Impact of Dissolved Oxygen on Metal Corrosion in Post-CMP Cleaning for Advanced Logic Structures

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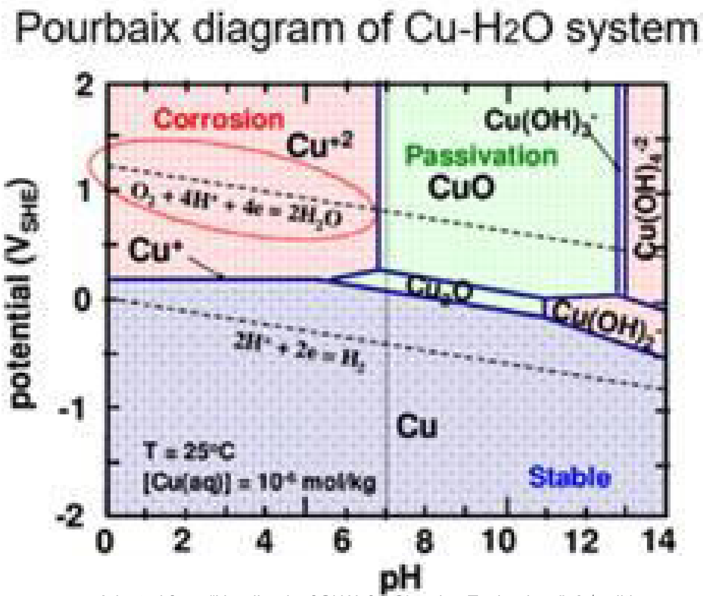
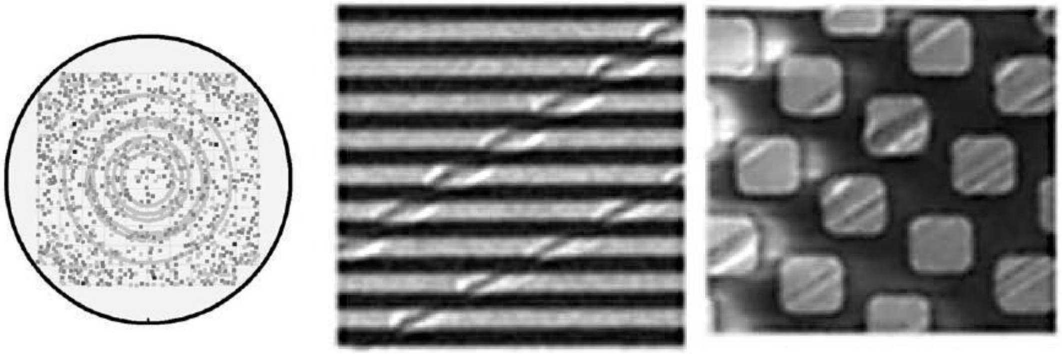
AGENDA

- Metal CMP cleaning challenges
- Electrochemical analysis of cleaning conditions
- Impact of dissolved oxygen on Cu corrosion current and surface oxygen content
- Chemistry delivery | Oxygen reduction and oxygen uptake
- Molybdenum CMP | Impact of dissolved oxygen

Metal Post-CMP Cleaning Challenges



Adapted from "Handbook of Si Wafer Cleaning Technology", 3rd edition
FIGURE 5.3-30 Potential – pH diagram of Cu-water system

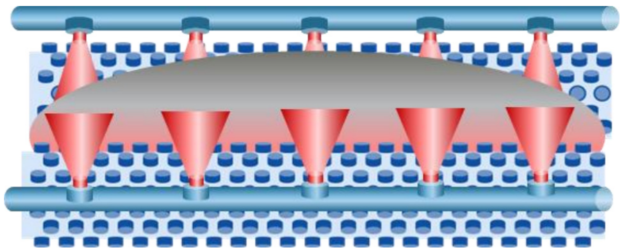


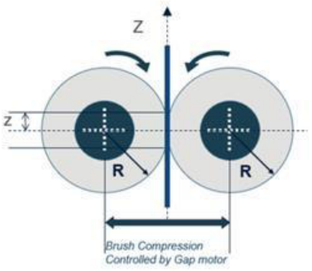
Published in "Handbook of Si Wafer Cleaning Technology", 3rd edition
FIGURE 5.2-16 (A) Wafer scan map of copper circular scratches generated by brush scrubbing. (B) SEM images of the scratches

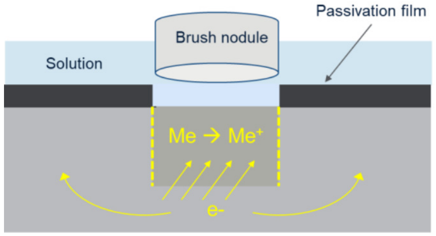
- Eliminate Cu corrosion
- Achieve high particle removal efficiency
- Prevent particle reattachment
- Avoid film damage

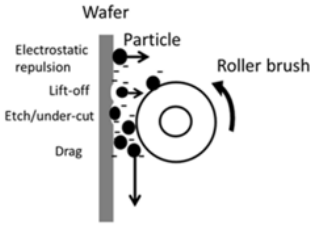
Unique characteristics of Cu metal present additional challenges for Post-CMP cleaning

Metal Post-CMP Cleaning | Wafer Center Corrosion Challenge



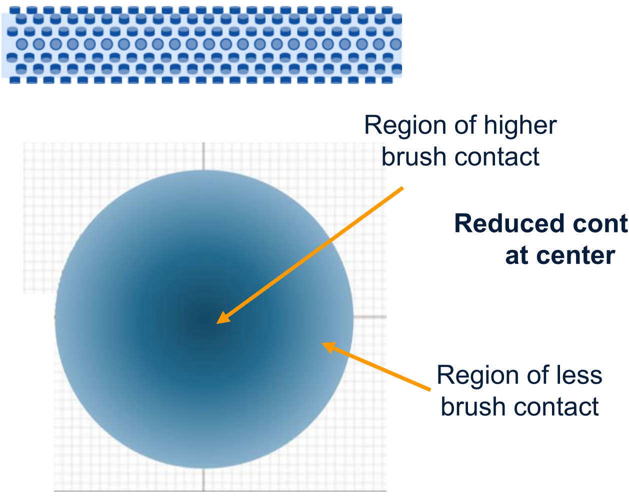




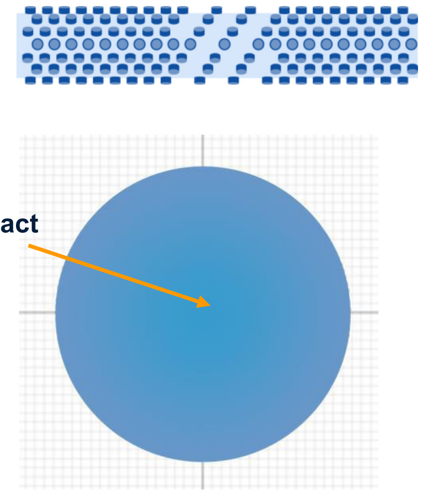


Excessive contact from the PVA brush can remove thin passivation Me_xO_y layer exposing underlying metal

Brush - Wafer Contact Uniformity



Reduced contact at center

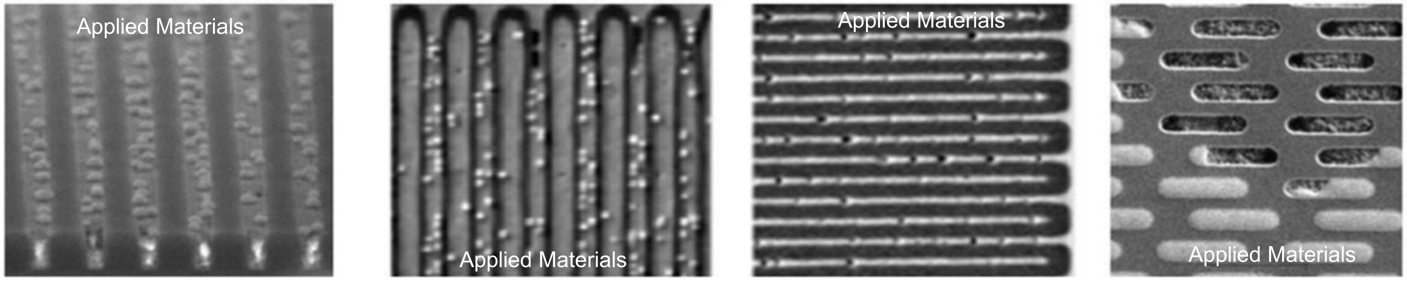


Small wafer center area receives heavier scrubbing duty cycle, with standard brush rollers

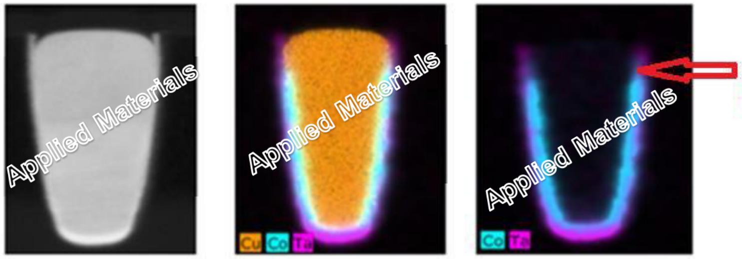
Modification of roller brushes for reducing wafer center defects

Metal corrosion at wafer center observed in advanced nodes with shrinking device geometry

Common Corrosion Related Defects



SEM images collected on internal Applied Materials test structures



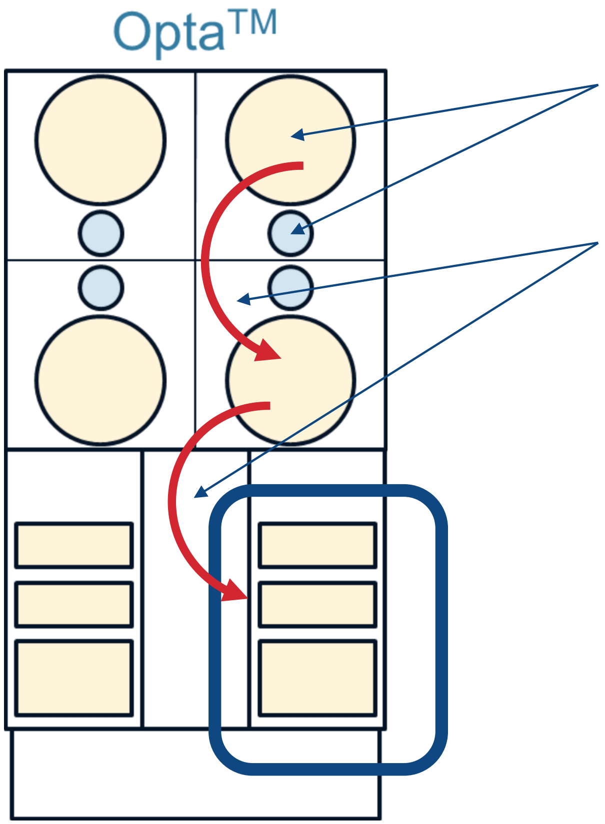
Co loss due to
Cu/Co Galvanic Corrosion

EDX Element Mapping:
Slit Divot Defect (Co Loss)

Cu Co Ta

Cu Oxidation, Corrosion, Missing metal, Divot Defects, Cu redeposition and dendrite growth

Holistic Approach Needed to Address Metal Corrosion



Post polish rinse optimization

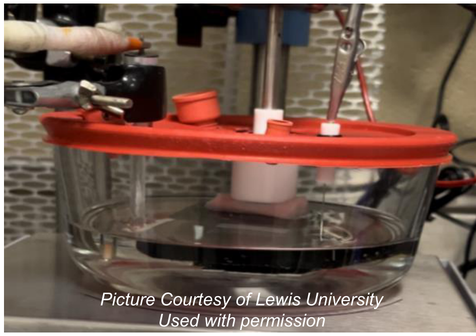
Airtime reduction

Optimization of mechanical action during clean

Chemistry optimization: (pH, corrosion inhibitors, zeta potential adjustors)

Focus: Reduce oxidation during chemical treatment through dissolved oxygen control

Electrochemical Analysis of Cleaning Conditions



Picture Courtesy of Lewis University
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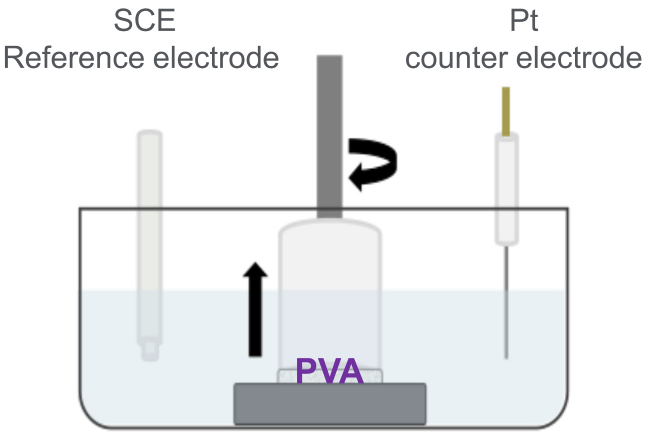
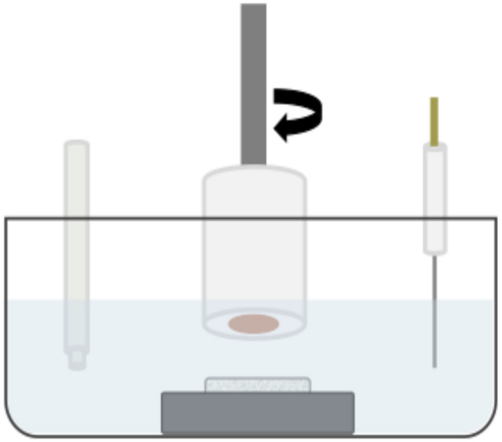
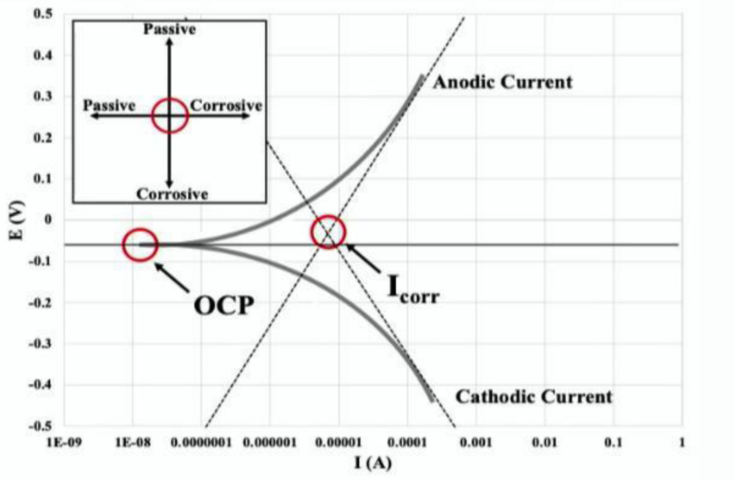
“Dynamic Cleaning” with Contact

“Static Cleaning” No Contact

Rotating working electrode in contact with PVA brush
Force equivalent to 2 mm displacement, 50 rpm

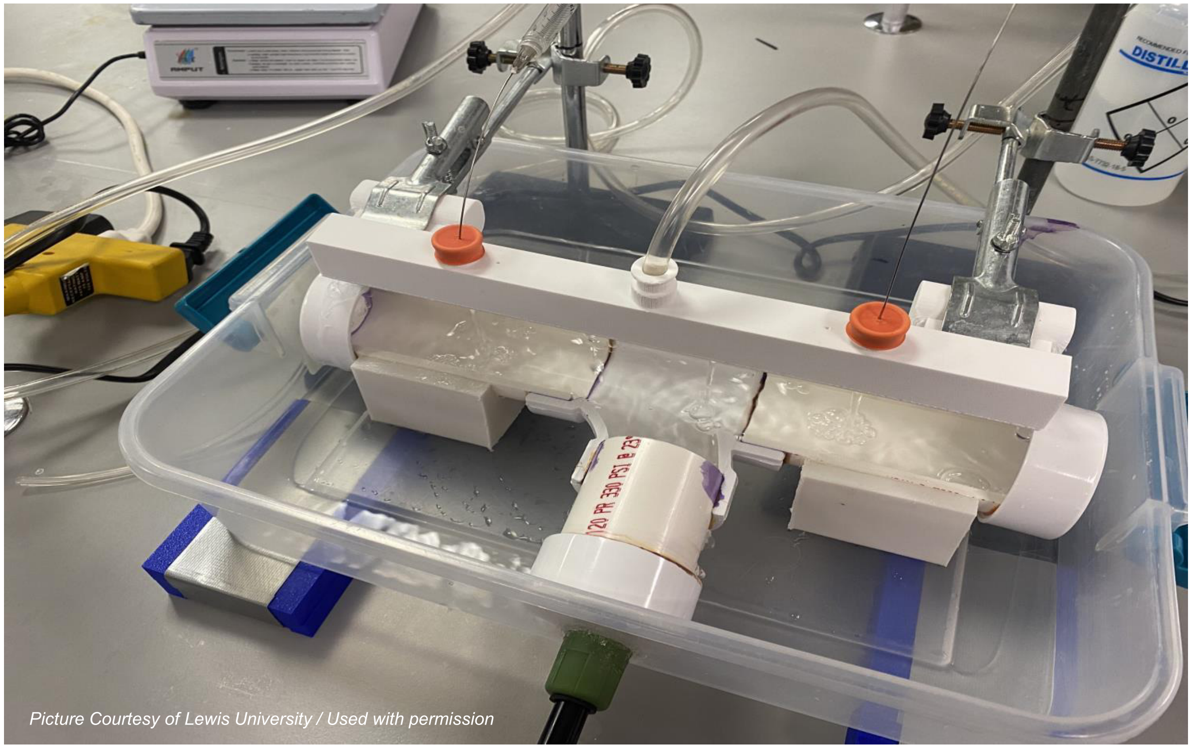






Electromedical characteristics are used to compare corrosion probability for different cleaning conditions

Dissolved Oxygen Measurements

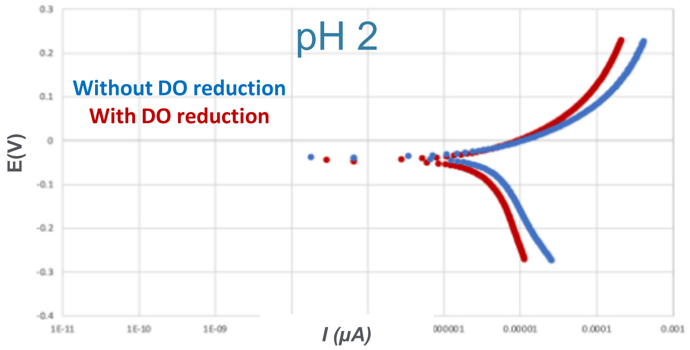


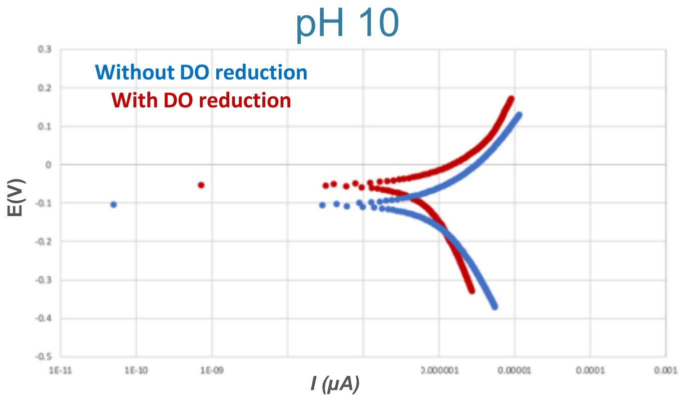
Picture Courtesy of Lewis University / Used with permission

Most of experiments are conducted using benchtop setups

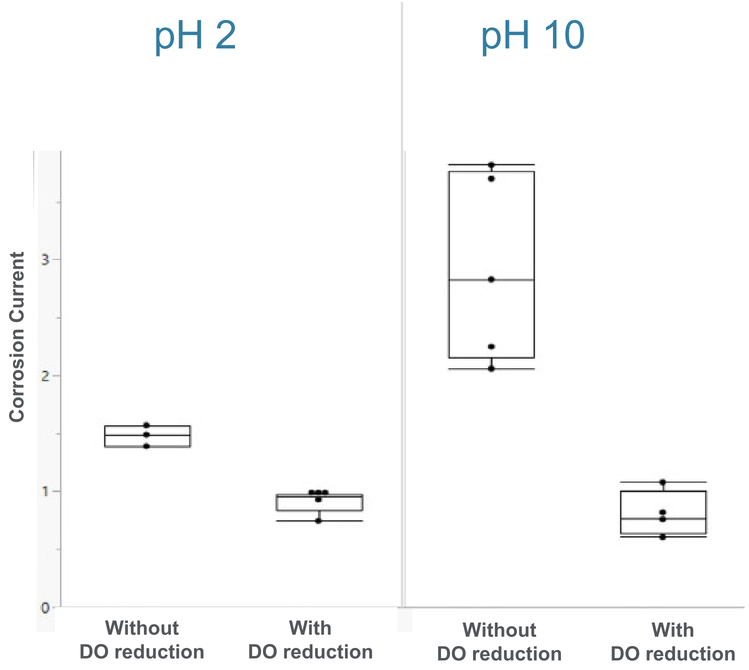
Cu | Dissolved Oxygen Impact on Corrosion Current

Effect of DO on Surface Redox Profile



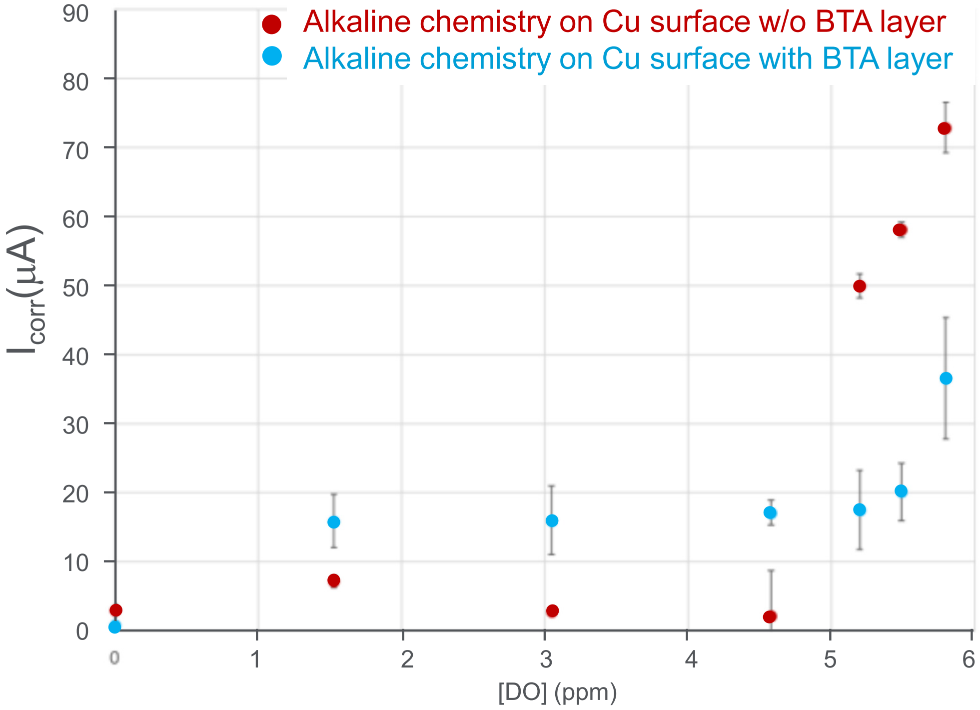


Corrosion current reduction on Cu surface in pH-adjusted DIW



Reduced DO correlates to reduced corrosion current

Cu | Corrosion Current Reduction in Alkaline Chemistry



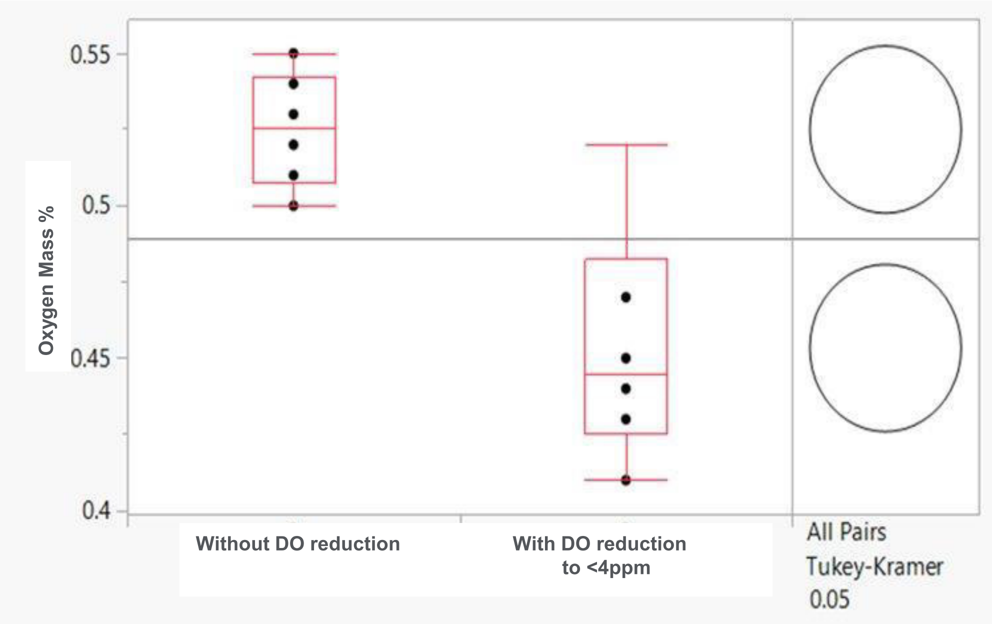
Environmental DO = 8 ppm
(no treatment)

Reducing DO from 8ppm to <4ppm suppresses corrosion current.

Benefit from further reduction is limited

Cu | Surface Oxygen Content on Cu surface

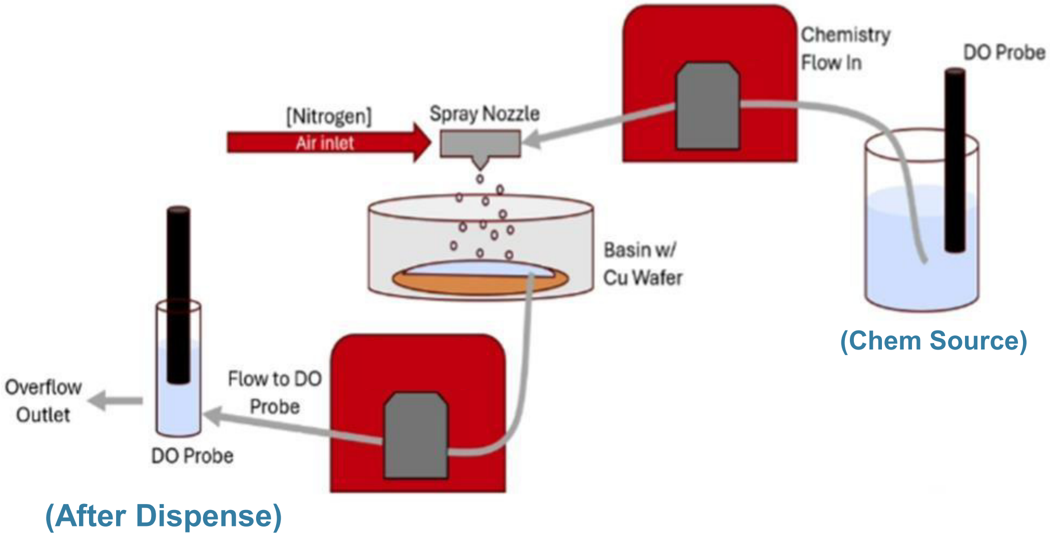
After alkaline chemistry treatment with and without oxygen reduction

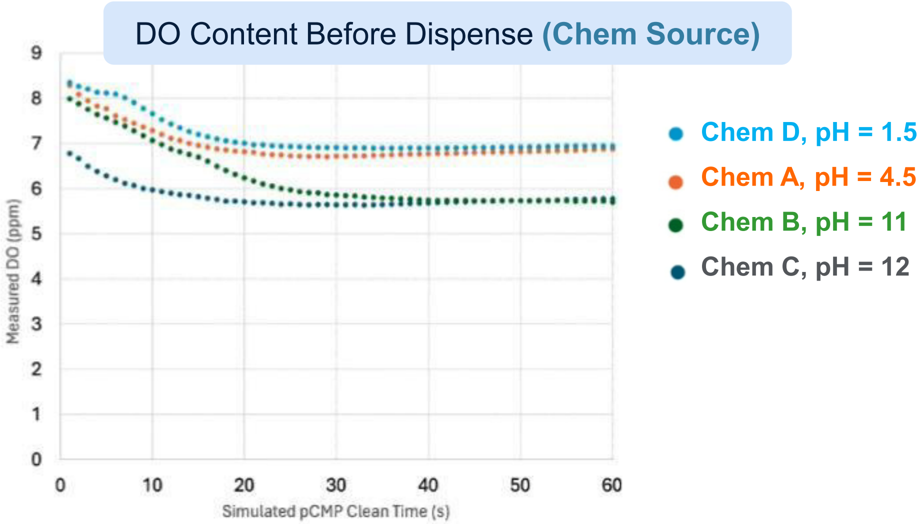


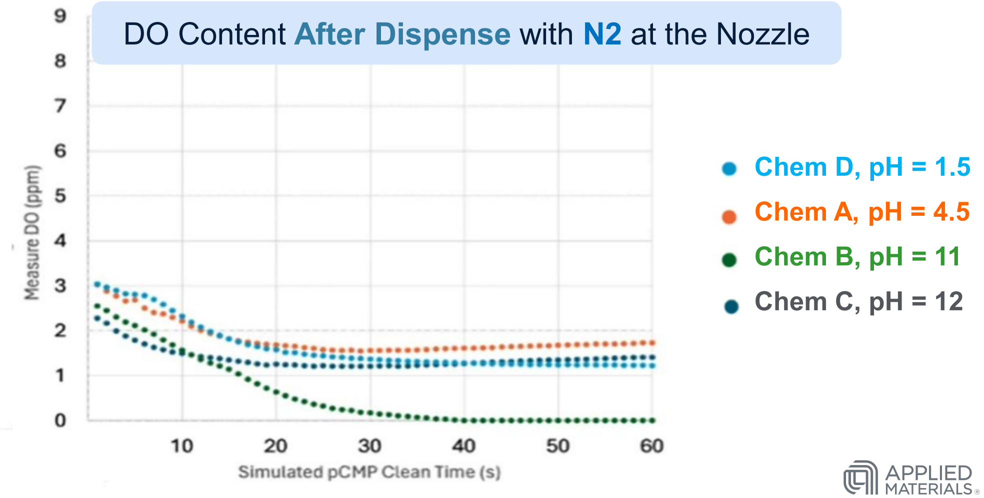
by SEM/EDS

Reduced DO in chemistry leads to reduction in oxygen content on treated surface

Dissolved Oxygen Reduction with Alkaline Chemistry Dispense from Jet Nozzle



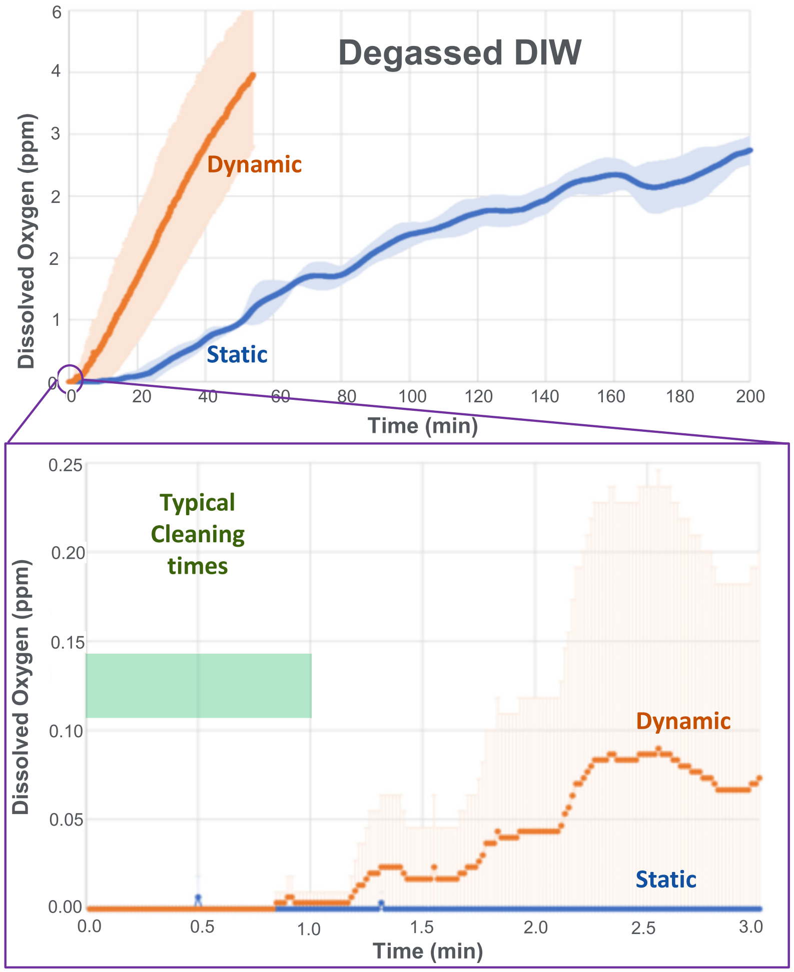




Using N2 in jet nozzle significantly reduces DO in dispensed liquid

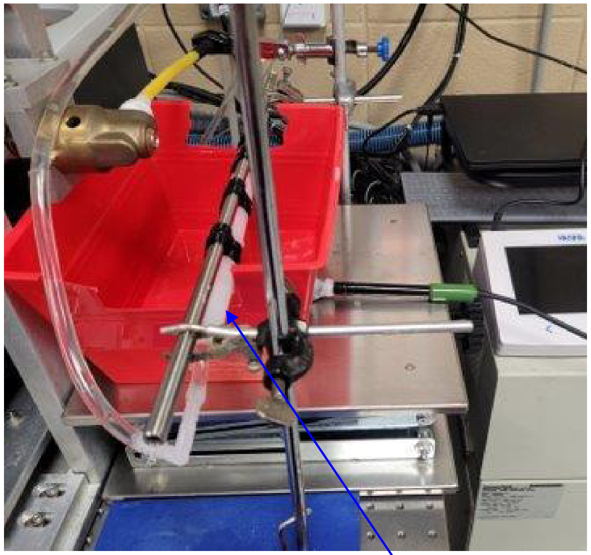
Presence of oxygen scavengers affects equilibrium DO concentration and DO drop under N2 purge

Oxygen Uptake in DIW under Static and Dynamic Conditions



Static

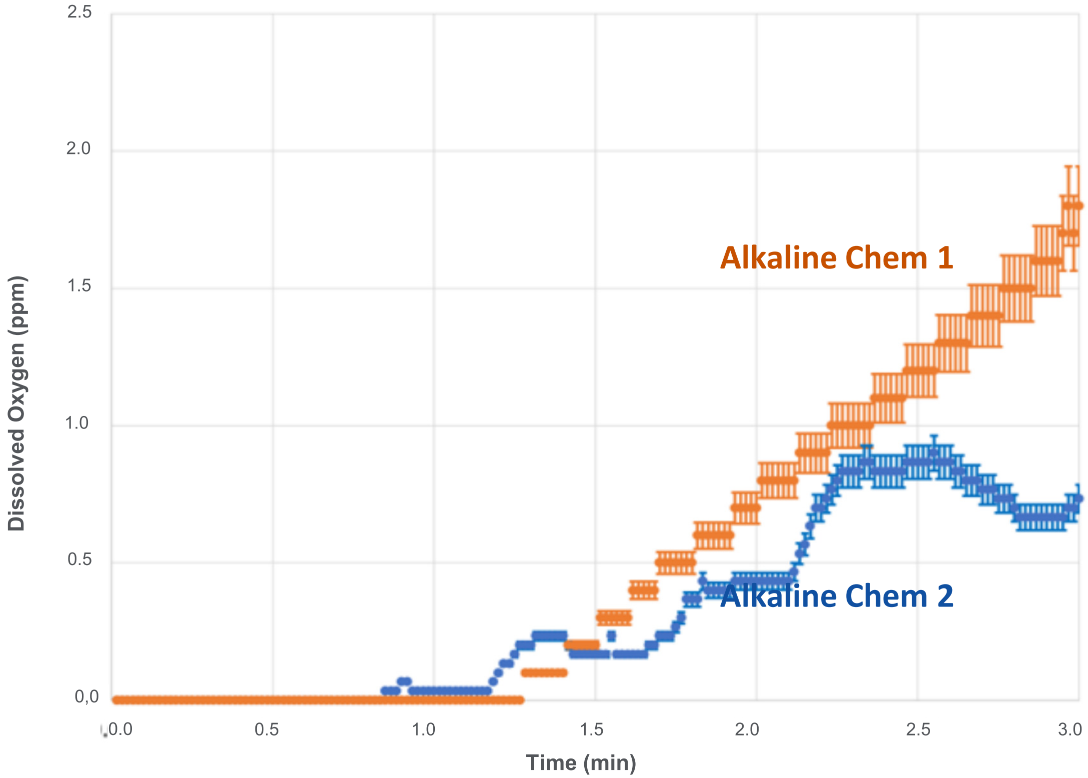
Dynamic



DIW flows out of Spray Bar

Even under dynamic conditions reoxygenation is slow

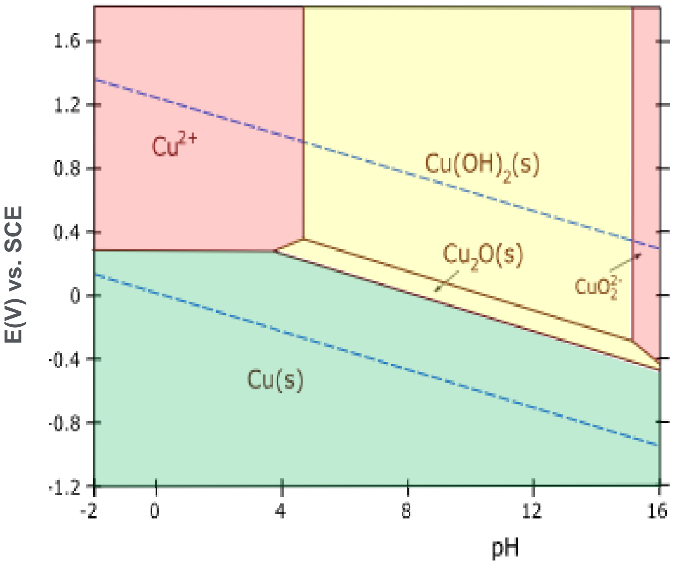
Oxygen Uptake in Cleaning Chemistry under Static and Dynamic Conditions



Similar to DIW, chemistry reoxygenation is slow

Molybdenum | Post CMP Cleaning Challenges

- Problem Statement: Metal corrosion in small features for advanced logic structures



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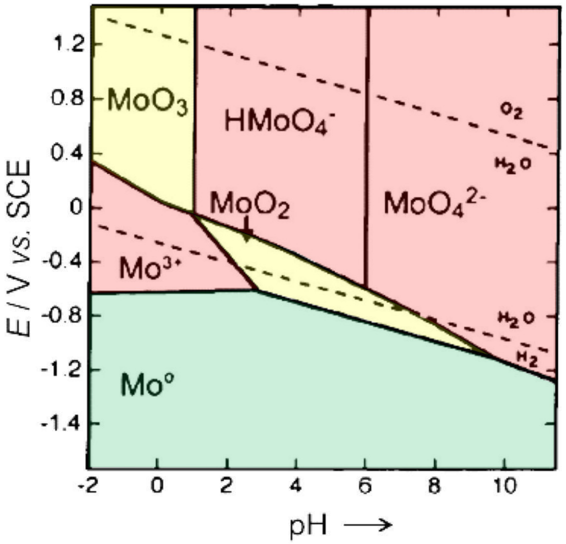


Adapted from "Molybdenum, Molybdenum Oxides, and their Electrochemistry", Viswanathan S. Saji and Chi-Woo Lee, ChemSusChem 2012, 5, 1146 – 1161

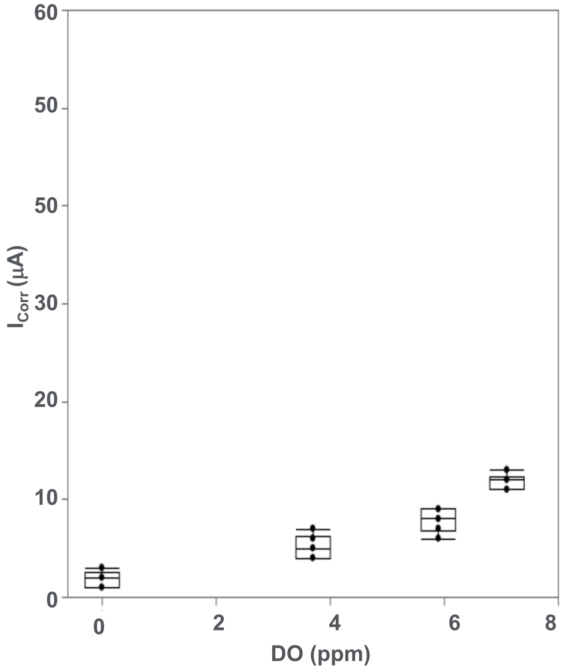
» In neutral and alkaline media, passivation is not effective due to the formation of soluble species $HMoO_4^-$, MoO_4^{2-}.

» In acidic solutions the passive film consisted mainly of MoO_2 together with MoO_3.

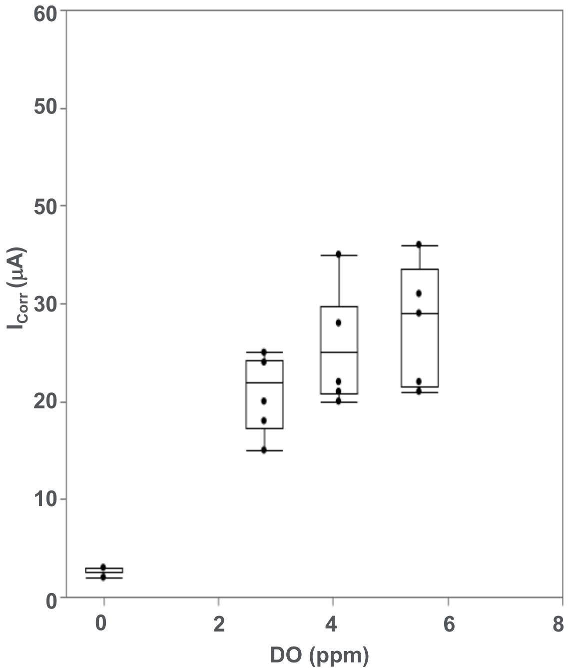
Approach: Minimize corrosion by reducing dissolved oxygen (DO) in liquids in contact with surface

Mo | Corrosion Current Reduction with Reduced DO

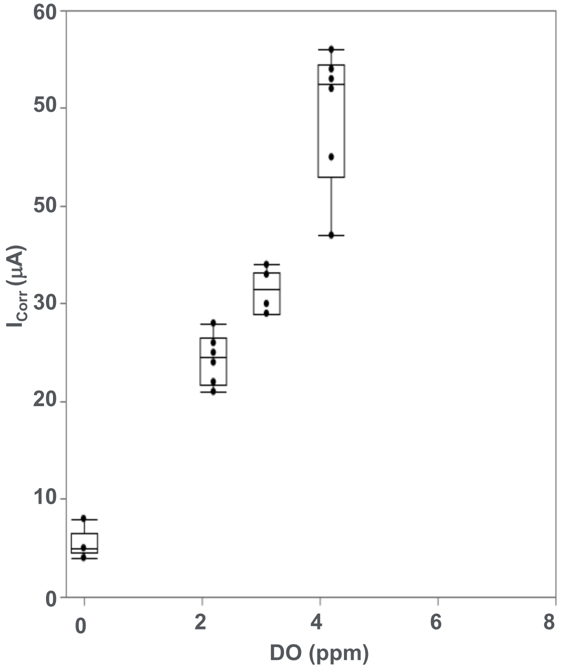
Chem B (pH=4.5)



Chem C (pH=11)



Chem D (pH=12)

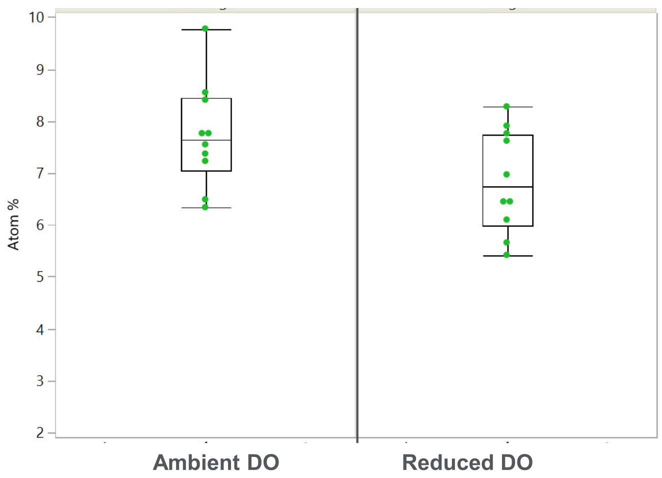


Reduced DO correlates to reduced oxidation of Mo, especially in alkaline solutions
DO reduction to less than 2 ppm is needed to minimize corrosion current.

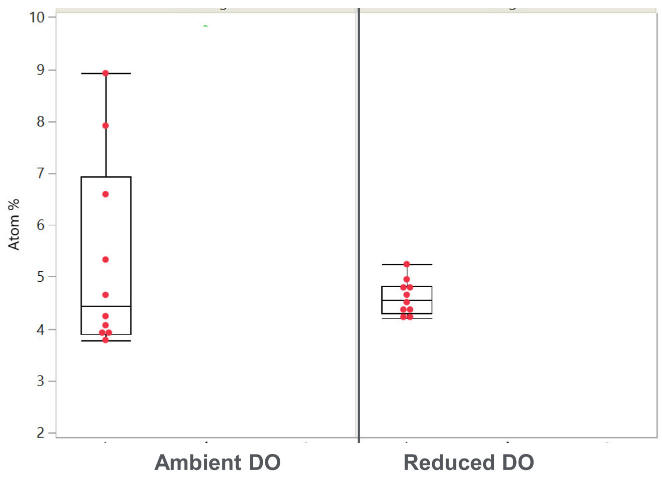
Ambient DO = 6-8 ppm, chemistry dependednt

Mo | Surface Oxygen Content with DO Reduction

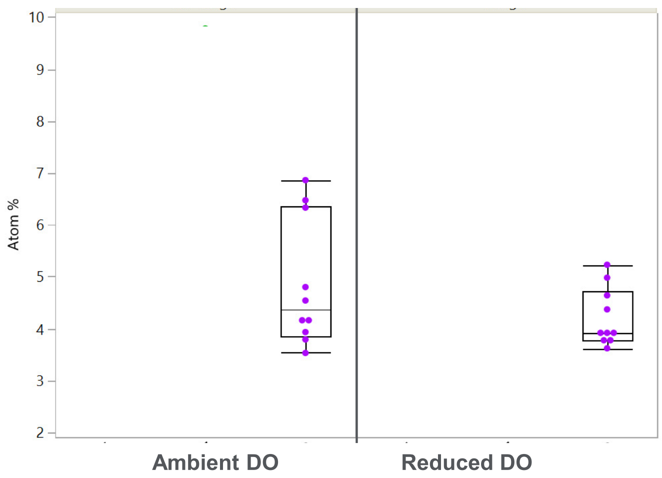
Chem B (pH=4.5)



Chem C (pH=11)



Chem D (pH=12)

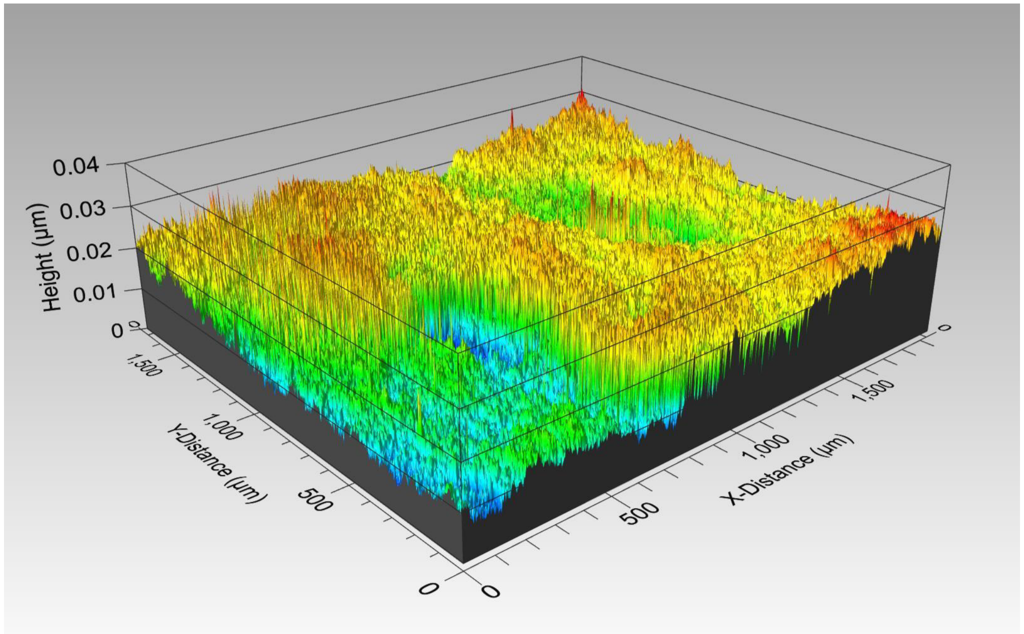


Reduced DO correlates to reduced and more consistent oxygen content on post CMP Mo surface

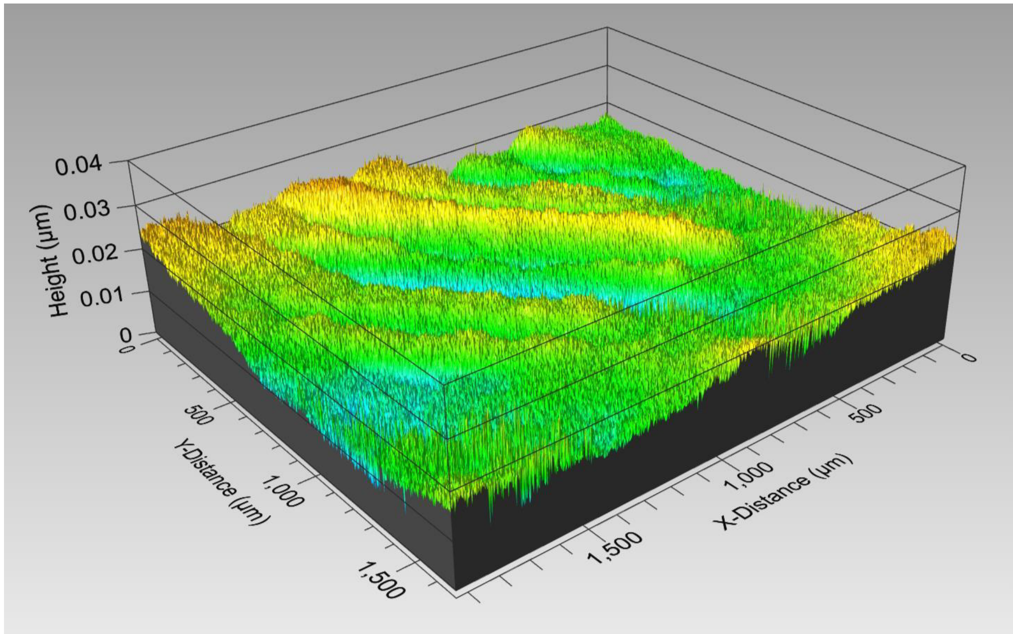
Ambient DO = 6-8 ppm, chemistry dependednt

Mo | DO Impact on Surface Roughness

Ambient Oxygen Content



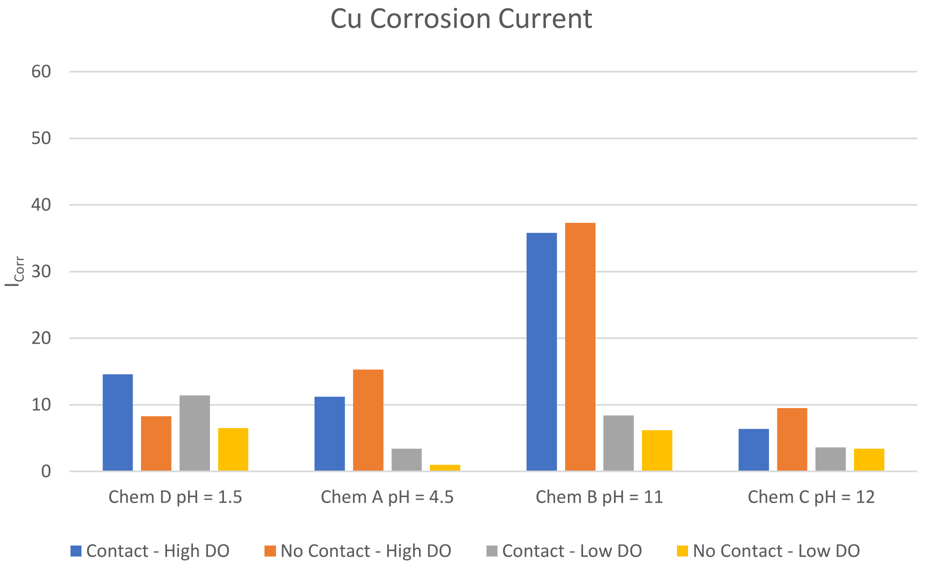
De-Oxygenated Chemistry

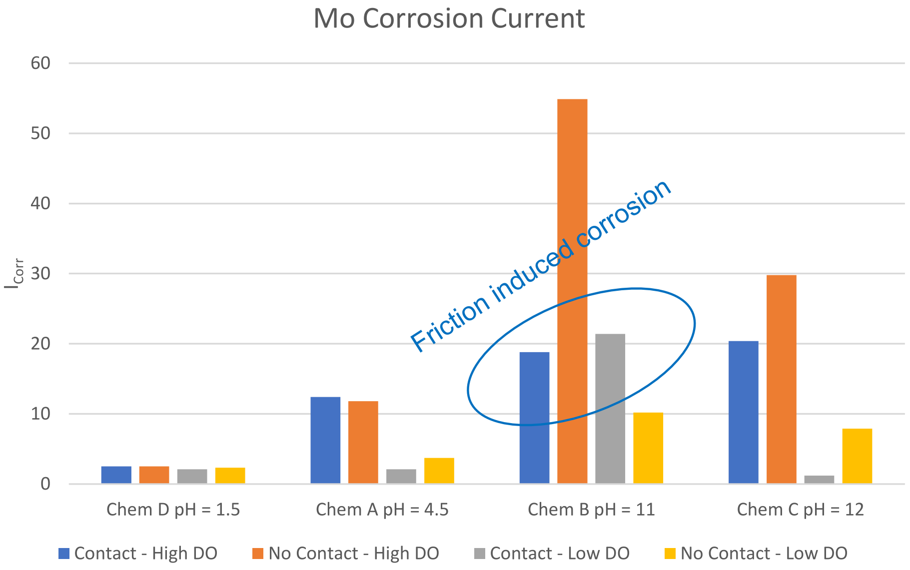


Wafer	Sa (nm)	Sq(nm)
No Purge	3.42±0.43	4.25±0.48
Purge	2.76±0.15	3.46±0.26

Using de-oxygenated cleaning chemistry yields smoother Mo surface

Cu and Mo Corrosion Current with and without Dissolved Oxygen





Reduction in Dissolved Oxygen leads to drop in overall corrosion current for both Mo and Cu

For alkaline chemistries, Mo has overall higher I_{Corr} compared to Cu

In certain chemicals, Mo exhibits friction induced corrosion (Chem B)

Key Learnings and Conclusions

- Metal Post-CMP cleaning is challenging, as it requires high particle removal efficiency to be achieved with reduced mechanical force and chemical aggressiveness.
- Reducing dissolved oxygen content in the cleaning chemical is beneficial for elimination of surface corrosion.
- For both Cu and Mo, reduction in dissolved oxygen leads to decrease in the overall corrosion current I_{Corr} and minimizes oxidative half-reaction.
- N2 purge is effective in removing DO from cleaning chemicals.
- Oxygen uptake into the chemicals is slow on a time scale typical for post-CMP cleaning processes, even with chemistry being dispensed through a standard spray bar

Acknowledgement

- This work is a result of outstanding collaboration between Applied Materials CMP Business Unit and Lewis University Prof. J. Keleher Research Group. Thank you, Team!

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