

Advanced CMP Cleaning Solutions

Surfactants, Metal Inhibitors, Oxygen Scavengers
& Particle Removers

By

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Contents

- Challenges of CMP Cleaning
- Background and Principles of CMP Cleaning
- New Concepts in CMP Cleaning
- Fab Experimental Results
- Summary

Challenges of CMP Cleaning Solution

- ❑ **Multiple materials in Dynamical CMP Systems**
 - Trace metals and ions: **Cu**, **W**, Ni, Fe, Ru, Ti, Cr, etc
 - Dielectric material: SiO₂, Al₂O₃, etc
 - Slurry residuals: PSD, MOx
 - Organic polymer materials
- ❑ **Cleaning Mechanism for Different Materials**
 - Cleaning chemistry vs. CMP chemistry; pH, corrosion & inhibitors
 - Metal surface cleaning
 - Dielectric surface cleaning
 - Wafer surface topography, structures, macro & micro-scratching
- ❑ **Cleaning Tool and Cleaning Functions**
 - Different tools, masonic, rinsibility & dry methods
- ❑ **Wafer Quality, CMP Process Performance**
 - Wafer aging, CMP process performance & recontamination
 - Partial dried wafers & wafer surface slurry residual pre-treated

Challenges of CMP Cleaning Solution

1 H hydrogen 1.008																	2 He helium 4.003
3 Li lithium 6.968	4 Be beryllium 9.012											5 B boron 10.81	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31	13 Al aluminum 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cl chlorine 35.45	18 Ar argon 39.95										
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.97	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.95	43 Tc technetium 98	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs cesium 132.9	56 Ba barium 137.3	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium 144.9	62 Sm samarium 150.4	63 Eu europium 151.9	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0	72 Hf hafnium 178.5
73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium 209	85 At astatine 210	86 Rn radon 222				
87 Fr francium 223	88 Ra radium 226	89 Ac actinium 227	90 Th thorium 232	91 Pa protactinium 231	92 U uranium 238	93 Np neptunium 237	94 Pu plutonium 244	95 Am americium 243	96 Cm curium 247	97 Bk berkelium 247	98 Cf californium 251	99 Es einsteinium 252	100 Fm fermium 257	101 Md mendelevium 258	102 No nobelium 259	103 Lr lawrencium 262	104 Rf rutherfordium 261
105 Db dubnium 268	106 Sg seaborgium 271	107 Bh bohrium 272	108 Hs hassium 277	109 Mt meitnerium 276	110 Ds darmstadtium 281	111 Rg roentgenium 280	112 Cn copernicium 285	113 Nh nihonium 284	114 Fl flerovium 289	115 Mc moscovium 288	116 Lv livermorium 293	117 Ts tennessine 292	118 Og oganesson 294				

MP Related Materials	
1	AlOx
2	SiOx
3	Cu
4	W
5	Al
6	MOx
7	Polymers
8	SiN
9	TiN
10	Redep

Key Issues of Cleaning Chemistry

❑ Unbalance of Hydrophilic/Hydrophobic of Surfactants

- Poor vehicle of slurry
 - Poor uniformity of slurry across pad
- Poor surface modification of particles, such as SiO_2 , CeO_2
 - Agglomeration of particles
 - Wide distribution of particles - macro and micro-scratching
- Residual slurry particles, Al_2O_3 , colloidal SiO_2 , and CeO_2
- Cleaning residual of BTA in Slurry

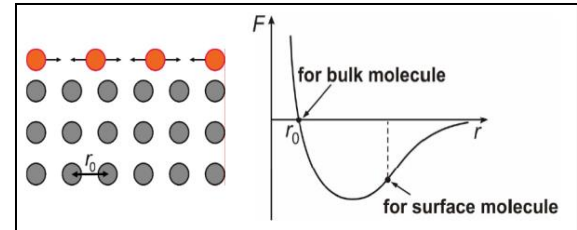
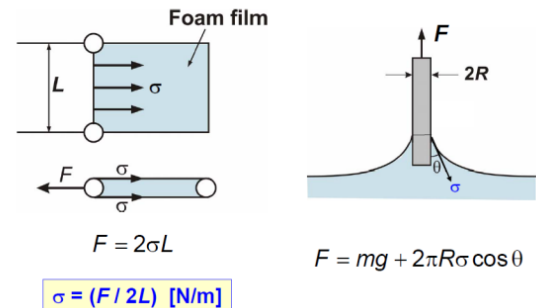
❑ Incompatible of Metal Inhibitors/Oxygen Scavengers

- Non-uniformity of particle dispersion in solution
 - Corrosion of metal, Cu, and W
 - Recontamination
- Aggressive chemicals, high or low pH
 - Corrosion
 - Macro or micro-scratching
 - Poor rinsibility

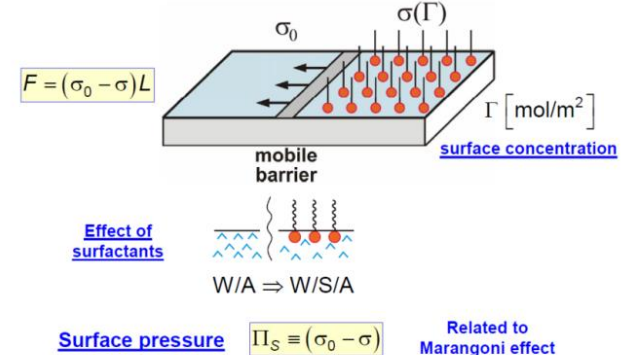
Cleaning Fundamentals

- ❑ **Cleaning Mechanism**
 - Hydrophilic/Hydrophobic balance
 - Surface tension
- ❑ **Metal Cleaning with Inhibitors (BTA)**
 - Better removing particle
 - Corrosion on metal
 - pH range
- ❑ **Classic Non-ionic Surfactants (NIS)**
 - Removing particles
 - Removing Organic Contaminations
- ❑ **Ionic Surfactants (IS)**
 - Aliphatic phosphorous surfactants
 - Metal surface protection
- ❑ **Chelating/Complex Chemicals**
 - Cleaning/removing metal ions and oxides

Surface tension of liquids as a tangential force



Surface tension of spread surfactant monolayers (Langmuir-trough)



New Cleaning Concepts

Surfactanized Metal Inhibitors with Cleaning Functions

❑ Surfactanized Metal Inhibitors

- Hydrophilic metal inhibitor on one side
- Short aliphatic hydrophobic tail
- Maximized protection on metals: **Cu**, W, Ru, Ni, Fe

❑ Surfactanized Oxygen Scavengers

- Long ethoxylated hydrophilic tail
- Hydrophobic oxygen scavenger
- Max scavenged oxygen throughout CMP process

❑ Special Surfactants

- Ethoxylated hydrophilic tail
- Short hydrophobic chain with chelating agent
 - Much better vehicle
 - No **amines (TMAH)** compounds

Briteclean System – How does it work?

Hydrophilic
Metal Inhibitor Head

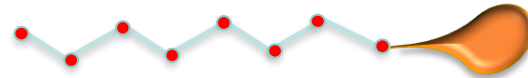
Aliphatic
Hydrophobic Tail



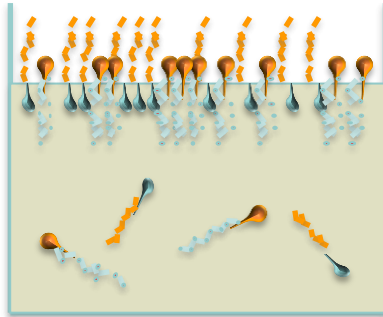
+

Ethoxylated
Hydrophilic Tail

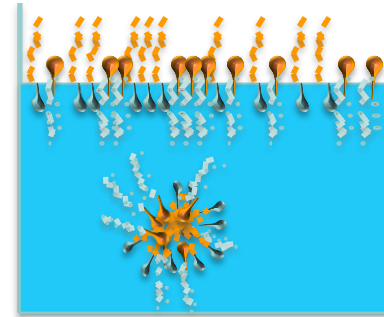
Anti-oxidant
Hydrophobic Head



Briteclean-0plus
Briteclean-Ultra



Briteclean-1



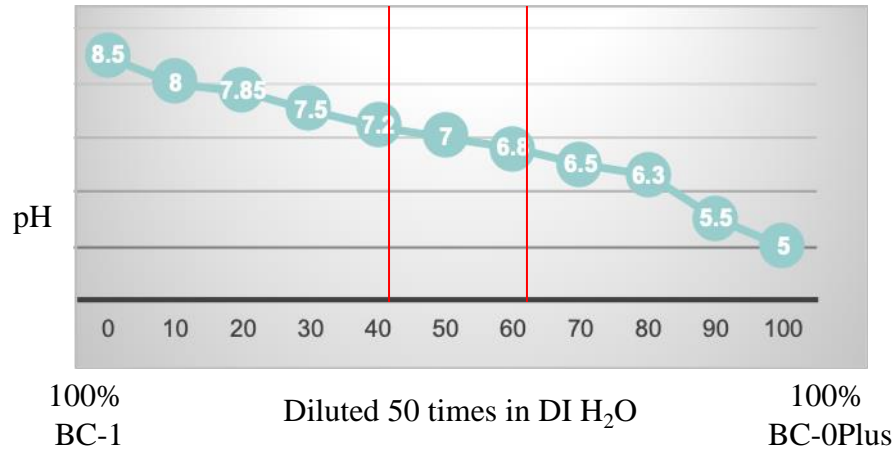
Briteclean-0plus/Ultra : Briteclean-1
= 1:1 Diluted 50 to 1

Briteclean-0 : Briteclean-1 = 1:1
No dilution

Phase Separation

Briteclean System

pH Control and Application Conditions



Recommendation: BC-0plus/BC-1 = 1:1; Diluted to 1%-2% with DI water

	Briteclean - 0/Plus	Briteclean - 1	Briteclean-ACP
Pre/Post Cleaning Process	YES	YES	YES
Slurry Additives	YES	YES	YES
Storage/Buffer	NO	NO	YES
Application	Need to mixing with BC-1 or BC-ACP	Need to mixing with BC-0/plus	Solely
Usage	1% - 5%	1% - 5%	1% - 4%

❑ Process Conditions:

- CMP Tool (8inch): Applied Mirra; Ebara; 6DSSP(Strausbaugh)
- Slurry: Cabot MH8xx system; ASL system
- Pad applied: IC1000; Sub IV
- Cleaning Tool: DNS, SSEC
- Cleaning solution: Briteclean-1; Briteclean-0plus
 - Mixed: Ratio 1:1 in 1.0% - ~2% Aqueous media
- Wafer: **Cu, W, TiN, TaN**, Ni, Fe, Low key, SiOx, Al₂O₃, Ru, etc

Briteclean-Ultra: pH~9.5
Briteclean-3D: pH~5.0

Metal and Cl Elements Content in Briteclean products

Metal Elements (ppb)	Briteclean-0+	Briteclean-1	Briteclean-ACP
Fe	<20	22	53
Cu	28	<5	25
Ni	18	<5	<5
Zn	<5	<5	<5
Pb	<5	<5	<5
Cr	<4	<4	5
Mn	<5	<5	<5
Co	<5	<5	<5
AS	<25	<25	<25
V	<25	<25	<25
Al	<20	32	25
Ti	<20	<20	<20
Mg	<20	<20	<20
Cl	<20	<20	<20

1: Cu, Ni, Zn, Ti, Pb, Mn, Co, V, As were analyzed by EPA Method 200.8 on an ICP-MS (Perkin Elmer DRC-e)

2: Fe, Al, Cr were analyzed by EPA Method 200.7 on an ICP-OES (Thermo iCAP 6300 DV)

3: Cl was analyzed by EPA Method 300.0 on an IC (Metrohm 850)

Note

1: ICP-MS Analysis

2: "<" means below detection limit

Corrosion Test – Cu Wafer

Testing Instrument

- Solution Fixture
- Std Corrosion testing Cell
- Solartro Electrochemical
- Corrosion testing interface



Cu Wafer

Corrosion Test Outputs

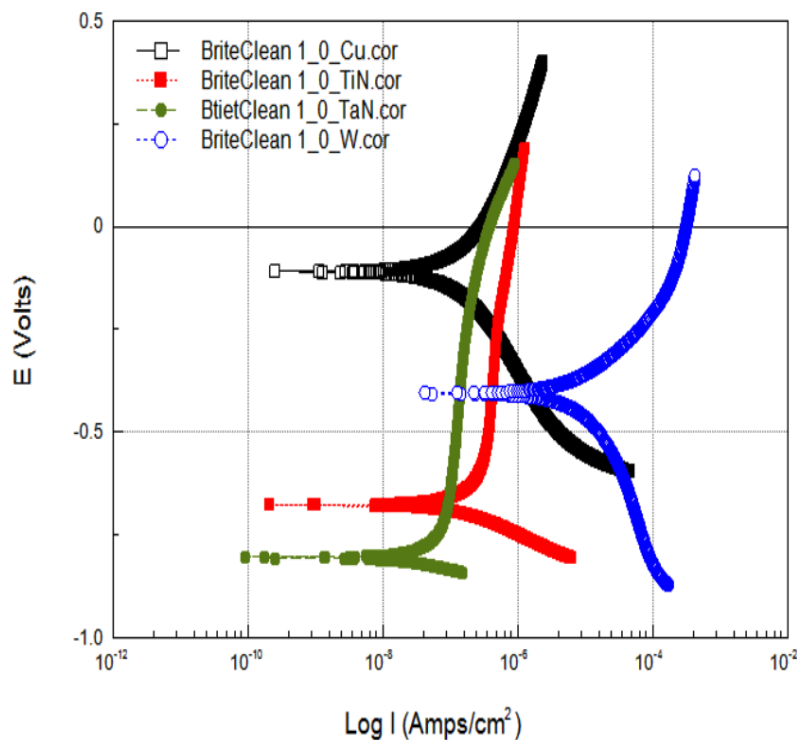
- Tafel/Linear Polarization – Corrosion Rate Measurements
- Galvanic Corrosion Current Measurements
- Electrochemical Impedance Spectroscopy
- Corrosion Rate Measurements under Abrasion

Corrosion Testing Results – Cu Wafer

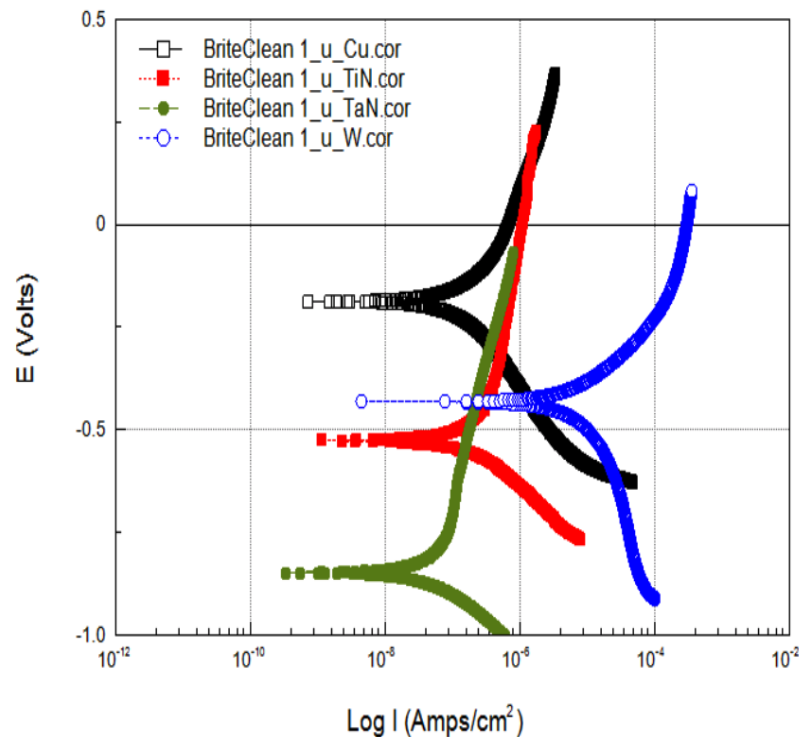
Solution	OCV (vs SCE)	RP (Wcm2) (from linear)	io (A/cm2)	ERR (Angstrom/mi n)
DI H2O	-0.0614	10.8	4.18E-06	0.9236
Best Competitor	-0.242	2135	1.22E-05	2.6845
Another Competitive	-0.294	685	3.76E-05	8.302
Briteclean-0+ /Briteclean-1 = 1:1 2% aqueous	0.1017	3645	7.05E-09	0.0016
Briteclean-0+ /Briteclean-ACP =1:1 2% aqueous	0.1585	2180	1.20E-08	0.0026

Corrosion Testing Results

BC-0plus, BC-1 and BC-Ultra on Cu, TiN, TaN and W Wafer



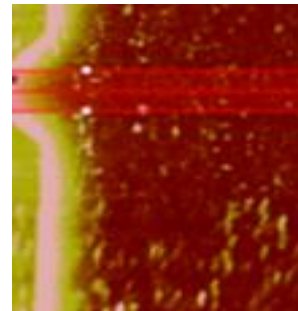
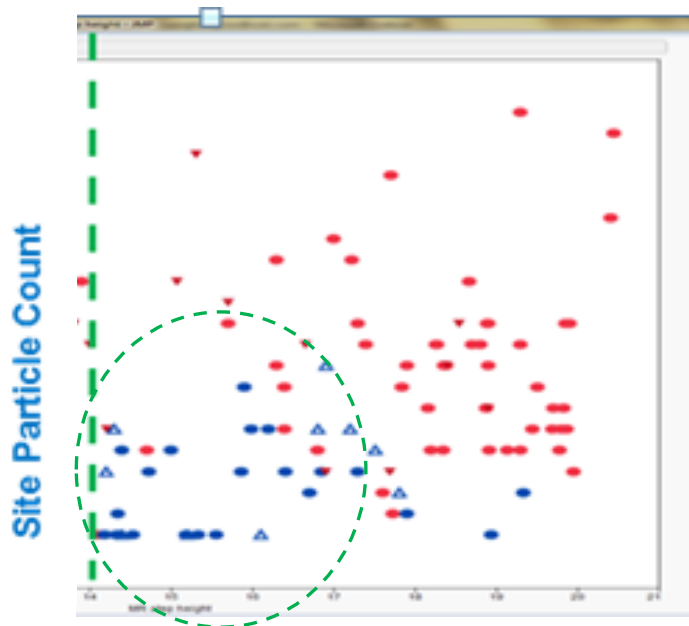
	BriteClean 1_0 (1:1:48)			
Substrate	Cu	TaN	TiN	W
E _{corr} (V)	-0.10764	-0.80145	-0.67662	-0.40374
I _{corr} (A/cm ²)	2.13E-07	8.45E-08	1.98E-07	9.31E-06



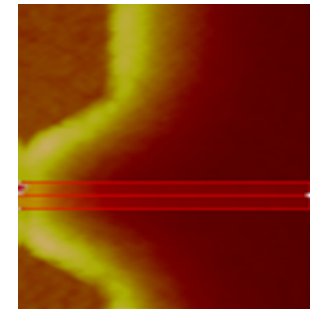
	BriteClean 1_Ultra			
Substrate	Cu	TaN	TiN	W
E _{corr}	-0.18517	-0.52489	-0.84506	-0.4298
I _{corr}	2.60E-07	3.29E-07	9.69E-08	9.14E-06

Briteclean System –Applications

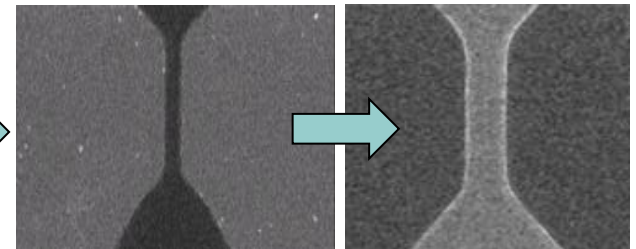
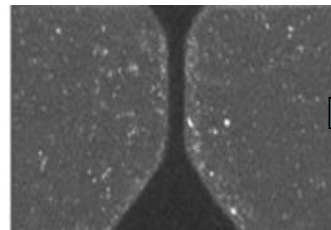
- ❑ Briteclean products are qualified on 7 Major US fab lines
- ❑ Particle Reduction
 - BC cleaning system showed better particle count reduction
 - BC cleaning system showed >40% particle reduction on device production wafers



BC-Product



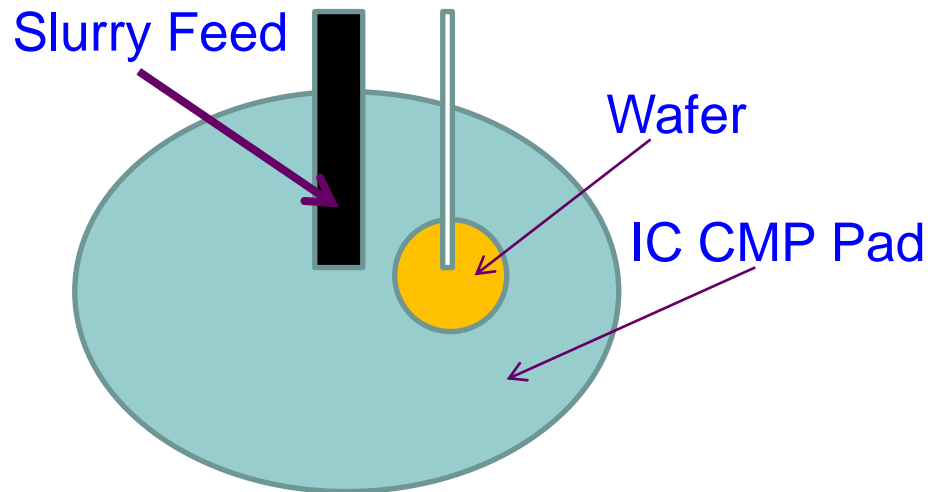
AFM



SEM

Principle of Slurry Additive for CMP Applications

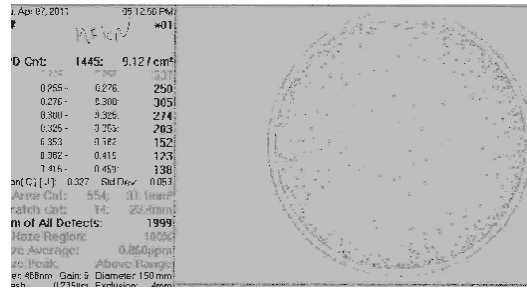
- Slurry distribution on polishing pads is a critical factor to achieve better WIW uniformity
- Adding Brizon products into CMP slurries, the slurry surface extension with IC series CMP pads was modified to form a uniformed slurry layer across the whole wafer



Surf-Clean Imaging For Competitor's Clean Solution

Pre-Treatment

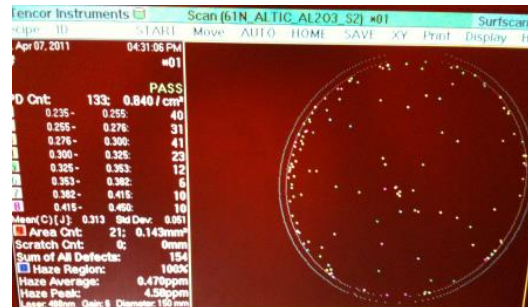
Alumina



Post-Treatment



Cu

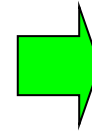
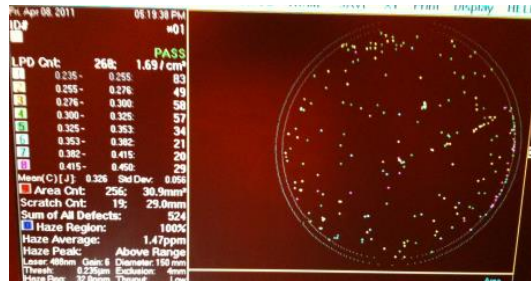


Surf-Clean Imaging For Briteclean Clean Solution

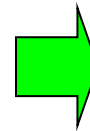
Pre-Treatment

Post-Treatment

Alumina



Cu



Different Slurry Cleanability of Briteclean vs Competitor's

BriteClean mixed Solution		
	Alumina	Cu
Con-1	-70	-66
Con-2	-22	-340
Competitor's Cleaning Solution		
	Alumina	Cu
Con-1	190	280
Con-2	1571	370

Different Method Cleanability of BriteClean vs Competitor's





BriteClean mixed Solution		
	Alumina	Cu
Roller	10	24
Pencil	-10	-6
Competitor's Cleaning Solution		
	Alumina	Cu
Roller	318	2985
Pencil	190	280

Average Particle counts for Briteclean Products on Cu Surface

Briteclean Products	AlOx	SiOx
Briteclean-0	-20	-6
Briteclean-0+	-30	-20
Briteclean-3D	-73	-56
Briteclean-Ultra	-154	-137

Note: Mixed with BC-1, 1:1 ratio (5%:5% in DI H₂O), on Pencil tool

Principle of Cleaning Process for CMP Applications

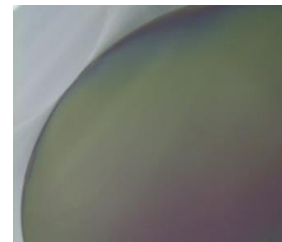
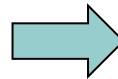
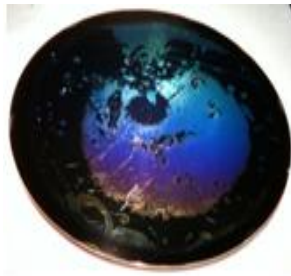
- ❖ Slurry:  Dissolved/Dispersed into Advanced Nonionic Surfactants, Slurry Chemistry
- ❖ Trace Metals:  Dispersed into Advanced Nonionic Surfactants
- ❖ Metal Ions:  Complex to Chelate in the Cleaning System
- ❖ Aggressive Corrosive High/Low pH:  Buffered by the Cleaning Solution

Briteclean System –Applications

❑ Surface Quality improved

- Prevent AlO_x wafer surface without pitting with BC products
- Metal surface improved

Full AlO_x film
pitting – long
time in DI water



No film pitting – x2
time in DI water +
Briteclean

Other Cleaning Solution

BriteClean Mixture



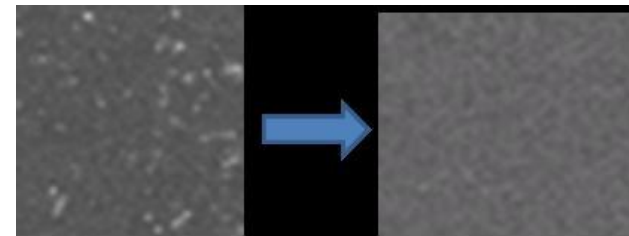
Average Roughness(N=3x3): Rms=0.34nm

Cu AFM Image

Average Roughness(N=3x3): Rms=0.29nm

Other Cleaning Solution

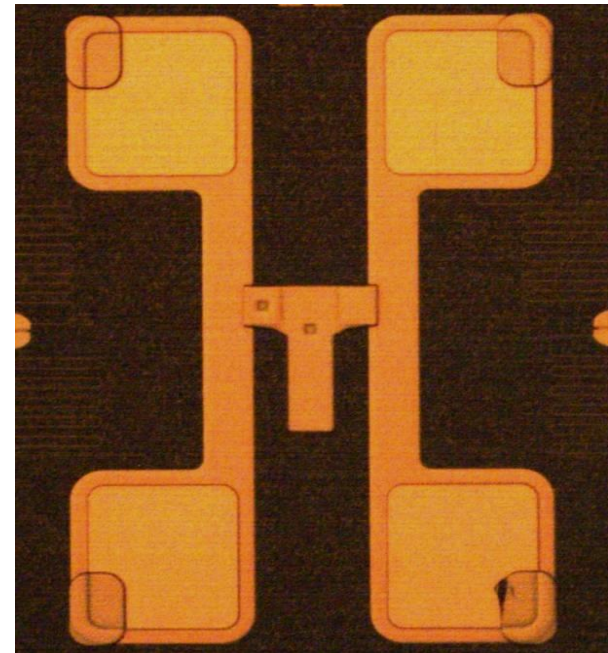
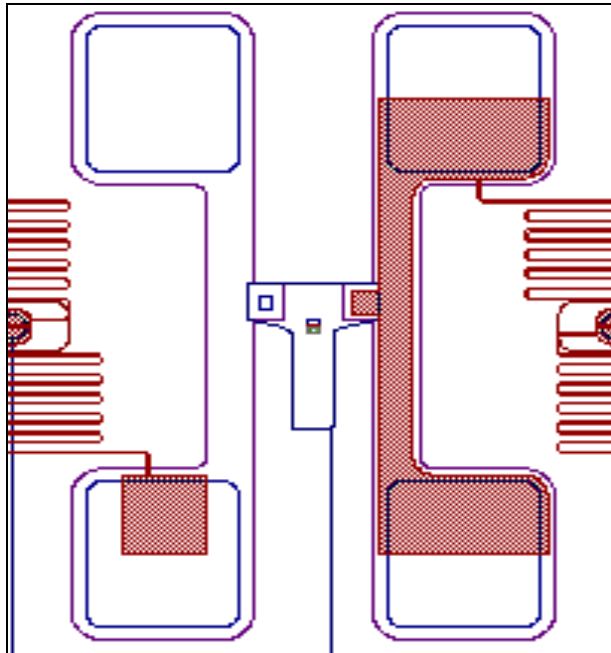
Briteclean Cleaner



Cu SEM Image

Briteclean System –Applications

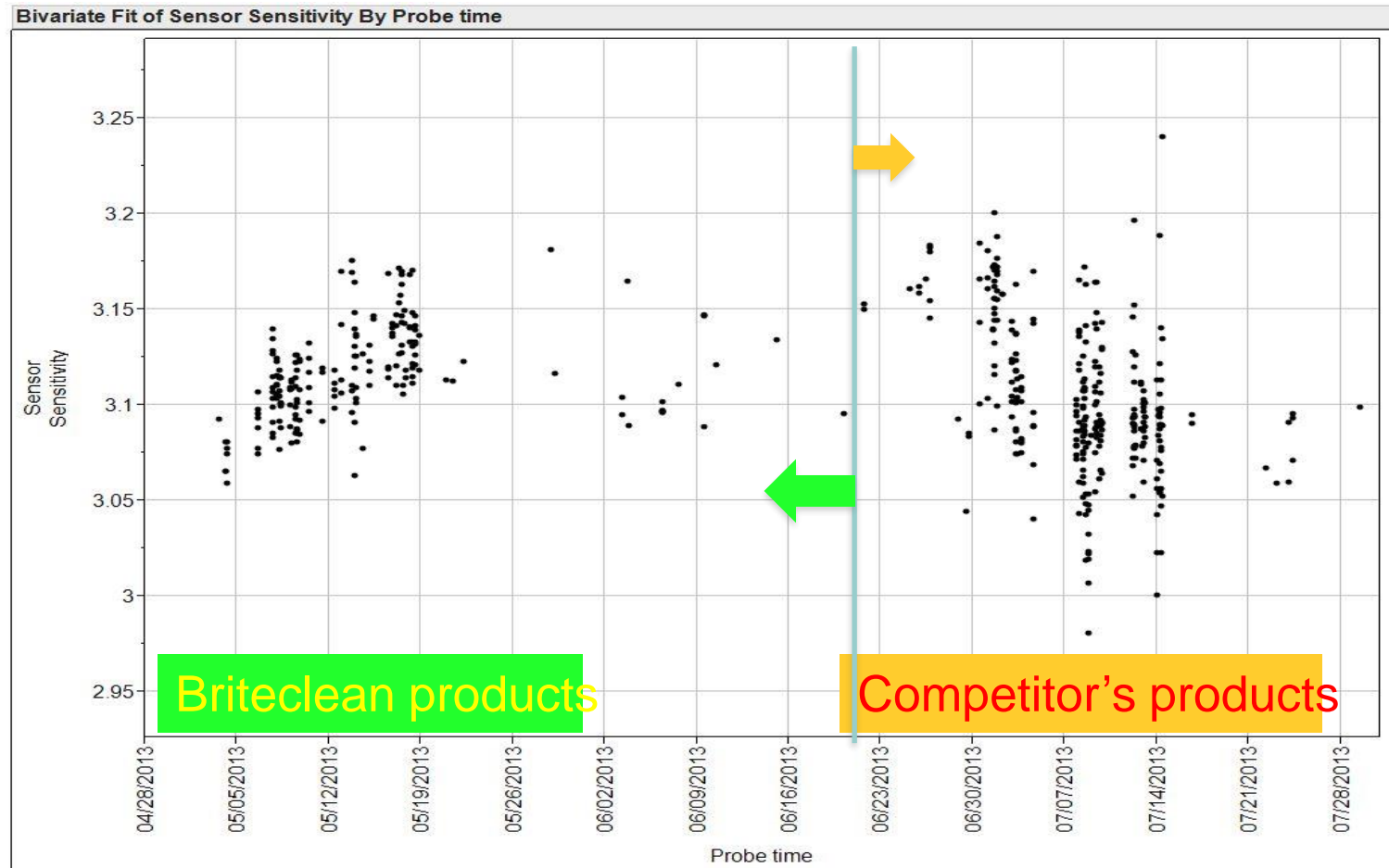
Sensor Circuit Measurement



- Sensor dimension was designed per different usages.
- 4-point scheme minimizes contact resistance during probing

Briteclean System –Applications

Sensitivity Measurement Trend Chart



Summary

- ❑ Briteclean Products use a new surfactanized metal inhibitor and anti-oxidant cleaning approach
- ❑ Cleans major metal surfaces, dielectrics materials, slurry & photo residues with one solution
- ❑ Highly efficient cleaning with significant particle reduction and better surface quality
- ❑ Easier to handle and simpler process on all tools
- ❑ Briteclean products in daily use on many fab lines for over 9 years
- ❑ Other advanced cleaning products also available