# Enabling Low Defectivity Solutions Through Co-Development of CMP Slurries and Cleaning Solutions for Cobalt Interconnect Applications

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# Versum Materials' pCMP Cleans Overview

- **Track record**
  - Since 1998, we have been a HVM supplier of pCMP products to leading IDMs and Foundries in NA, EU and Asia
  - Ashland →Air Products (DA Nano)→ Versum Materials
- **Differentiations**
  - Integrated Slurry and Clean Co-design and Co-optimization
  - Only post-CMP Cleans supplier with combined CMP slurry and pCMP cleans product development in one location
  - Depth of understanding of roles of surfactant, chelating agent, corrosion inhibitors and particle (removal / defect control) for pCMP Cleans
- **Commercialized pCMP product applications**
  - BEOL and MOL Metals (Copper, Tungsten, Cobalt, Al HKMG) including barrier
  - BKM for AMAT CMP tool (BEOL)
  - FEOL / STI for logic devices

# Outline

- Challenges in replacing copper with cobalt
- Overview of cobalt CMP and pCMP processes
- Cobalt pCMP cleaning: Corrosion and Defect control
- Simultaneous Optimization of Slurry and pCMP cleans to meet customer requirements

# Interconnects at sub-10nm devices

- **Challenges with copper at sub-10 nm  technology nodes**
  – Increased copper resistivity as grain size reduces
  – Less volume of copper available for electrical conduction as barrier and seed layers do not scale
- **Advantages with cobalt**
  – Superior electro-migration resistance
  – Lower overall resistance compared to copper in small structures resulting from
    - Reduced barrier layer requirements
    - Shorter mean free path of electrons
  – Ability to electroplate with bottom-up fill
  – Already integrated as barrier liner and cap layers in older technology nodes
- **Copper, tungsten local interconnects → Cobalt**

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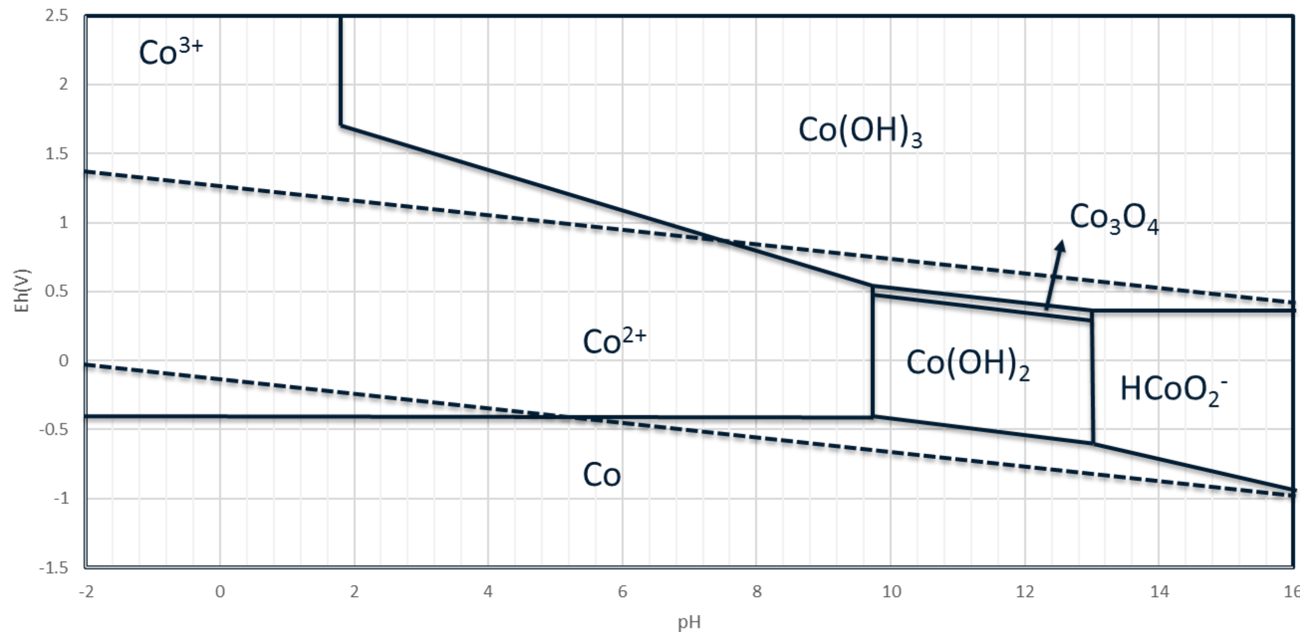
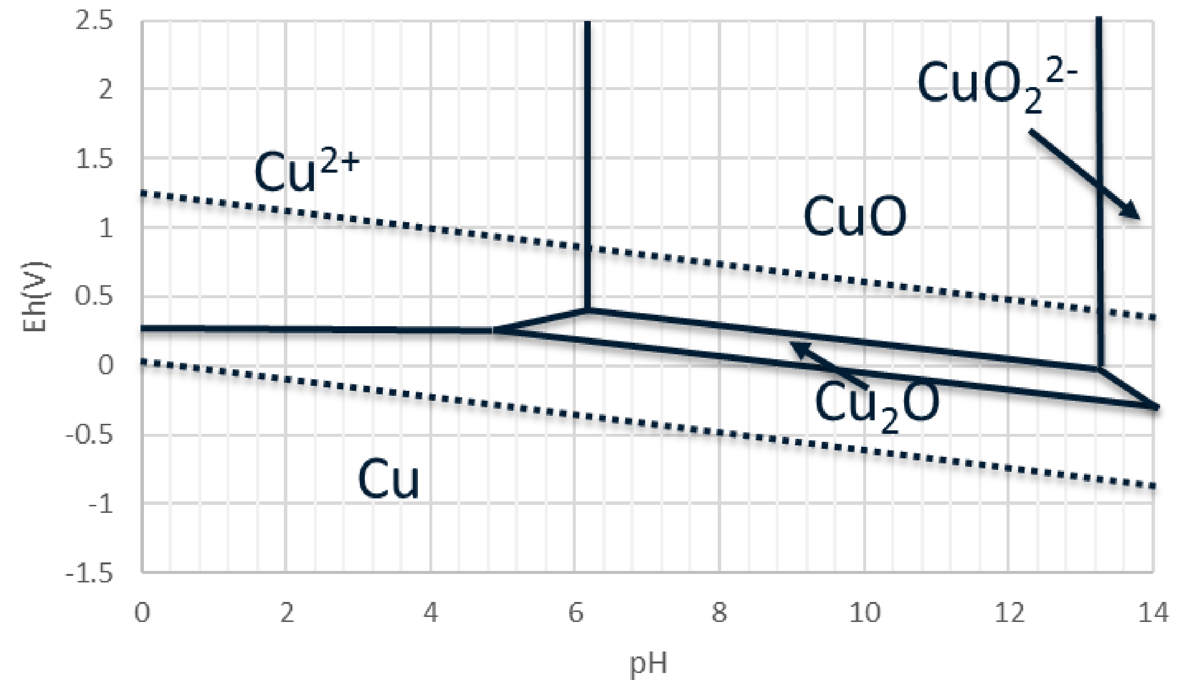
# Challenges with Cobalt




- Cobalt electrochemically very active material
- Thermodynamically cobalt forms stable aqueous species over a wide Eh-pH range
- Stable passivity regime extremely limited

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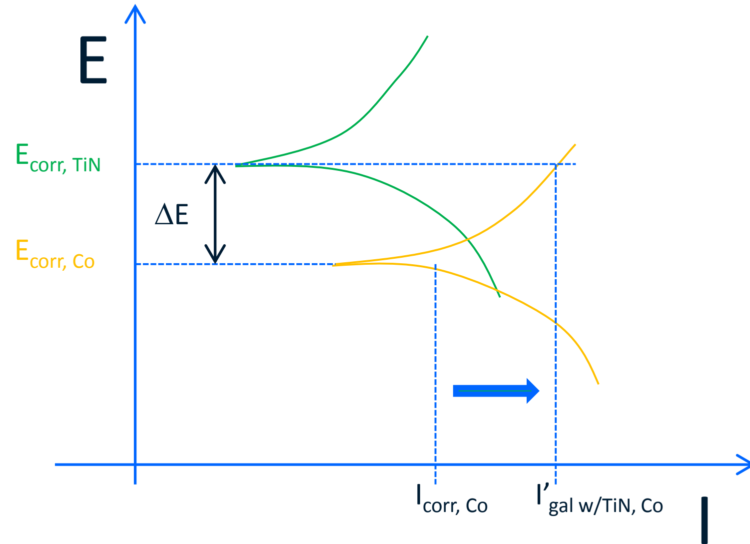
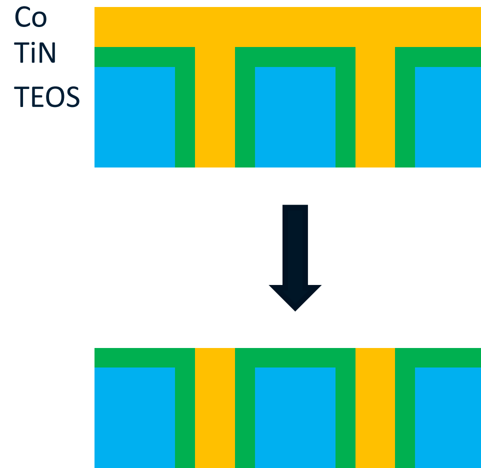
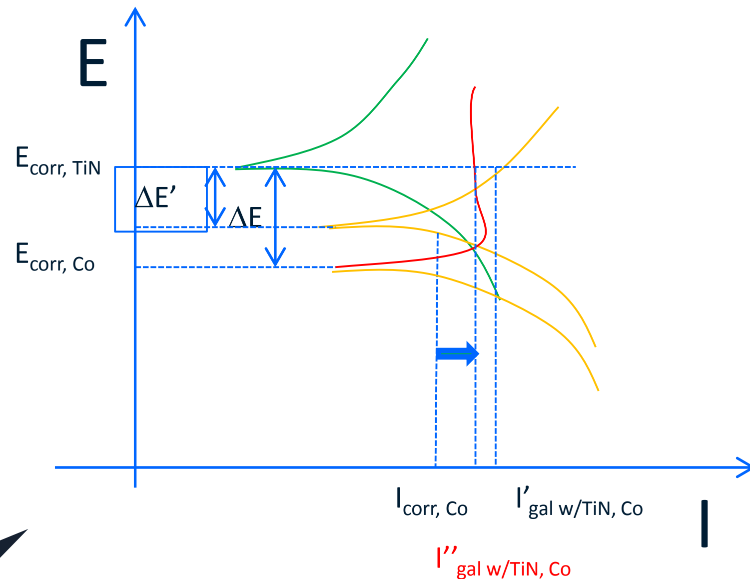
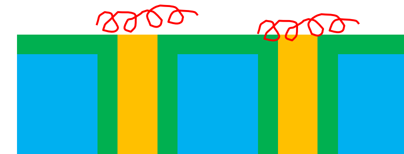
# Galvanic Corrosion




In term of exposed area ratio, Co corrosion potential might be raised as high as TiN potential, so as to dramatically increase Co corrosion current.



The Co galvanic corrosion can be reduce by reducing galvanic potential difference (ΔE→ΔE') or Co surface passivated by suitable passivation method

Accelerating Factor

$AF = I_{gal\ w/\ TiN,\ Co} / I_{corr,\ Co}$

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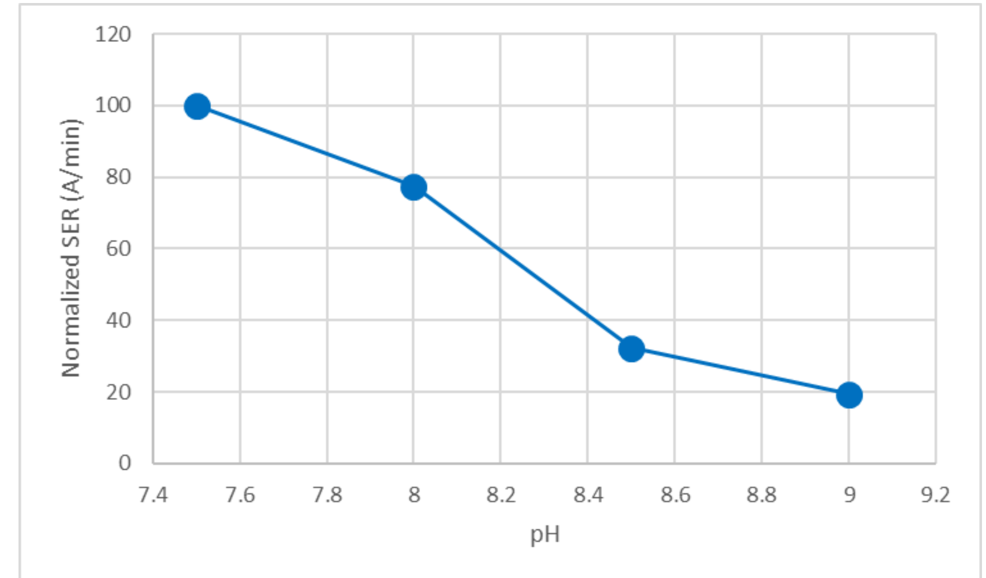
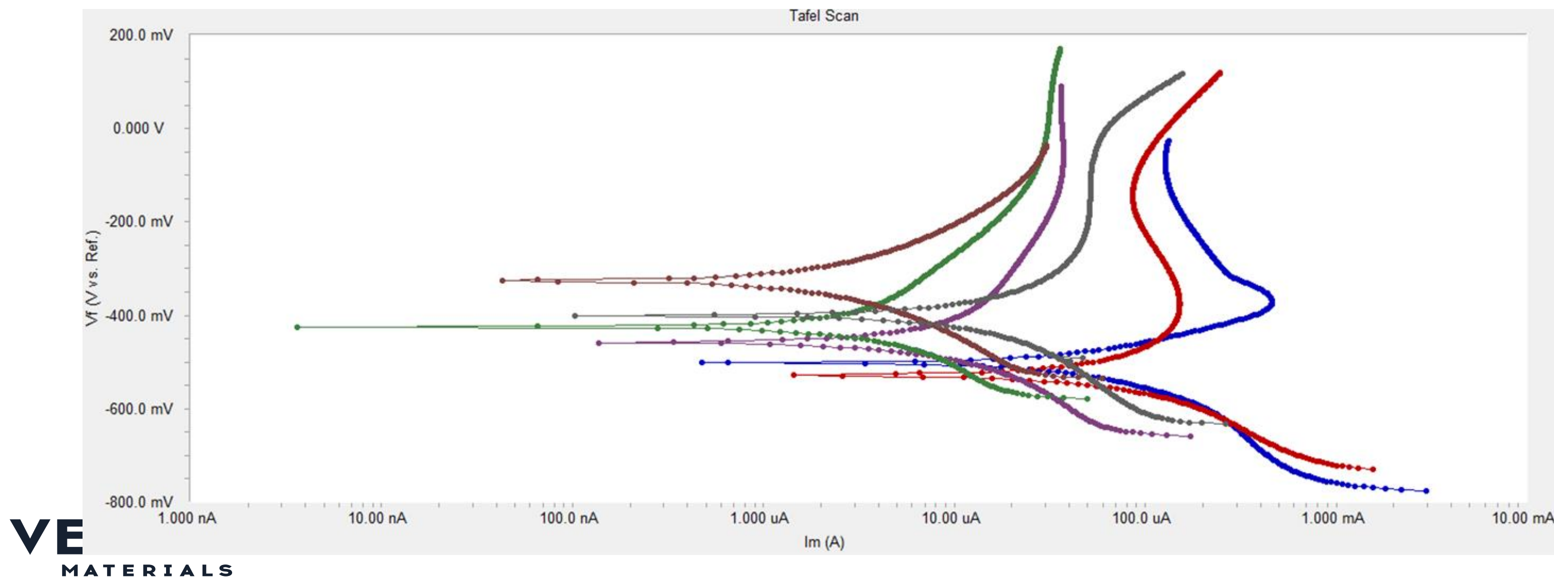
# Corrosion Minimization Strategies

- pH
- Corrosion Inhibitors
- Cobalt oxidation control




Optimization of corrosion inhibitors and pH to reduce corrosion current density and increase the open circuit potentials

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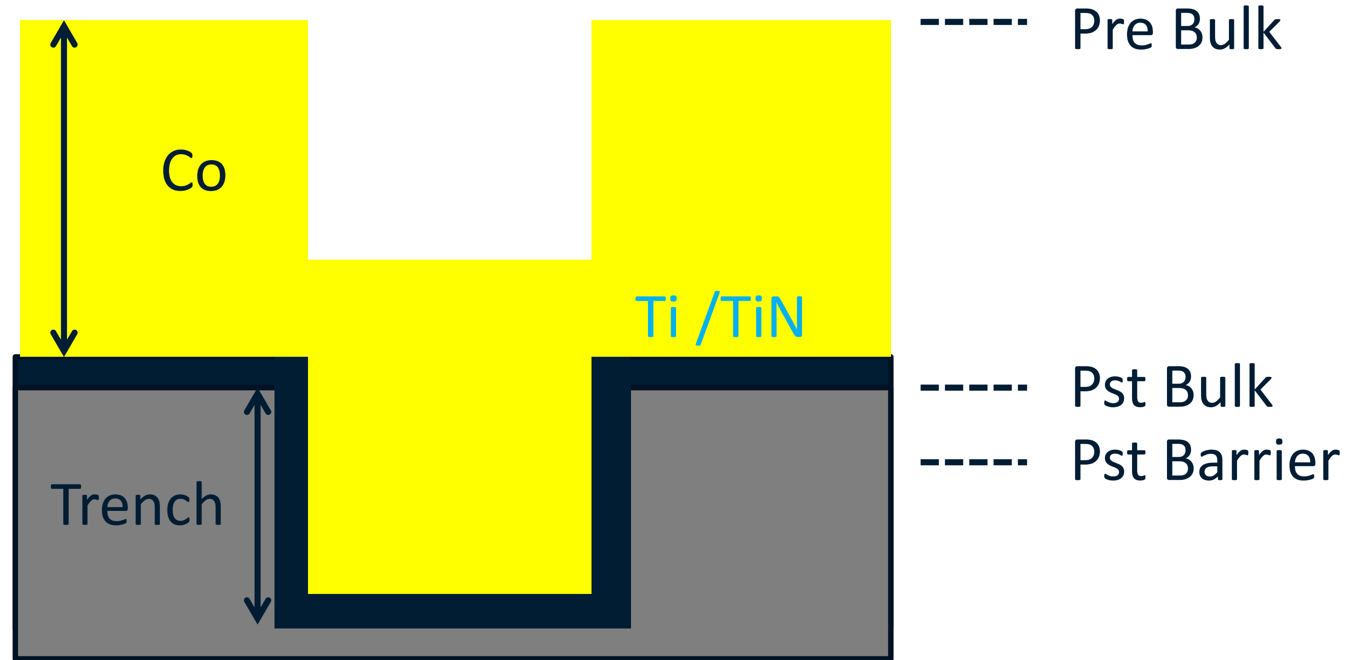
# Typical Cobalt CMP Process




- Bulk Cobalt Polish
- Barrier/Buff
- Post-CMP Clean

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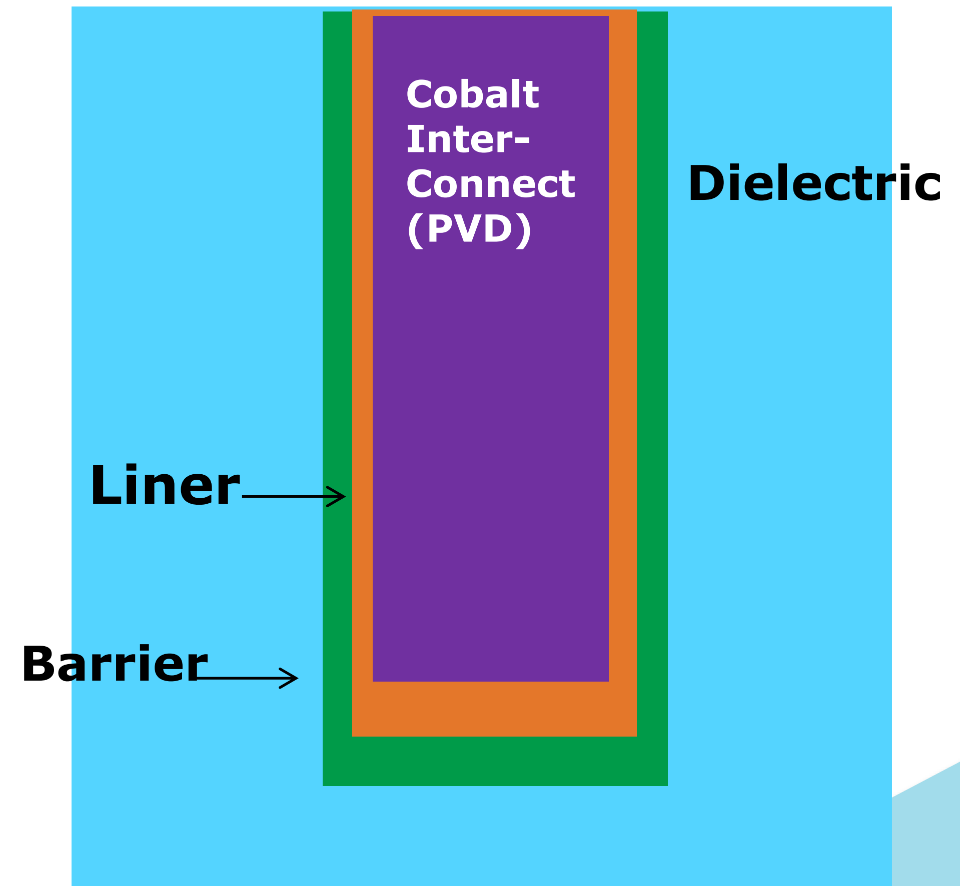
# Bulk Cobalt CMP Challenges

- Integration scheme requires new slurries for bulk cobalt polish step
- Challenges in Co CMP include
  - Corrosion
  - Defectivity
  - Roughness
  - Dishing
  - Selectivity
  - Co RRs on different types of Co films

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# Barrier Polish Challenges

- Complex integration schemes
  - New materials being introduced to serve various functions including polish-stop, liner, hard-mask
- Stringent targets for material loss
- Reduced down-force requirements
- Galvanic corrosion between various new materials
- Surface roughness
- Residue defects

# Post-CMP Challenges

- Cobalt corrosion protection
  - Prevent copper line loss
  - Galvanic corrosion with barrier/liners
  - Provide stable surface after the cleaning process
- Very low organic and slurry residue defects

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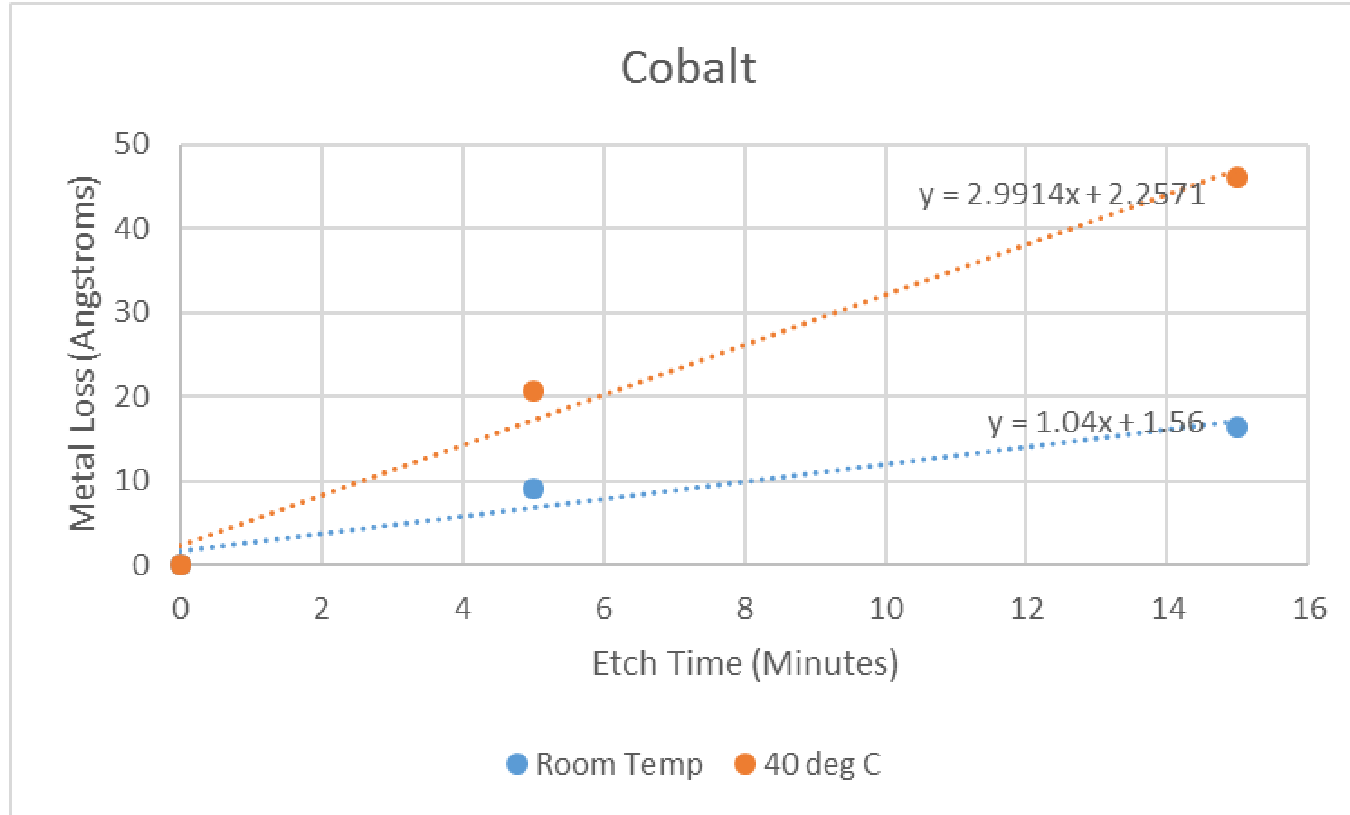
# Cobalt Corrosion Protection in the Cleaning Chemistry




| Temperature | Static Etch Rate (Å/min) |
|---|---|
| Room Temperature | 1.04 |
| $40^0$C | 2.99 |

Wafers pre-treated with 0.1 wt% citric acid for 1 minute prior to etch rate measurements

- Etch rates very low even at higher temperatures, indicating slow kinetics of cobalt corrosion

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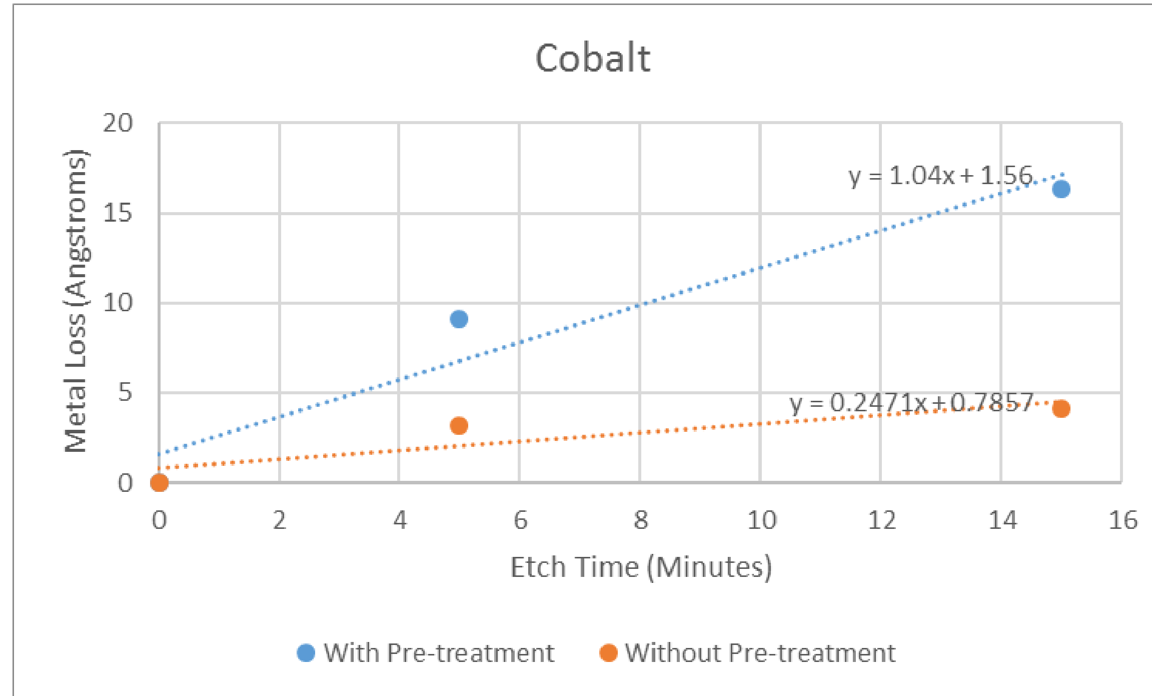
# Effect of Native Oxides on cobalt etching




Etch rates at room temperature

- Post-Polish cobalt surface would likely have an oxide layer on the surface
- In the absence of pre-treatment to remove native oxide layers, etch rates are even lower due to protection by native oxides

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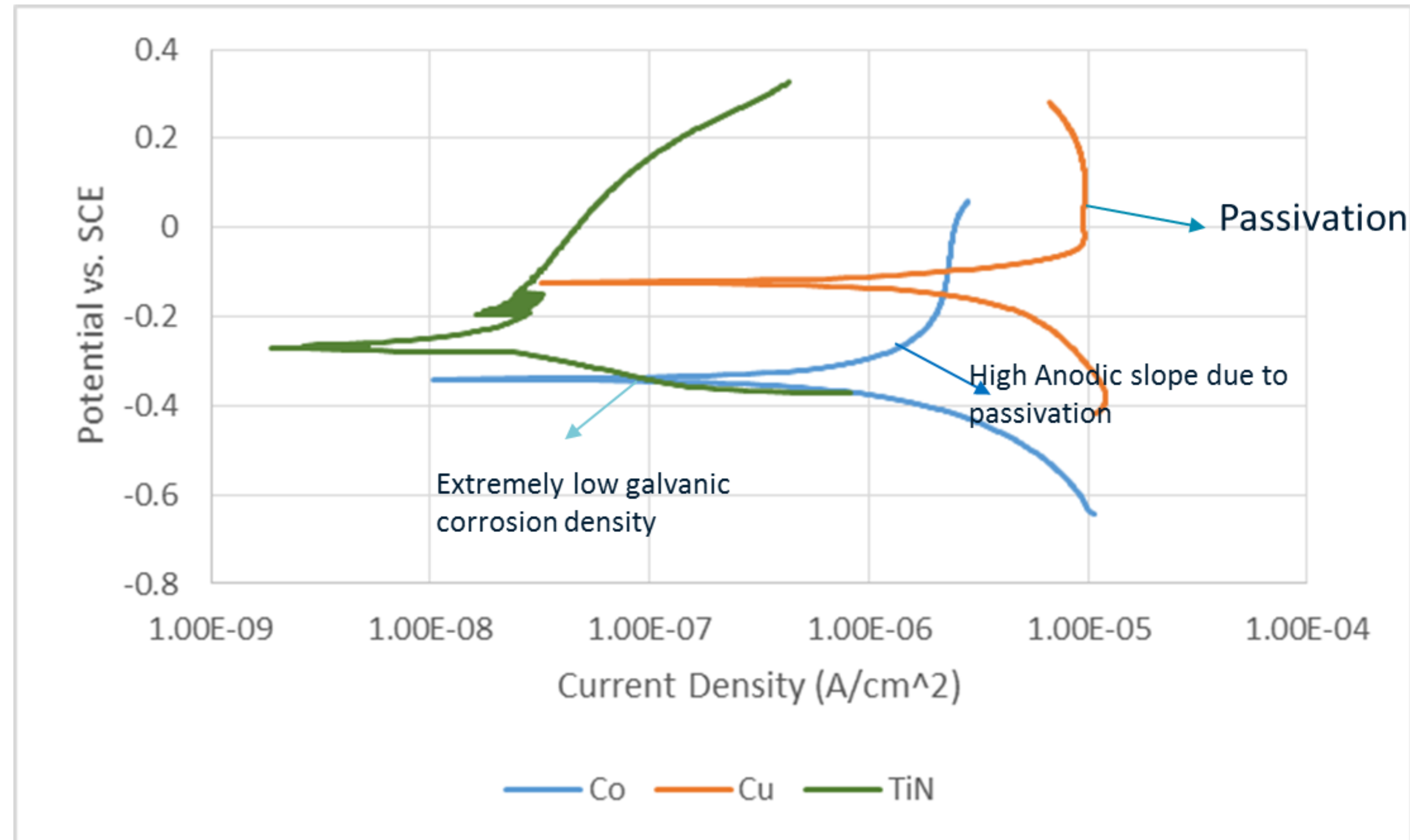
# Electrochemical Polarization




- Cobalt shows slower kinetics of corrosion even compared more noble copper surface

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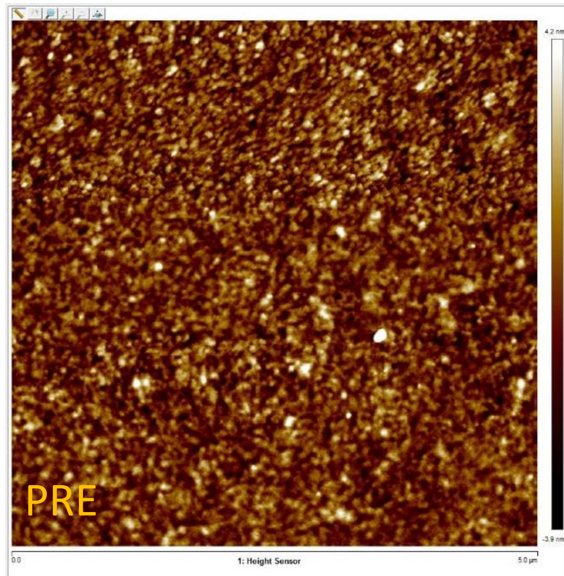
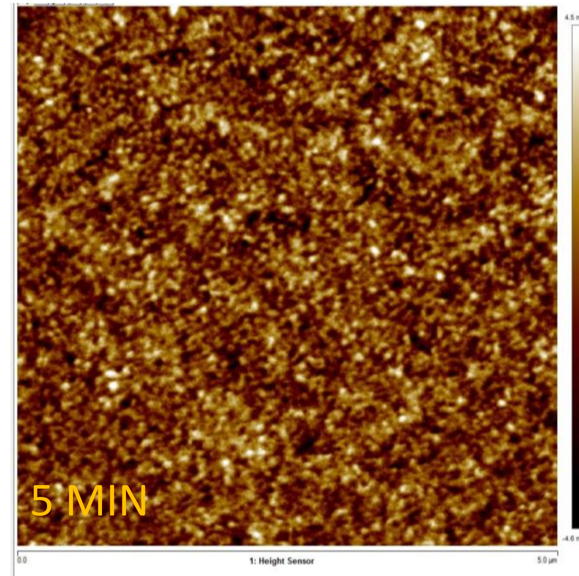
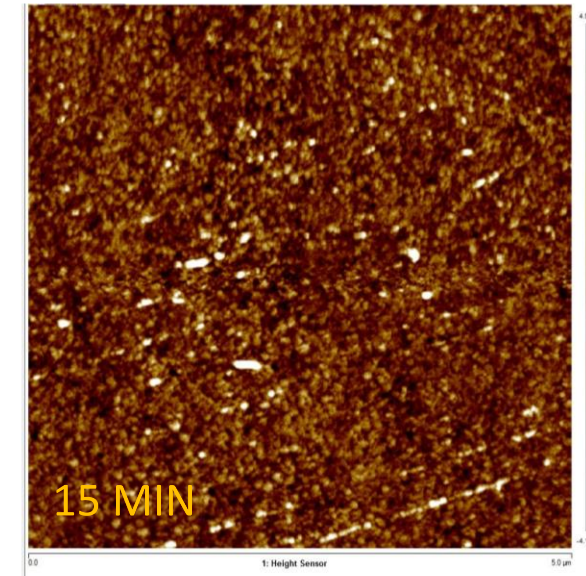
# Effect of Cleaning Chemistry Immersion at room temperature on Cobalt surface roughness




| Immersion Time | $R_q$ (Angstroms) |
|---|---|
| Pre | 13.5 |
| 5 minute | 11.5 |
| 15 minute | 16 |

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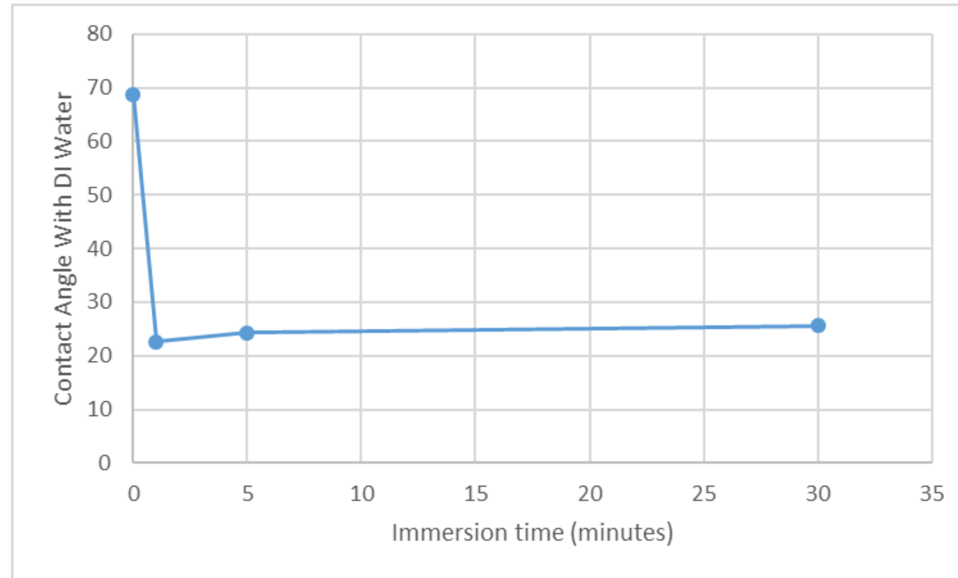
# Effect of Immersion on Cobalt Surface




- Immersion in cleaning chemistry leads to lowering of contact angle due to removal of adventitious contamination from film surface by the cleaning surface
- Stability of cobalt surface in the post-CMP cleaning solution is evident from virtually no changes in the contact angle of the surface with long immersion times

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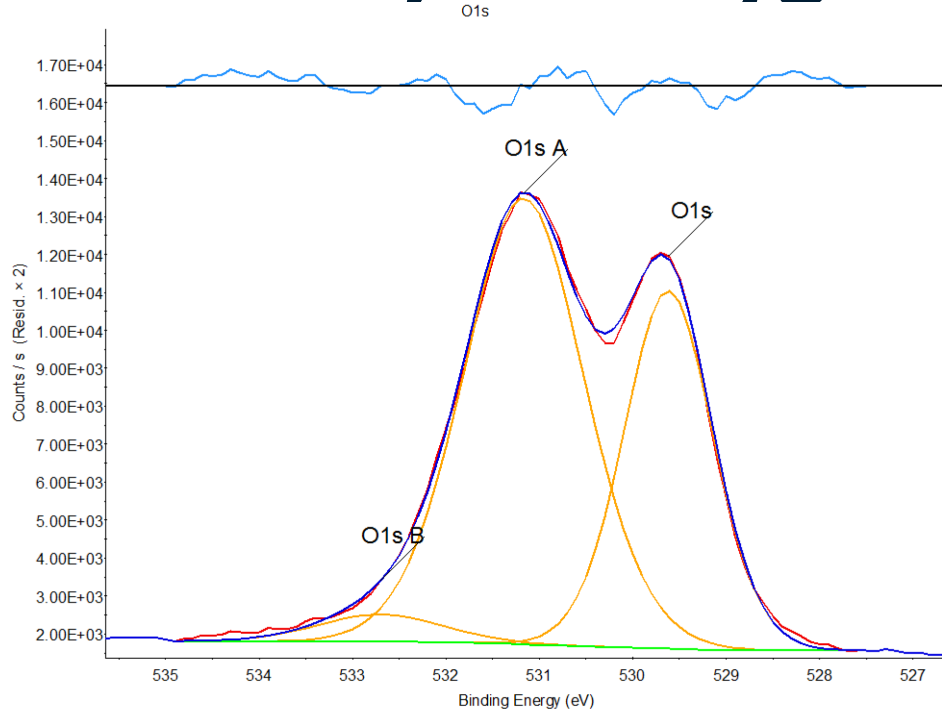
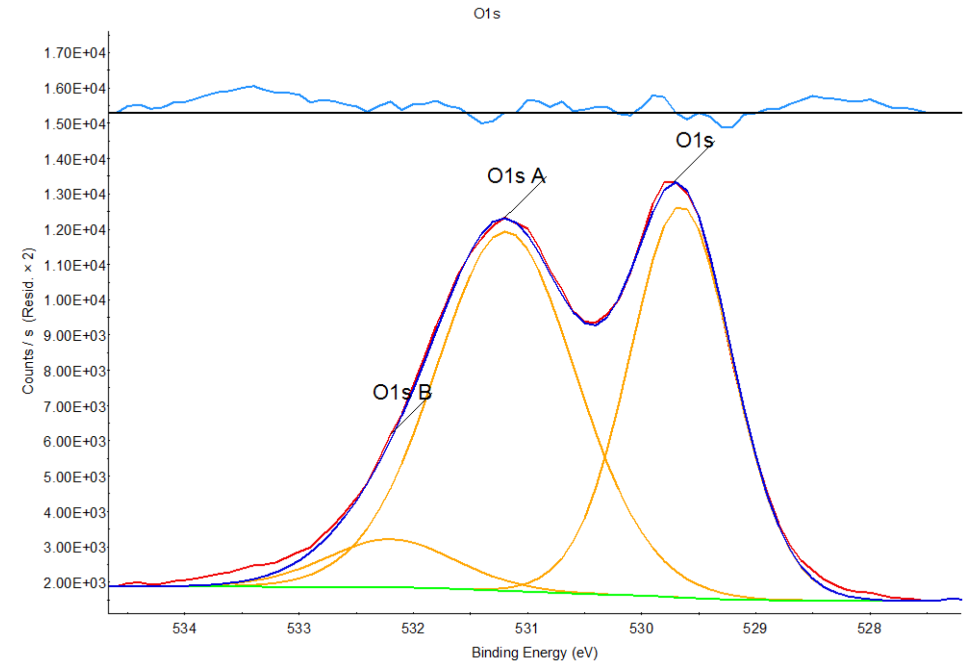
# XPS Analysis: Oxygen Spectra




As Polished (Spin-Rinse Dry)




Polished + Post-CMP Clean

| | As polished | Polished + Post-CMP Clean |
|---|---|---|
| Relative ratio of oxygen in oxides to hydroxides | 0.59 | 0.8 |

Cleaned wafers shows higher fraction of cobalt hydroxide

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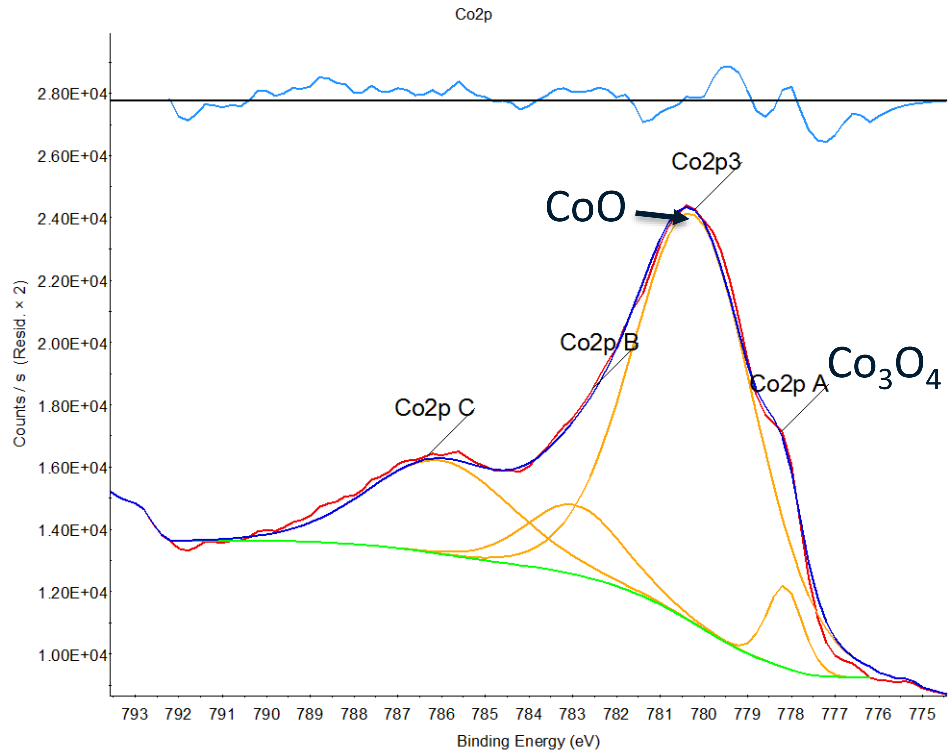
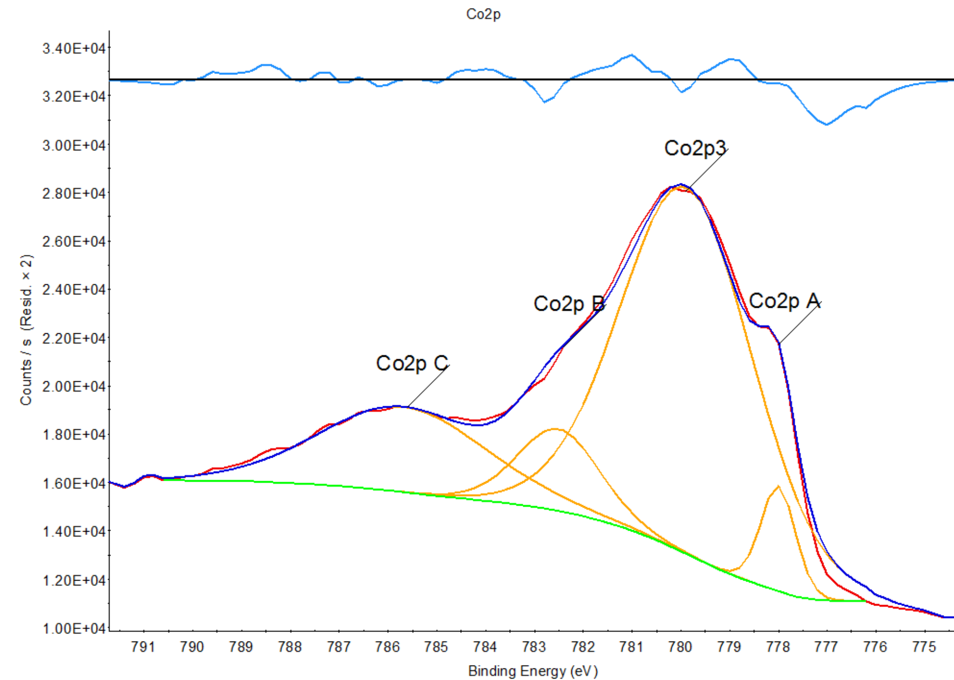
# XPS Analysis on Cobalt Surfaces




As Polished (Spin-Rinse Dry)




Polished + Post-CMP Clean

| | As polished | Polished + Post-CMP Clean |
|---|---|---|
| Relative ratio of cobalt in Co3O4 vs CoO | 0.06 | 0.07 |

Small fraction of CoO is converted into $Co_3O_4$

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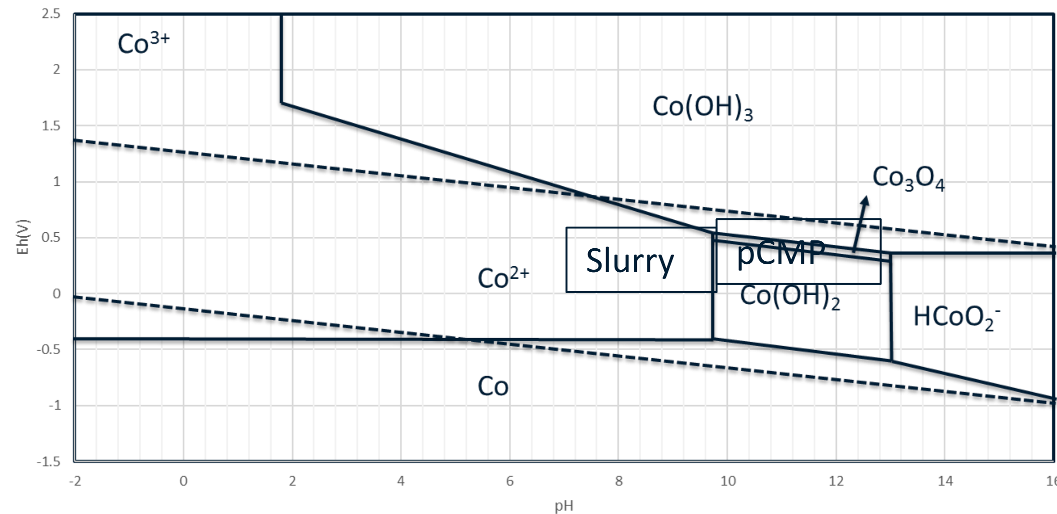
# Surface Oxide Speciation in Cobalt CMP




- pCMP cleans operate at higher pH regime where there is more stability for cobalt oxides
- Passive oxides can offer cobalt protection even in the absence of film forming agents

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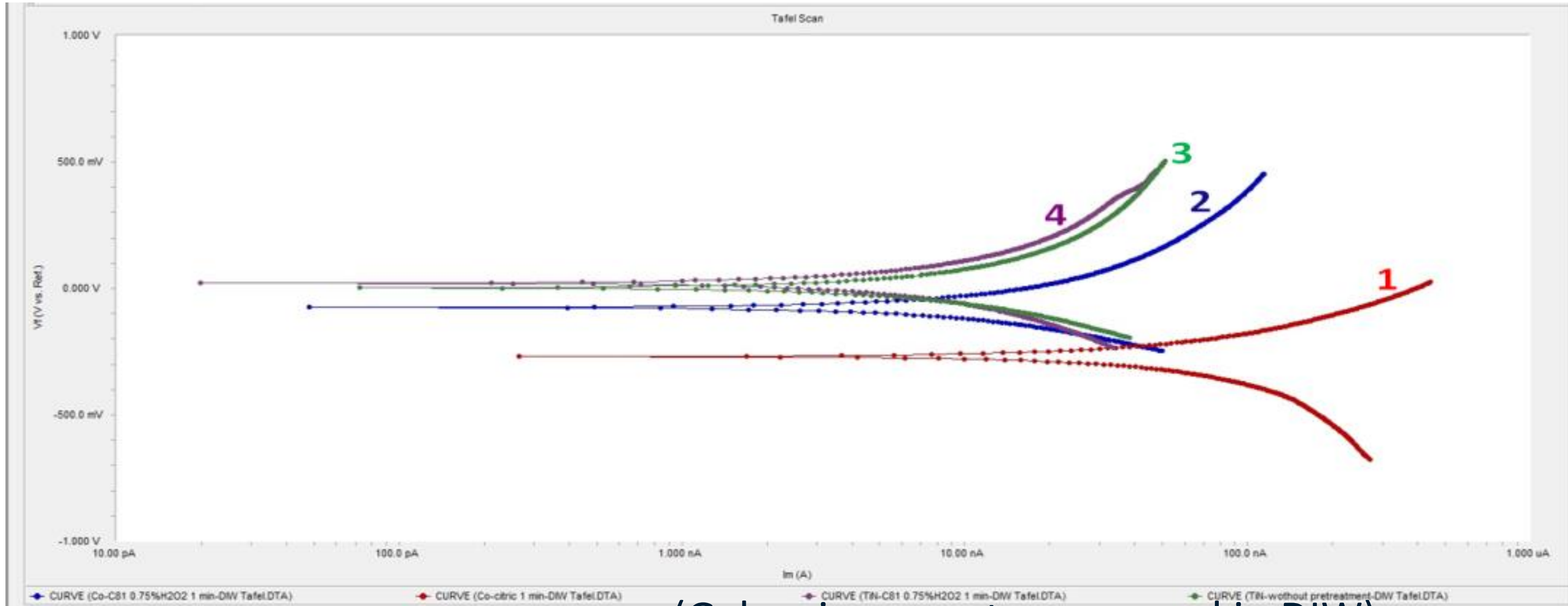
# Post-Polish Reduction of Corrosion by Barrier Slurries




(Galvanic currents measured in DIW)

Passivating layer formed on the cobalt slurry with barrier slurry treatment reduces the corrosion currents and galvanic corrosion with titanium nitride

| | | Pre-treatment | Ecorr (mV) | Icorr (nA) | TiN-Co Potential difference |
|---|---|---|---|---|---|
| 1 | Co | Citric Acid | -268 | 275 | 270 |
| 2 | Co | Barrier Slurry | -75 | 45 | 96 |
| 3 | TiN | Citric Acid | 2 | 39 | n/a |
| 4 | TiN | Barrier Slurry | 21 | 42 | n/a |

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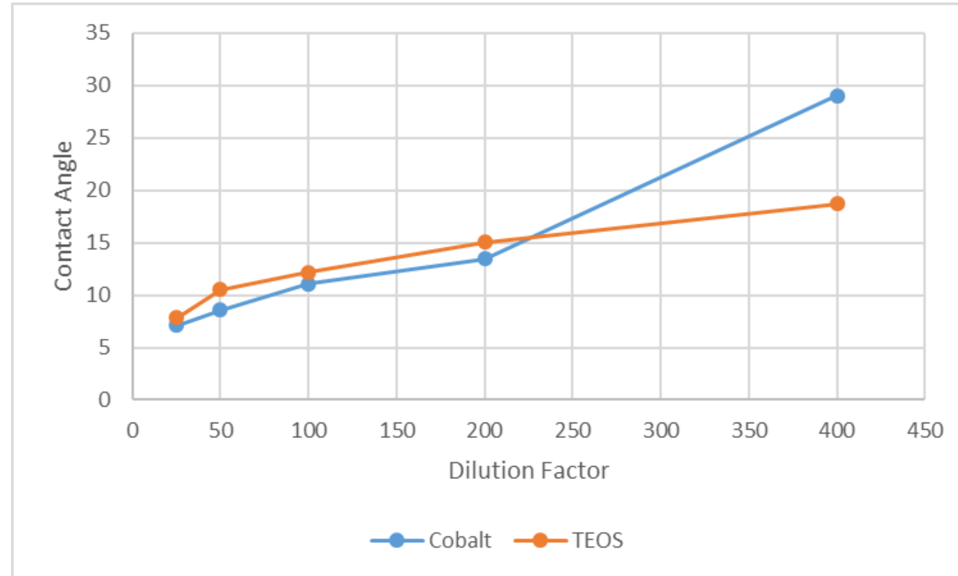
# Factors contributing to superior cleaning




- Very low surface tension and contact angle enable excellent cleaning ability even as the chemistry is getting diluted on the tool

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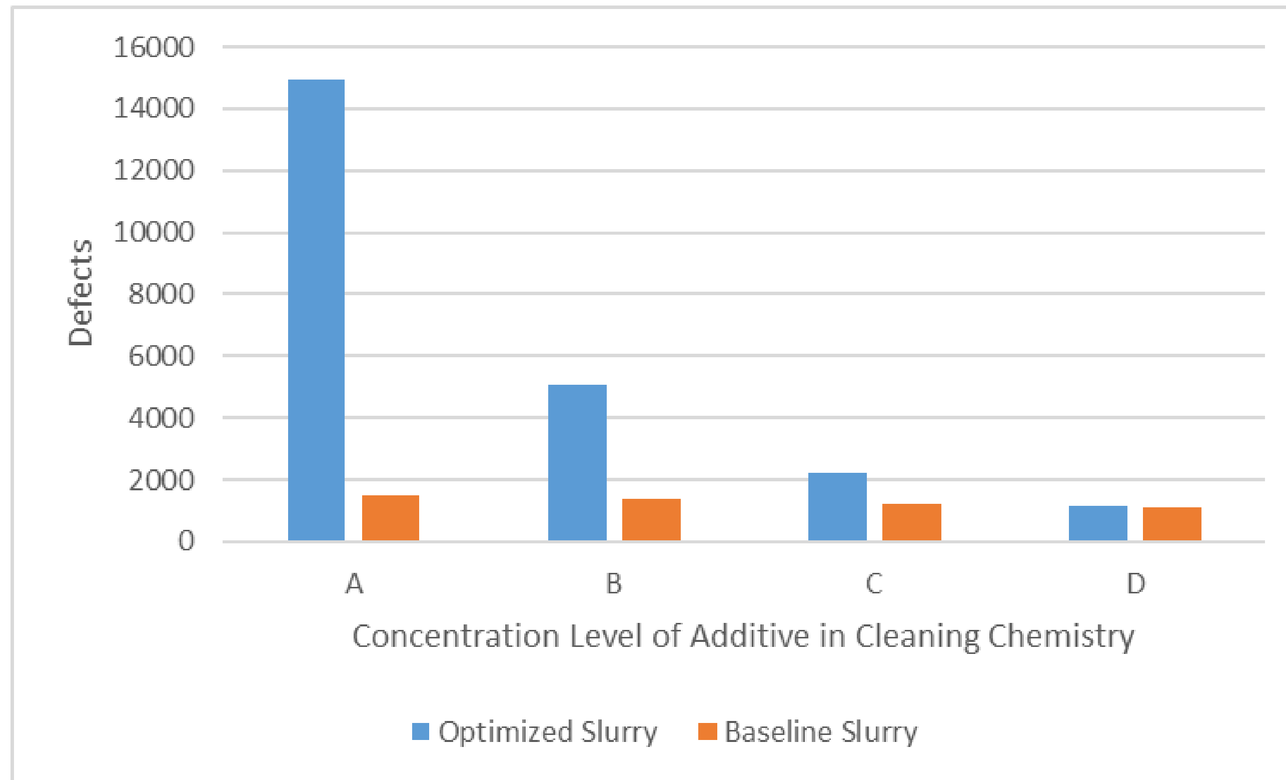
# Simultaneous Optimization of Slurry and Cleaning Chemistries

- Slurry Performance Objectives
  - Increased removal rates of oxide films
  - Reduce removal rates of cobalt and increase corrosion protection
  - Maintain the defects as baseline
- Slurry removal rate objectives achieved through
  - High abrasive loading
  - Higher corrosion inhibitor concentrations
- However factors that lead to improved CMP performance also lead to higher defects
- Simultaneous optimization of cleaning chemistry enable reduction of defects to baseline level

# Defect Reduction through cleaning chemistry optimization




- Defectivity with baseline slurry is less sensitive to additive concentrations due to low reduced levels
- By tailoring the component concentrations, defectivity with the optimized slurry can be brought to baseline levels

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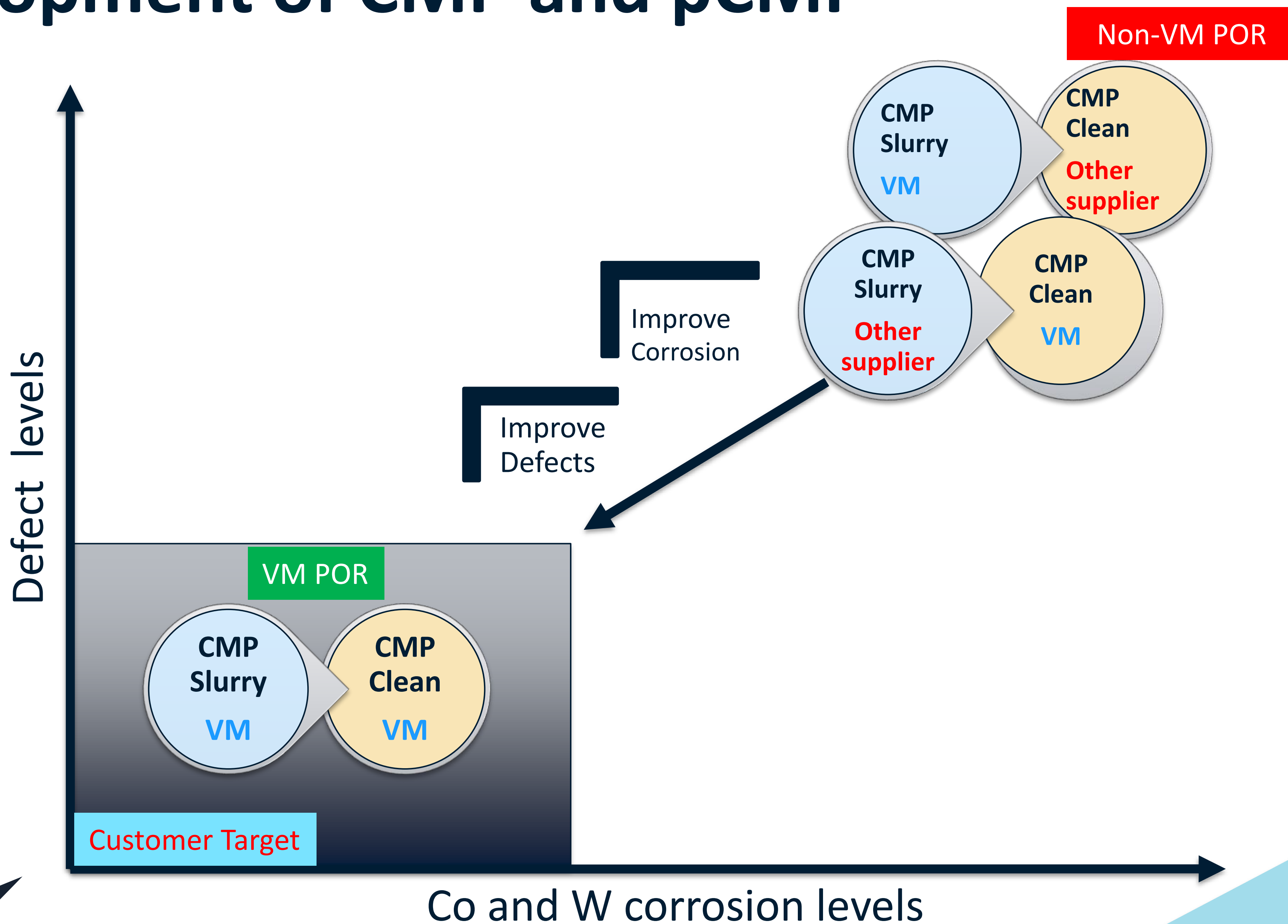
# Co-development of CMP and pCMP

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