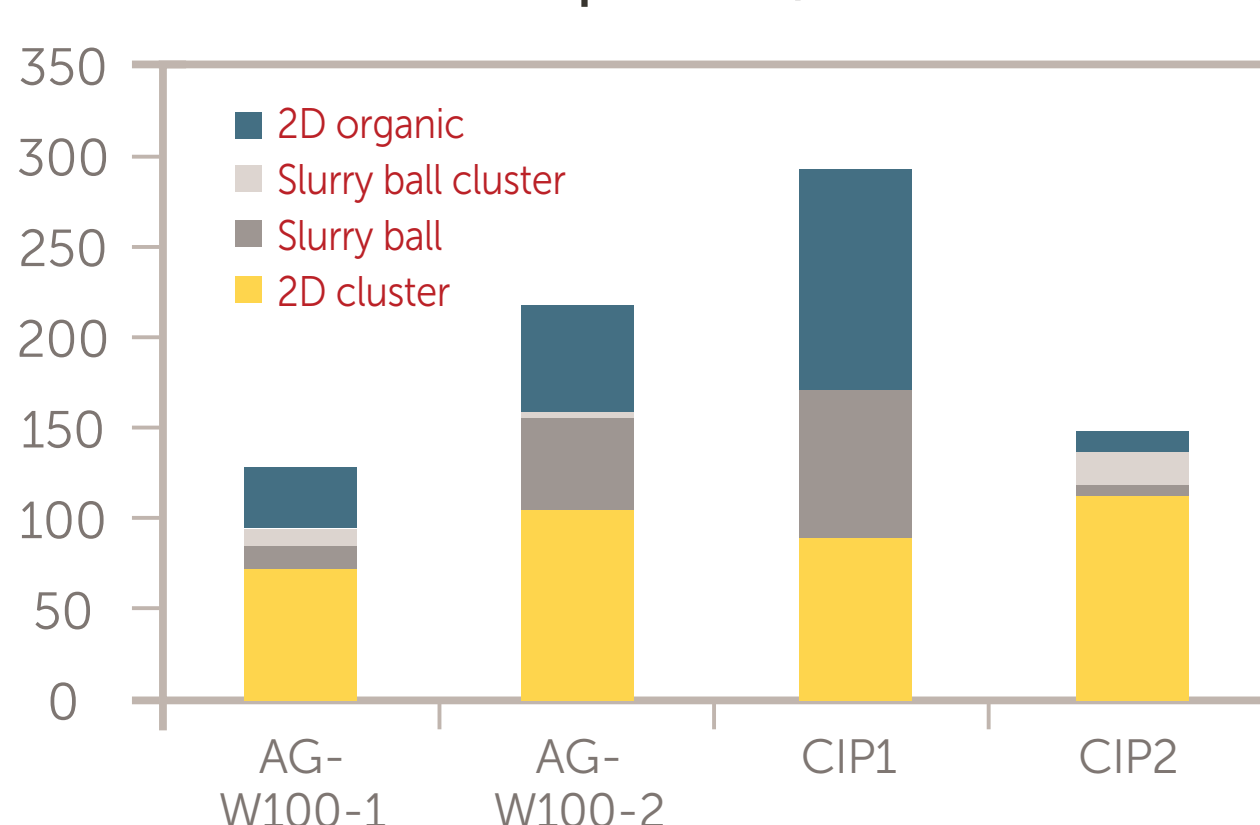


Figure 2: Number of defects (particles and organic residue) pareto on W blanket wafers.

Number of defects pareto (≥ 60 nm defects)



Number of defects pareto (≥ 65 nm defects)

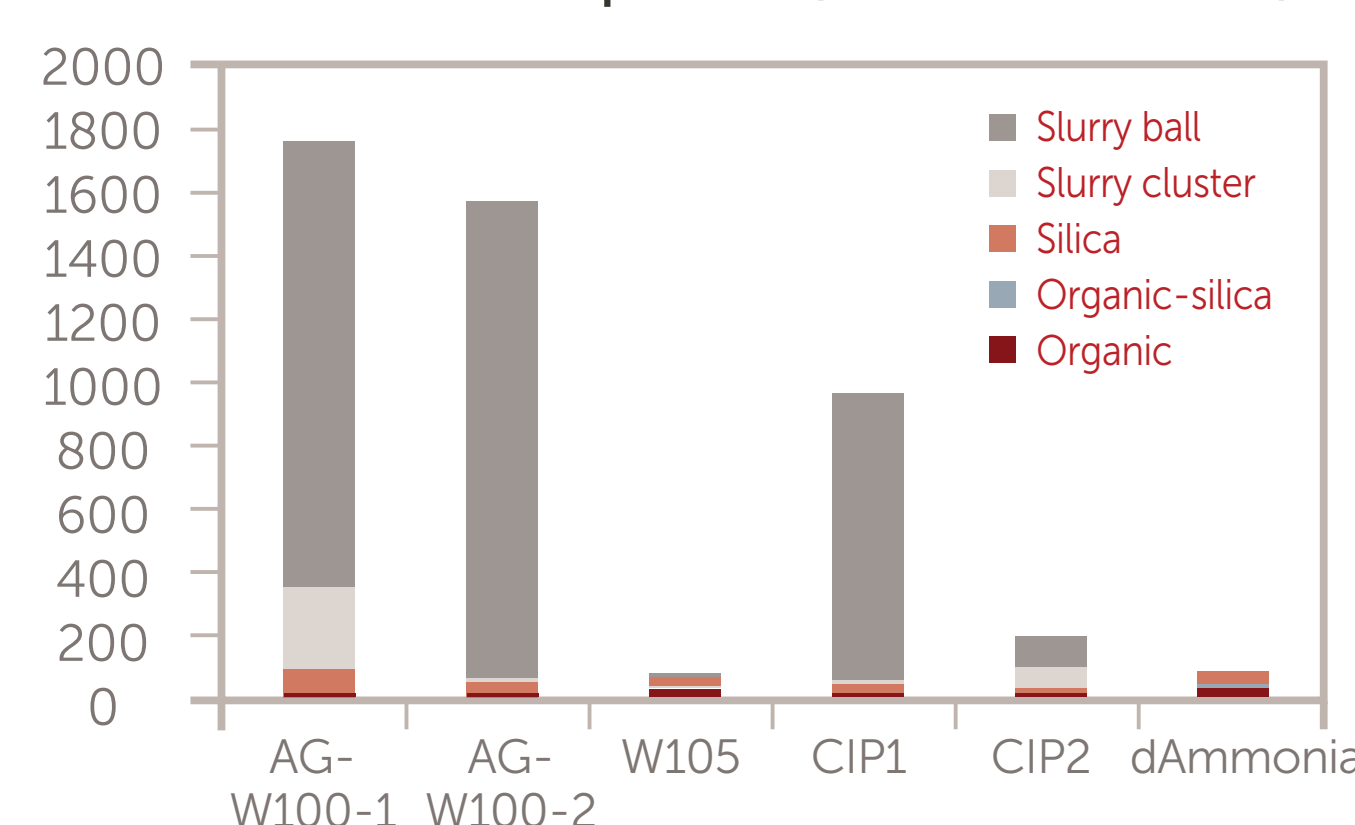


Figure 3: Number of defects (particles and organic residue) pareto on SiO_2 blanket wafers.

APPROACH

Two main cleaning approaches:

- (1) **W surface charge reversal**, using cleaning additives able to adsorb at the W surface. Other cleaning additives prevent residue redeposition.
- (2) **Particle charge reversal** and electrosteric protection using organic additives $\rightarrow$ strongly negative charged surfaces $\rightarrow$ best cleaning.

CMP slurry abrasive:

- Al_2O_3 $\zeta > 0$ mV;
- Surface-treated silica (ST-SiO_2) $-\zeta > 0$ mV;
- Silica ($\zeta > 0$ mV)

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

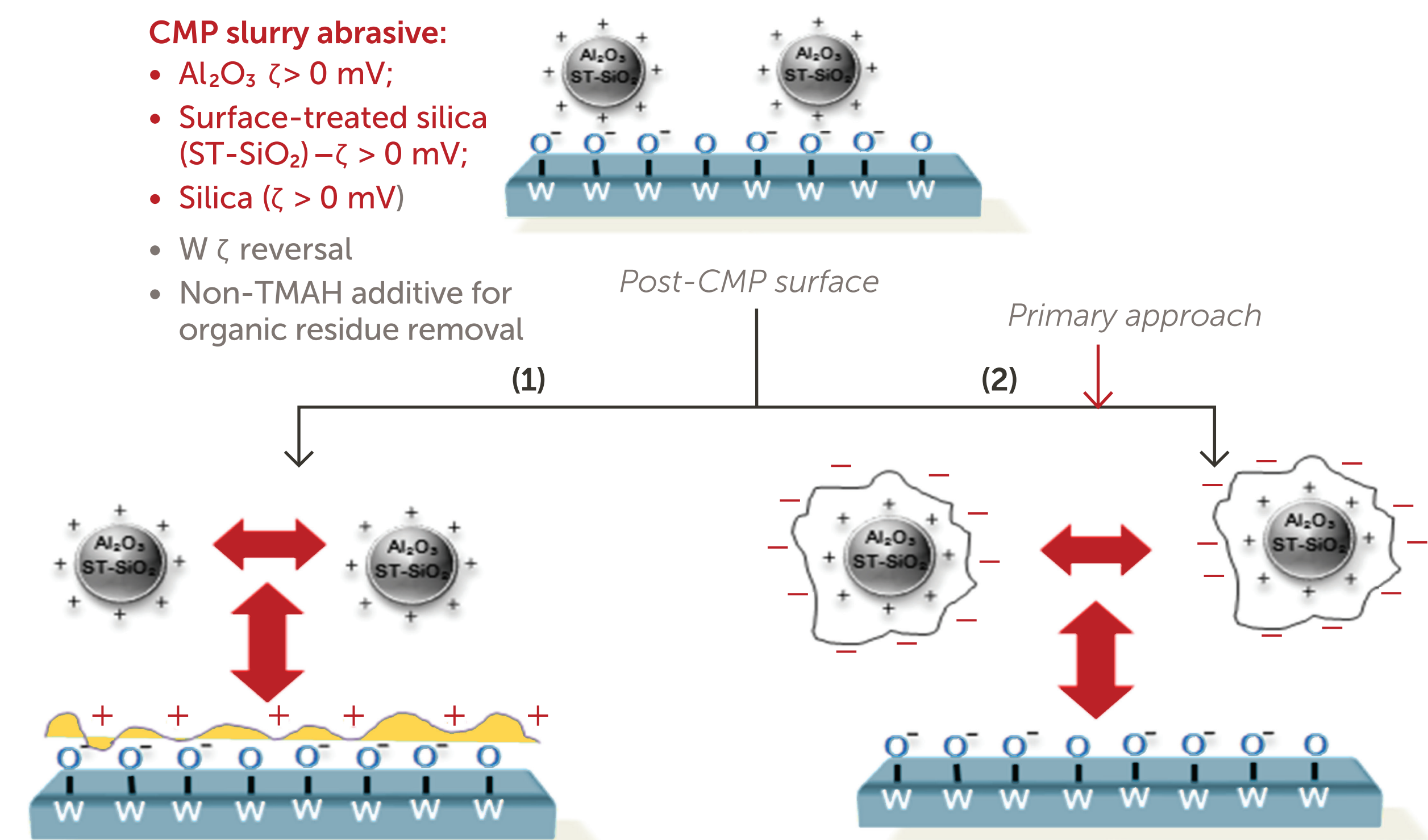
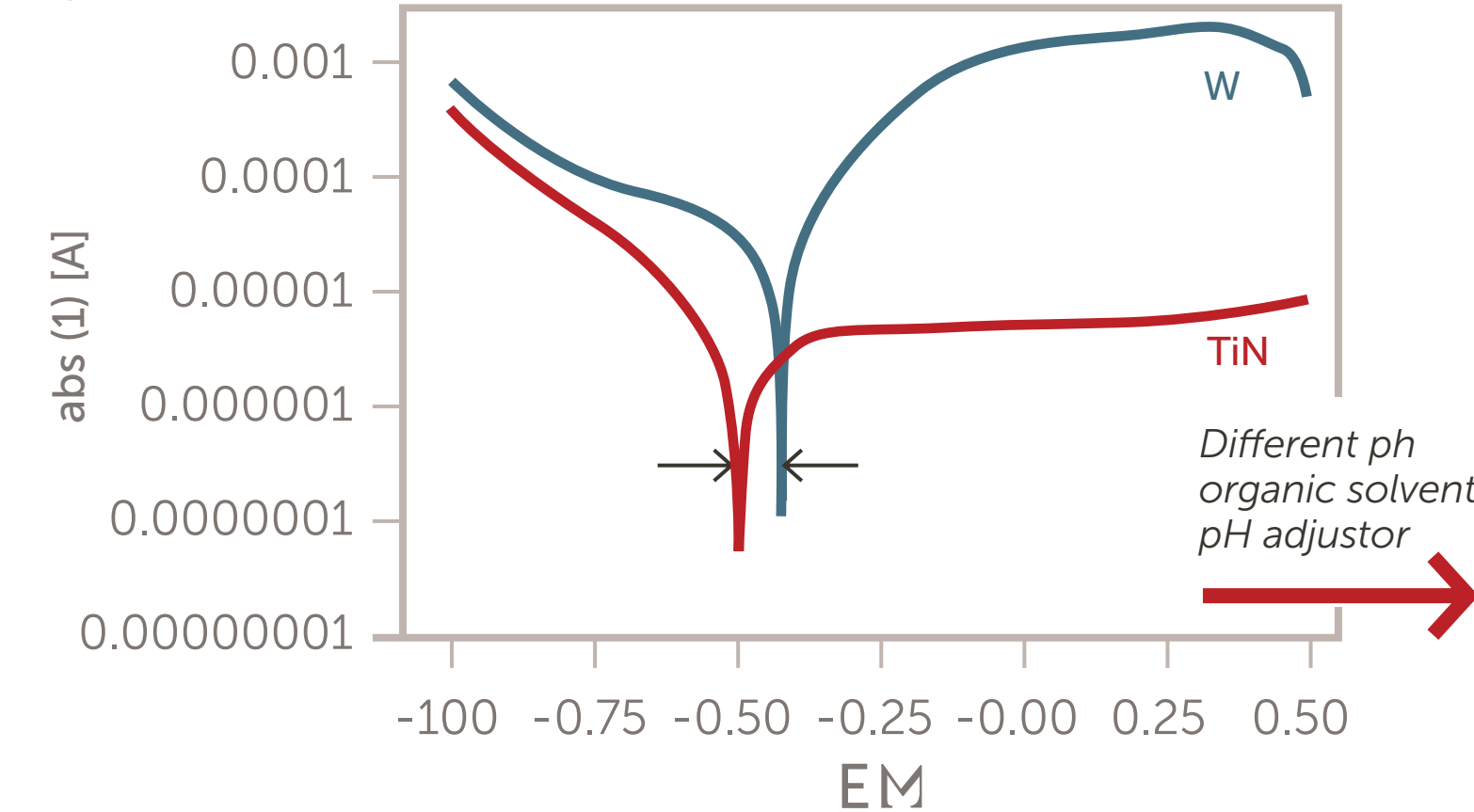


Figure 4: W post-CMP cleaning formulation – mechanistic design concepts

CIP-1



CIP-2

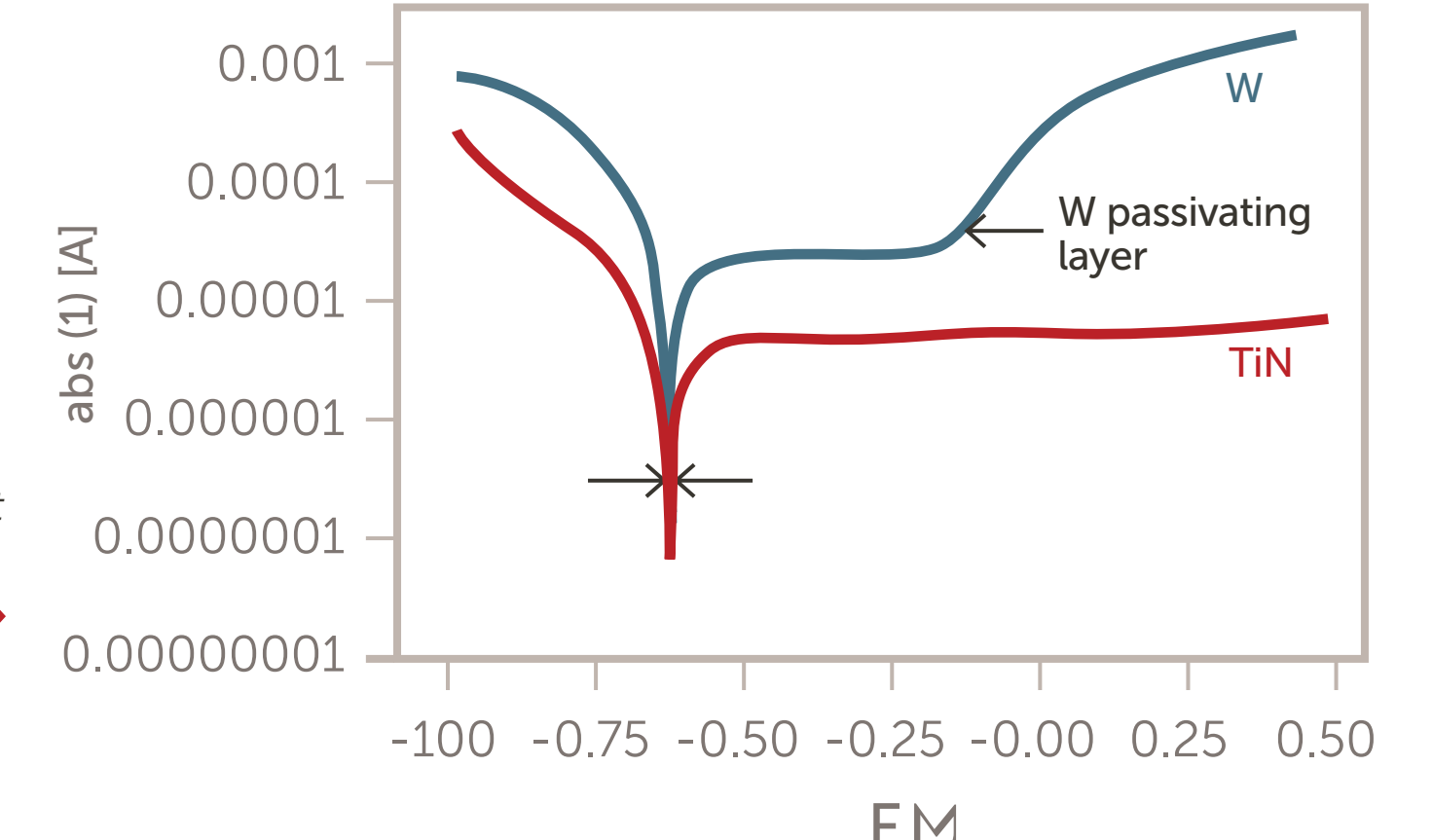


Figure 5: Tunability of the galvanic corrosion W/TiN for PlanarClean AG W-100 type formulations

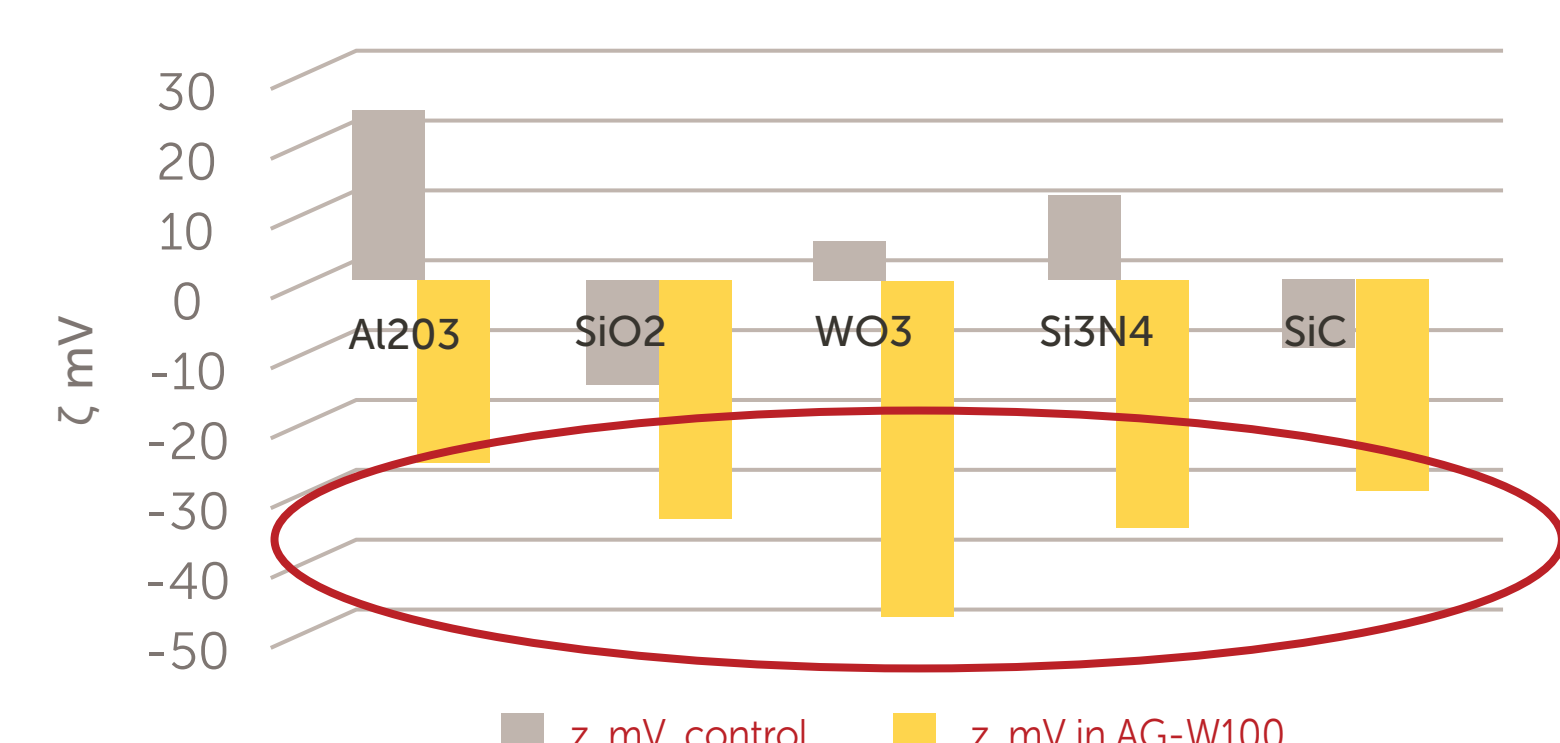


Figure 6: Zeta Potential, ζ , (mV) for slurry abrasives (alumina, silica), W and dielectrics surfaces in contact with AG-W100 formulation.

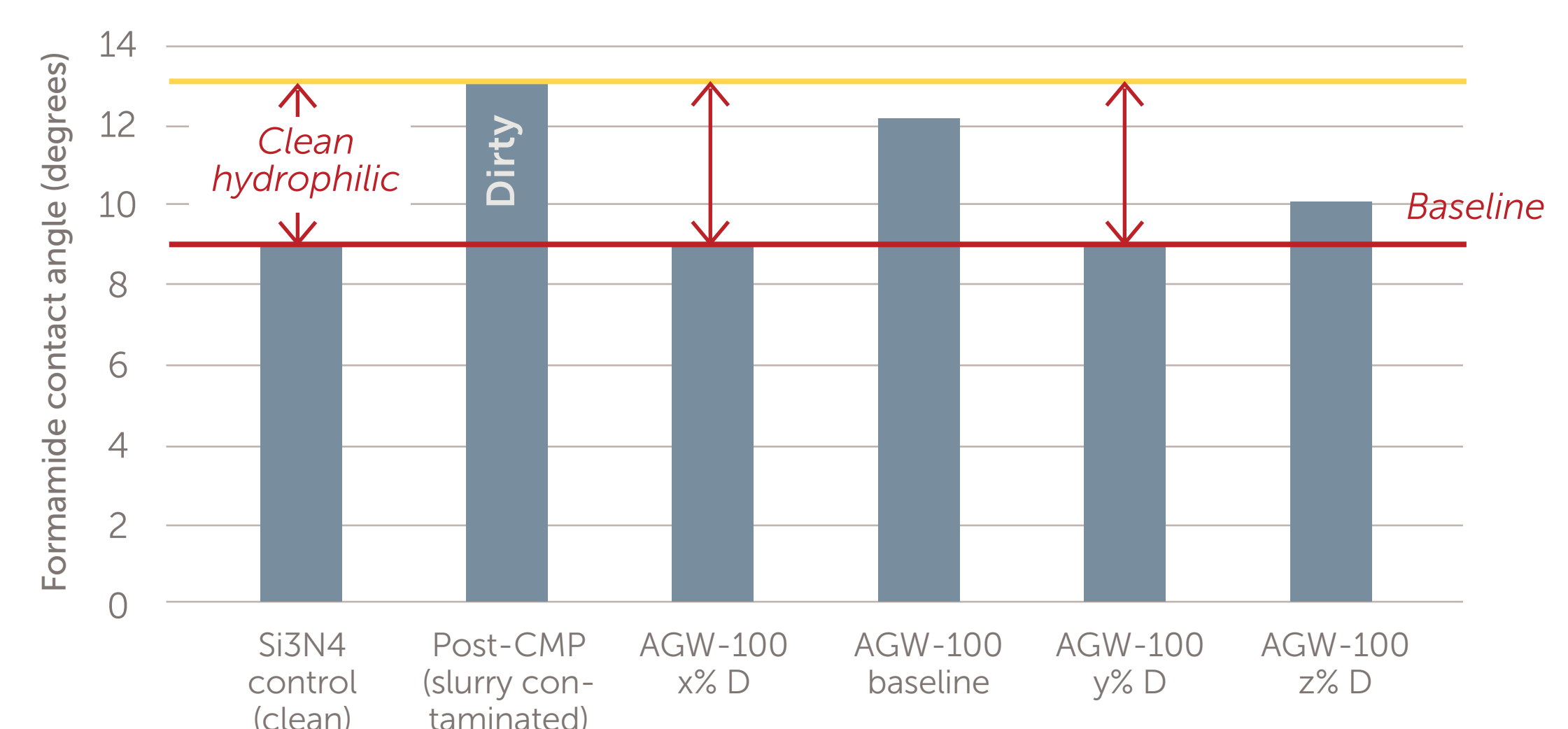


Figure 7: Formamide contact angle measurements on contaminated and cleaned SiN surfaces.

SUMMARY

- Two main approaches followed: (1) reverse W surface charge; (2) particle charge reversal.
- Latter approach results in strongly negative charged surfaces and best cleaning.
- AG W-100 represents a significant improvement in cleaning.
- CIP2 shows the best performance on W, SiN and SiO_2 blankets.
- This feature enables advanced node W cleaning for memory devices.