Surface and Electrochemical Evaluations for Barrier and Packaging Level CMP Optimization

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Advancements in CMP Applications and Research

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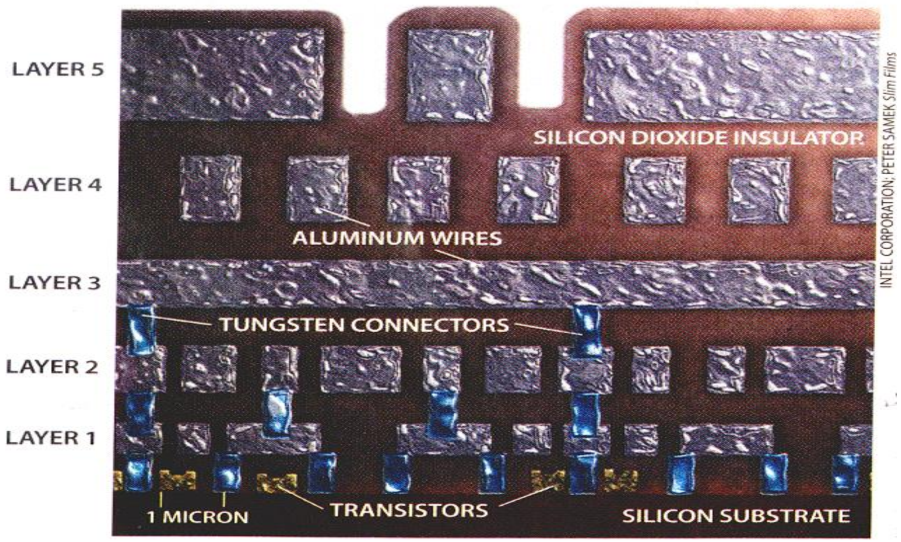
Application of CMP Beyond 10 nm Technologies

Multi Level Metallization

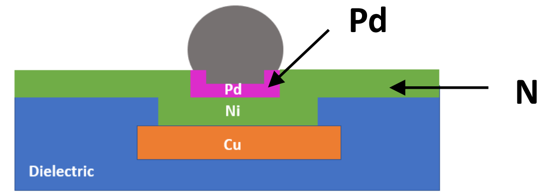


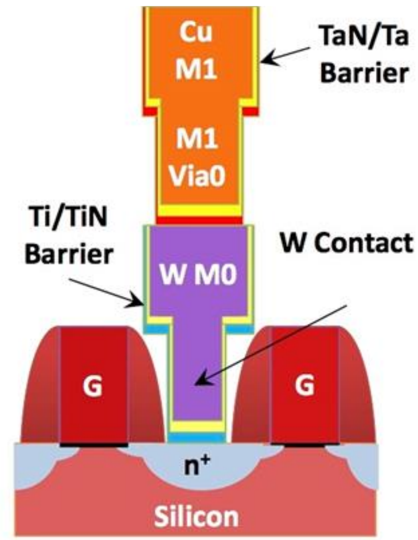
$$RC = \rho\varepsilon\frac{l^2}{td}$$

Resistance; Capacitance; Resistivity; Permittivity; Line length; Thickness

- CMP achieves global planarity enabling multi level metallization.

Barrier Materials





- Shrinking sizes of the plugs reduce the volume of tungsten, increasing ρ
- Use of palladium (Pd) plated lead-frame for packaging has improved the processing cost and reliability by simplifying the process integration*.

* Kajija, I.V., Absy, J.A., Maisano, J.J., Kudrak, A.J., Shimada, S. “Thin Multilayer Palladium Coating for Semiconductor Packaging Applications. Part I: Solderability. NASF Surfcae Technology White Papers, 80 (6), 6-19 (2016).

Introduction

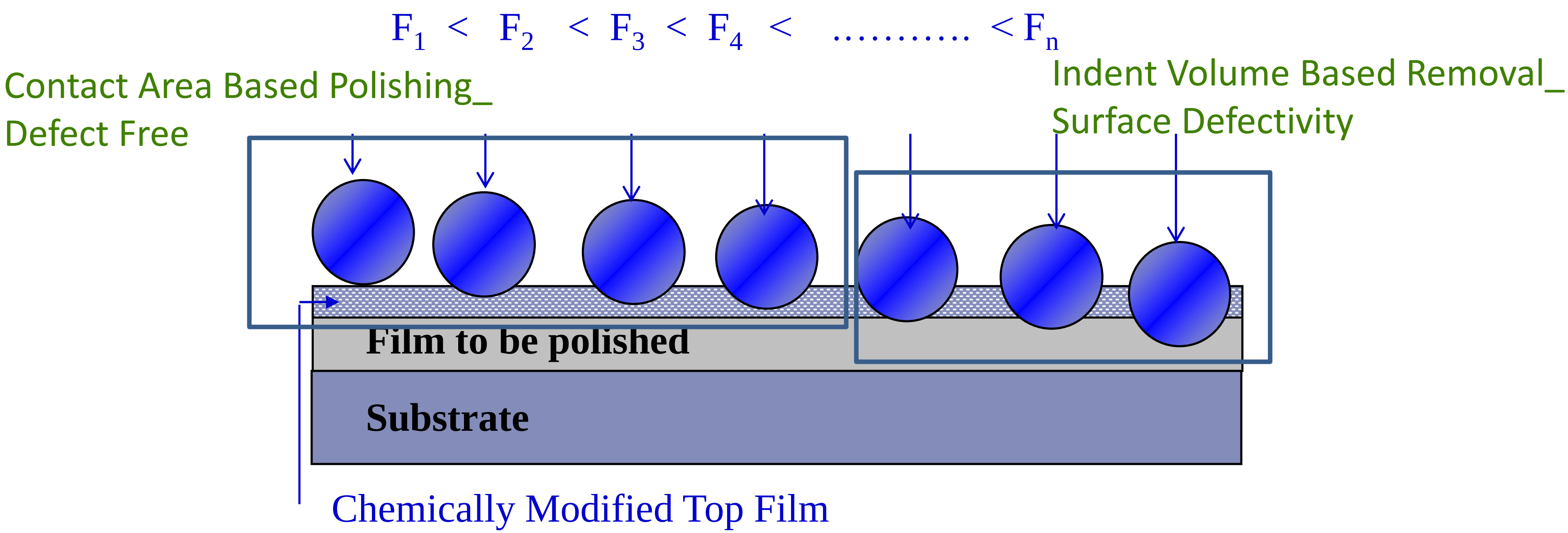
- Chemical Mechanical Planarization (CMP) process development for 10nm nodes and beyond demands a systematic understanding of atomic-scale chemical and mechanical surface interactions for the control of material removal, selectivity, and defectivity.
- CMP of barrier/liner films is challenging with new materials introduced to better adhere the contact metal at the interface and limit the probability of metal diffusion to the transistors.
- The relative selectivity of the CMP removal rates of the barrier materials against the contact metal needs to be controlled depending on the integration scheme.

Objectives

- Utilize ex-situ electrochemical evaluations to evaluate the corrosion/passivation rates in various slurry formulations as a function of the slurry chemistry and the abrasive particle solids loading.
- Optimize selectivity to obtain 1:1:1 MRR on W/Ti/TiN films.
- Implement the fundamental understanding on Cu barrier film evaluations for packaging level CMP applications.

Role of Polishing Slurry in CMP Applications

Formation and deformation of the chemically modified thin films



Chemistry: Changes the top film properties

Oxide*: Hydrated layer formation
Metal**: Passivated layer formation

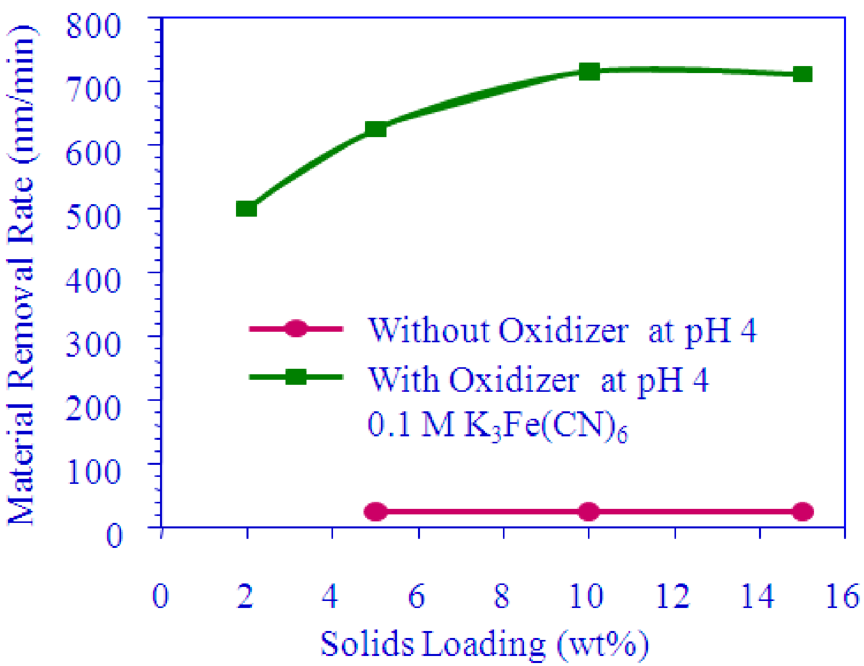
Mechanics: Determines the type of deformation

- It is necessary to determine mechanical properties of the chemically altered film to evaluate the CMP performance.

Functionality of Chemically Modified Film in CMP Applications

Enables Material Removal

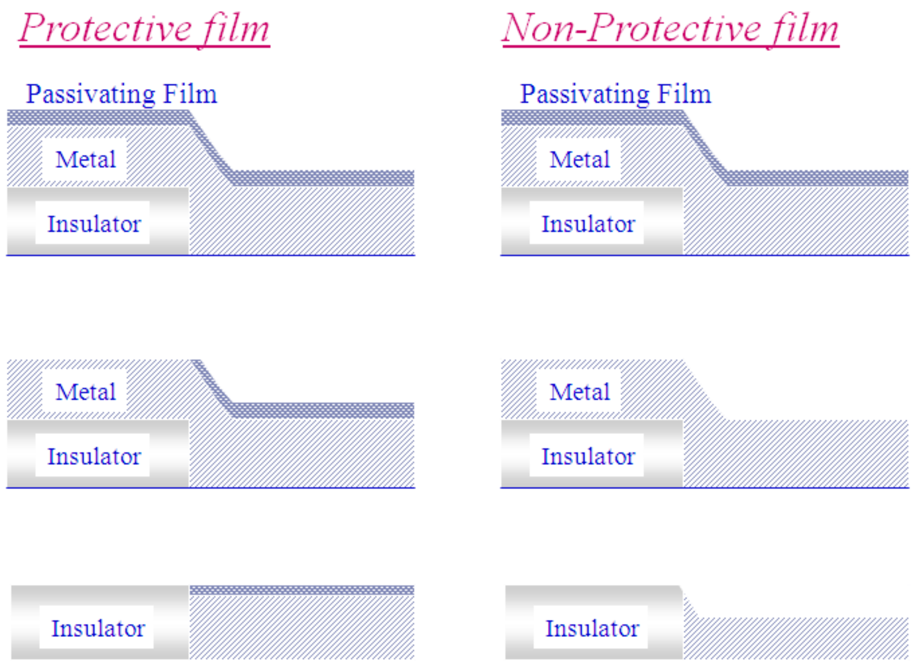
(Effect of Oxidizer on Tungsten CMP)



- There is no material removal in the absence of oxidizer

Enables Topographic Selectivity

(Effect of Self-Protective Oxide in CMP)



- Chemical etch stops
- Chemical etch continues

Metal Oxide Thin Film Formation on Polished W wafers _P-B ratio analysis (XRR)_

	1 M KOH		0.05 M H_2O_2		0.075 M H_2O_2		0.10 M H_2O_2	
	T	D	T	D	T	D	T	D
Layer 0	15	4.5	7	4.8	7	4.4	8	4.5
Layer 1	122	5.0	51	12.4	53	12.2	53	12.5
Layer2	20	14.7	43	14.5	40	15.6	42	15.8
W substrate		17.6		17.8		18.4		18.6

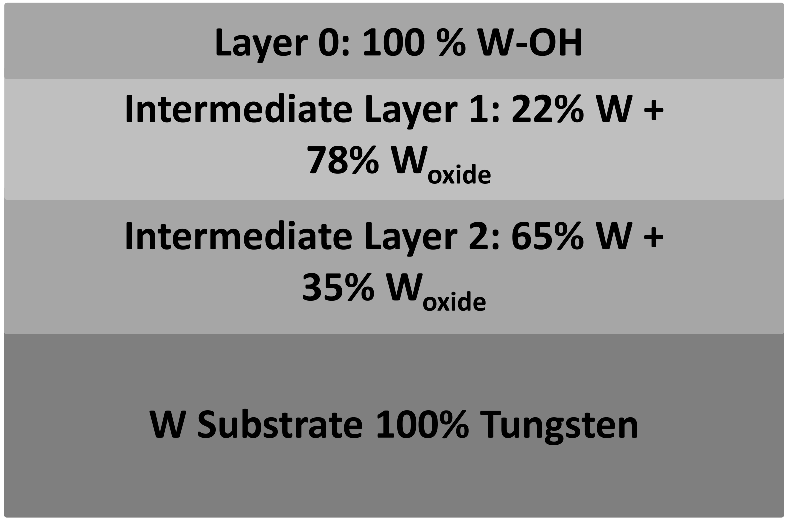
T: Thickness (Å).
D: Density (g/cm^3).

P-B Ratio

3.64

1.35

1.25



Interfacial Stress

3.84 GPa

2.03 GPa

2.48 GPa

- W forms protective oxide films

- Only the very top metal oxide layer is abraded during CMP.

Pressure on 0.2 µm particle ~0.024- 2.38 GPa*

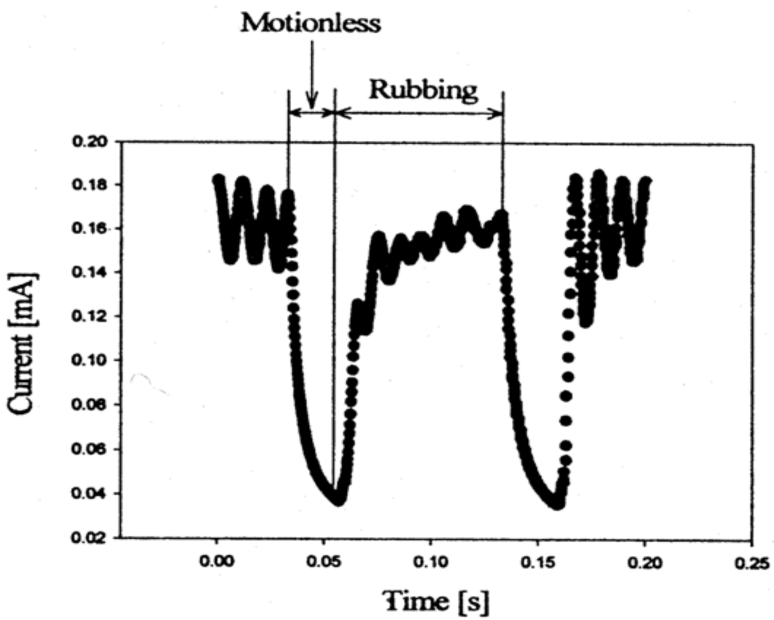
➢ W forms a protective oxide in slurries containing oxidizers and the top layer is removed.

* A. Karagoz,, V. Craciun, and G. B. Basim*, Characterization of Nano-Scale Protective Oxide Films: Application on Metal Chemical Mechanical Planarization, *ECS Journal of Solid State Science and Technology*, 3 (12) P1-P8 (2014)

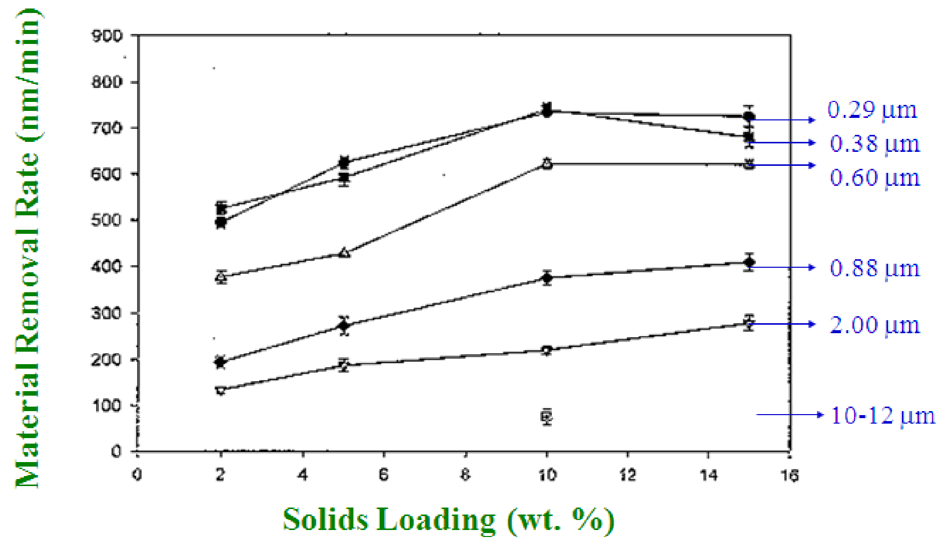
Evaluation on Tungsten CMP

Passive Layer Formation in Tungsten CMP

0.5 M H_2SO_4, + 2 V Anodic Potential
(0.2 s sphere motion cycle)



Diffusion limited layer thickness = 5 -7 nm**

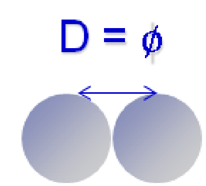


$$A \propto C_o^{1/3} \cdot \Phi^{-1/3}$$

Contact area mechanism is predominant

<u>0.3 µm over 10wt.%</u>

MRR = 750 nm/min = 12.5 nm/s



<u>Number of abrasions/sec</u>

$V/D = 1.4\ 10^6 (\mu m/s) / 0.3 (\mu m) = 4.7\ 10^6$ abr./s **x 0.0033**

$t_{abrasion} = 0.65\ 10^{-4}$ sec/abrasion

- Oxidation takes place as the fresh surface is exposed to the slurry (Diffusion limited growth)
- Only 1 in a 1000 or 10000 particles can remove material during CMP.

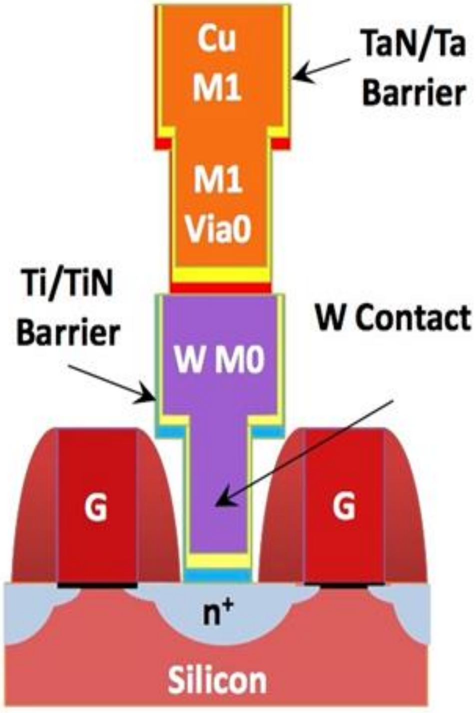
* M. Bielman, U. Mahajan, R. K. Singh, P. Agarwal, S. Mischler, E. Rosset, D. Landolt, Mater. Res. Soc. Proc. 566, p. 97.
** E.A. Kneer et al. J. Electrochem. Soc. V 144, p. 3041 (1997).

Barrier Layer Evaluation for W Plugs

- Ti/TiN are typical diffusion barriers for W via due to their thermal and chemical stability and their ability to passivate, which creates an oxide layer that promotes adhesion.

- The TiO_2 films presents acceptable properties:
  - Low leakage current density of 1.0×10^{-5} A/cm at 1 V.
  - Band gap of 4.6 eV.
  - High insulation or leakage resistance of 5×10^{5} Ω.
  - Applied in gate oxide in metal oxide semiconductor field effect transistors (MOSFETs) and in thin film capacitors.

- Alternatives are;
  - replacing the W plugs with the Co
  - introduction of new W based material that can serve as both barrier and liner film is tested to allow the gap to be filled with more W rather than consuming the volume by the Ti/TiN layers.



*Derbyshire, K. (2017). Managing Parasitics for Transistor Performance. [online] Semconductor Engineering.

Materials and Methods

- W/Ti/TiN wafers were used for electrochemical evaluations as a function of oxidizer concentration (H_2O_2)* to evaluate the passivation rates in various slurry formulations as a function of the slurry chemistry and the abrasive particle solids loading.
- Cu ECD/Ni/TaN/Pd water coupons were evaluated for electrochemical responses in commercial bulk Cu and a barrier slurry.

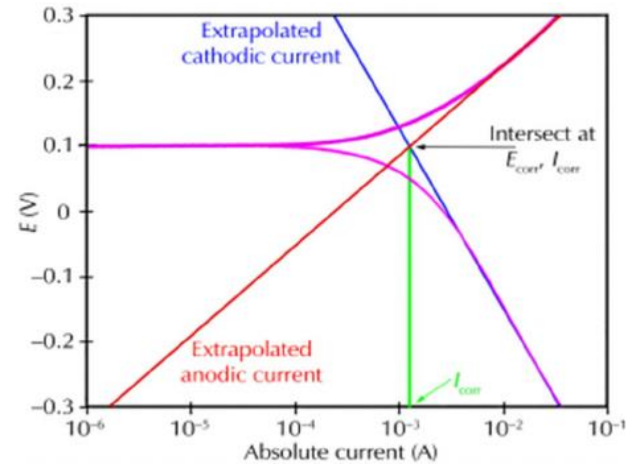
Ex-situ Electrochemical Measurement Set-up

- Gamry flat specimen holder was used to maintain consistency in exposed sample surface area (circular area with 1 cm diameter) and electrochemical response.
- Saturated Calomel Electrode (SCE) connected with a Luggin capillary, and a 26-gauge thick Platinum wire (99.90% Pure) served as the reference and the counter electrodes, respectively.
- Measurements were recorded by using a Gamry reference 3000 potentiostat system and the dedicated Gamry Echem Analyst software.

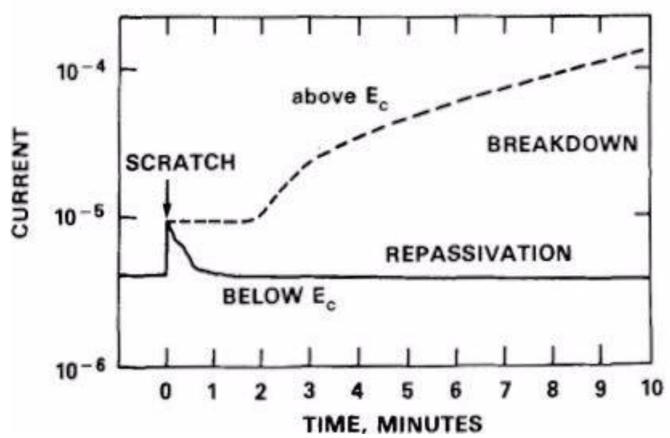
** Yagan, R., Basim, G.B., "A Fundamental Approach to Electrochemical Analyses on Chemically Modified Thin Films for Barrier CMP Optimization," ECS J. Solid State Sci. Technol. 8-5, P3118-P3127, 2019.*

Electrochemical methods for surface passivation evaluation

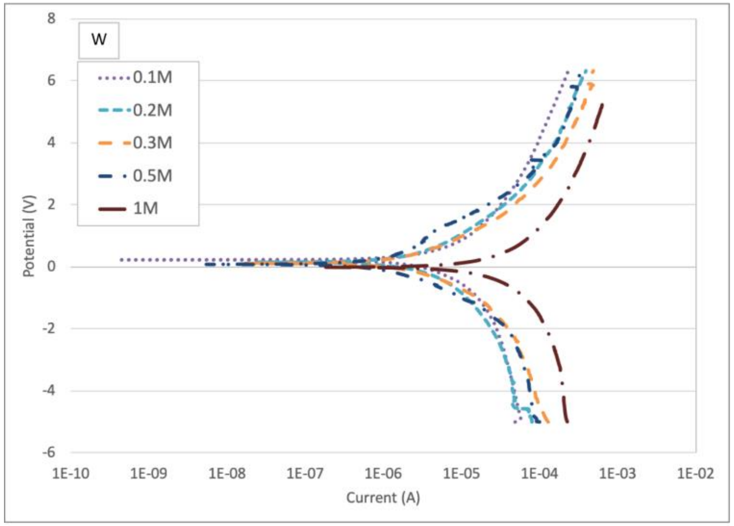
- **Potentiodynamic polarization** measurements is a commonly used technique to simulate corrosion characteristics of metals during CMP
  - Both anodic and cathodic polarizations are involved
  - From both branches Tafel slopes can be plotted -> E_{corr} and I_{corr} .
  - Butler-Volmer equation is used for Corrosion rate,
  - A relationship between corrosion currents and CMP removal rates can be developed.

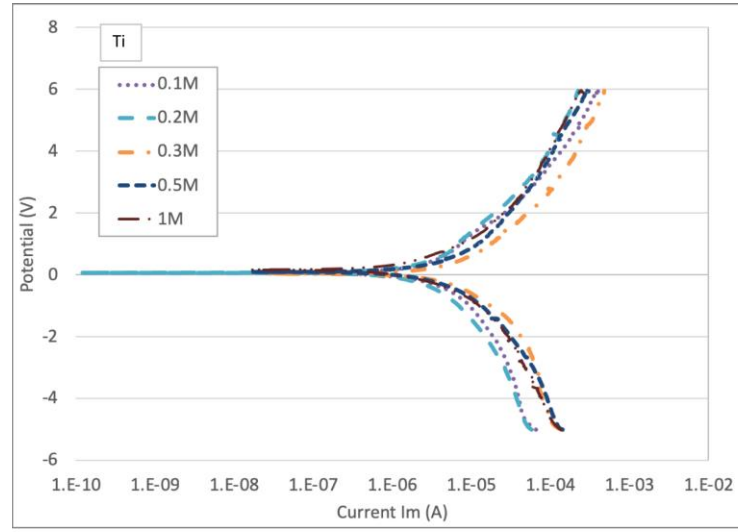


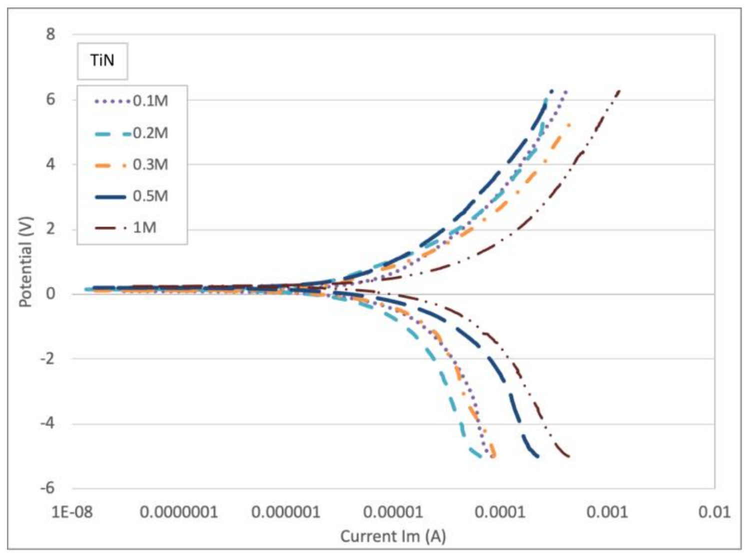
- **Potentiostatic scan (current vs. time transients)**
  - Current measured by applied potential can depict film growth characteristics.
  - Surface metal oxide film passivation can be determined.
  - Passivated films are self-protective oxides of the underlying metal.



Potentiodynamic Polarization Curves of W, Ti and TiN

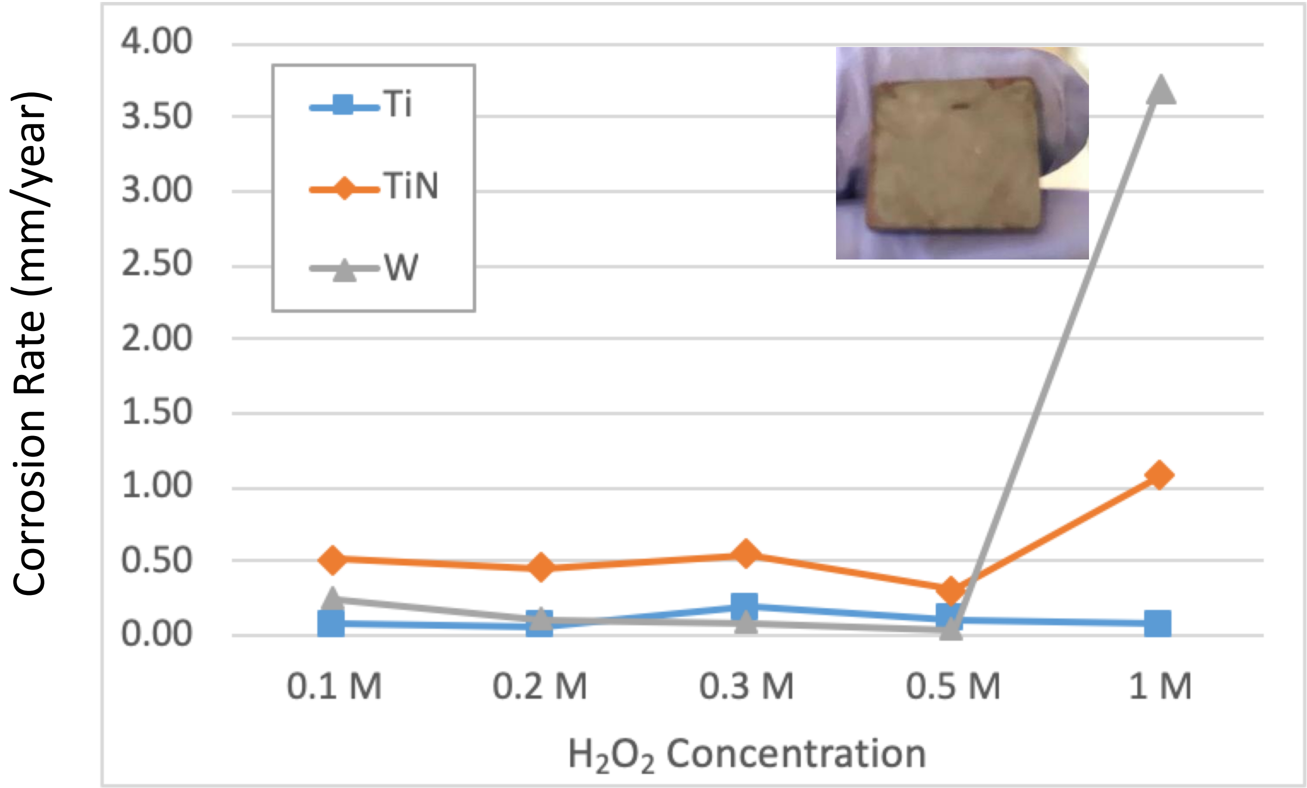






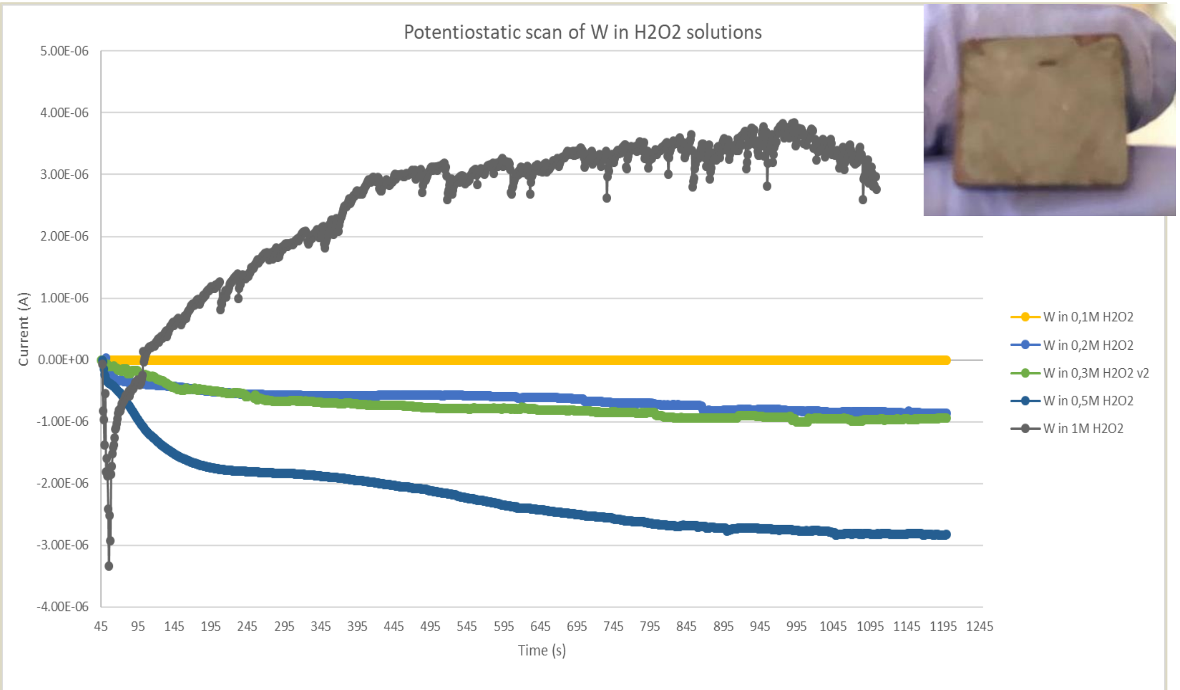
- The measured current on the film surfaces decreased as the applied potential reached the zero value and started progressing into the anodic polarization portion of the curve

Corrosion Rate Calculations based on Potentiodynamic Measurements on W, Ti and TiN



- Tungsten showed relatively low corrosion rates up to 0.5 M H_2O_2 addition, whereas, a high rate of 3.7 mm/year was observed at 1M.
- Titanium wafers showed much consistent corrosion rate which can be attributed to the protective nature of the titanium oxide surface layer
- TiN is considered to be more of a ceramic material in its chemical nature and oxidizes into TiO_2 in the presence of oxygen or at high temperatures

Potentiostatic transient response of W in H_2O_2 solutions

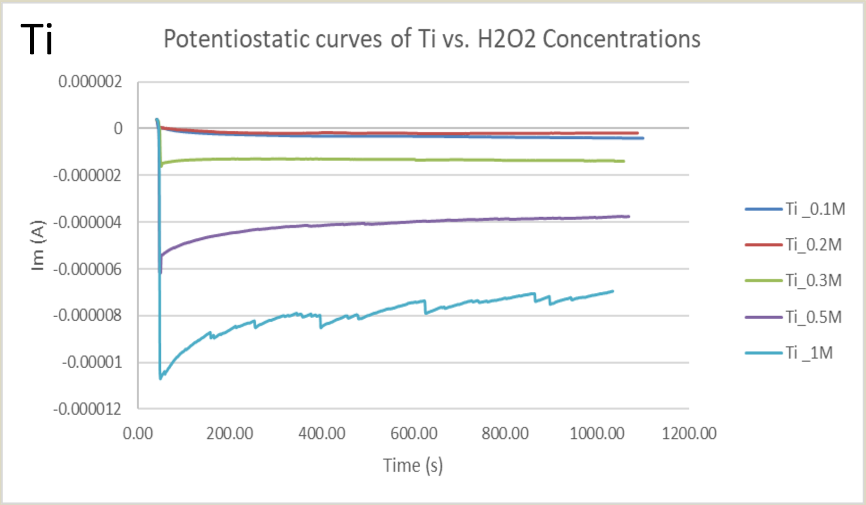


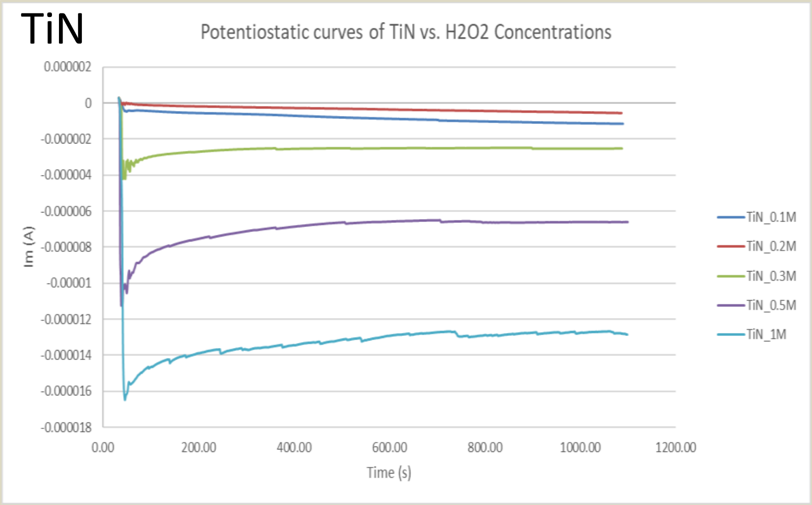
Oxide concentration	Slope (W) A/s
0.1 M	2.416-14
0.2 M	4.175-10
0.3 M	5.87E-10
0.5 M	2.059E-09
1 M	2.85E-07

- As the oxidizer concentration increases, curve settles at lower current levels due to faster nucleation and better passivation.
- Steady state levels of passivation are reached for all concentrations other than 1 M.
- All concentrations of oxidizer addition satisfy protective oxide formation other than 1 M as observed in earlier studies*.

** A. Karagoz, A., V.. Craciun, and Basim, G. (2014). Characterization of Nano-Scale Protective Oxide Films: Application on Metal Chemical Mechanical Planarization. ECS Journal of Solid-State Science and Technology, 4(2), pp.P1-P8.*

Potentiostatic transient response of Ti/TiN in H_2O_2 solutions

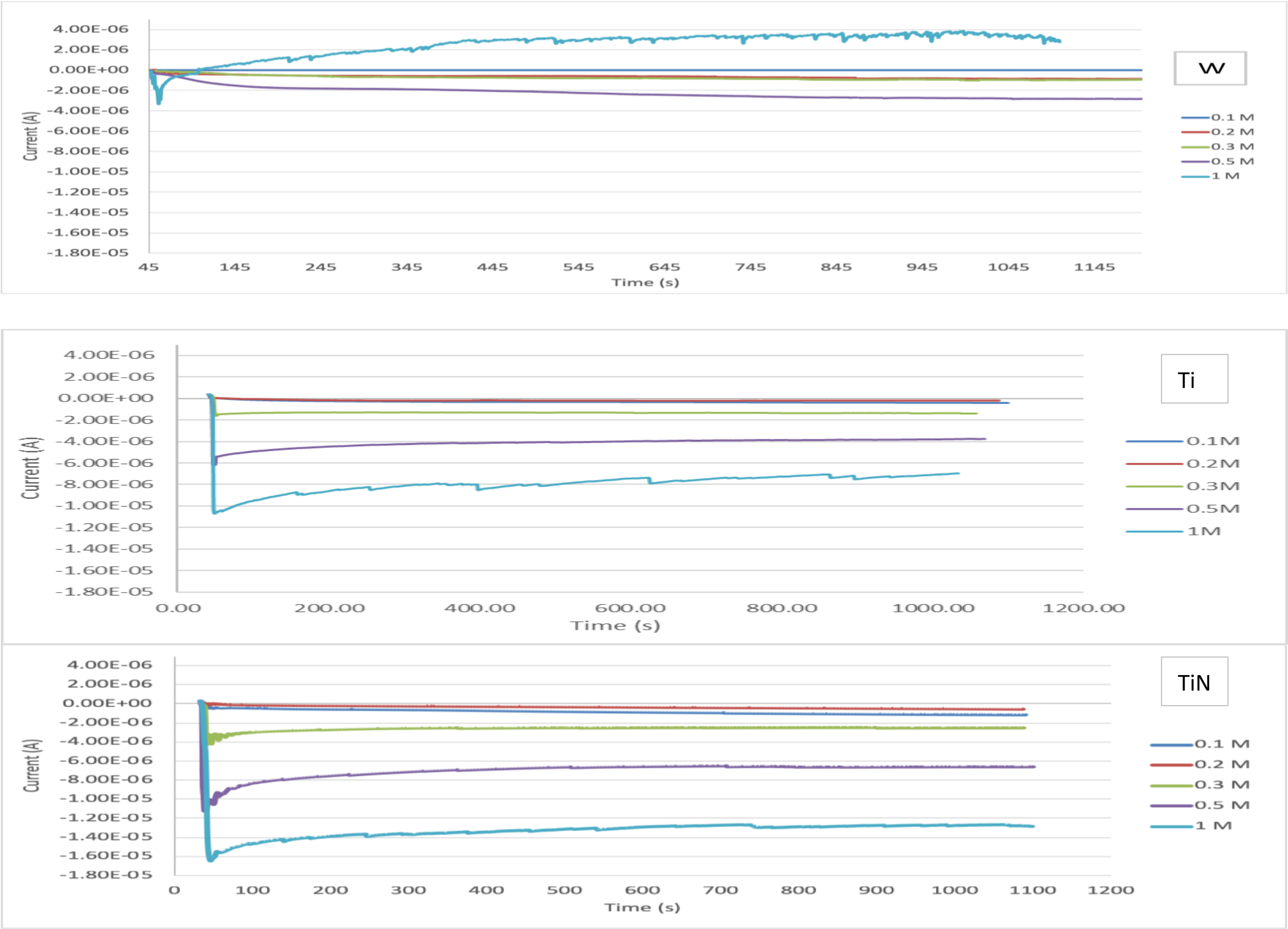




Hydrogen Peroxide Concentrations	Titanium Slope (A/s) abs	TiN Slope (A/s) abs
0.1 M	7.25E-09	5.88E-08
0.2 M	8.98E-09	2.36E-08
0.3 M	6.33E-08	5.13E-07
0.5 M	3.17E-07	8.96E-07
1 M	1.45E-06	1.69E-06

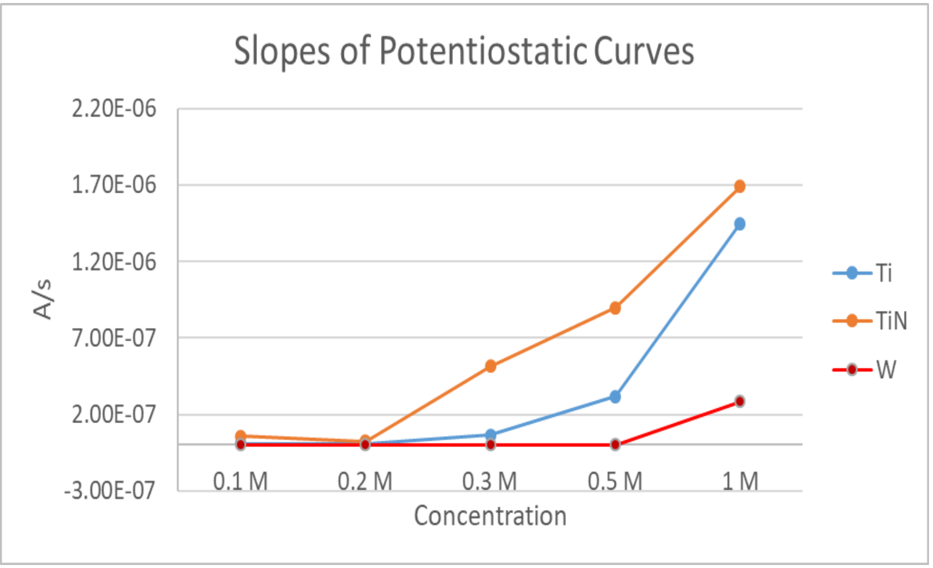
- Similar passivation response for Ti and TiN.
- Similar passivation rates at 0.1 and 0.2 M.
- Ti shows lower passivation currents as compared to W.
- TiN shows lower passivation since it is a ceramic material.
  - the oxygen present in the environment still forms a passive film of titanium dioxide (TiO_2) on TiN.

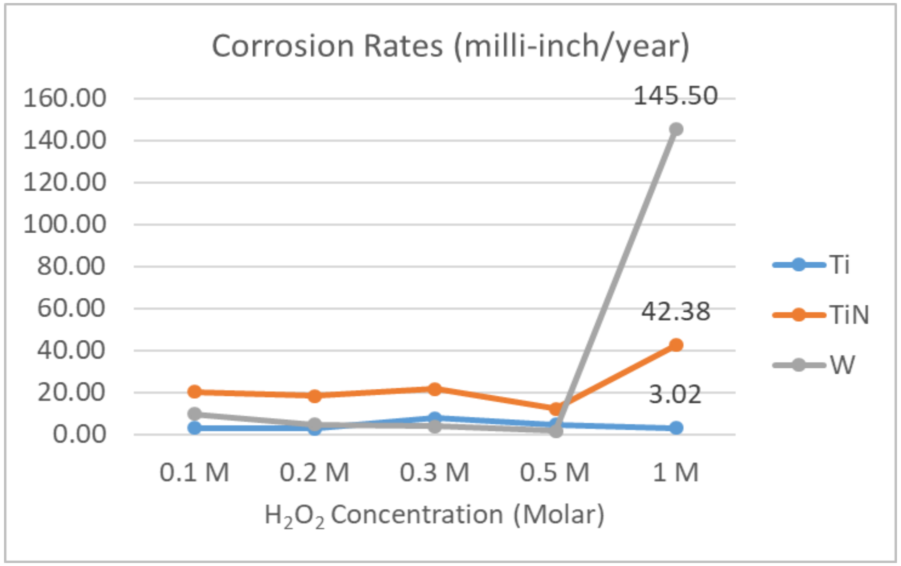
Potentiostatic transient response of W, Ti, TiN in H_2O_2 solutions



➢ Passivation slopes are similar up to 0.2 M oxidizer addition for W, Ti and TiN films.

Comparison of Electrochemical Responses of Tungsten, Titanium and TiN Films





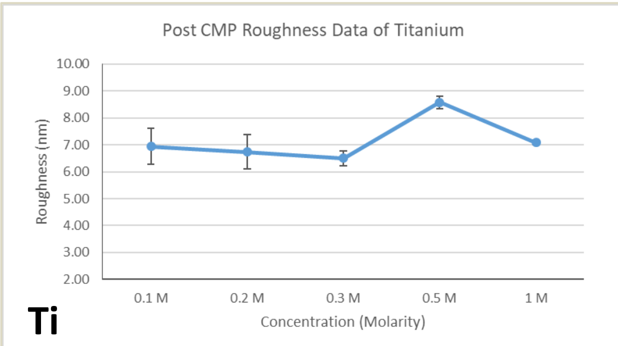
- Passivation responses of all W/Ti/TiN films are similar up to 0.2M, which should correlate with the Material Removal Rates during CMP applications.
- Ti and W films correspond similarly up to 0.5M oxidizer concentration for corrosion rates.
- TiN passivation is nor as pronounced as Ti and W since it is not a metallic layer.

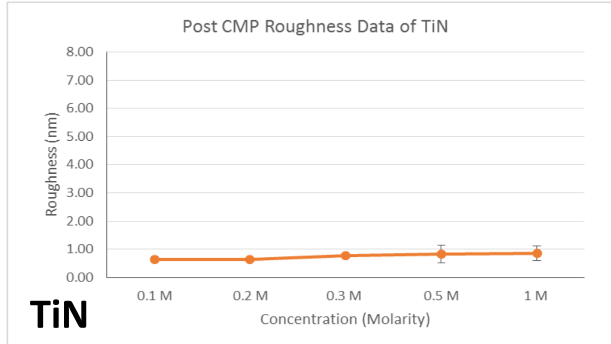
CMP Material Removal Rate Comparison

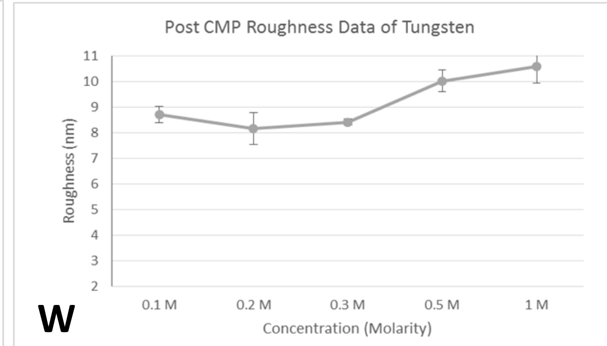
H_2O_2 Concentrations	Ti MRR (nm/min)	TiN MRR (nm/min)	W MRR (nm/min)
0.1 M	41.82	83.48	184.09
0.2 M	74.94	79.16	76.40
0.3 M	86.53	188.40	396.05
0.5 M	275.54	88.27	140.22
1 M	204.68	221.88	73.27

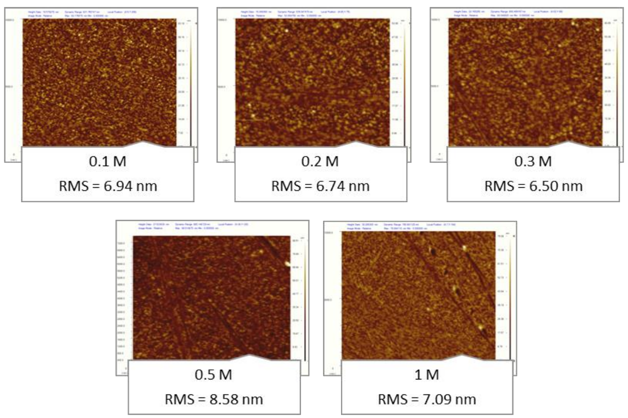
- Ti Removal rates increase with increasing H_2O_2 concentration in the polishing slurry
- All the materials show similar MRR responses at 0.2M oxidizer concentration with 3wt% polishing slurry at pH 9 with the given CMP set-up.
- This correspondence provides 1:1:1 MRR selectivity.
- Variation of the MRR responses relate to the nucleation and growth mechanisms of oxide on the different materials.

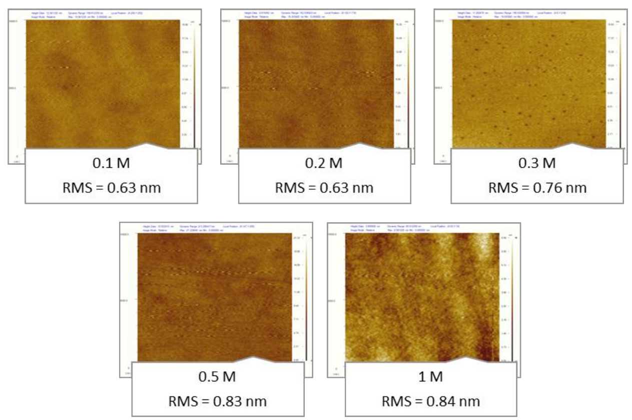
Characterization of post CMP surface quality (Ti and TiN)

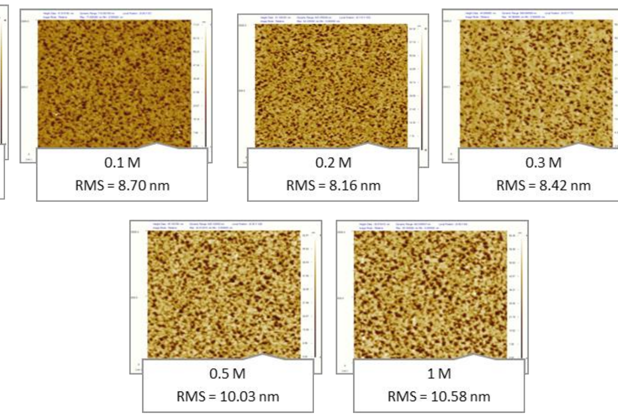






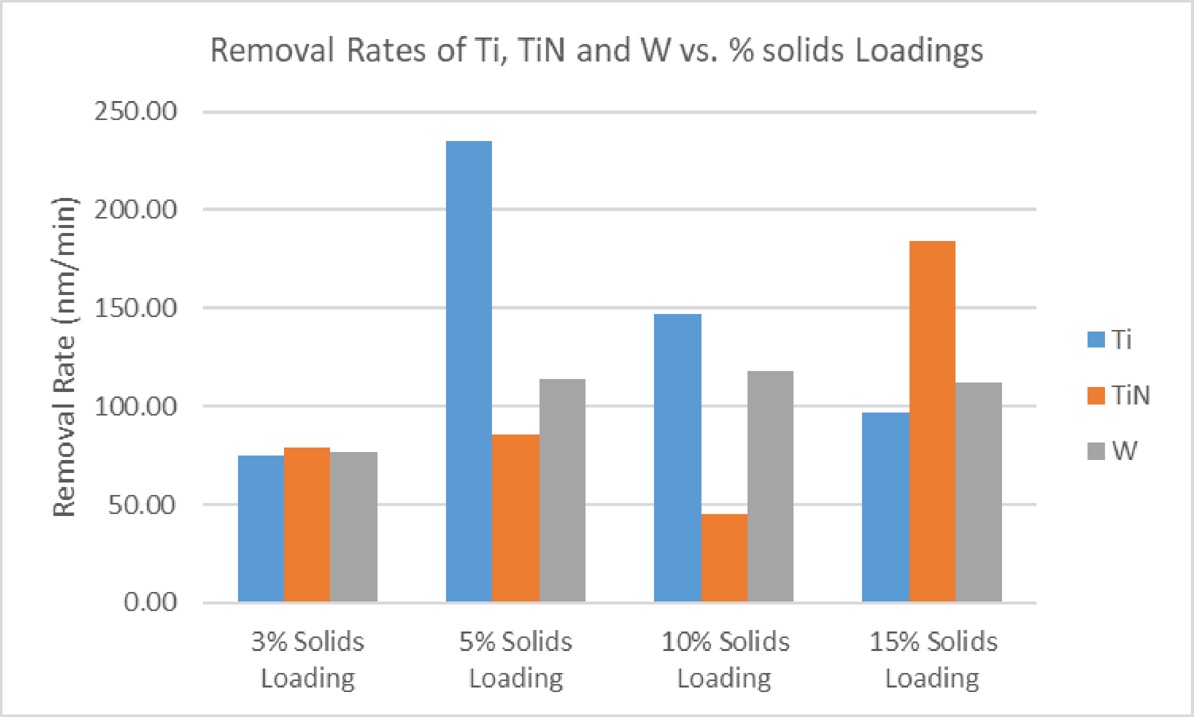






- Ti and W show similar roughness values post CMP application
- TiN has ~6-10X better surface roughness as compared to Ti and W.
- Surface roughness correlates to the passivation behavior of the materials.

Effect of Slurry Solids Loading on CMP Performance by Oxidizer Concentration



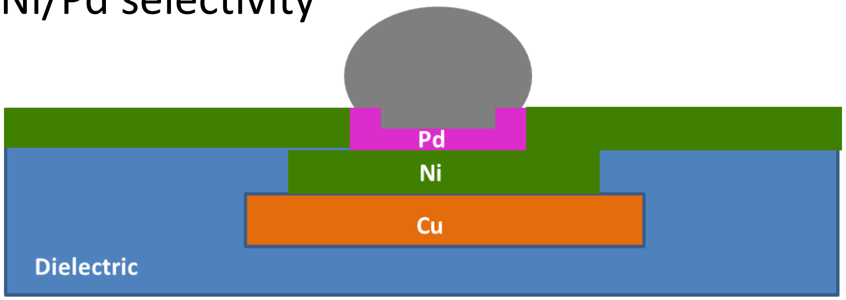
- Optimal 1:1:1 MRR selectivity at 0.2 M oxidizer concentration with 3%wt slurry abrasive (silica) solids loading.
- Variation of the mechanical abrasion activity requires the optimization of the chemical activity.
- Selectivity can be optimized by controlling both the chemical and the mechanical components of the CMP process.

Barrier Layer Evaluation for Packaging Level

- The yield of chip packaging operations is a function of the surface finish that is solderable and wire bondable.
- Palladium (Pd) plated lead-frame for packaging has improved the processing cost and reliability by simplifying the process integration. It forms a Ni(Pd)Si allowing a lower morphology*.
- Pd can also be used as a sacrificial layer to protect the copper (Cu) substrate material from oxidation and interdiffusion before the SnPb solder application.
- The new integration schemes of Pd into the circuitry at the packaging level also require a CMP application where the Pd is deposited on the dielectric layer with bond-pad recess and polished to form a Pd based pad surrounded by Ni**.

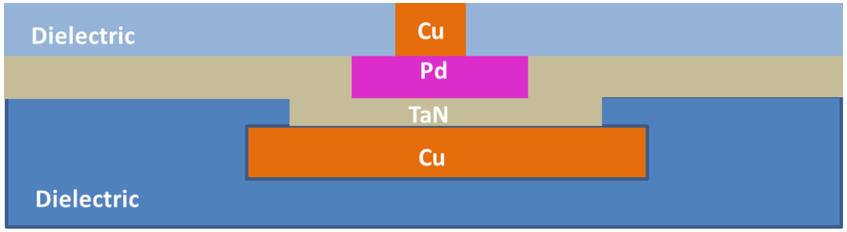
Bond Pad Pd Integration

Ni/Pd selectivity



Interconnect Pd Integration

TaN/Pd selectivity

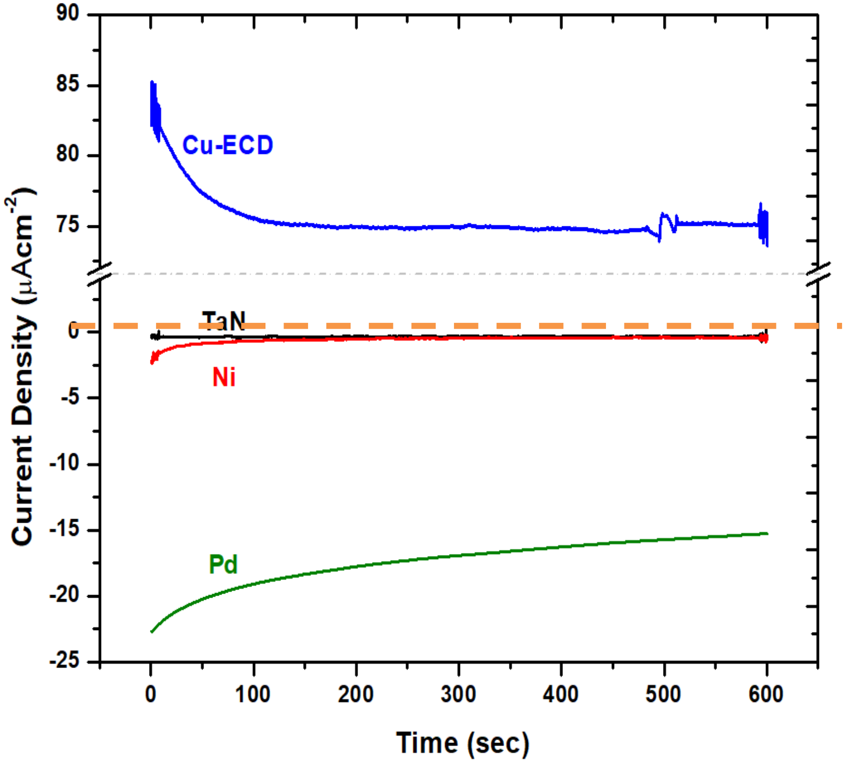


** Karabko, A., Dragasius, E. Nisi and Ni(Pd)Si as possible interconnect and electrode material for film bulk acoustic resonators and microelectromechanical systems. Journal of Vibroengineering, 15 (1), 2013.*

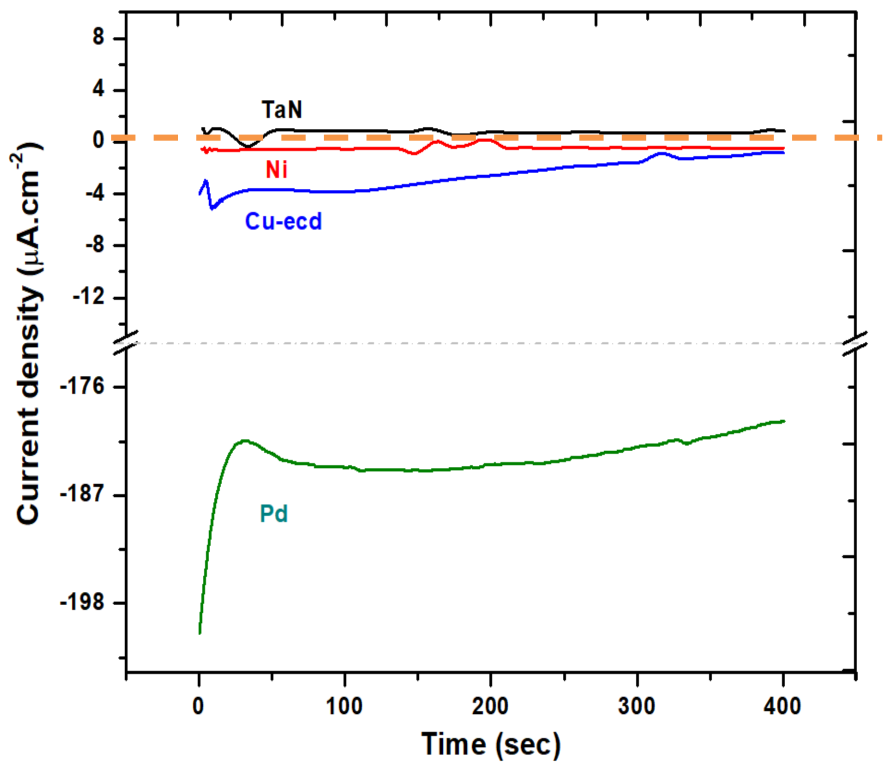
*** Eisa, M., Zinn, B. "Aluminum Enhanced Palladium CMP Process" US Patent 8,288,283, October 16, 2012.*

Potentiostatic Evaluations on Cu, Ni, TaN and Pd wafers in Bulk Cu Slurry and Barrier Slurry with 2% H_2O_2

Potentiostatic measurements in Bulk Cu Slurry with 2% H_2O_2

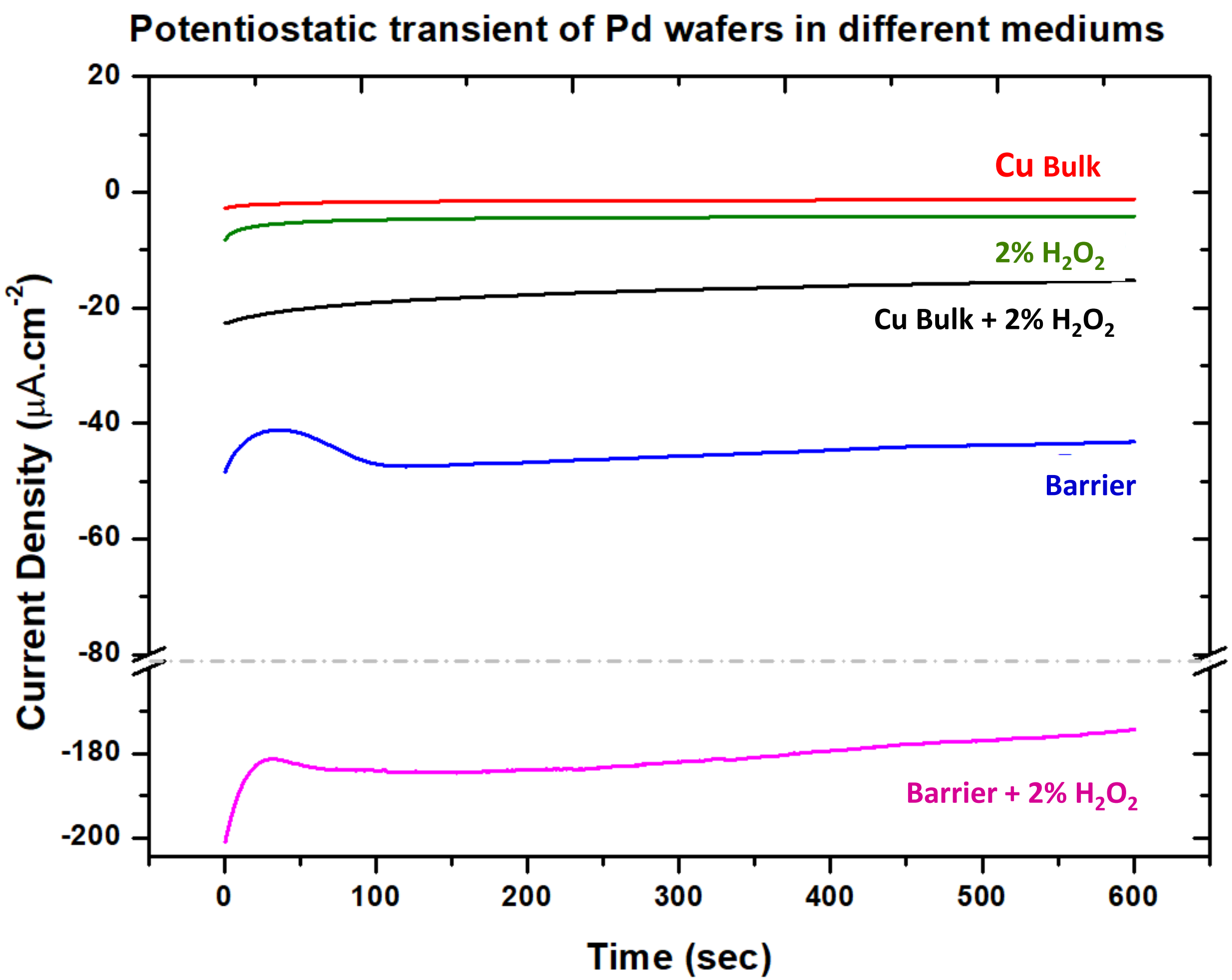


Potentiostatic measurements in Barrier Slurry with 2% H_2O_2



- Cu bulk slurry is corrosive against Cu that helps removal rates.
- Pd strongly passivates in both bulk and the barrier slurries with more pronounced effect in the barrier slurry.

Potentiostatic Evaluations on Pd wafers in Different Mediums



- Pd passivation ranges with the type of slurry and the oxidizer concentration that can be tuned to the specified integration needs.

Summary

- Electrochemical analyses of metal and barrier films were explored as a function of oxidizer concentration through potentiodynamic and potentiostatic methods on a model W/Ti/TiN system.

- Potentiostatic sweeps showed passivation of the surfaces indicating the formation of chemically modified oxide layers. The initial passivation slopes were stable up to 0.2 M H_2O_2 concentration.

- It was observed that at 0.2 M oxidizer addition, a 1/1/1 removal rate selectivity of W/Ti/TiN was achieved indicating a slurry formulation suitable to a single step metal barrier layer planarization.

- Pd selectivity against Ni and TaN in Cu integration also shows promising results to be evaluated with the same approach.

- Advances in the CMP development for new barrier materials and integration schemes can benefit from the experimental approach outlined in this research.

QUESTIONS/COMMENTS?

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