Semiconductor Manufacturing Going Green – Role of Chemical Mechanical Planarization (CMP)

The 18th U.S.-Korea Forum on Nanotechnology:
Sensors Related to Human Cognition and Sustainability in Semiconductor Manufacturing

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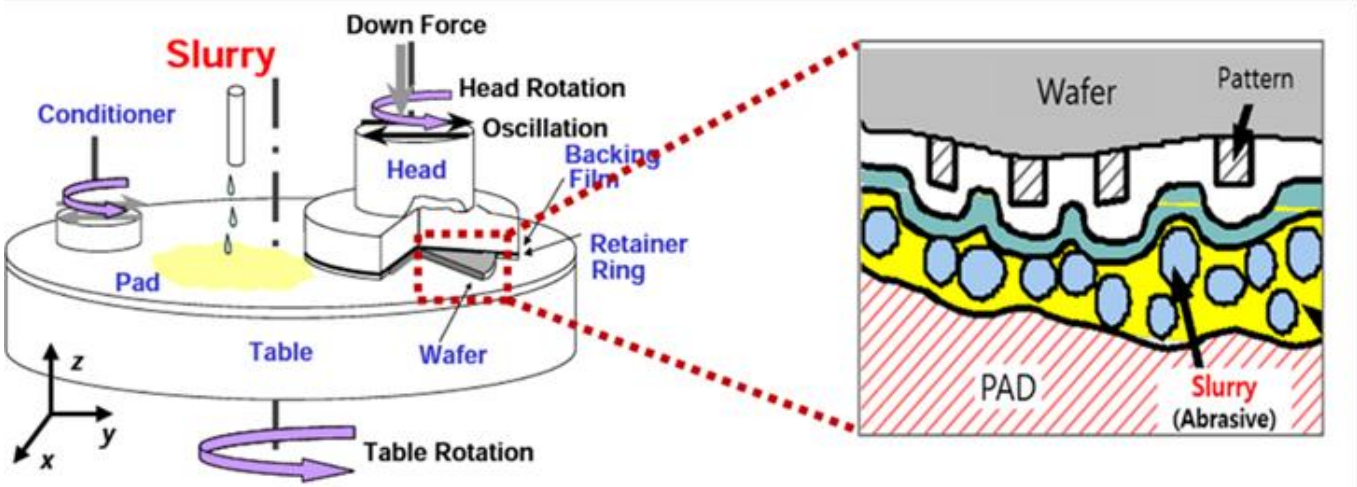
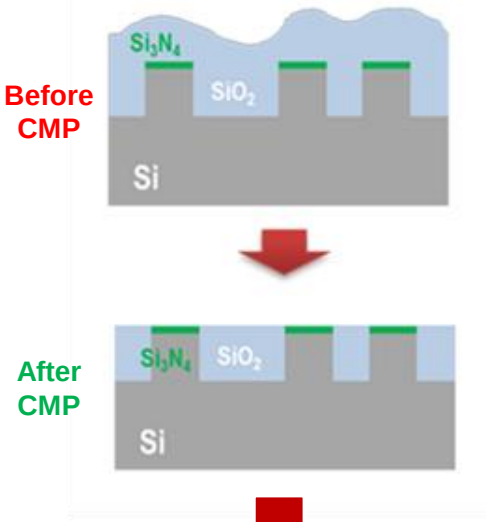
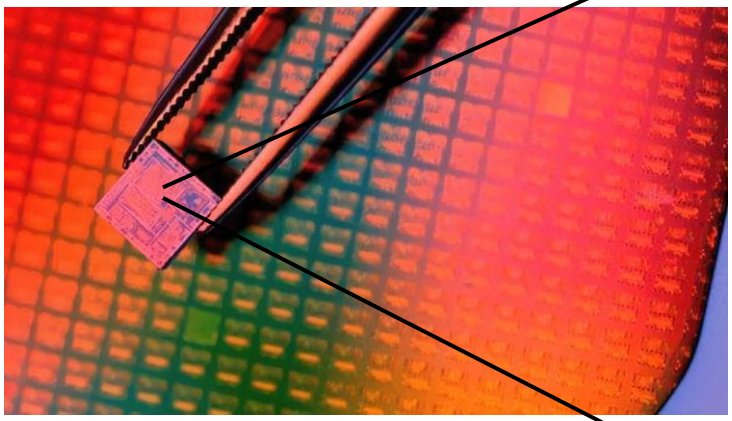
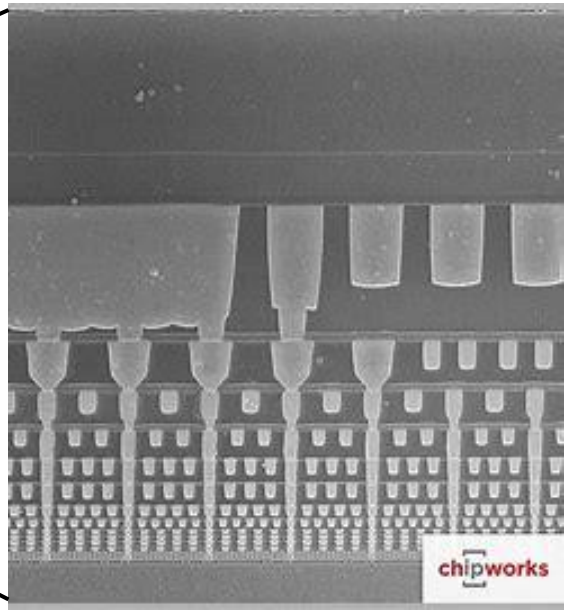
September 23-24, 2024

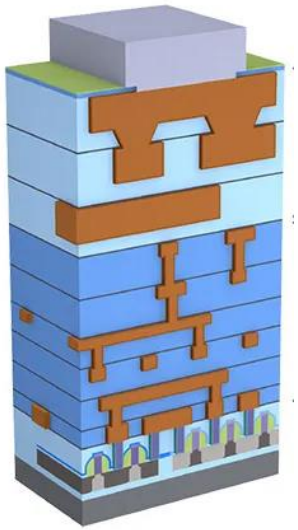
What is CMP and how does CMP contribute to the semiconductor industry?









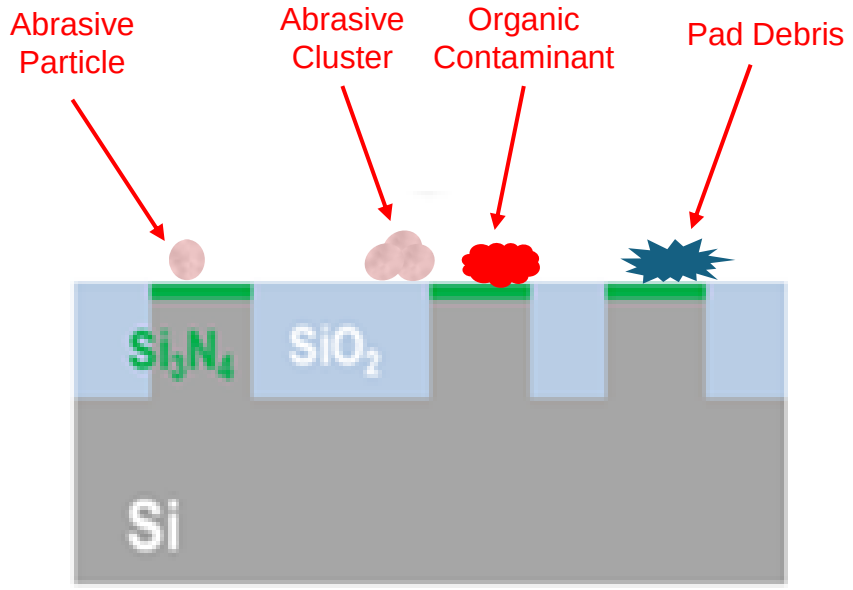


CMP can achieve global planarization !!!

Zhao L, in All about Interconnects, *Semi Engineering*, 2017

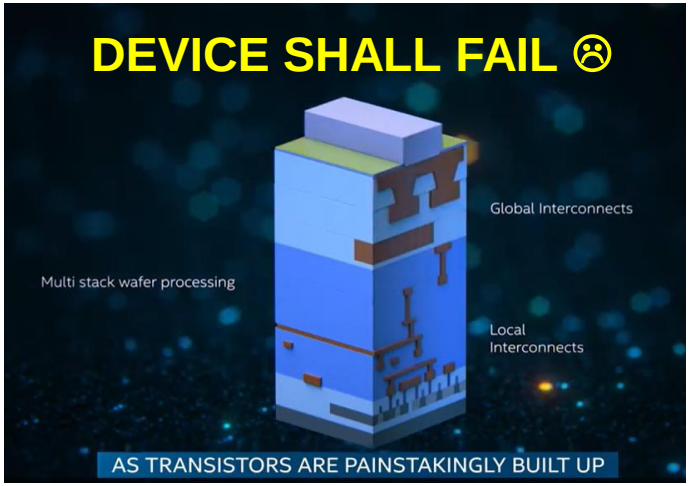
Kim J Y, Post Cleaning Chemical of Tungsten Chemical Mechanical Planarization for Memory Devices, 2014

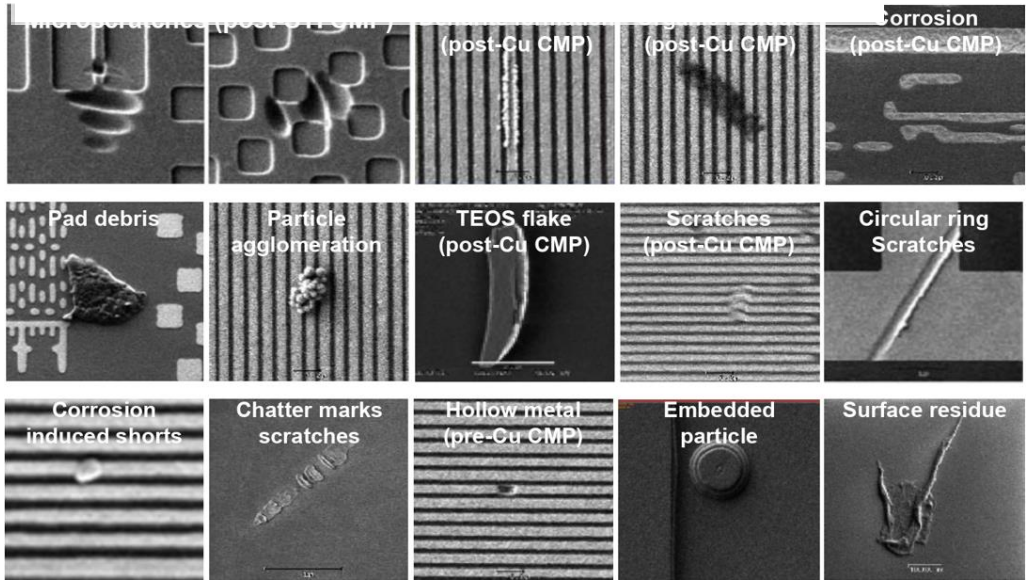
Why Post CMP Cleaning?

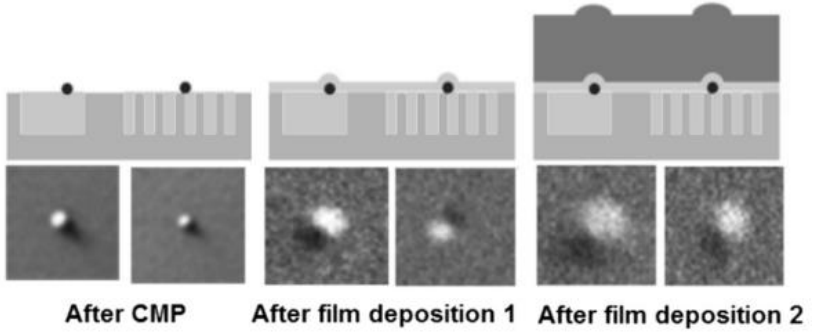


Inadequate residue removal leads to –

- → **poor adhesion of subsequent layers**
- → **electrical shortage or leaking**
- → **insufficient device reliability**





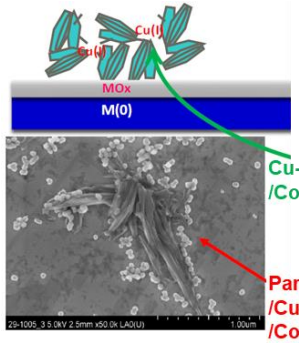


Post-CMP Cleaning to the Rescue!

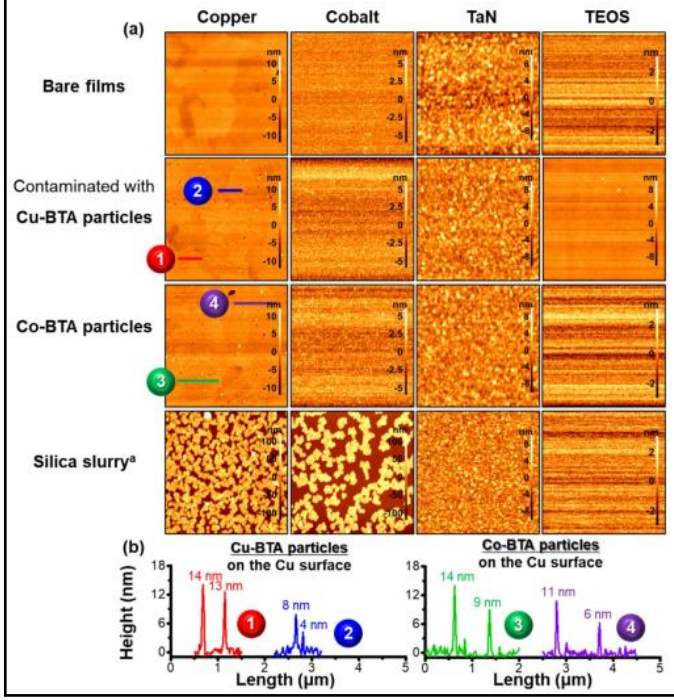
W.-T. Tseng, in S. V. Babu, *Advances in Chemical Mechanical Planarization (CMP)*, Woodhead Publishing, 2016

Strategies for Post-CMP cleaning of Cu and Co films

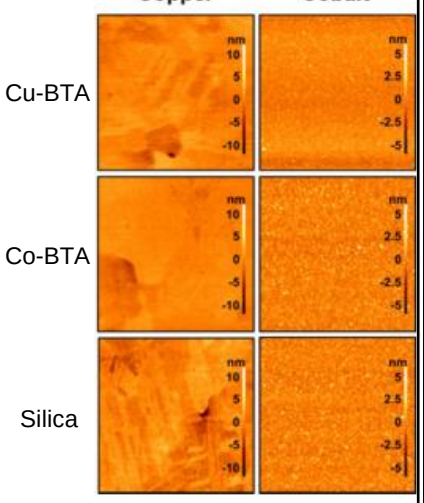
Post-CMP Cleaning solutions for the removal of contaminants



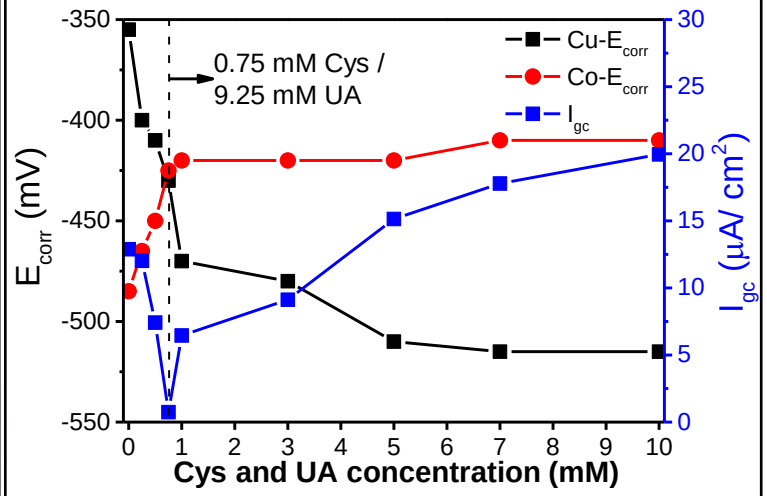
Chelating agents	Stability constants Cu(II)	Co(II)
Citric acid	6	4
Glycine	8	5
EDTA	19	16
En	19	14
BTA	4.9[a]	2.7–3.9[b]

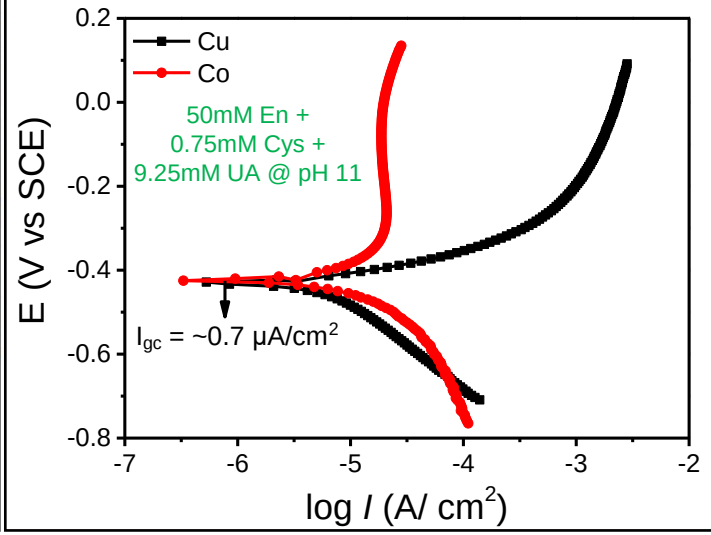


Cleaning with
50mM En + 0.75mM Cys +
9.25mM UA @ pH 11



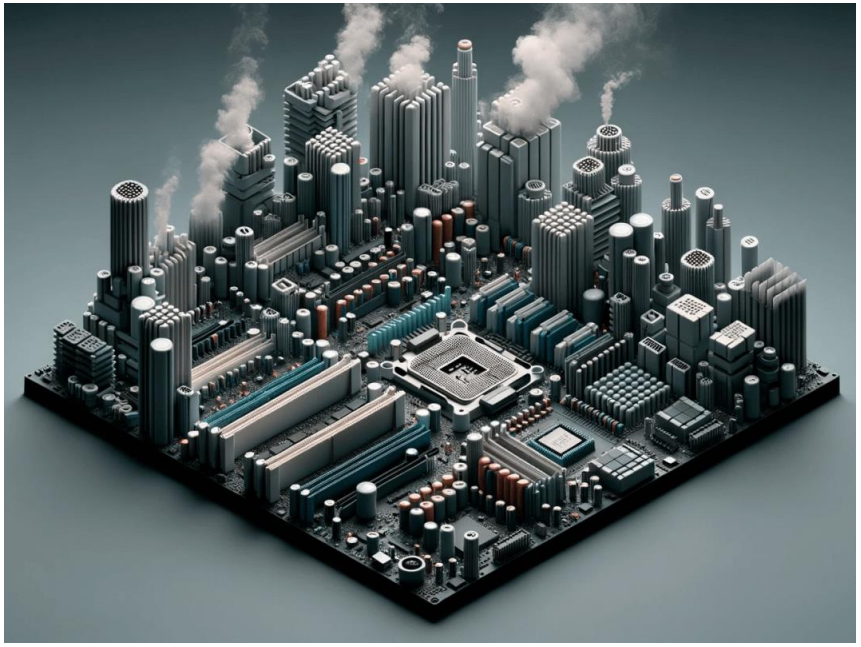
Control of galvanic corrosion of Cu-Co





Source: Jihoon Seo, **S. S. R. K. Hanup Vegi**, and S.V. Babu, *ECS J Sold State SC*, 8(8), P379-387,2019

How Do We Reduce the Semiconductor Carbon Footprint?



Safety first

Quality follows

Micron · intel capital · Lam Research Capital · M. Ventures · ASML · Applied Ventures · Samsung · KLA · TEL

SEMI member companies joined forces to seek out and partner with the world's top startups to bring new sustainability technologies to semiconductor operations in:

Energy efficiency	Water	Material usage and sustainability
at tool, manufacturing processes, and supply chain levels	sustainability technologies to increase manufacturing process efficiencies, reclamation, reuse and restoration in industrial treatment centers	including alternative chemistries for wafer processing, materials recycling and waste stream abatement

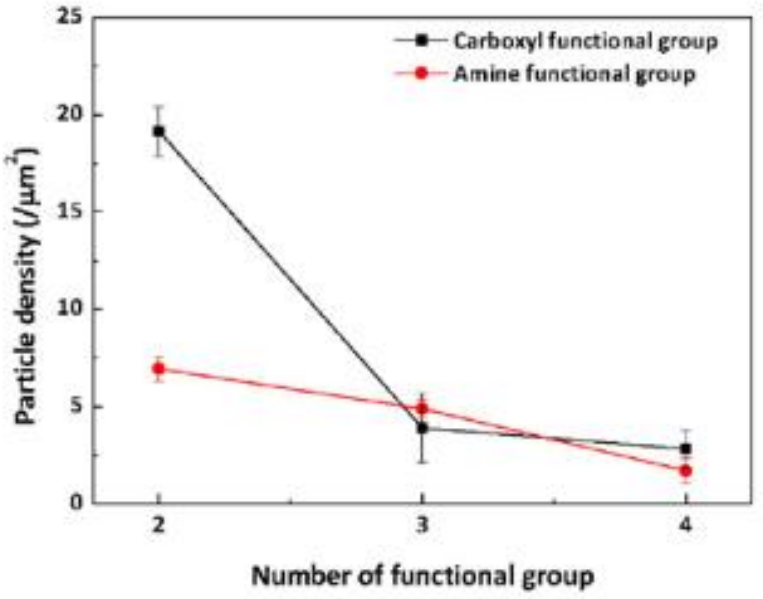
Environmentally benign products are the need of the hour.

This significantly lowers the energy consumption that is spent on the treatment of various hazardous chemicals before their discharge.

Dean Freeman in "How Do We Reduce the Semiconductor Carbon Footprint?", 3DInCites blog, SEMI.

Choosing the apt chemistry – effective and safe too!

Chelating Agent	Stability Constant *,† (Co^{2+}) log [K_{eq} (mol^{-1})]
Oxalic Acid	4.7
Glycine	5.2
Citric Acid	4.4
EDTA	16.3
En	14



Aliphatic diamine as chelating agent	# of metal complexes*
Ethylenediamine (DE)	>3000
1,3 propane diamine (DP)	182
1,4 butane diamine (DB)	18
1,6 hexane diamine (DH)	0

Ability to chelate decreases

Are the long chain amines effective for the removal of organic residues?

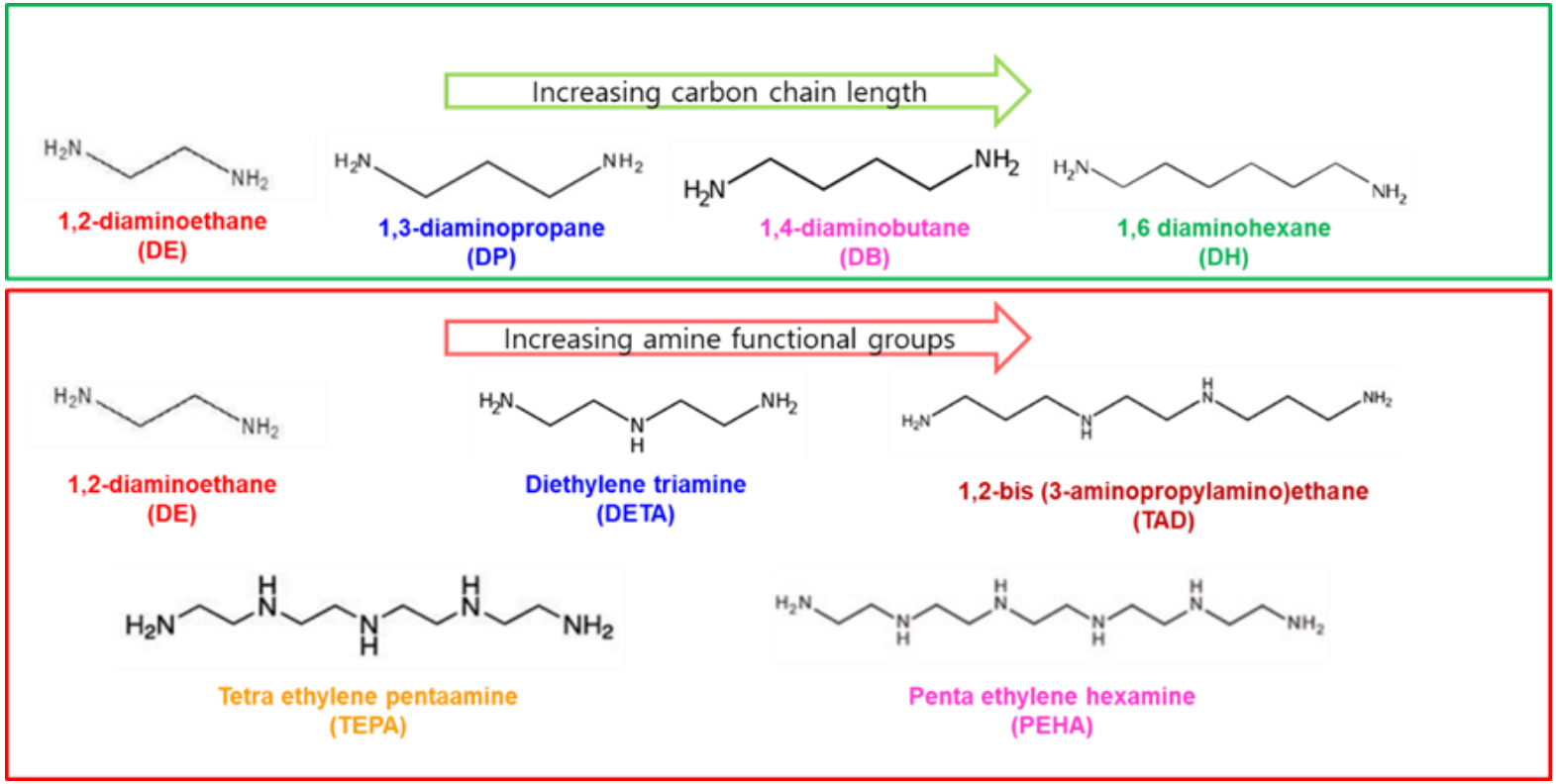
▶Our primary goal while developing post-CMP cleaning solution is to break the metal complex bond by promoting ligand exchange between the chelating agent and inhibitor molecule with the metal ion and control corrosion, while we choose less toxic chemistries.

▶Based on the literature, not all amines can readily form complexes with metal ions. Hence, choosing the right amine as the chelating agent in the cleaning solution is important.

A. E. Martell, *NIST critically selected stability constants of metal complexes database*, National Institute of Standards & Tech(1998); Lutsenko et al., *Complexation $Zn^{2+}$and $Co^{2+/3+}$ with primary diamines: Synthesis, structure and thermal properties*, Polyhedron 190 (**2020**).

Lee et al, *The effect of TAD based cleaning solution on post Cu CMP process,* Microelectronic Engineering 162 (**2016**).

Amines identified for the study



▶ Primary amines of different alkyl chain lengths and amines consisting of both primary and secondary amine groups are chosen to study their ability to break the metal complex.

▶ In this study, we refer to DE and DP as short-chain amines and DB and DH as long-chain amines.

▶ Toxicity of these amines are in the order DE > DP > DB > DH, with DE being most toxic. Among the secondary amines, TAD is the least toxic compared to others, hence preferred in the post-CMP cleaning chemistry.

Summary

	DE	DP	DB	DH	DETA	TAD
Type of amine	Linear, Short chain	Linear, Short chain	Linear, Long chain	Linear, Long chain	Linear, Short chain	Linear, Long chain
MW (gm)	60	74	88	116	103	189
# of amine functional groups	2	2	2	2	3	5
Mass fraction of amine groups	0.53	0.43	0.36	0.28	0.47	0.41
I_{corr} - Co film ($\mu A/cm^2$)	180	120	1	1	120	40
Co Cleaning Efficiency	High	Low	Very Low	Very Low	High	High
Toxicity	Most toxic	Toxic	Toxic	Toxic	Toxic	Least toxic

▶While the long chain amines (DB and DH) inhibit film corrosion, the short chain amines (DE and DP) promote film corrosion.

▶ Amine functional groups also help in modulating the metal film corrosion currents that helps in removing the adsorbed organic residue layer from the film surfaces.

▶ Both DETA and TAD show high cleaning efficiency and preserve the film surface quality post cleaning. Moreover, TAD is less toxic and preferred in the post-CMP cleaning chemistry.