Versum Materials' Tungsten Chemical and Mechanical Planarization Technology

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Agenda

- Versum Materials' diverse CMP and pCMP clean product offerings
- W CMP
    - Balance of chemical and mechanical aspects
    - Importance of fundamental and mechanistic investigation
    - W removal kinetics
        - Characteristics of oxidized W surface film and RR model
        - Strong temperature dependence: in-process heat generation, incubation and activation behavior
- Performance table of exemplary VM's W CMP products
- Conclusive remarks

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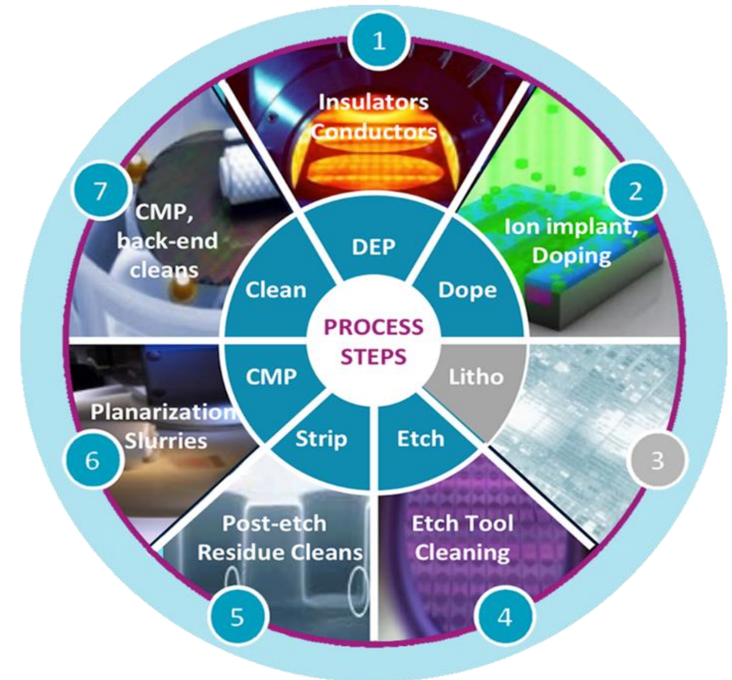
FOCUSED PURE PLAY WITH STRONG PORTFOLIO AND CAPABILITIES

- Focus on the semiconductor (IC) materials space where materials provide low cost in use/high value in use
- Leverage technology leadership, global scale, quality and reliability capabilities, and partnership with customers and OEMs to develop and commercialize the next generation technologies which will advance the industry
- Expand into adjacent segments within IC



Versum Materials participates in six of seven key semiconductor process steps

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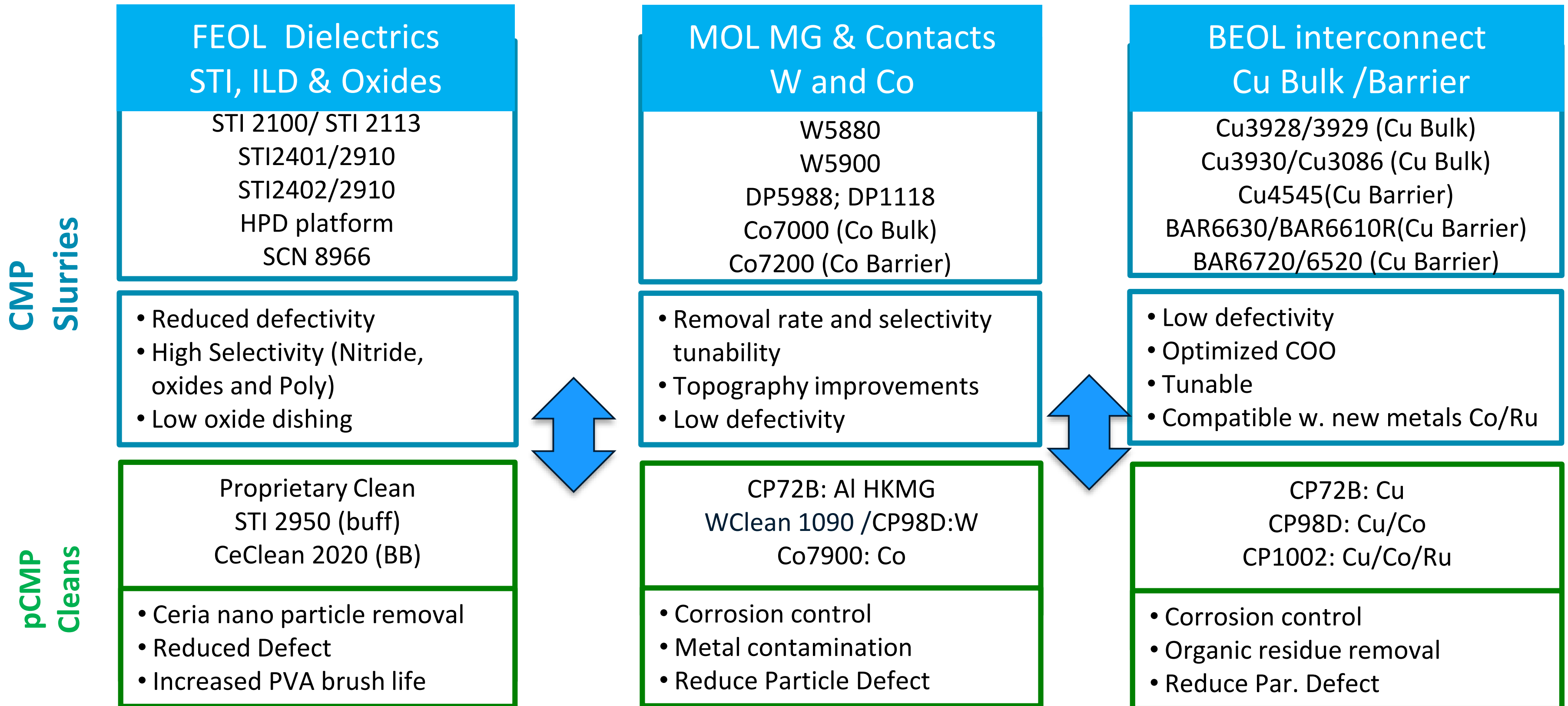
VM's Broad Product Offerings in FEOL and BEOL Slurries and Post CMP Cleans



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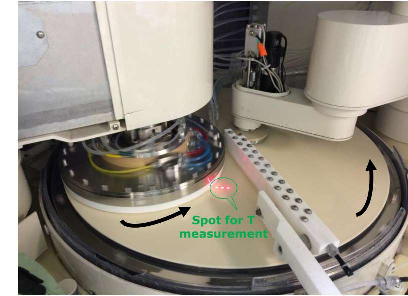
Tungsten CMP



Ice

slush

Too hard to deal with

Chemically creates soft surface layer

Mechanical removal of the soft layer

W

Oxidant + Catalyst

WOxHy

W

Abrasive particles

W

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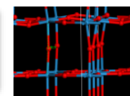
Fundamental and Mechanistic Investigation

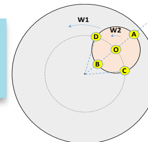
Differentiated W Products with Speed, Quality and Reduced Cost

Applied Polish Assessment

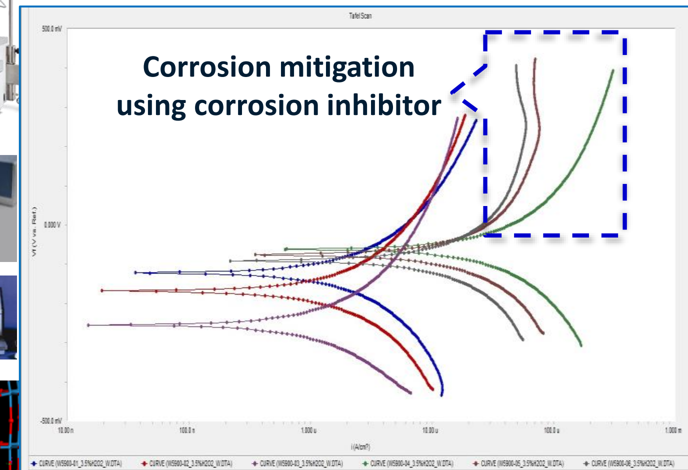
Fundamentals & Mechanism

- W corrosion/mitigation
- W oxidation kinetics
- Interfacial interactions
- Colloidal chemistry
- Computation modelling
- Fluid dynamics

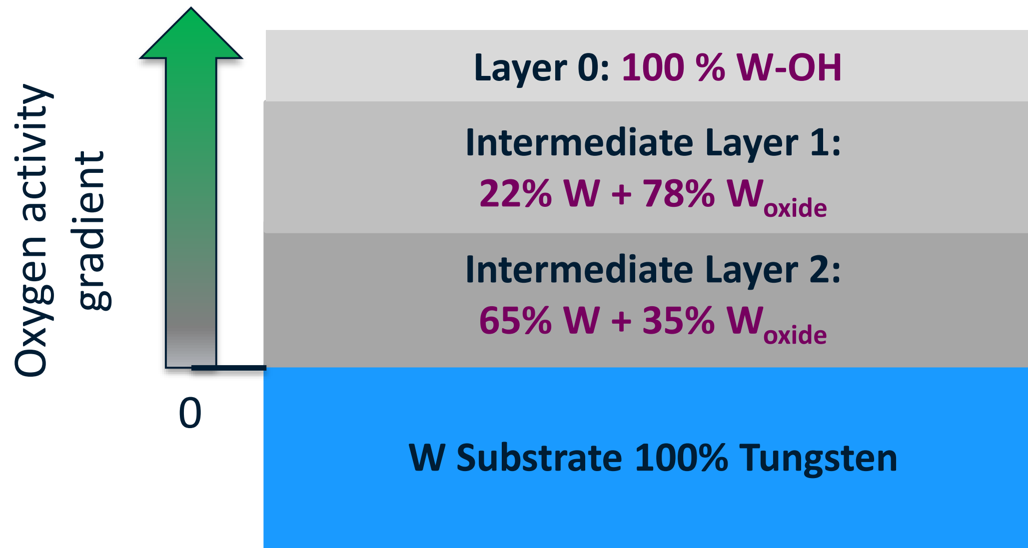




Electrochemistry: Tafel plots



Layered-structure of an Oxidized W Surface



- **Only the very top metal oxide layer is abraded during CMP.**
- **W forms protective oxide films**

**Small, Volume 4, Issue , pages 87–91, January 18 (2008)*
*****Basim G.B.**,"Formulation of Engineered Particulate Systems for Chemical Mechanical Polishing Applications", PhD Dissertation, UF, Florida, FL (2002)*

- *Thickness and density of the oxidized tungsten films determined by **X-Ray Reflectivity** analyses after oxidizing with H_2O_2 addition and post cleaning in 1 M KOH.*

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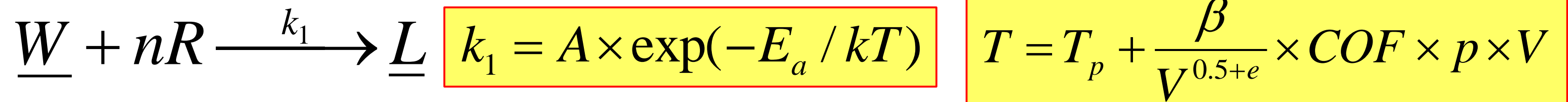
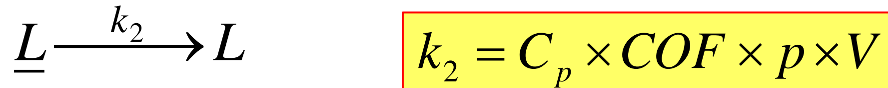
W Removal Rate Model

- **Modified Langmuir-Hinshelwood (LH) model:**
  - **n moles of reactant R in the slurry react at rate k_1 with tungsten film on the wafer to form a product layer L on the surface**



  - **Product layer $\underline{L}$ is subsequently removed by mechanical abrasion with rate k_2**



  - **Abraded material *L* is carried away by the slurry**

- **RR in this sequential mechanism therefore <u>is a function of both chemical and mechanical attributes of the process</u>**

$$RR = \frac{M_w}{\rho} \frac{k_1 k_2}{k_1 + k_2}$$

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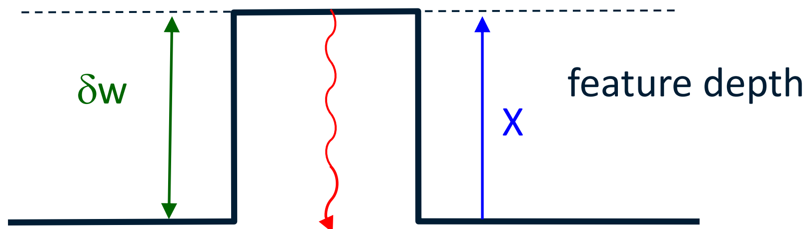
In collaboration with professor Ara Philipossian

W Removal: An Thermally Activated Process

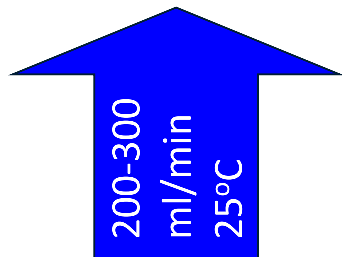
Heat is generated by ***friction*** and ***exothermic oxidation.*** Temperature at the wafer surface is constantly changing.

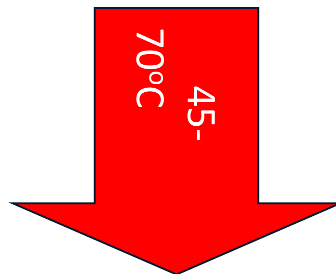


Reaction 2,000Å/min = 24 W

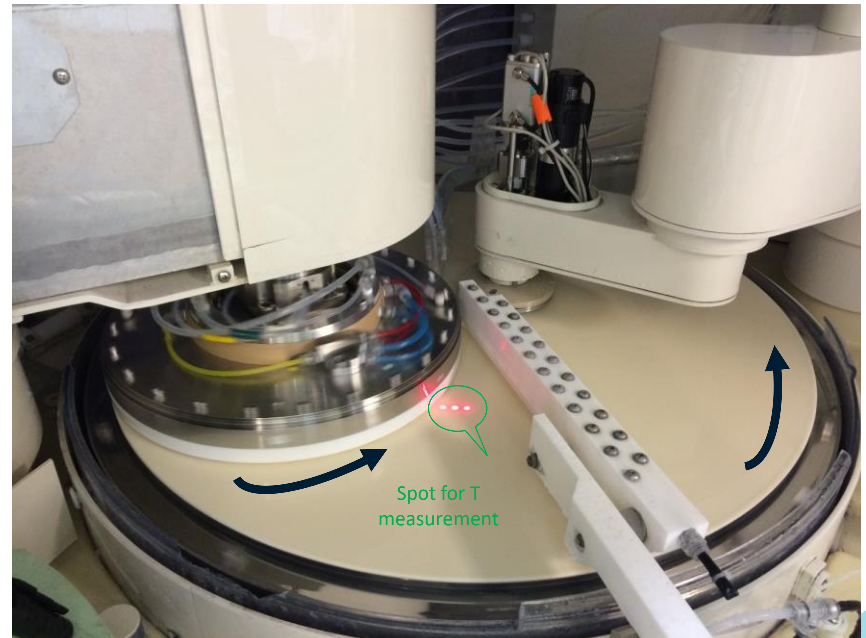
Friction = 200-400 W

Heat generation is dominated by ***friction***



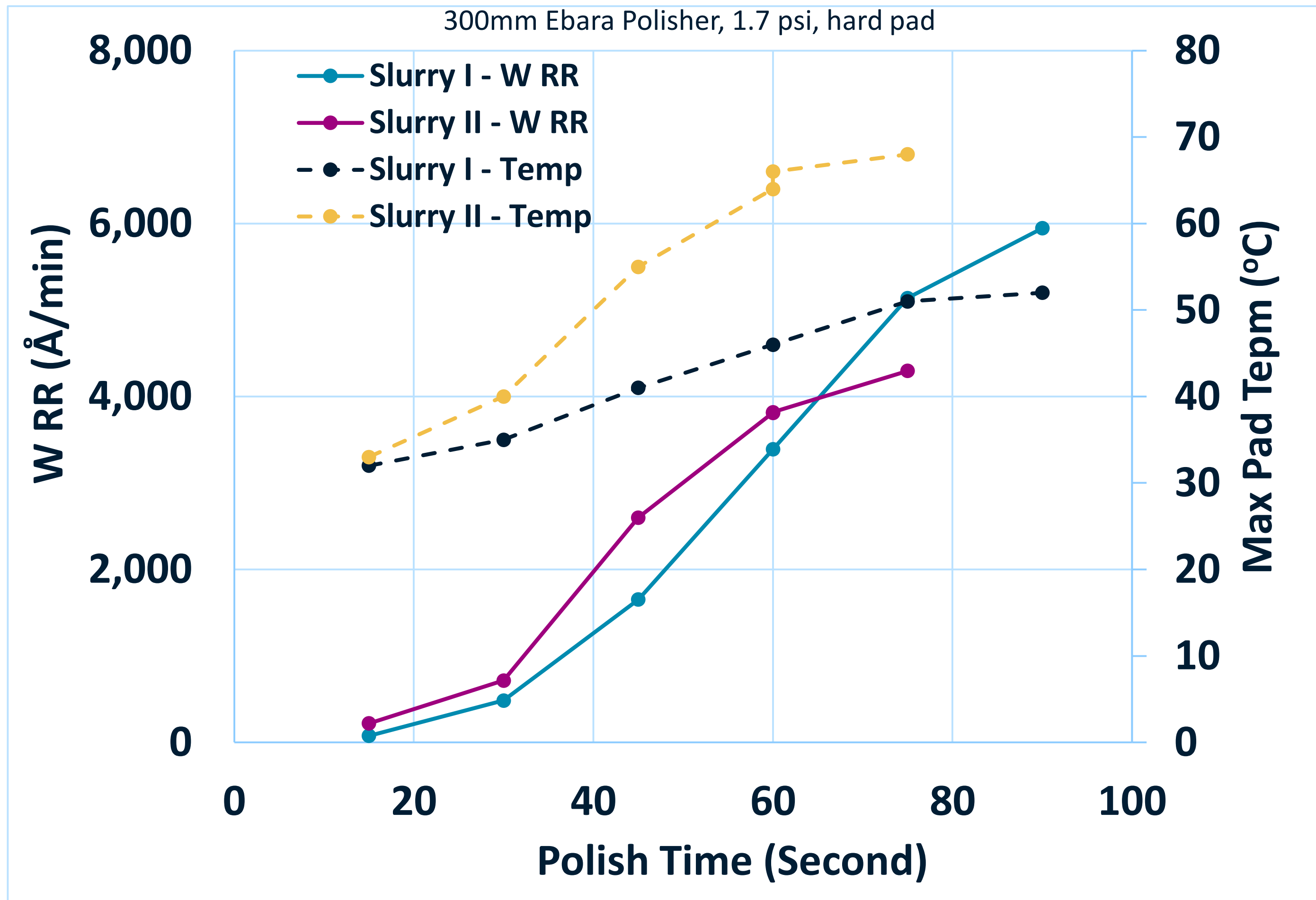


Establishment of Temperature Monitor Capability on an Ebara Polisher



Incubation and Activation Behaviors of W CMP

W RR and max. pad temperature of time-polishing using different W slurries



Ea (eV)	Slurry I	Slurry II
	1.7	0.7

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Blanket RRs and W/Oxide Selectivity of VM's Exemplary W CMP Products

Product ID	Down Force (psi)	W RR (Å/min)	Oxide RR (Å/min)	W/Oxide Selectivity
W5880 **Bulk**	3	2000 - 2600	480 - 640	3 - 6
DP5988 **Bulk**	3	2500 - 3900	< 50	50 - 80
W5900 **Bulk**	1.7 – 4	2600 -5200	< 15	>100
DP1118 **Barrier/Buff**	3.4	200~700	700 ~ 1000	0.2 - 1

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Conclusive Remarks

- Versum Materials (VM) offers broad spectrum of CMP and pCMP clean products including tungsten (W) slurries.
- Optimal W removal balances chemical oxidation of hard metallic W into softer oxidized surface layer(s) and subsequent removal of the oxidized layer(s) by mechanical motions of abrasive particles.
- W CMP is a highly thermally activated process, showing incubation and activation behaviors that can be tuned by slurry chemistries.
- Fundamental and mechanistic understandings empower VM to develop differentiated W products per customers' requirements.

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