Tackling Critical Requirements for Advanced Post-CMP Cleans

Paul Bernatis

May 16, 2012

EKC Technology

DuPont Electronics & Communications

DUPONT

The miracles of science™

Outline

Introduction

- Product roadmap
- Copper post-CMP cleaning
  - Critical requirements

Cleaning and Compatibility

- Physical displacement, charge-charge repulsion, dissolution
- Dielectric compatibility, spontaneous and galvanic corrosion

Stability

- Dendrite mitigation
- Minimization of heavy oxide growth

Summary and Path Forward

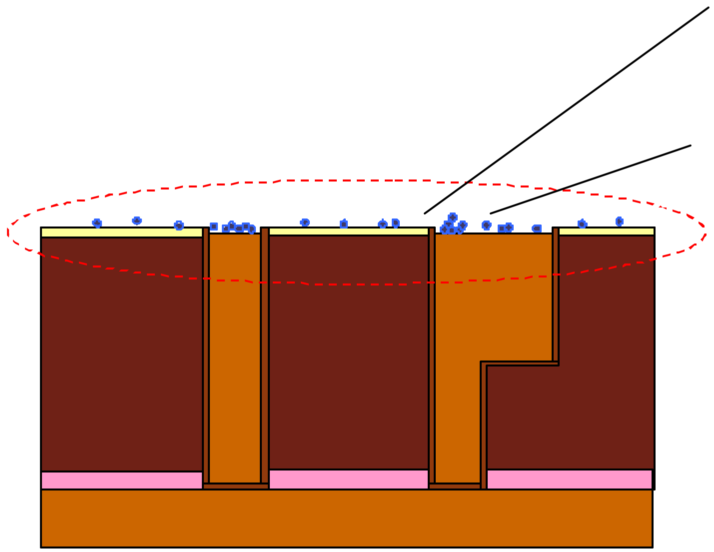
DuPont-EKC PCMP Product Roadmap

EKC Technology: Copper Interconnect Technology Roadmap									
	Advanced Technology Customer Roadmaps								
Year	2007	2008	2009	2010	2011	2012	2013	2014	2015
Production Node	45nm		32nm			22nm		16 nm	
Cu Post-CMP Cleaning									
GEN I PRODUCTS	PCMP 4000/ PCMP 5000 SERIES								
GEN II PRODUCTS	**PCMP5510™**								
GEN III PRODUCT: GEN III-N									
GEN III PRODUCT: GEN III-A									
GEN IV PRODUCTS: 22 nm: Co						**PCMP 5600 / 5610™**			
TDP: Al PCMP									
TDP: TSV PCMP									
Research Project: Particle Adhesion Studies									
Research Project: Organic Defect Studies									

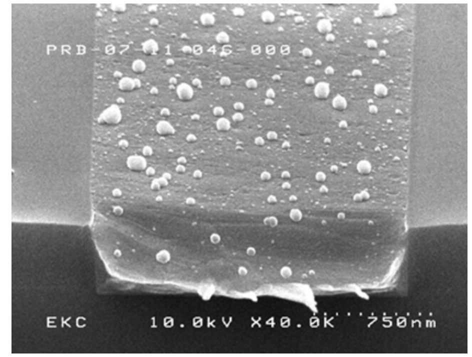
= Technology Development Program
= Commercialized
= Extendibility
= Research Project

The Need for Post-CMP Cleaning

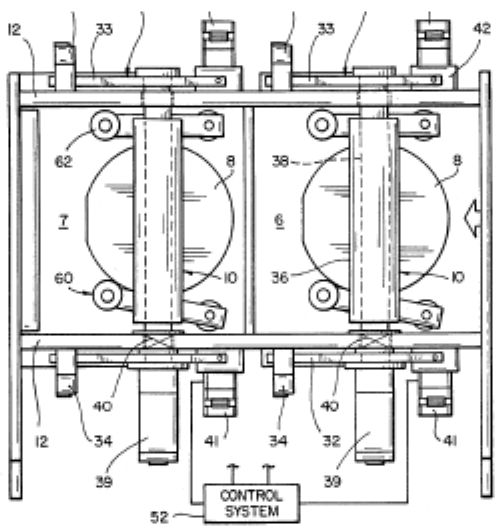
Inadequate residue removal leads to:
–poor adhesion of subsequent layers
–electrical shorting or leakage
–insufficient device reliability



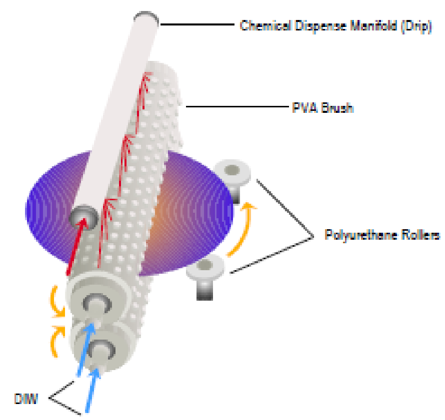
Pre-CMP Clean



Residues include:
–SiO_2 particles
–organics
  – from slurry
  – pad and brush
–metal ions
–organometallics



Top down view of brush module(s)

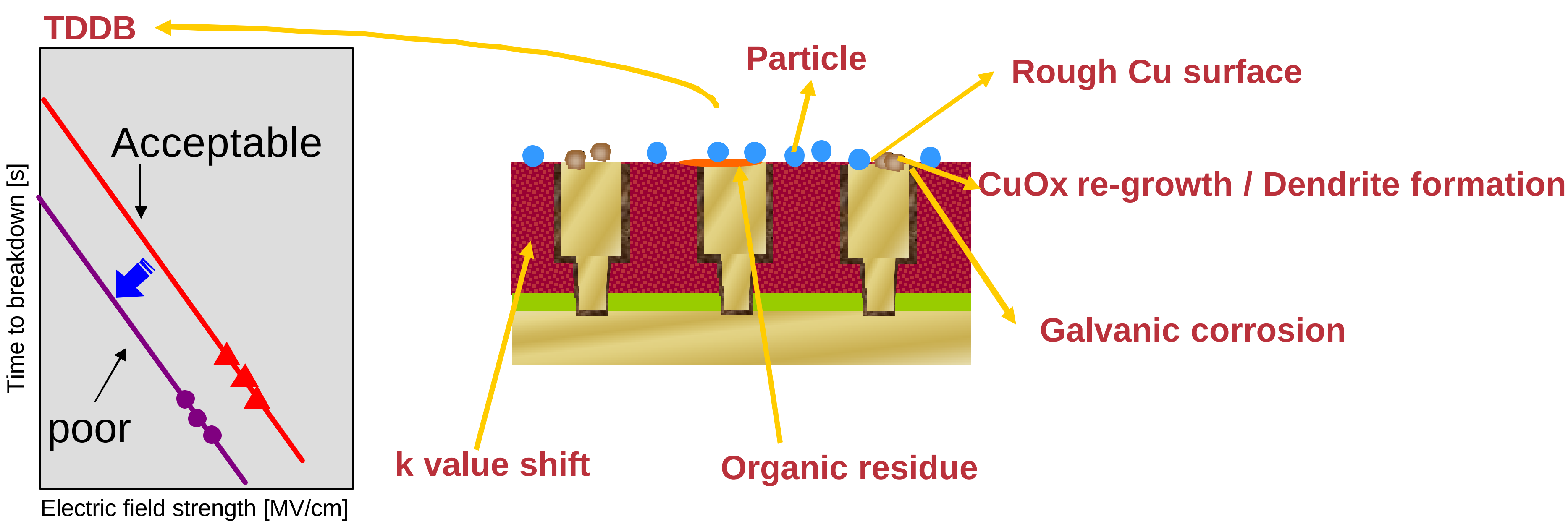


Side view of brushes

Critical Requirements for Post-CMP Cleaners

1. Removal of particles
   - Slurry
   - Organic residues
2. Remove metal ions
3. Minimal corrosion and etching of the conductor
4. No dendrite growth
5. Mitigate copper oxide protrusion growth on the cleaned surface during storage
6. No modification of the dielectric which could lead to k-value shift
7. No increase in line resistivity or decrease in device reliability
8. Safety
   - No TMAH or other highly toxic components
   - No components with potential environmental issues
9. One year shelf life and one week pot life
10. Low cost of ownership

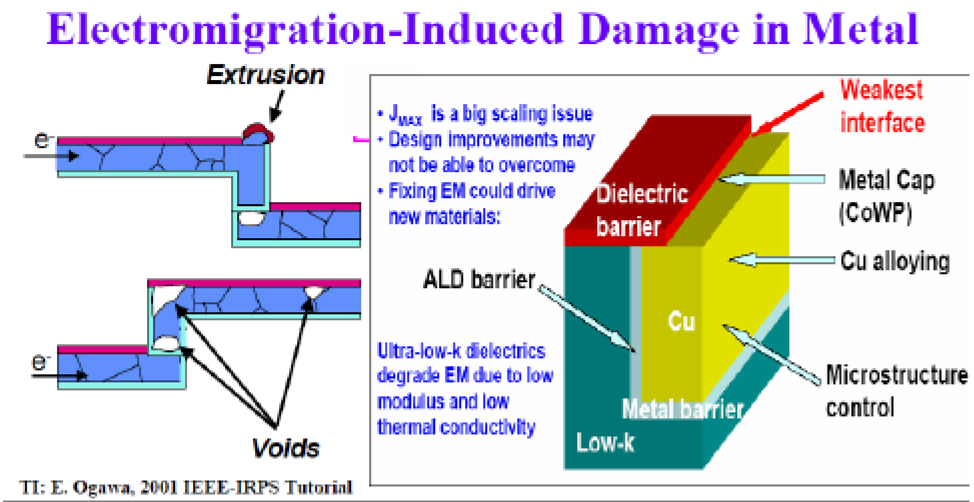
Design of EKC™ PCMP5600 (Gen IV Cleaner)

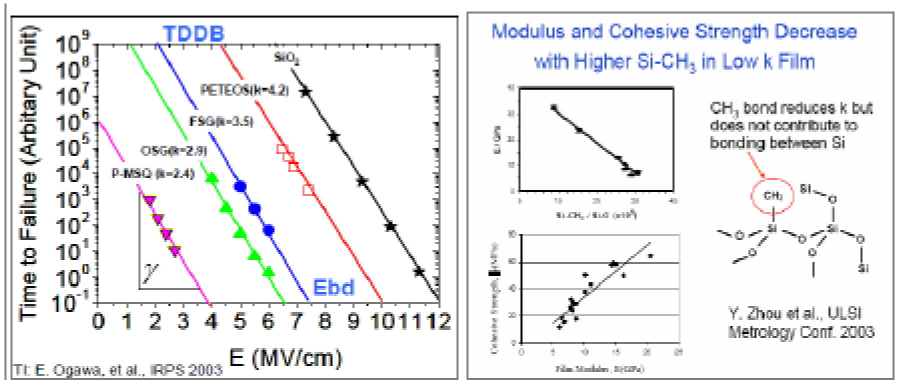


1. **Removal of slurry (or abrasive) on dielectric** by physical displacement and maximizing zeta potential
2. **Removal of slurry (or abrasive) on Cu** by mild undercut, physical displacement, and maximizing zeta potential
3. **Removal of impurity metals** by dissolution and sequestration with chelating agents
4. **Removal of Cu-Organic complex (ex. Cu-BTA) and CuOx** by
   1) displacement with chelating agent
   2) dissolution with ligands
5. **Smooth Cu surface and prevention of oxide re-growth** by inclusion of non-aggressive passivating ions
6. **Advanced barrier material compatibility** by controlling OCP, pH, and including passivating agents

Factors Affecting TDDB

1. **Poor adhesion between capping layer and copper or dielectric**
2. **Metal migration along the liner**
3. **Dielectric modification and breakdown**





- **Lower-k silica-based materials generally have lower Ebd and TDDB**
- **Lower-k materials generally have lower modulus and lower mechanical strength**
- **UV and/or e-beam shown to be effective at increasing strength/hardness**

Images from presentation on internet site by J.W. McPherson http://videos.dac.com/43rd/slides/12-1slides.pdf

Particle and Residue Removal

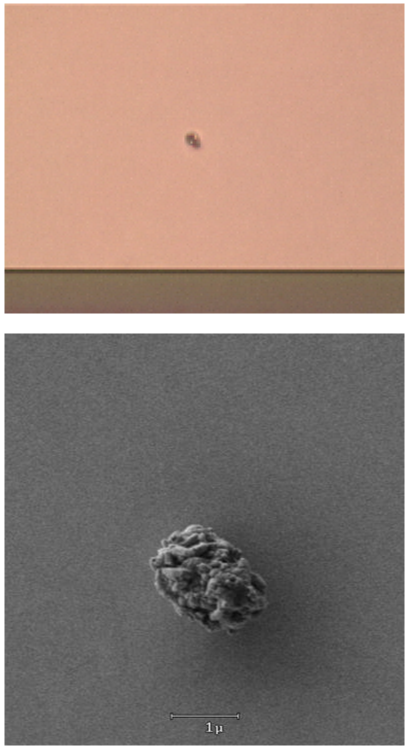
Formulation Design and Key Components

Class	Ligands	Function
Group 1 dissolution agents	highly water soluble mono and polydentate acids	facilitate metal ion removal, prevent crystallization and dendrite formation
Group 2 dissolution agents	mixed amines	facilitate organic residue removal including BTA, disrupt bonds to copper oxide via weak etch, block re deposition via competitive bonding
base / pH adjuster	hydroxide base with highly water soluble counterion	maintain high pH and zeta potential preventing particle re-deposition, facilitate BTA removal

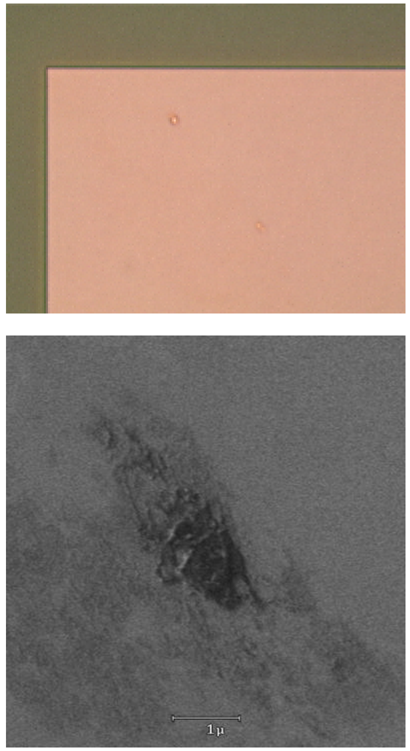
Chemical Properties

- Aqueous, alkaline pH = 10 ~ 12
- Contains proprietary chelating agents and anions to remove metallic impurities and organic residues
- No TMAH
- Optional : surfactant

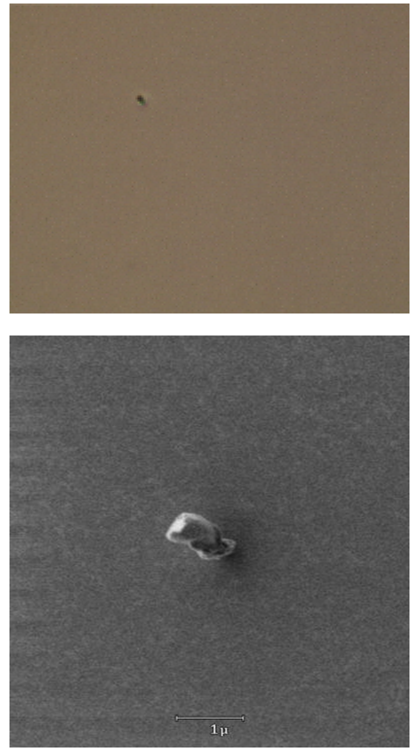
Particle Residues Observed On Patterned Wafers



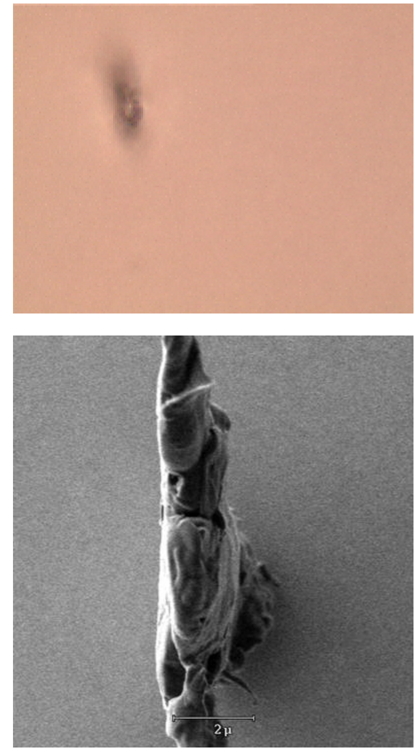
Typical



Atypical



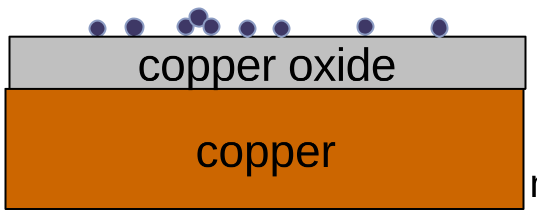
Typical



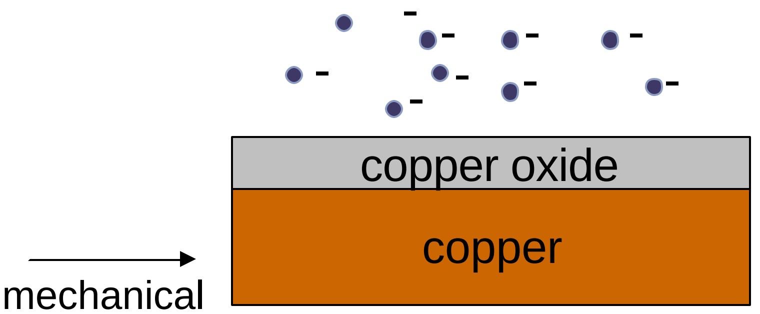
Typical

Typical residues appear to be loosely held “fall on” residue. A smaller amount of embedded residues are observed. The majority of defects are on the copper lines.

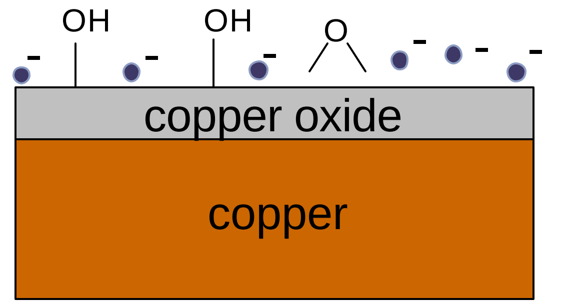
Zeta Potential in EKC 5600/5610 Was Optimized for Charge-Charge Repulsion



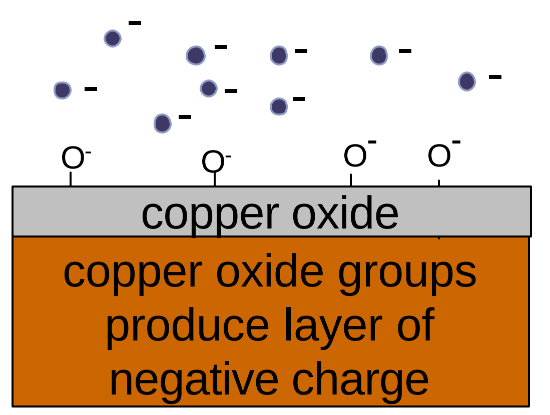
Residues on post-CMP surface



mechanical displacement of slurry with brush



Re-deposition can take place on uncharged surface at lower pH



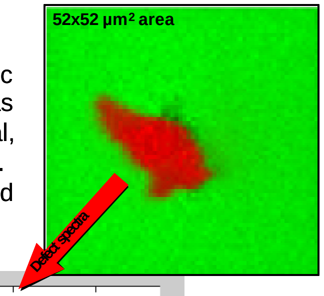
Charge-charge repulsion of negatively charged copper oxide and negatively charged particle prevents slurry re-deposition at high pH

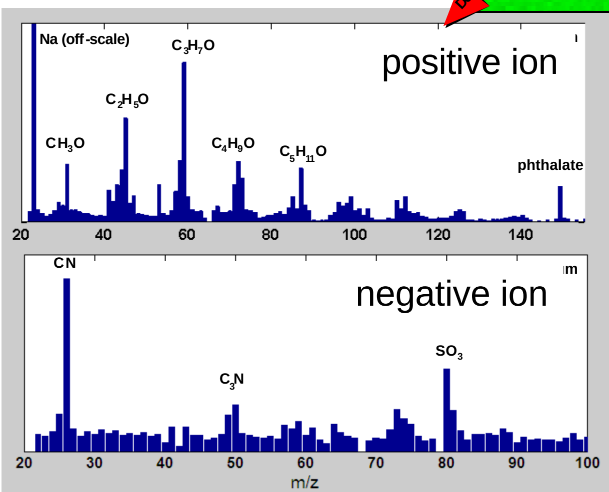
DUPONT

ToF-SIMS Characterization of Residues

Organic Defect

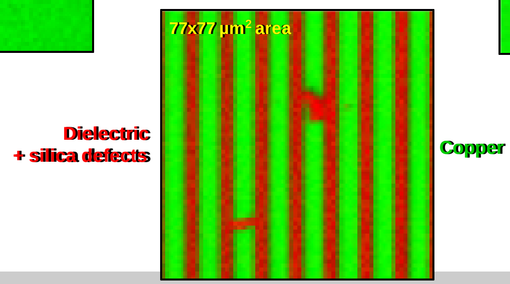
This defect exhibits ions characteristic of either cellulose or glycol as well as degraded nitrogen-containing material, with surfactant compounds mixed in. One possibility is degraded CMP pad plus backing.

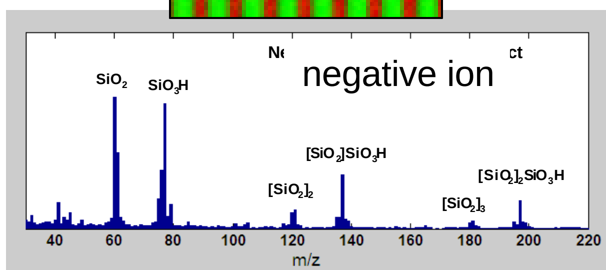




Silica Defects

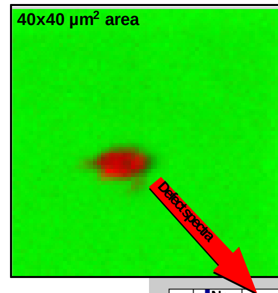
Many defects are agglomerated silica from polishing slurries. The spectral signature is similar to that of the carbon-doped silica dielectric.

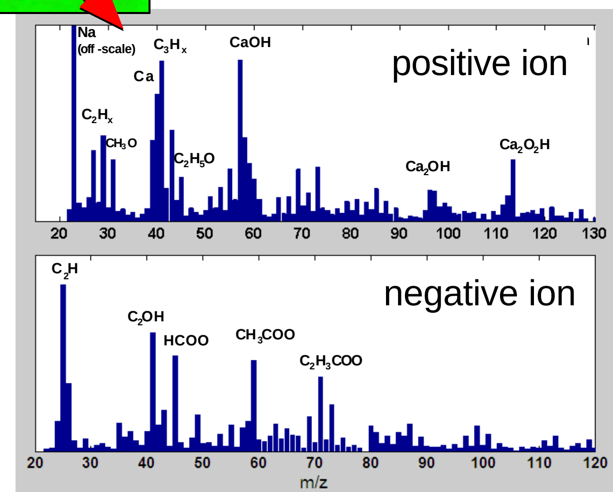




Organic/Inorganic Defect

This defect exhibits ions characteristic of carboxylate/acetate functionality plus calcium oxide/hydroxide. One possibility is degraded post-CMP cleaning brush plus entrapped inorganic material.



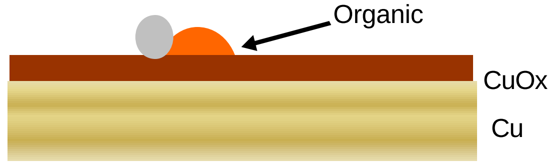


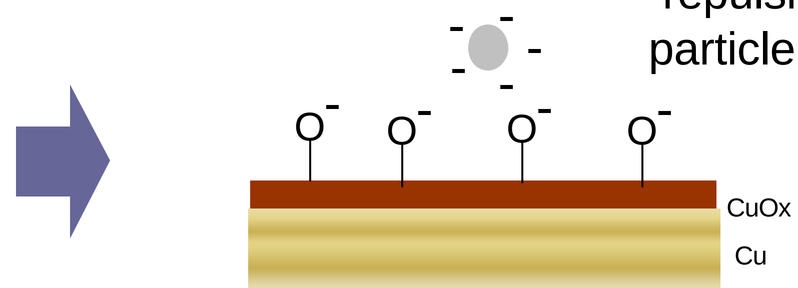
A definitive match between the residues and control samples of pad and brush were not seen. Particles sloughed from the pad or brush might be more degraded than the intact material making it impossible to ever completely match control and residue spectra.

Small Particle Removal With EKC 5600/5610

CASE 1 : Mixture of organic and inorganic [embedded]

•attachment of particle through organic surface residue



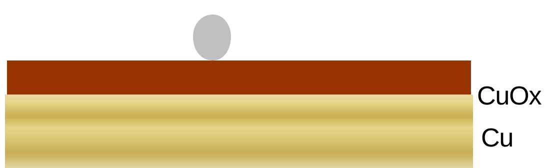


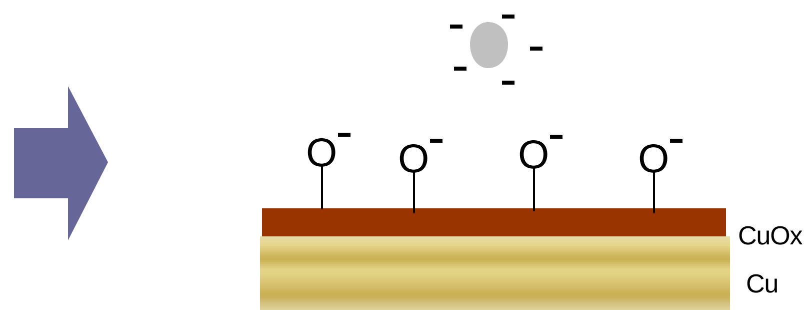
charge-charge repulsion between particle and surface

Mild undercut to release particle

CASE 2 : Physically attached

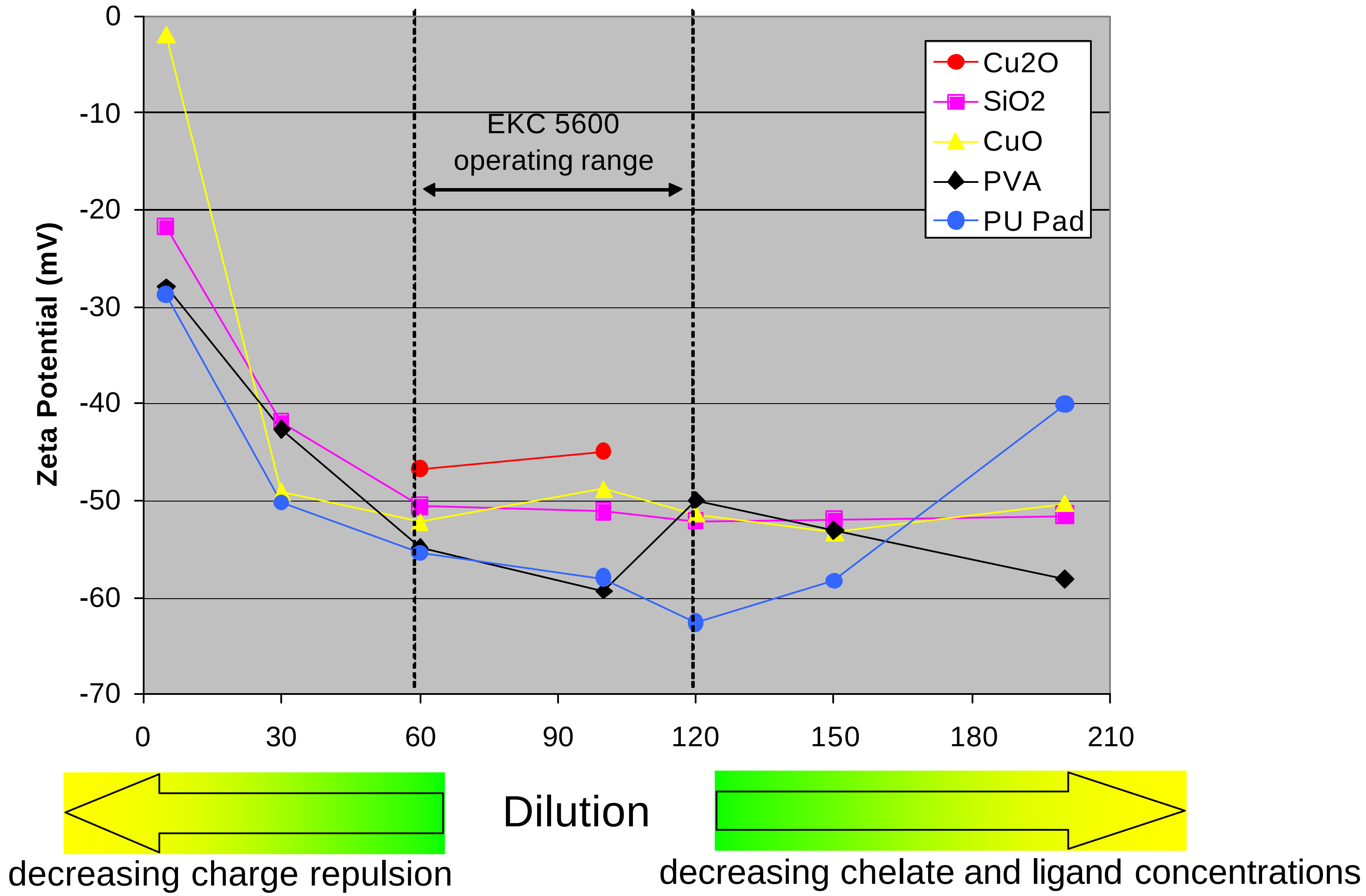
- Physically attached on surface
- Re-deposited due to poor ZP.





Mechanical displacement and strong zeta potential to prevent re-deposition

Zeta Potential of Particle Residues and Wafer Surfaces in EKC 5600 at Dilution Extremes



Brush particles were made from a AION PVA brush
Pad particles were made from a IC 1000 polyurethane polish pad

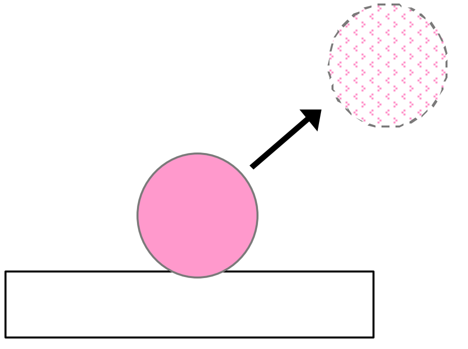
Dissolution and Solubilization of Contaminants

A) Ligand Facilitated Metal and Organic Contamination Removal

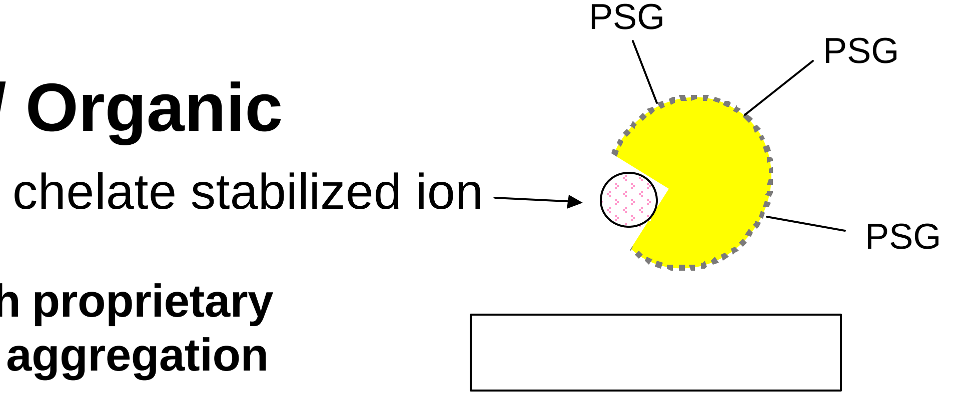
Dissolution, decomposition

Cu(L')n (insoluble) + L ⟶ Cu(L)n (soluble)

L' = BTA or other poorly soluble group



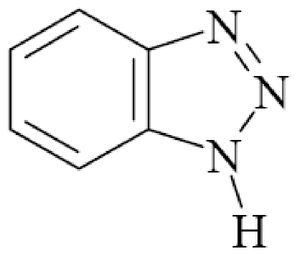
B) Prevention of Metal / Organic Re-deposition



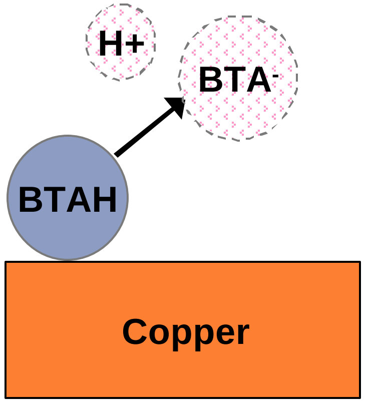
Chelation of contaminant ions with proprietary blend of chelating agents prevent aggregation and precipitation

PSG = polar solubilizing group

Basic pH Favors BTA Removal and Solubilization



•pKa (25 °C) pKa 8.2



Copper Surface BTA Removal

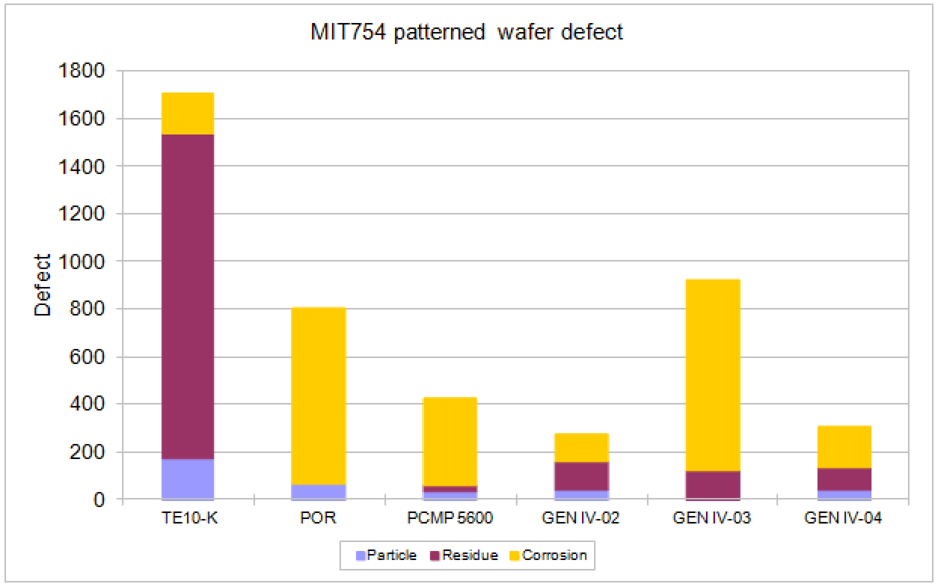
$$BTAH + OH^{--} \rightleftharpoons BTA^{--} + H2O$$

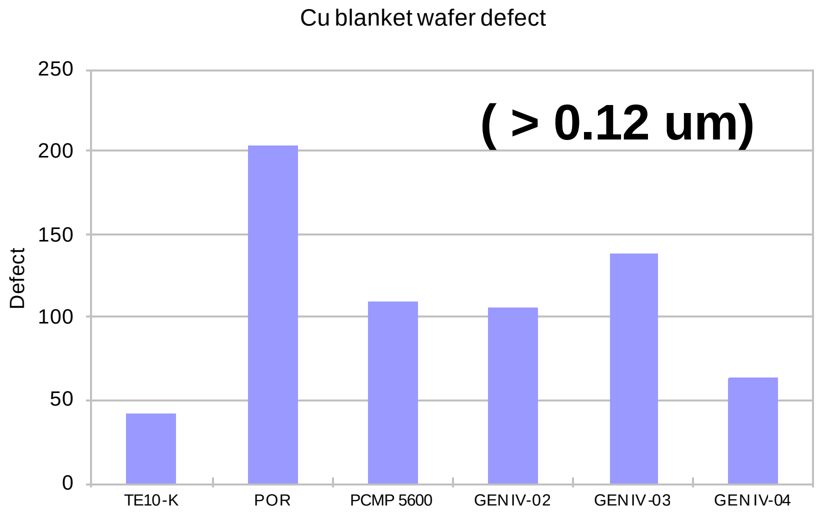
Inhibitor residues from slurry typically include a thin layer of chemisorbed BTA. EKC™ PCMP5600/5610 has a pH 10.3 / 11 respectively allowing it to extract the proton from the weak acid BTAH and remove the film through:

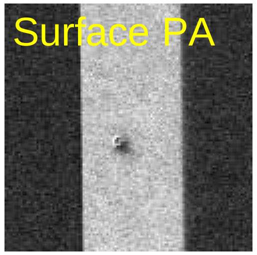
- •mild copper oxide undercutting and release
- •competitive bonding of ligands in the cleaner that impede re-deposition of BTAH or BTA^-.

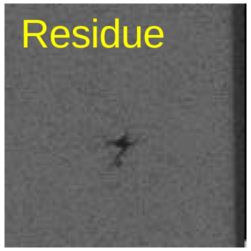
1)-1 Defect Data on Patterned and Blanket Wafers

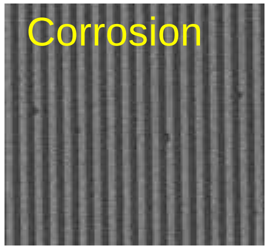
Tool : 300 mm commercial CMP tool









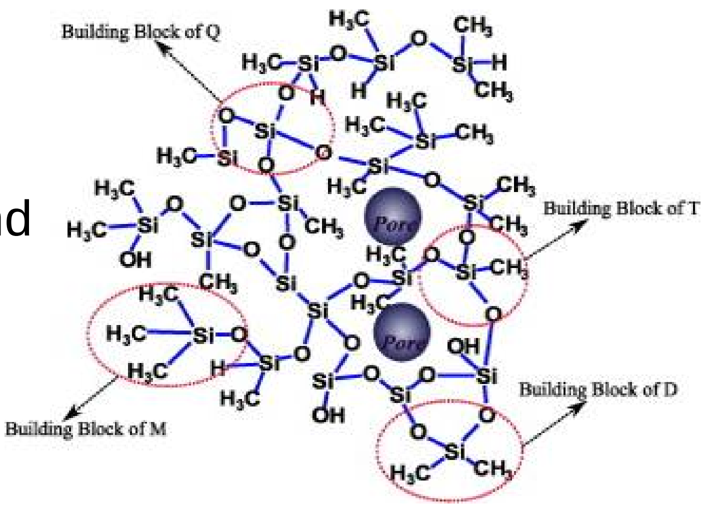


Particles classified with SEMVISION G4 and measured on a SP2 or AIT

Post-CMP Clean
Substrate Compatibility

Key EKC™ PCMP5600/5610 Design Criteria: Clean Fragile ULK Without Damaging Porous Framework

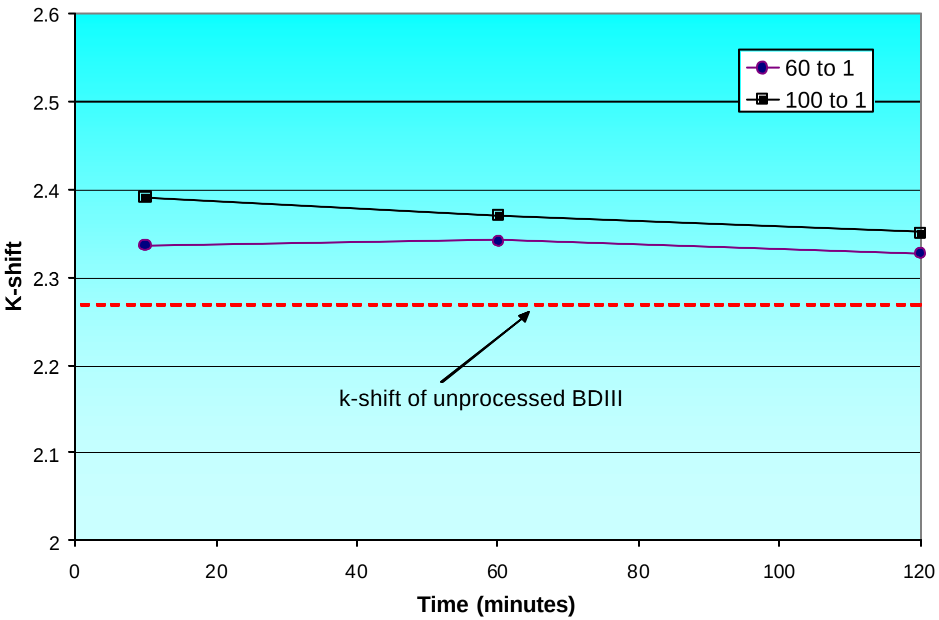
Black Diamond series



Structure from ***Microelectronics Reliability*** 47, 2007, 1483.

Cleaning challenges:

1) Minimal k-shift
2) No dielectric cracking
3) No harmful residues
4) No undesirable chemical modification of the dielectric

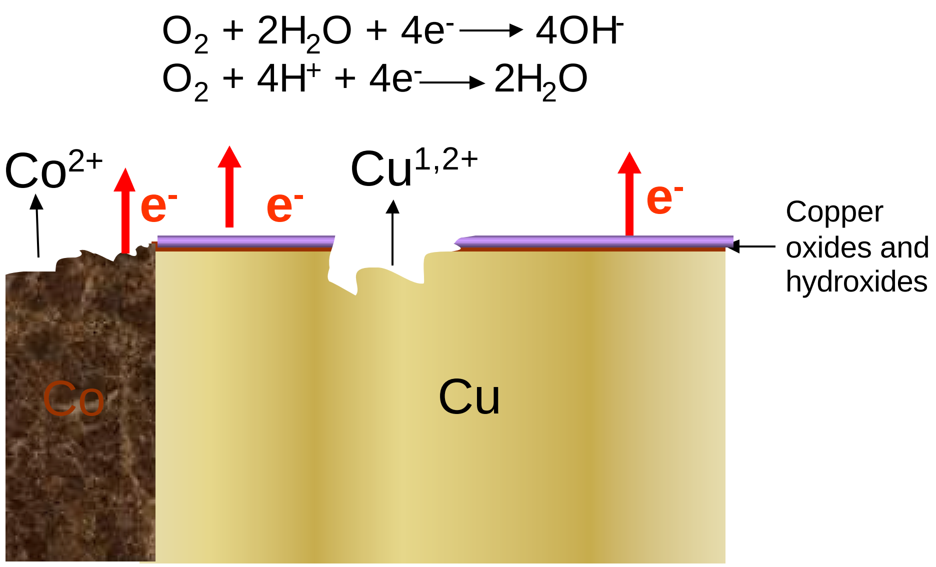


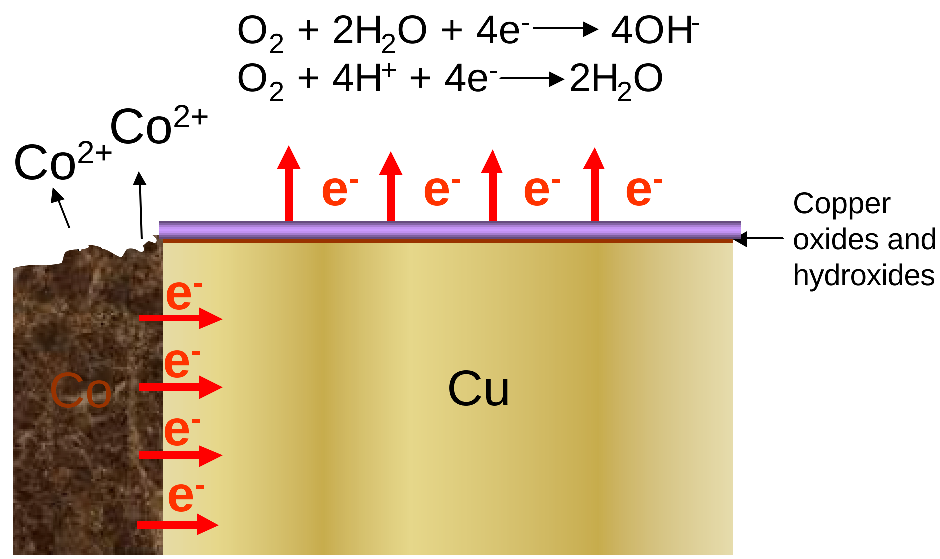
Almost no k-shift observed for EKC™ PCMP5600/5610 and BDIII even at greatly extended intervals

K-shift measured on Four Dimensions mercury probe

DUPONT

Factors Affecting Cobalt Corrosion





OCP [V] : V_{Co} @ V_{Cu}

Primary factors for spontaneous corrosion

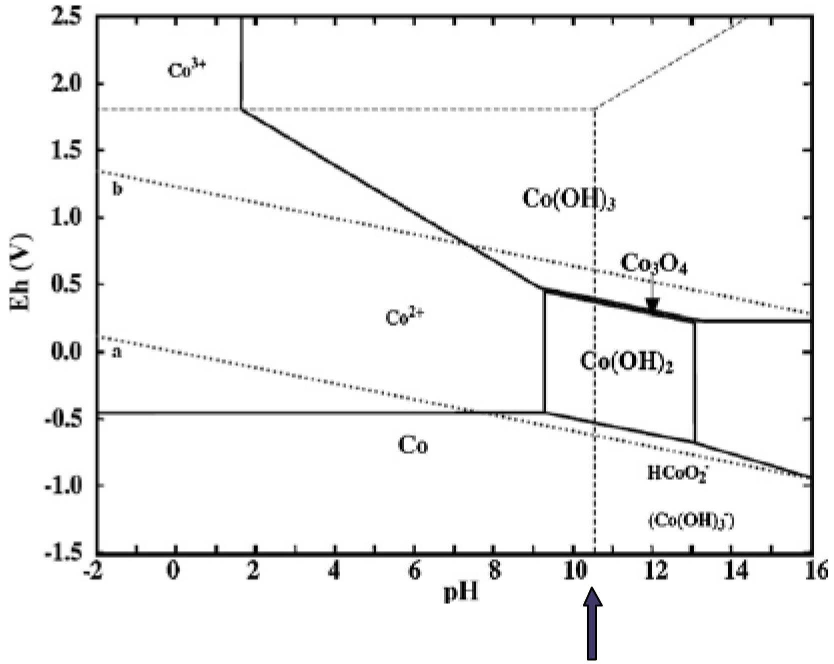
1. Oxidation potential of metal
2. Self passivation via oxide formation
3. Aggressiveness of ions in solution
4. pH

OCP [V] : V_{Co} < V_{Cu}

Primary factors for galvanic corrosion

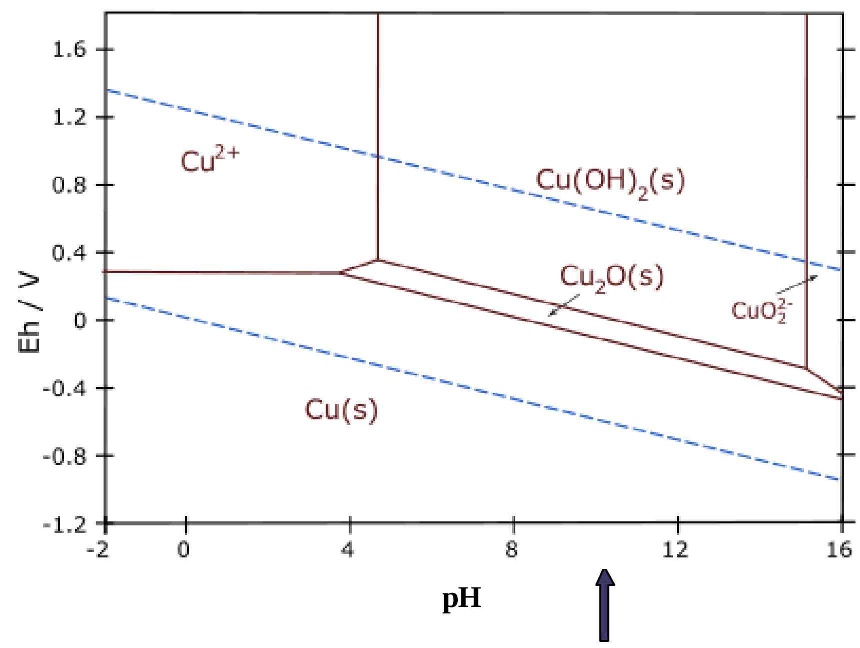
1. OCP difference between two metals
2. Electrical conduction of solution
3. Exposed area ratio (can be affected by ligand coverage)

At the High pH of EKC™ PCMP5600/5610 Cobalt is Less Susceptible to Etching



EKC[TM] PCMP5600/5610 pH at POU = 10.3

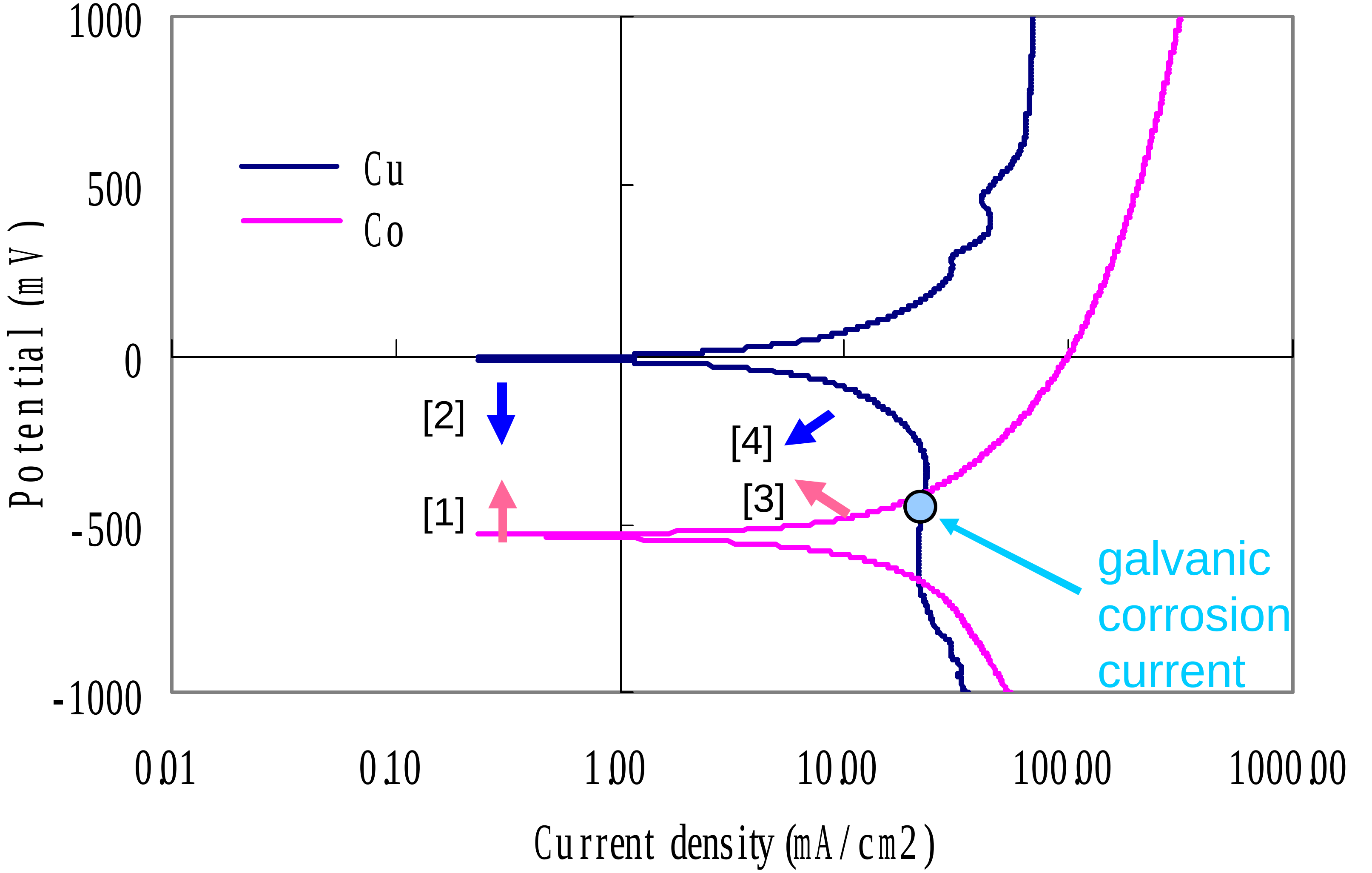
Pourbaix Diagram for Cobalt



EKC[TM] PCMP5600/5610 pH at POU = 10.3

Pourbaix Diagram for Copper

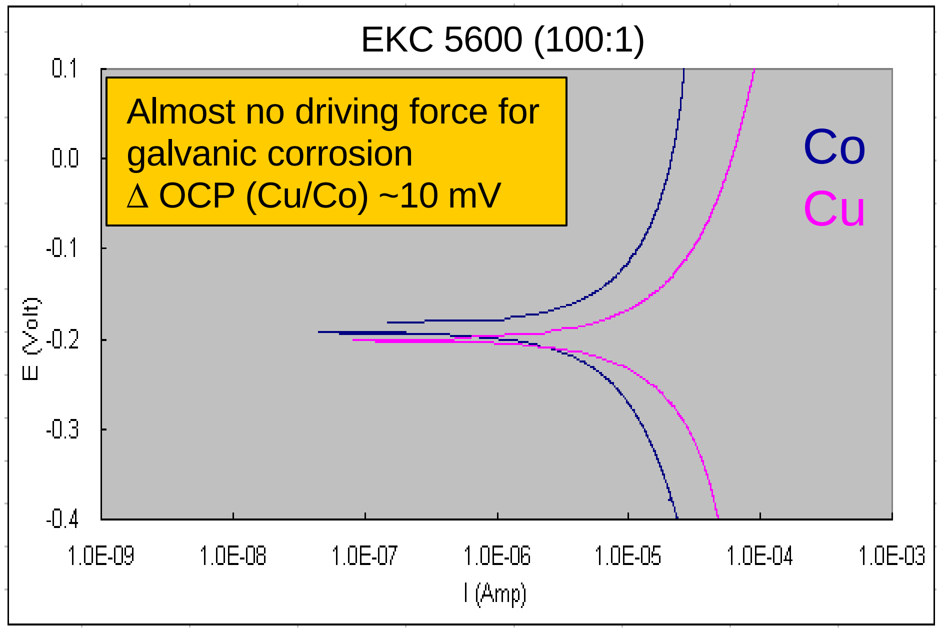
Approaches To Reduce Galvanic Corrosion



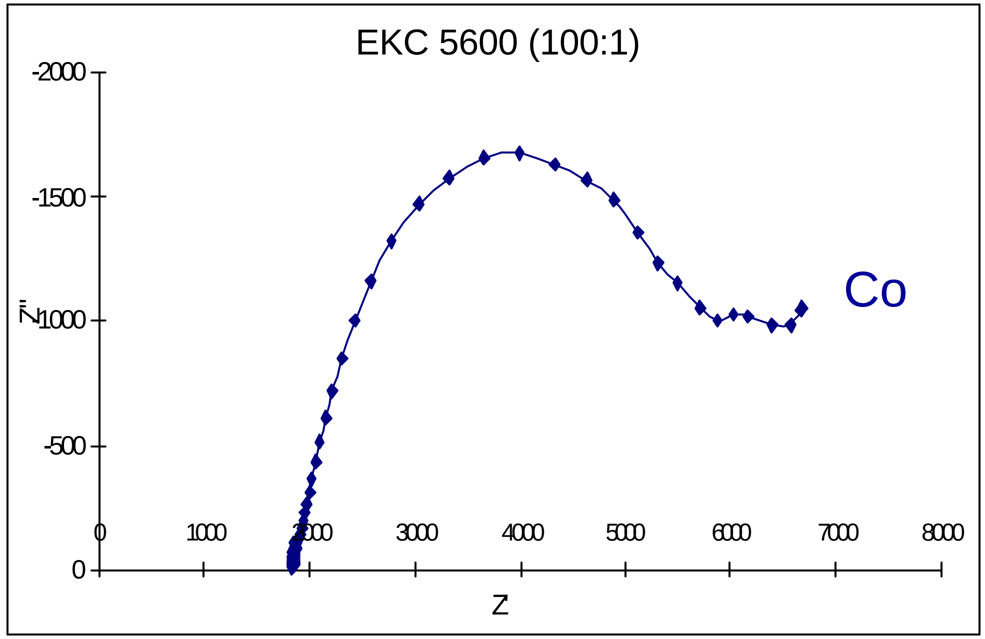
Approaches to reduce galvanic current

1. Increase Co OCP
2. Decrease Cu OCP
3. Reduce Co anodic current
4. Reduce Cu cathodic current

Advanced Barrier Material Compatibility



Tafel plots for copper and cobalt in EKC™ PCMP5600/5610



AC impedance data for copper and cobalt in EKC™ PCMP5600/5610

Ligands that interacted with the surface of the metals shifted their open circuit potential (OCP). Ligands were chosen for EKC™ PCMP5600/5610 that minimized the OCP difference between metals and therefore the thermodynamic driving force for galvanic corrosion.

In Stress Test, Device With Cobalt Liner Extracted With EKC™ PCMP5600/5610 Was Almost Completely Un-etched After 30 Minutes

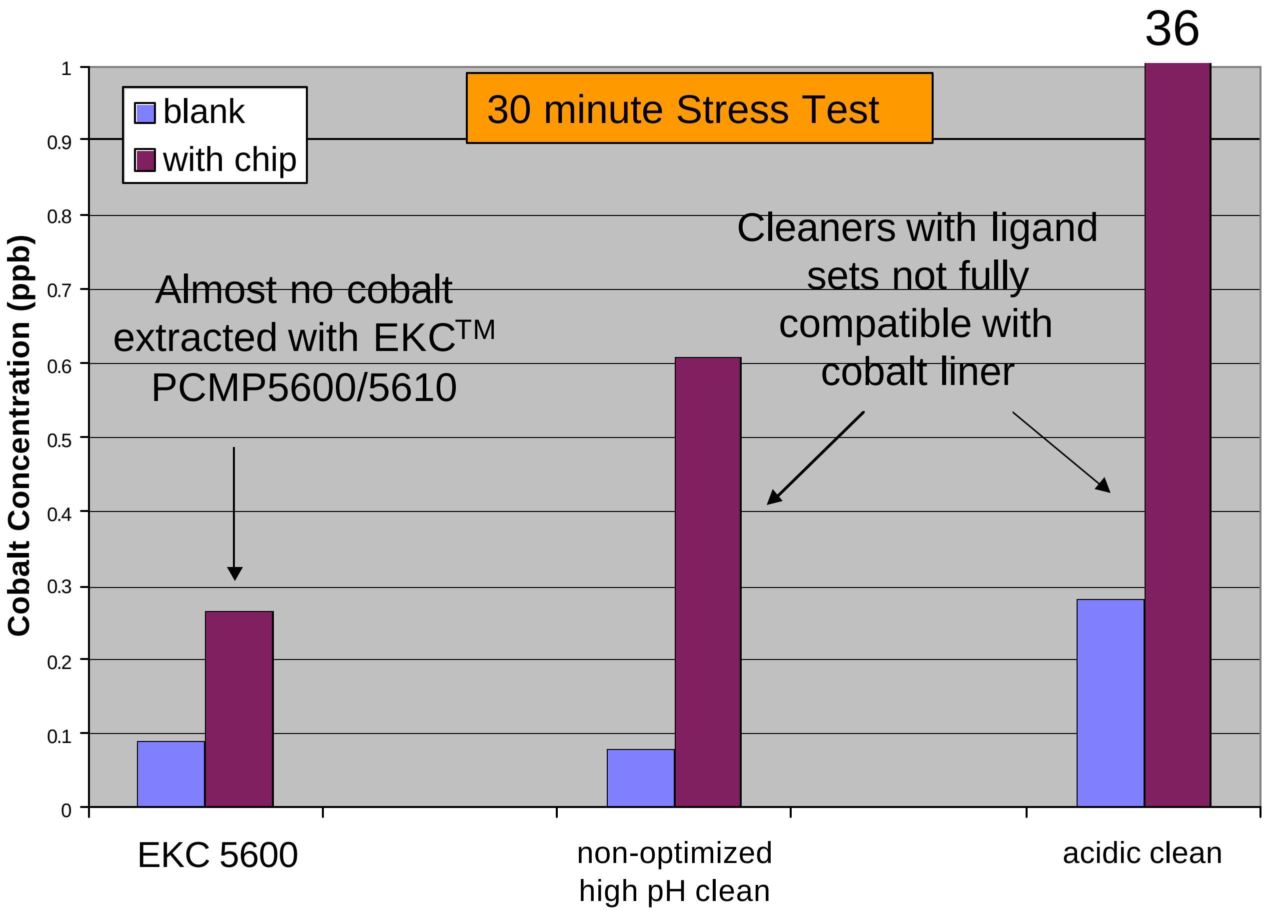
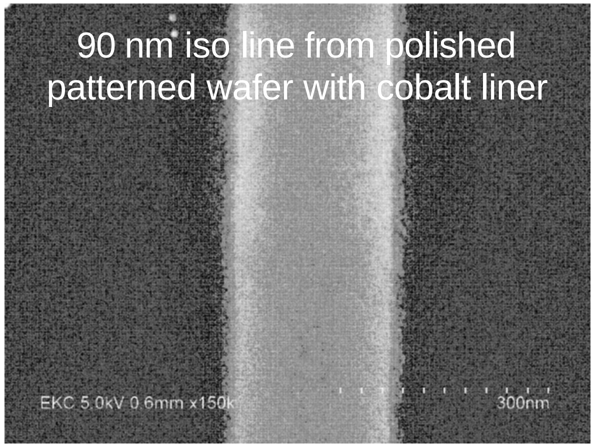


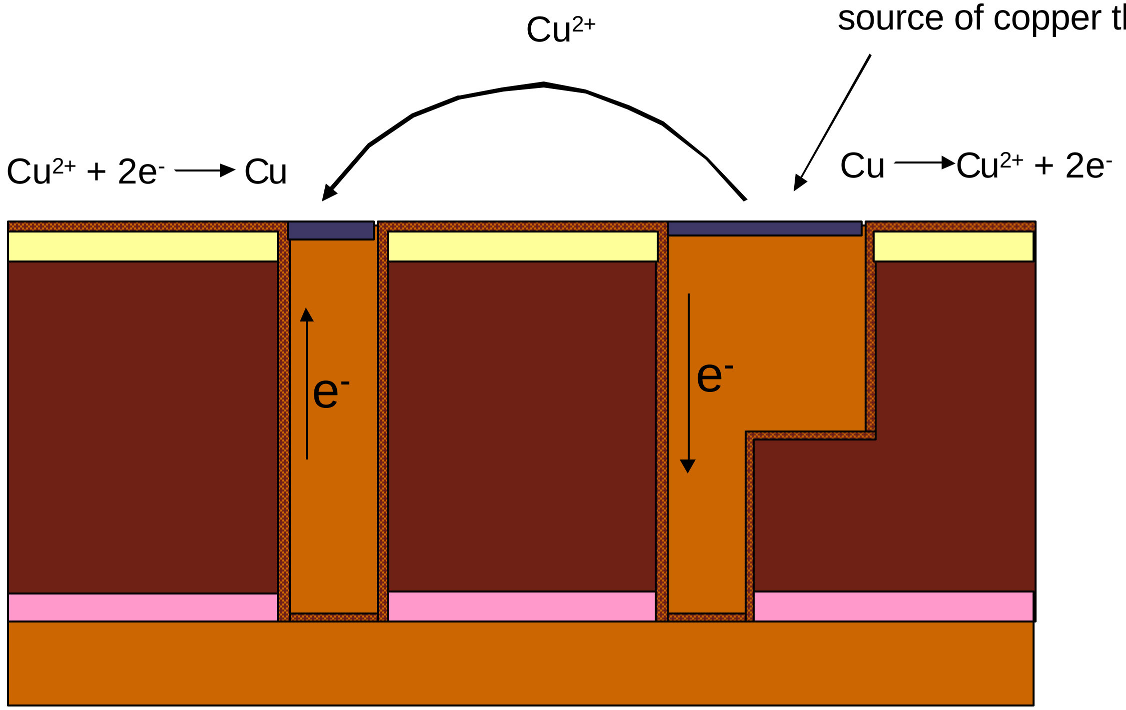
Chart showing amount of cobalt extracted from patterned wafer chip with cobalt liner that was suspended in stirred solution of cleaner for 30 minutes.

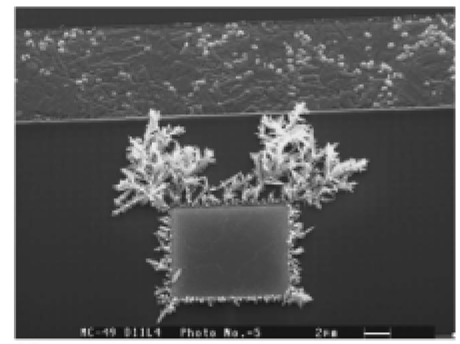


Under normal process conditions (~2 min clean) no corrosion was observed by SEM with EKC™ PCMP5600/5610

Stability of Cleaned Substrates

Potential Mechanisms for Mitigation of Dendrite Formation by EKC™ PCMP5600/5610





From Ostermann, R. et al. J. Electrochem. Soc. 154, H393, 2007

Example of dendrite growth from literature

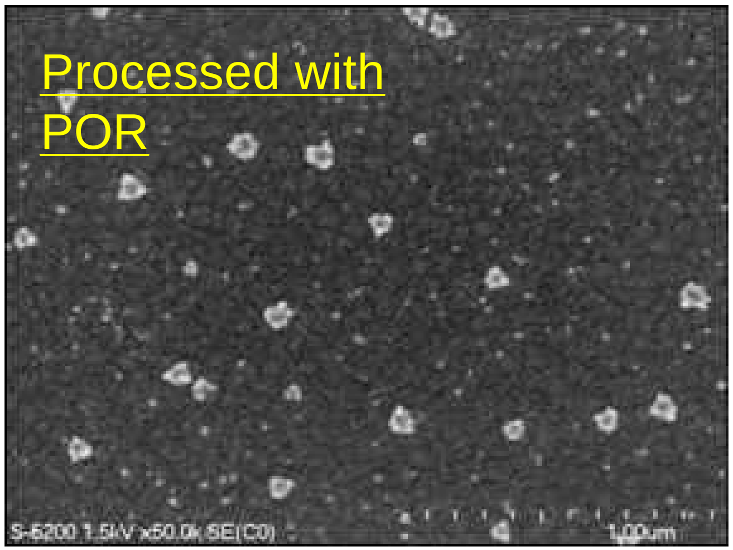
- During cleaning, components in the EKC™ PCMP5600/5610 formulation affect the copper oxide structure as it is mildly etched and reformed during cleaning altering the oxide density and stability.
- The structure and stability of CuO_x as it grows on the surface has been shown to be greatly affected by the nature of ions present in solution. See for example Kang, M. C. et al. Electrochem. Solid-State Lett. 12, H433, 2009; Grimes, C. A. et al. Mater. Lett. 65, 2011, 1949.
- Copper ions on strongly passivated surfaces are less available for electrochemical reduction and dendrite formation.

At POU the pH is 10.3 for EKC 5600. CuO_X is predominant copper species on surface

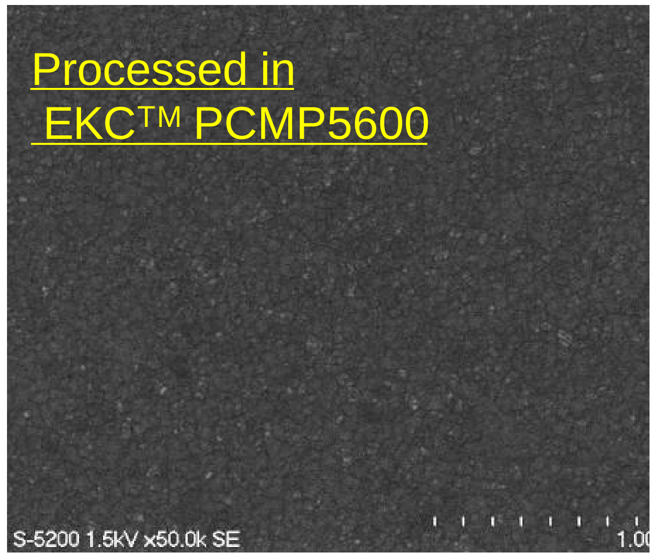
Copper Re-oxidation Characteristics

(accelerated condition)

- **Sample: Wafer Coupon**
- **SEM (S-5200)**
- **Process : Cleaner 1min -> DIW5min**



Growth of structures on surface without EKC™ PCMP5600/5610 gives evidence for ion mobility and general instability



Unpolished blanket copper wafers which were dipped in cleaner and then stood in DI water before being examined by SEM for oxide growth and protrusions

Summary of Key Features Associated with The Cleaning Ability of EKC™ PCMP5600/5610

- In EKC™ PCMP5600/5610, the conductor and dielectric surfaces have a strong negative zeta potential that prevents re-deposition of negatively charged slurry

- Ligands and chelates facilitate contaminant dissolution and prevent aggregation and precipitation that would lead to re-deposition.

- No evidence is seen for degradation of the dielectric even at greatly exaggerated cleaning times.

- Through tuning of the proprietary ligand set the driving force for galvanic corrosion was almost completely eliminated.

- The ligand set favorably interacts with copper oxide and data indicates ion dissolution and migration is suppressed that can lead to dendrite formation.

The miracles of science™