

Protecting Against Cobalt Corrosion in Advanced CMP Slurries

James McDonough, Ph.D.

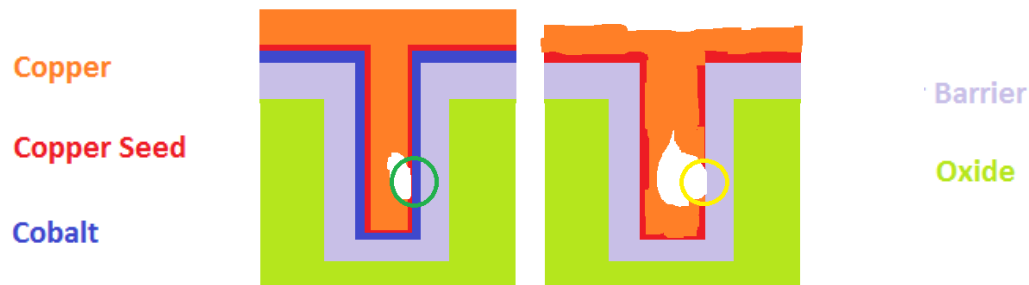
Richard Wen, Ph.D., Luling Wang, Ph.D.

Fujifilm Planar Solutions, LLC

7/10/2013

- Increasingly, Co is attracting interest from chipmakers for use in IC's, especially due to:
 - Favorable adhesion of Co to Cu seed layers
 - Ease of conformal Co deposition
 - Most importantly, as Cu line sizes continue to shrink, trenches can be harder to fill without voids/keyholes. Co ensures conductive linings inside trenches even if Cu voids are present

**NOT TO
SCALE**



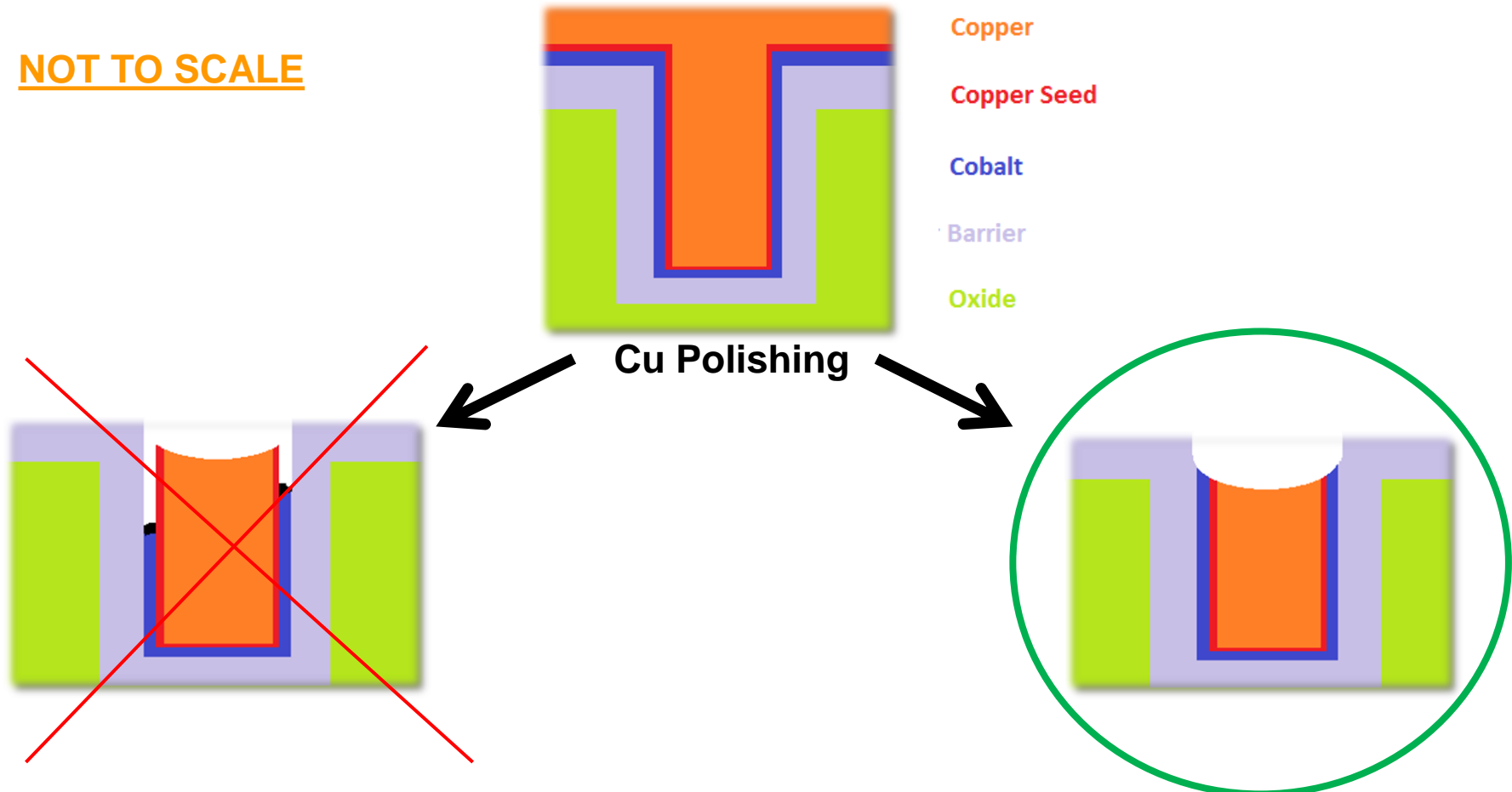
- Novel stacking structures present new challenges for CMP slurries. Slurry interactions with Co becoming increasingly significant!

- Co does not self passivate and is susceptible to corrosion
 - Pitting corrosion problems on blankets
 - Galvanic corrosion on patterns
 - Co ions quite reactive
- Thus, a solution is the essentially provide a protective layer on Co via additives
 - Additives should be selective for Co over Cu, so as not to compromise slurry performance
 - Only takes a small concentration of additive for large effect

	Oxidation Potential vs SHE	Oxidation Reaction	Comments
Ru	-0.46	$\text{Ru} \rightleftharpoons \text{Ru}^{2+} + 2\text{e}^-$	Ru hard to oxidize
Cu	-0.34/-0.52	$\text{Cu}^+/\text{Cu}^{2+}$	Oxidizer added to slurry, forms passivation layer
Co	0.28	$\text{Co} \rightleftharpoons \text{Co}^{2+} + 2\text{e}^-$	No passivation, continuous oxidation
Ta	0.75	$2\text{Ta} + 5\text{H}_2\text{O} \rightleftharpoons \text{Ta}_2\text{O}_5 + 10\text{H}^+$	Passivation prevents further oxidation
Ti	1.63	$\text{Ti} \rightleftharpoons \text{Ti}^{2+} + 2\text{e}^-$	Ti readily removed by slurry

- Co thermodynamically oxidizes and does not self passivate. Corrosion continues unless Co is protected.

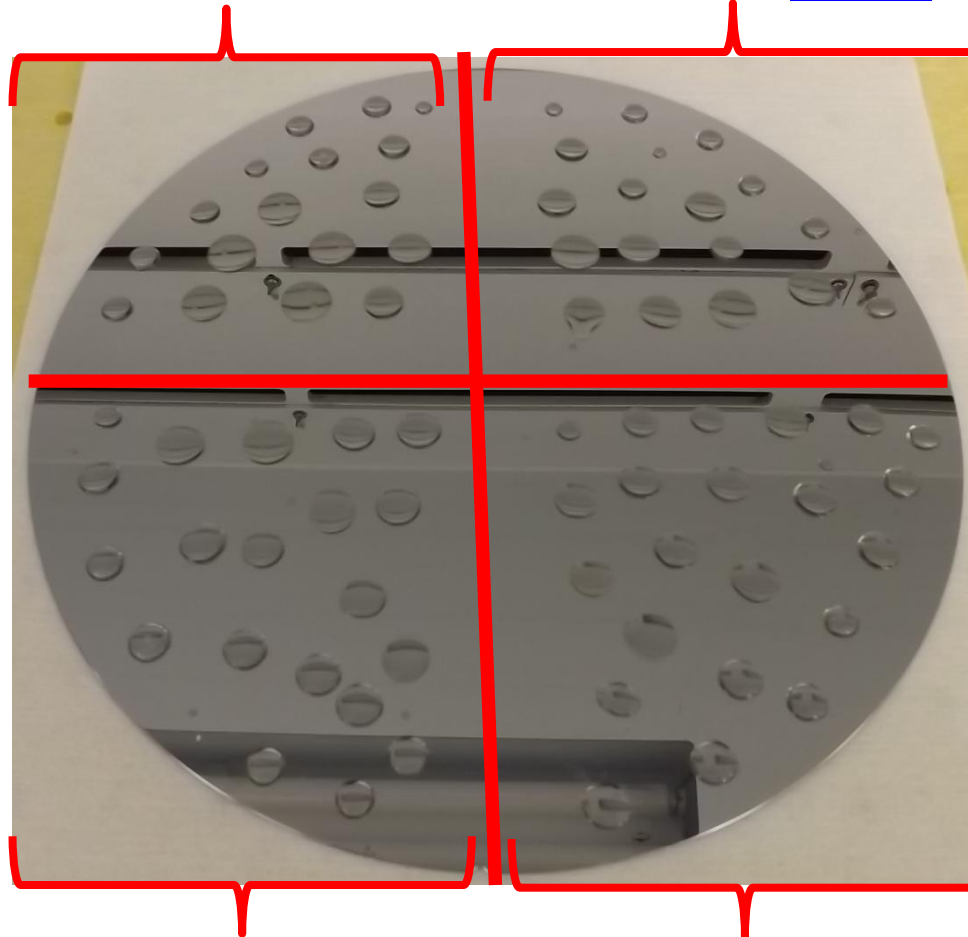
NOT TO SCALE



- If Co corrosion can be suppressed and/or the Co RR can be decreased, Co on the trench walls can be protected

DIW/Higher Oxidizer Conc ONLY

DIW/Lower Oxidizer Conc ONLY

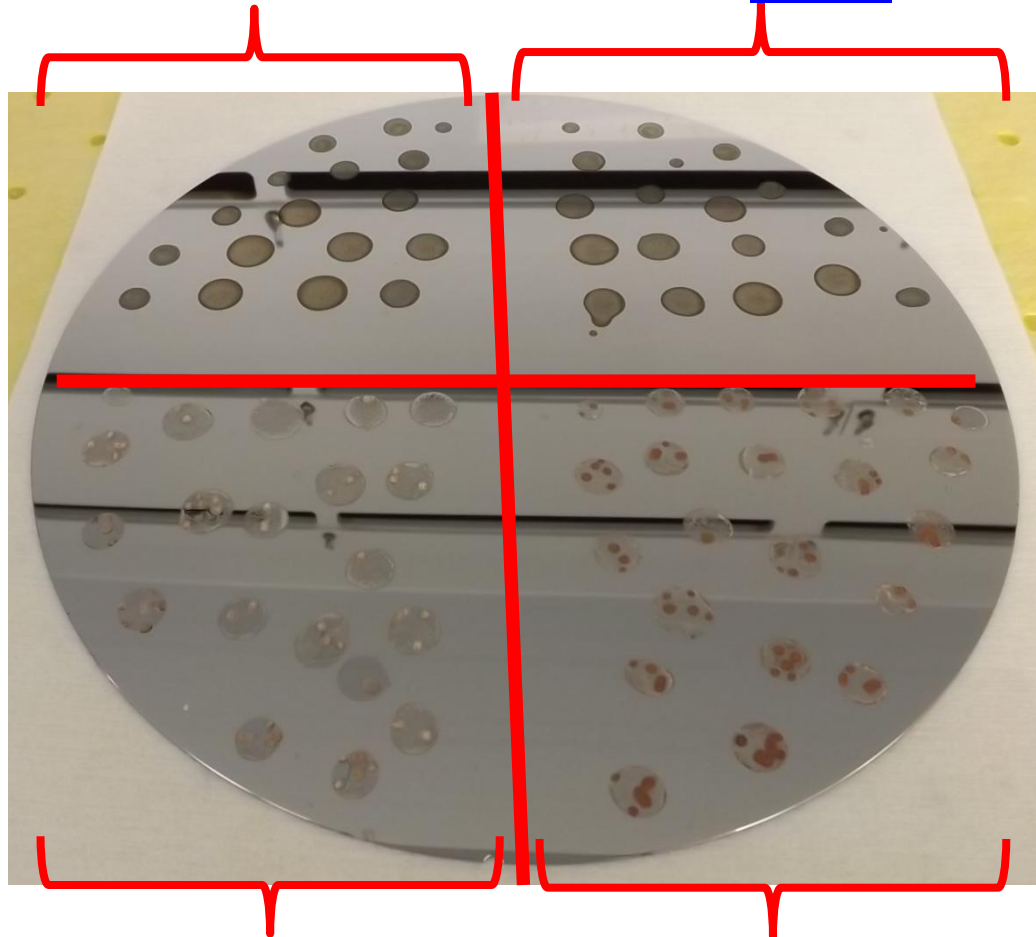


Cu Slurry with Co suppressor

Legacy Cu Slurry

DIW/Higher Oxidizer Conc ONLY

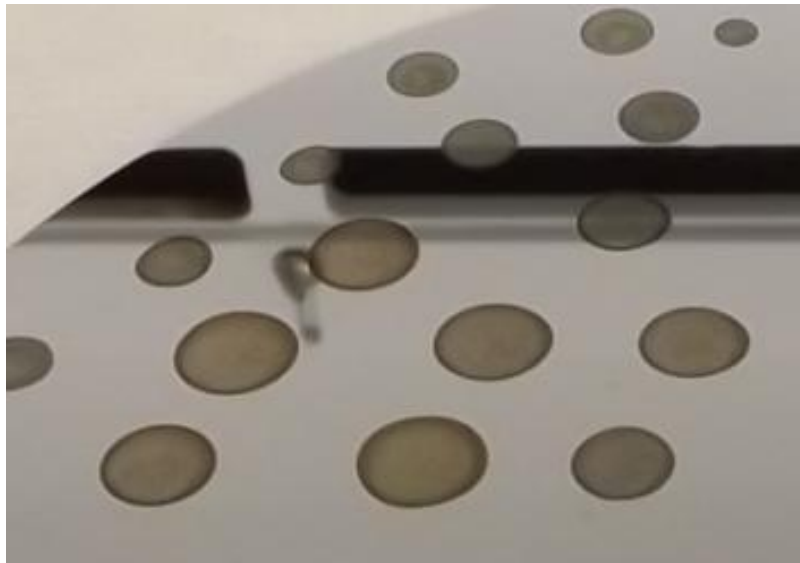
DIW/Lower Oxidizer Conc ONLY



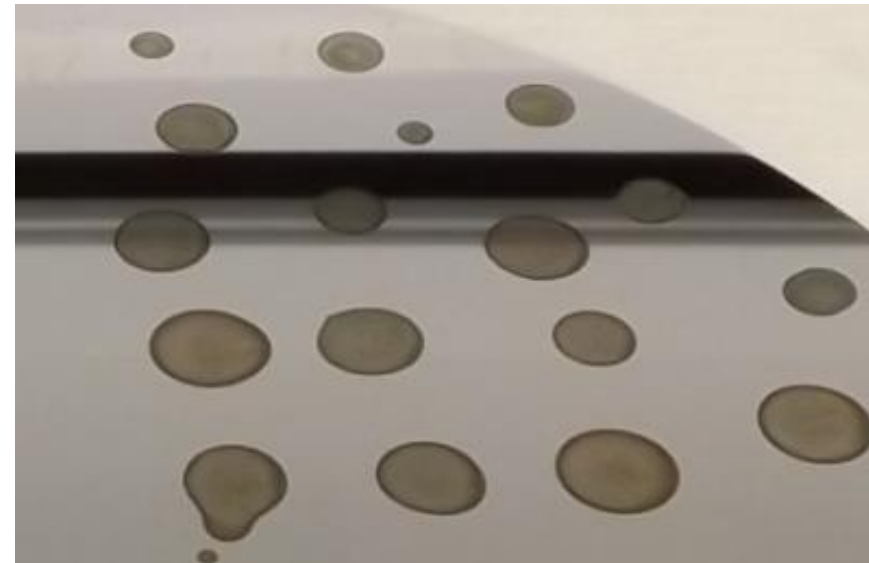
Cu Slurry with Co suppressor

Legacy Cu Slurry

DIW/Higher Oxidizer Conc ONLY



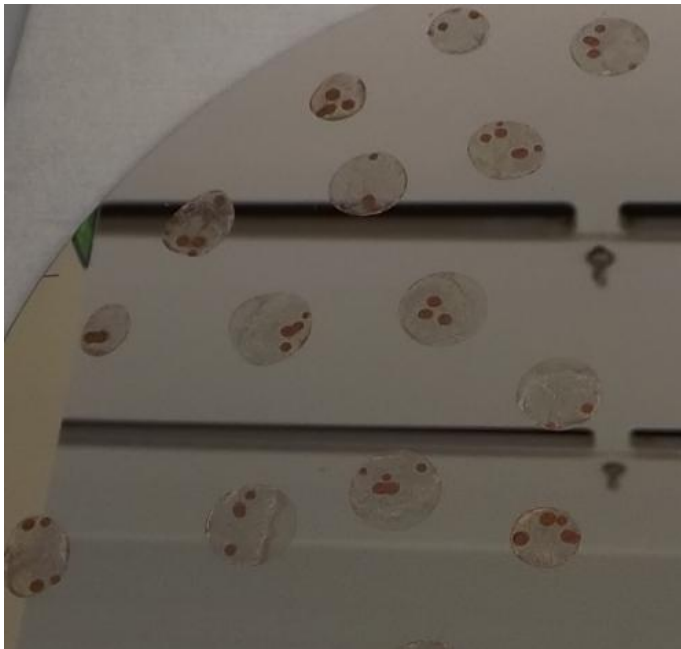
DIW/Lower Oxidizer Conc ONLY



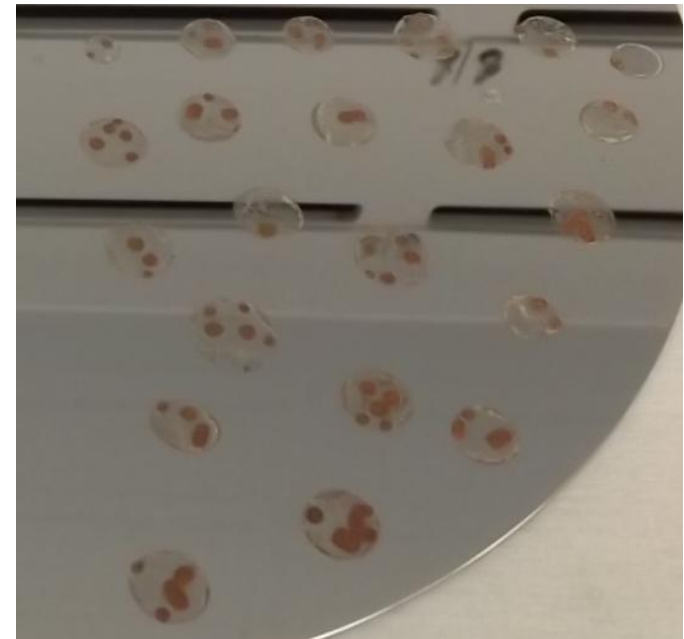
Cobalt is easily corroded by slurry oxidizer in DIW, regardless of concentration. Brown byproduct is observed.

Oxidizer concentrations slightly above and below POU oxidizer concentrations

Legacy Cu with higher oxidizer concentration



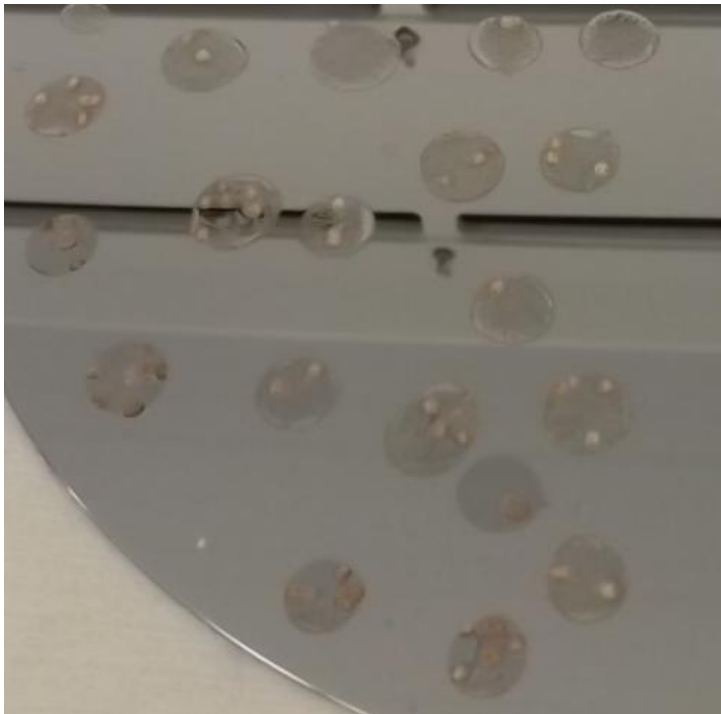
Legacy Cu with lower oxidizer concentration



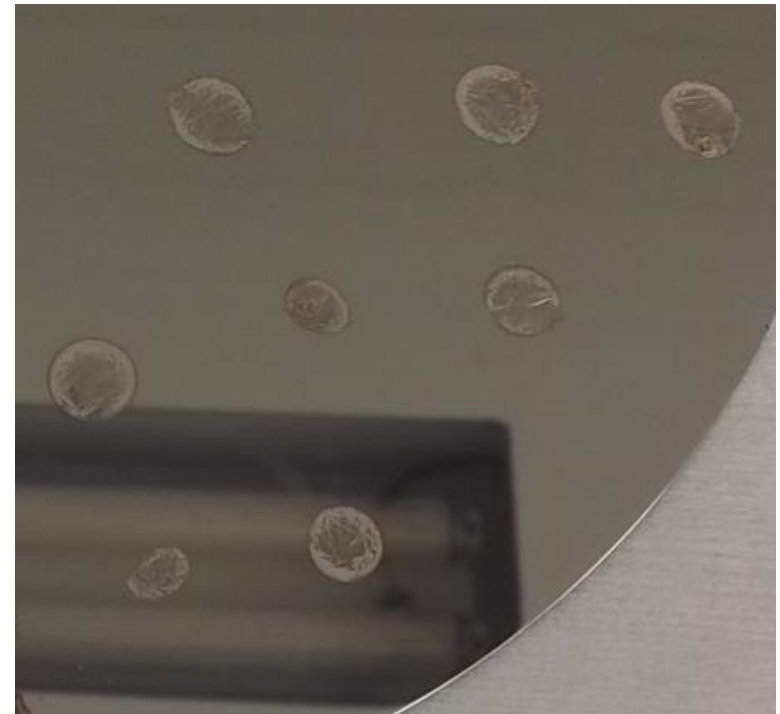
Brown byproducts of cobalt corrosion are observed, **although the byproducts are suppressed compared to DIW/oxidizer solution only**

Protection against Co corrosion unchanged with oxidizer concentration

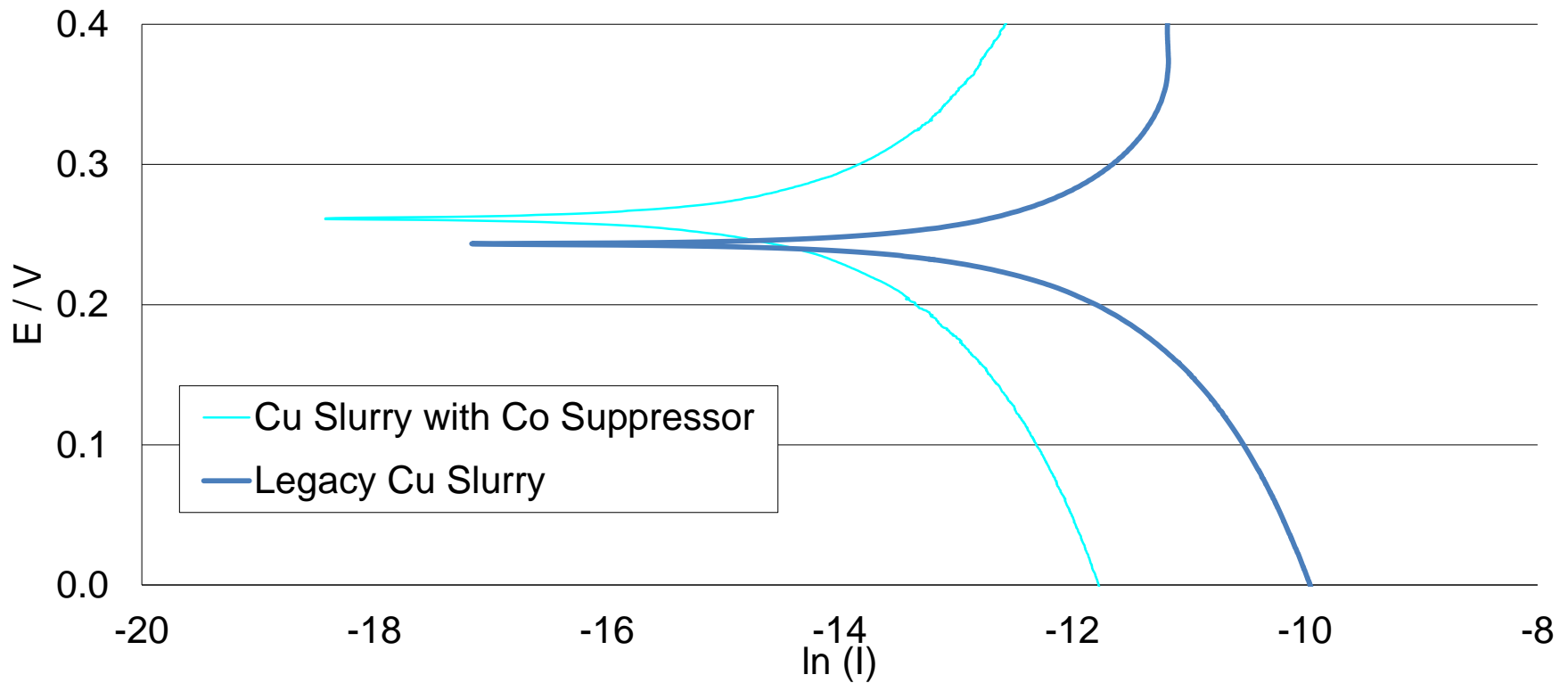
Cu Slurry with Co suppressor, higher oxidizer concentration



Cu Slurry with Co suppressor, lower oxidizer concentration



Reduction in brown byproducts of cobalt corrosion at both oxidizer levels

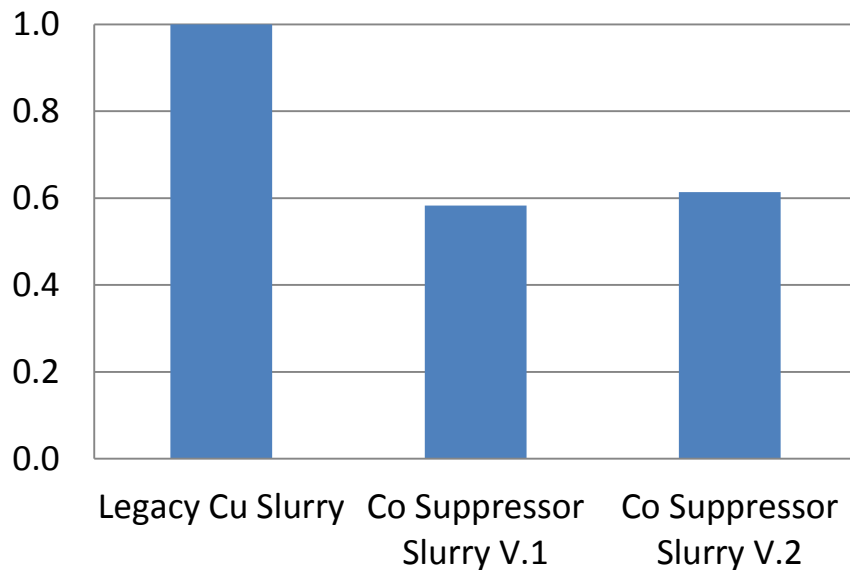


Current exchange density ~2 orders of magnitude lower for the case with the Co corrosion suppressor, meaning that corrosion happens less rapidly (**kinetics**)

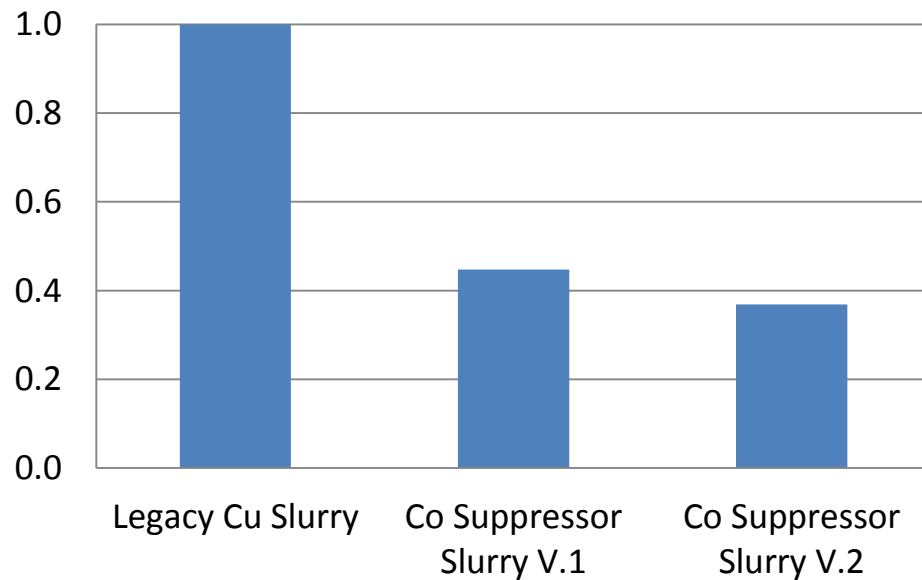
Corrosion potential higher for case with suppressor, meaning more energetically difficult (**thermodynamics**)

- Compare static etch rates for legacy Cu slurry vs Cu slurry with Co corrosion suppressor

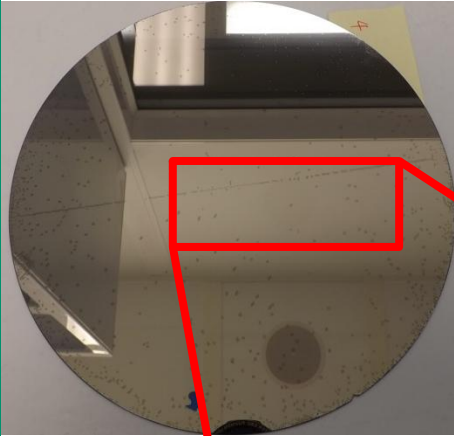
20C Normalized Co Static Etch Rates



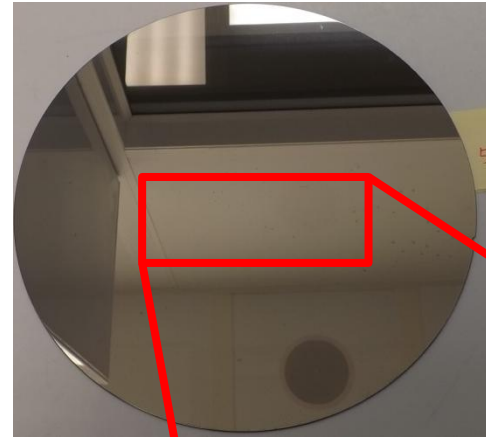
40C Normalized Co Static Etch Rates



Legacy Cu Slurry



Cu Slurry with Co Corrosion Suppressor

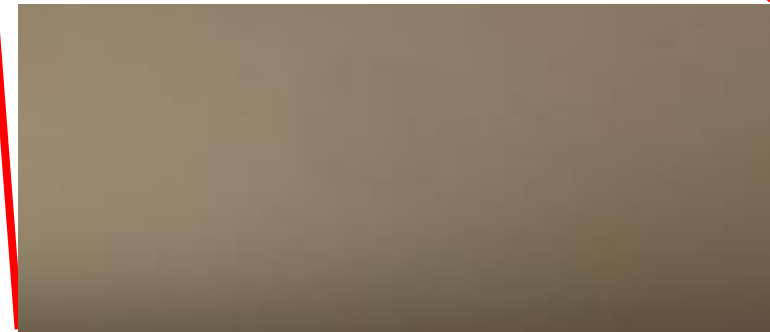
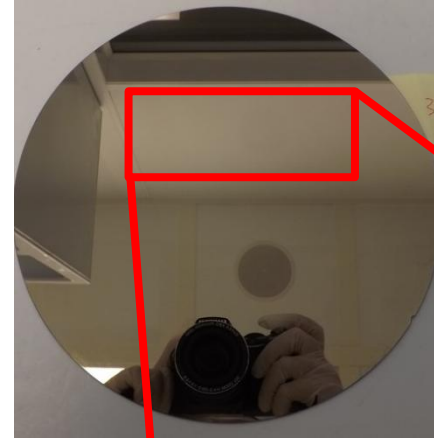


- Pitting corrosion mollified by Co corrosion suppressor

Legacy Cu Slurry

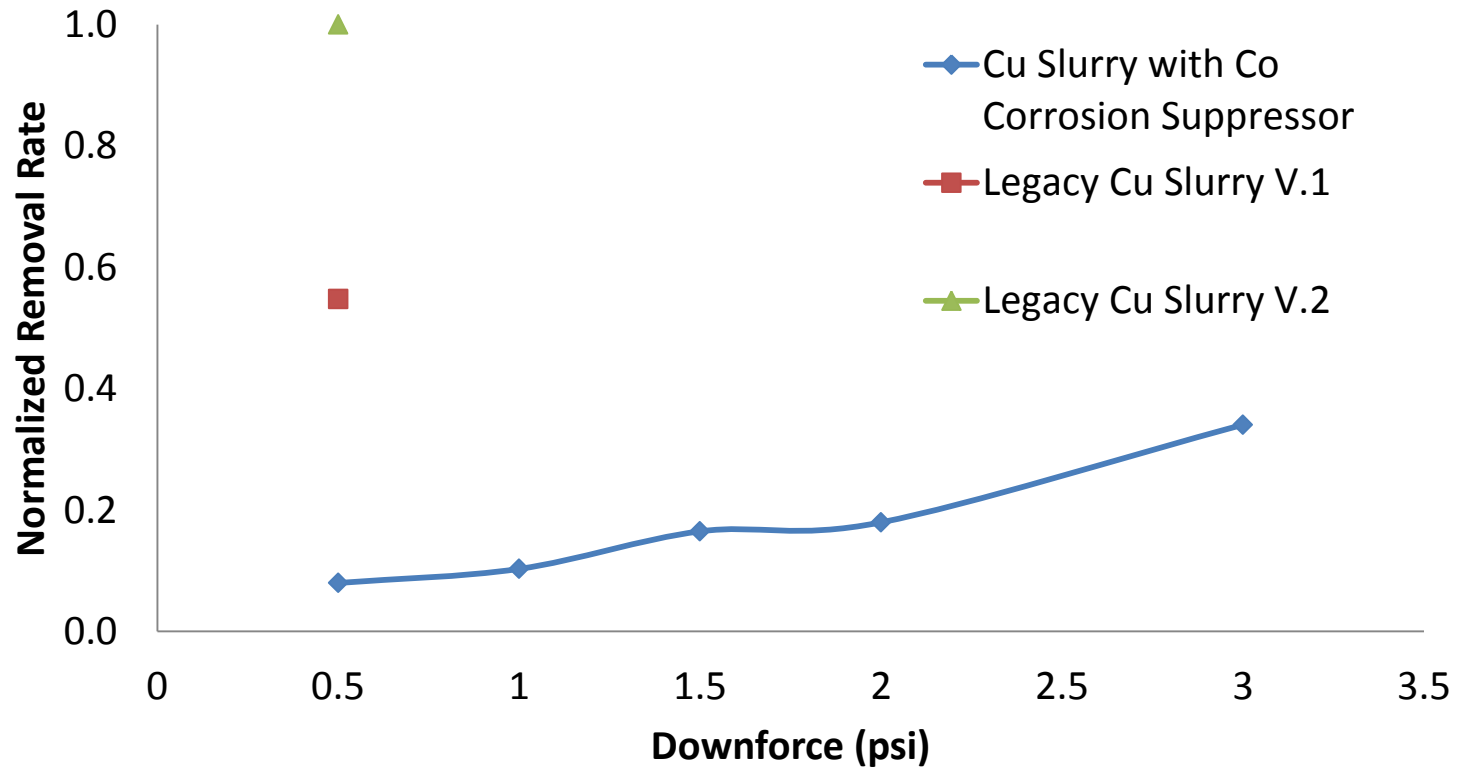


Cu Slurry with Co Corrosion Suppressor



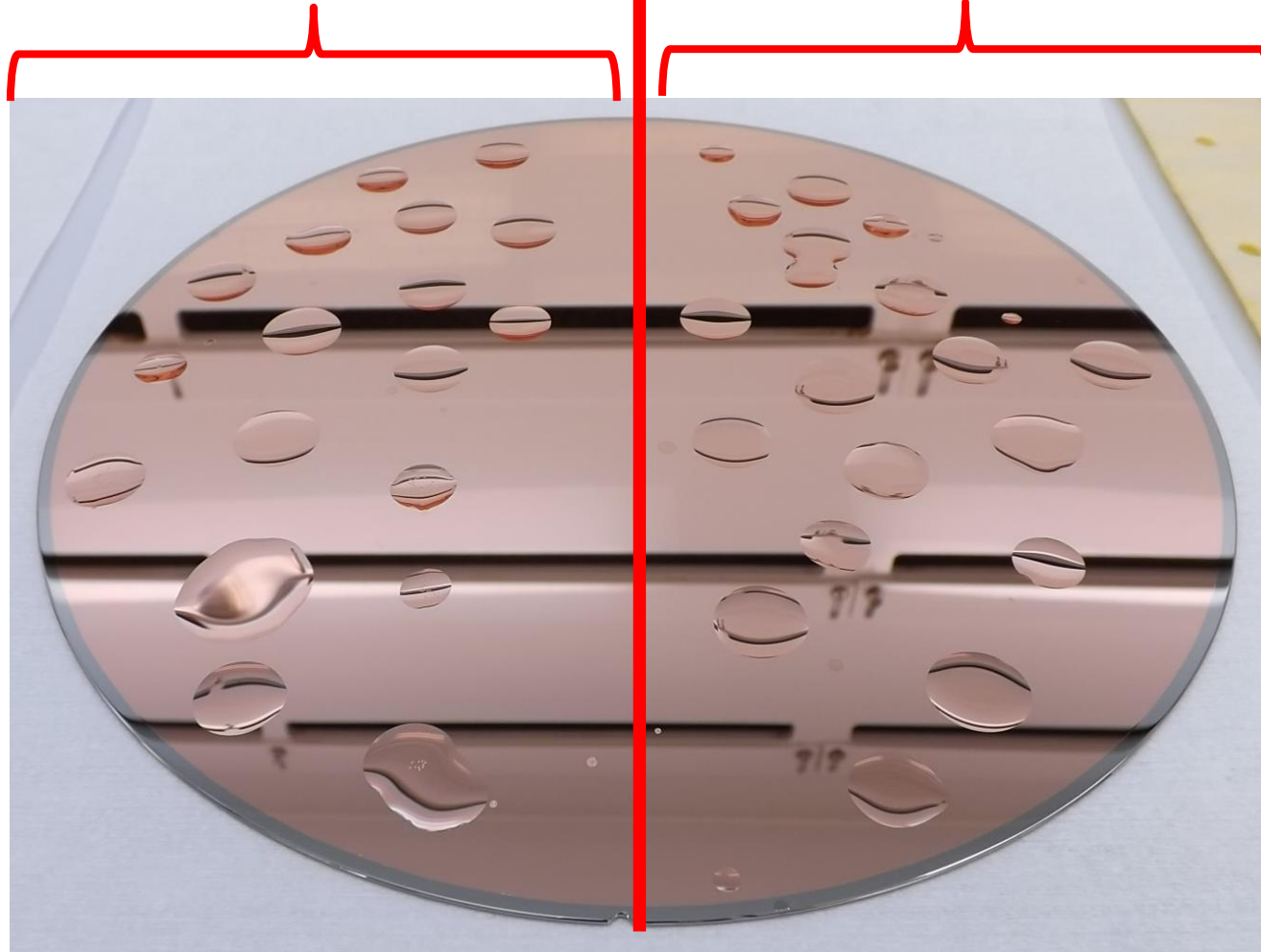
- Pitting corrosion mollified by Co corrosion suppressor

- Co wafers had same initial thicknesses, **Co wafers cleared for legacy slurries between 1-3 psi**



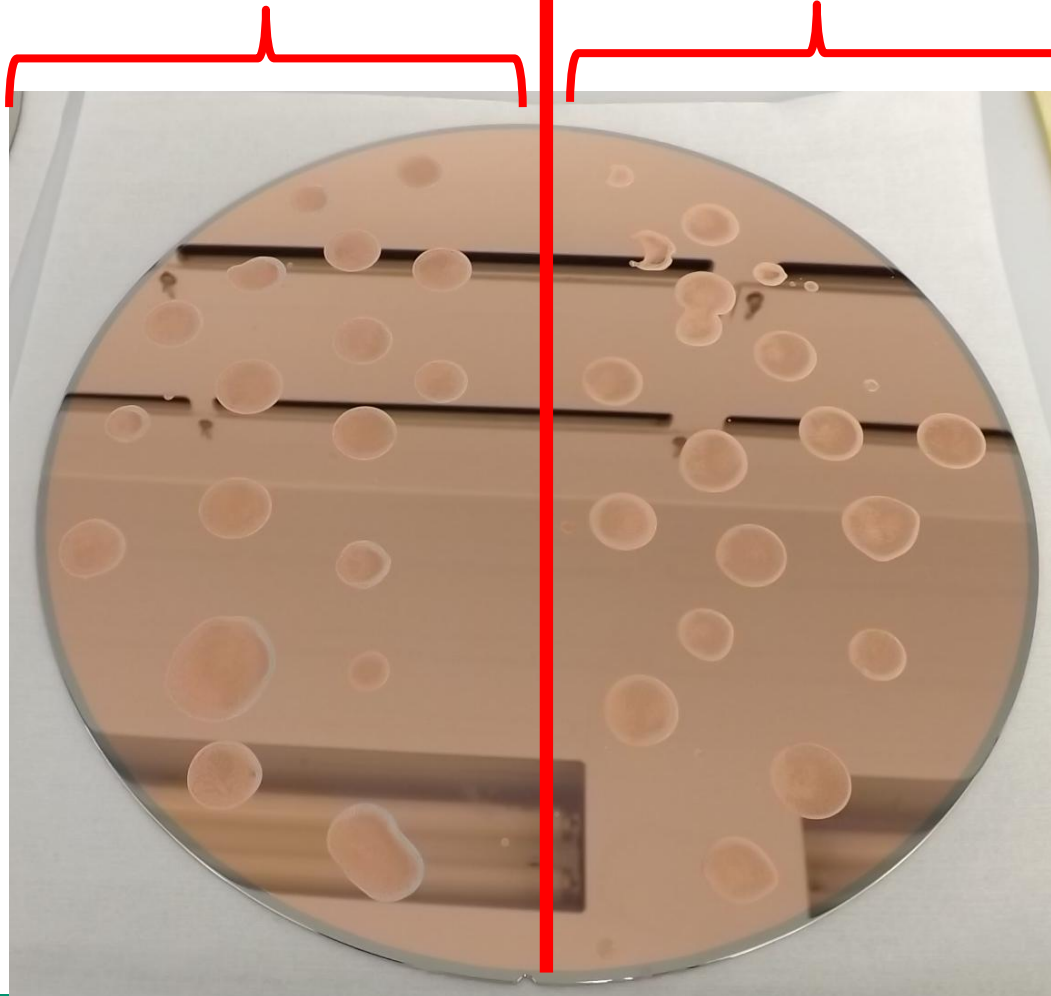
Legacy Cu Slurry

Cu Slurry with Co suppressor



Legacy Cu Slurry

Cu Slurry with Co suppressor



Similar Cu behavior, no added undesirable Cu interactions

- The addition of novel components to Cu CMP slurries can improve compatibility with Co, which is becoming a growing need for the industry
 - Lower static etch rates
 - Lower polishing rates
 - Higher corrosion potential and lower exchange current density
 - Copper polishing performance not compromised