Surface and Electrochemical Evaluations for Barrier and Packaging Level CMP Optimization

Prof. G. Bahar Basim

*Debashish Sur, Kimberly Beers, John Langhout*

NSF Center for Particle and Surfactant Systems (CPaSS) & Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611

Advancements in CMP Applications and Research

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Application of CMP Beyond 10 nm Technologies

**Multi Level Metallization**

\[
R C = \frac{\rho \varepsilon}{t d} \quad l^2
\]

- CMP achieves global planarity enabling multi level metallization.
- Shrinking sizes of the plugs reduce the volume of tungsten, increasing \( \rho \)
- Use of palladium (Pd) plated lead-frame for packaging has improved the processing cost and reliability by simplifying the process integration*.

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_

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

Chemistry: Changes the top film properties

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

Mechanics: Determines the type of deformation

\[ F_1 < F_2 < F_3 < F_4 < \ldots \ldots < F_n \]

Contact Area Based Polishing
Defect Free

Indent Volume Based Removal
Surface Defectivity

Film to be polished
Substrate
Chemically Modified Top Film

➢ 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

_Enable Material Removal_
(Effect of Oxidizer on Tungsten CMP)

_Enable Topographic Selectivity_
(Effect of Self-Protective Oxide in CMP)

➢ There is no material removal in the absence of oxidizer
➢ Chemical etch stops
➢ Chemical etch continues

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Enables Material Removal

Enables Topographic Selectivity

Effect of Oxidizer on Tungsten CMP

Effect of Self-Protective Oxide in CMP

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Metal Oxide Thin Film Formation on Polished W wafers

_P-B ratio analysis (XRR)_

<table>
<thead>
<tr>
<th>Layer</th>
<th>1 M KOH</th>
<th>0.05 M H₂O₂</th>
<th>0.075 M H₂O₂</th>
<th>0.10 M H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>D</td>
<td>T</td>
<td>D</td>
<td>T</td>
</tr>
<tr>
<td>Layer 0</td>
<td>15</td>
<td>4.5</td>
<td>7</td>
<td>4.8</td>
</tr>
<tr>
<td>Layer 1</td>
<td>122</td>
<td>5.0</td>
<td>51</td>
<td>12.4</td>
</tr>
<tr>
<td>Layer 2</td>
<td>20</td>
<td>14.7</td>
<td>43</td>
<td>14.5</td>
</tr>
<tr>
<td>W substrate</td>
<td>17.6</td>
<td></td>
<td>17.8</td>
<td></td>
</tr>
</tbody>
</table>

T: Thickness (Å). D: Density (g/cm³).

<table>
<thead>
<tr>
<th>P-B Ratio</th>
<th>Interfacial Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.64</td>
<td>3.84 GPa</td>
</tr>
<tr>
<td>1.35</td>
<td>2.03 GPa</td>
</tr>
<tr>
<td>1.25</td>
<td>2.48 GPa</td>
</tr>
</tbody>
</table>

- W forms protective oxide films

**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.

Evaluation on Tungsten CMP

Passive Layer Formation in Tungsten CMP

0.5 M H₂SO₄ + 2 V Anodic Potential (0.2 s sphere motion cycle)

Diffusion limited layer thickness = 5 - 7 nm**

➢ 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.

Material Removal Rate (nm/min)

Solids Loading (wt. %)

\[ A \propto C_0^{1/3} \cdot \Phi^{-1/3} \]

Contact area mechanism is predominant

0.3μm over 10wt.%

MRR = 750 nm/min = 12.5 nm/s

Number of abrasions/sec

\[ \frac{V}{D} = 1.4 \times 10^6 (\mu m/s) / 0.3 (\mu m) = 4.7 \times 10^6 \text{ abr./s} \times 0.0033 \]

\[ t_{\text{abrasion}} = 0.65 \times 10^{-4} \text{ sec/abrasion} \]


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 TiO₂ 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 5×10⁵ 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.

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.

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 $\rightarrow E_{\text{corr}}$ and $I_{\text{corr}}$.
  - 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.
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 $\text{H}_2\text{O}_2$ 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.
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*.

Potentiostatic transient response of Ti/TiN in H$_2$O$_2$ solutions

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

➢ 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$_2$O$_2$ 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 not as pronounced as Ti and W since it is not a metallic layer.
CMP Material Removal Rate Comparison

<table>
<thead>
<tr>
<th>$H_2O_2$ Concentrations</th>
<th>Ti MRR (nm/min)</th>
<th>TiN MRR (nm/min)</th>
<th>W MRR (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>41.82</td>
<td>83.48</td>
<td>184.09</td>
</tr>
<tr>
<td>0.2 M</td>
<td>74.94</td>
<td>79.16</td>
<td>76.40</td>
</tr>
<tr>
<td>0.3 M</td>
<td>86.53</td>
<td>188.40</td>
<td>396.05</td>
</tr>
<tr>
<td>0.5 M</td>
<td>275.54</td>
<td>88.27</td>
<td>140.22</td>
</tr>
<tr>
<td>1 M</td>
<td>204.68</td>
<td>221.88</td>
<td>73.27</td>
</tr>
</tbody>
</table>

- 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**.


Potentiostatic Evaluations on Cu, Ni, TaN and Pd wafers in Bulk Cu Slurry and Barrier Slurry with 2% H₂O₂

- 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.
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 H₂O₂ 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?

gbbasim@ufl.edu