Slurry Activation Through Flucto-CMP®

Kiana A. Cahue¹, Fritz Redeker², Yasa Sampurno³, Ara Philipossian³, and Jason J. Keleher¹

¹ Lewis University, Romeoville IL USA
² Independent Consultant, Livermore CA USA
³ Araca, Inc., Tucson AZ USA
Our Vision

- Today, the same HVM CMP tool must be able to planarize substrates by removing 2 to 2E7 nm of a single layer without compromising performance – 7 orders of magnitude difference!

- In addition to platen temperature modulation, there are very few mechanical knobs (e.g., controls, hydraulics, pneumatics, kinematics and the like) that can be perfected in a polisher – Yet the chemical options are nearly infinite!

- For 2 years, Araca has been working to partially merge the polisher and slurry roadmaps via our patent-pending Flucto-CMP® technology. Here, the combined slurry-polisher strengths complement each other to overcome their individual inherent weaknesses such as defects, gross vibrations, COO, slurry waste, RR, selectivity and WIWRRNU.

- IC makers wish to migrate to a slurry whereby its main properties (such as copper-to-barrier RR selectivity) can be toggled instantaneously and on-demand.

- Flucto means WAVE in Latin – We now provide on-demand off-the-shelf slurry activation using megasonic waves through:
  - Add-on polisher equipment (subject of today’s discussion) – Can also be combined with,
  - The addition of Sono-Activated® chemicals (some nuggets presented today).
Numerous studies of the interaction of BTA with copper reveal that the BTA molecule forms a coordination polymer above the surface featuring a Cu(I) center bridging between two BTA molecules.

This polymerization leads to the formation of a DENSE and RUGGED passivation layer that causes large levels of vibration and requires significant mechanical action to remove at appreciable polish rates.
Non-Covalent Passivation Dynamics of Flucto-CMP®

- In Flucto-CMP®, when it comes to material removal, it’s all about one’s ability to control the interface.

- Enhanced CMP performance evolves from a balance of kinetic and thermodynamic processes. Modulation of these processes get activated by external stimuli such as sonication.

- The subsequent softer and less dense film formation dynamics results in effective material removal at less mechanically-aggressive conditions. This reduces vibration as well as wafer-level defects.

Sono-Activation® of the Reactive Oxidizing Species (ROS)

$\begin{align*}
\text{Cu}_2\text{O}/\text{CuO} & \xrightarrow{k_{\text{oxidation}}} \text{Cu}^0 \\
\text{Cu}^0 & \xrightarrow{k_{\text{corde}}} \text{Cu}^+ \\
\text{Cu}^+ & \xrightarrow{k_{\text{corde}}^* [\text{OX}]} \text{Cu}^{2+} \\
\text{Cu}^{2+} & \xrightarrow{k_{\text{MLC}}} \text{Metal-Ligand Complexes} \\
[\text{OH}] & \rightarrow [\text{O}_2] \\
[\text{H}_2\text{O}_2] & \rightarrow [\text{IO}_2] \end{align*}$

BTA Layer

$= \text{ROS} \quad = \text{Cu}^{2+} \quad = \text{Complexing Agent}$
The Flucto-CMP® Setup at Araca

• The new Araca-Fujikoshi RDP-500® and APD-800 tools are the POR in-house polishers for Flucto-CMP®.
• Equipped with two highly-confidential continuously flowing closed megasonic reactors connected in parallel.
• Flucto-CMP® can be easily retrofitted on any HVM AMAT or Ebara polisher.

Flucto-CMP® Reactors with 1 MHz Transducers and a Power Density of 1 W/cm²

Day-Tank Containing off-the-Shelf Cu, Ta or W Slurry with H2O2

Activated Slurry
APD-800 Polisher and Tribometer for R&D and Low-Volume Manufacturing
Reactive Oxidizing Species Creation – Luminol® Tests

Supplier A – Bulk Copper Slurry with $\text{H}_2\text{O}_2$ – After 5-sec (left) and 60-sec (right) exposure to Flucto-CMP®

Supplier A – Bulk Copper Slurry Post Flucto-CMP® – Without $\text{H}_2\text{O}_2$ (left) and with $\text{H}_2\text{O}_2$ (right)
Reactive Oxidizing Species Creation – Luminol® Tests

No Flucto-CMP® at 30 sec

Flucto-CMP® at 30 sec
RR with Flucto-CMP® on Blanket Substrates – Off-the-Shelf Slurries

- Early results (on 100-mm wafers):
  - Bulk Cu RR increase – 40% (Supplier A, C, D)
  - TSV Cu RR increase – 15% (Supplier A)
  - W RR increase – 25% (Supplier A, B)
  - Ta RR increase – 25% (Supplier A)
  - ILD RR increase – 100% (Supplier A STI CeO2)

- APD-800 polisher with one or two Flucto-CMP® reactor (on 300-mm wafers):
  - Bulk Cu RR increase – 15% (Supplier A)
  - W RR increase – 10% (Supplier A)
  - Great RTR repeatability →
  - DRACO® hard mask – 35% (Supplier C)

- RDP-500 polisher (on 200-mm wafers) with two Flucto-CMP® reactors:
  - Bulk Cu RR increase – 35% (Supplier A)
  - W RR increase – 15% (Supplier A)
  - Great RTR repeatability →

### Copper Run Results

<table>
<thead>
<tr>
<th>Run</th>
<th>Mean COF</th>
<th>Mean Pad Temp. (°C)</th>
<th>Mean Removal Rate (A/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.56</td>
<td>25.5</td>
<td>9190</td>
</tr>
<tr>
<td>2</td>
<td>0.532</td>
<td>25.8</td>
<td>8844</td>
</tr>
<tr>
<td>3</td>
<td>0.571</td>
<td>25.8</td>
<td>9025</td>
</tr>
<tr>
<td>4</td>
<td>0.543</td>
<td>25.7</td>
<td>8858</td>
</tr>
<tr>
<td>5</td>
<td>0.551</td>
<td>25.6</td>
<td>9175</td>
</tr>
<tr>
<td>6</td>
<td>0.562</td>
<td>26</td>
<td>9215</td>
</tr>
<tr>
<td>7</td>
<td>0.548</td>
<td>25.6</td>
<td>8957</td>
</tr>
<tr>
<td>8</td>
<td>0.542</td>
<td>25.7</td>
<td>9041</td>
</tr>
<tr>
<td>9</td>
<td>0.562</td>
<td>26.2</td>
<td>9038</td>
</tr>
<tr>
<td>10</td>
<td>0.554</td>
<td>26.2</td>
<td>8854</td>
</tr>
<tr>
<td>11</td>
<td>0.539</td>
<td>25.9</td>
<td>8958</td>
</tr>
<tr>
<td>12</td>
<td>0.565</td>
<td>25.5</td>
<td>9124</td>
</tr>
<tr>
<td>Average</td>
<td>0.552</td>
<td>25.8</td>
<td>9023</td>
</tr>
<tr>
<td>Standard Deviation (%)</td>
<td>2.2%</td>
<td>0.9%</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

### Tungsten Run Results

<table>
<thead>
<tr>
<th>Run</th>
<th>Mean COF</th>
<th>Mean Pad Temp. (°C)</th>
<th>Mean Removal Rate (A/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.318</td>
<td>37.8</td>
<td>2435</td>
</tr>
<tr>
<td>2</td>
<td>0.299</td>
<td>37.2</td>
<td>2503</td>
</tr>
<tr>
<td>3</td>
<td>0.309</td>
<td>36.6</td>
<td>2453</td>
</tr>
<tr>
<td>4</td>
<td>0.308</td>
<td>36.9</td>
<td>2579</td>
</tr>
<tr>
<td>5</td>
<td>0.316</td>
<td>37.8</td>
<td>2471</td>
</tr>
<tr>
<td>6</td>
<td>0.301</td>
<td>36.9</td>
<td>2402</td>
</tr>
<tr>
<td>7</td>
<td>0.307</td>
<td>36.5</td>
<td>2475</td>
</tr>
<tr>
<td>8</td>
<td>0.294</td>
<td>37.1</td>
<td>2527</td>
</tr>
<tr>
<td>9</td>
<td>0.302</td>
<td>36.4</td>
<td>2481</td>
</tr>
<tr>
<td>10</td>
<td>0.294</td>
<td>36.9</td>
<td>2446</td>
</tr>
<tr>
<td>11</td>
<td>0.302</td>
<td>36.7</td>
<td>2490</td>
</tr>
<tr>
<td>12</td>
<td>0.301</td>
<td>37.6</td>
<td>2538</td>
</tr>
<tr>
<td>Average</td>
<td>0.304</td>
<td>37.0</td>
<td>2483</td>
</tr>
<tr>
<td>Standard Deviation (%)</td>
<td>2.5%</td>
<td>1.3%</td>
<td>2.0%</td>
</tr>
</tbody>
</table>
Electrochemical Analysis of Flucto-CMP®

Cu Supplier A

Cu Supplier C

Cu Supplier D
AFM Tip Indentation Depth of the Passivation Layer

- **Approach**
- **Retract**

**N = 12 wafers**

**Cu Supplier A**
- Conventional
- Flucto-CMP®

**Flucto-CMP® Power (Watt/cm²)**

- 0.0
- 0.5
- 1.5

**Indentation Depth (nm)**

- N = 12 wafers
- Flucto-CMP® at 1 W/cm²

**Cu Supplier A**: Blue bar for Conventional, Red bar for Flucto-CMP®

**Cu Supplier C**: Blue bar for Conventional, Red bar for Flucto-CMP®

**Cu Supplier D**: Blue bar for Conventional, Red bar for Flucto-CMP®
Slurry Supplier Performance Comparison

REMINDER – THE FASTER YOU POLISH, THE LESS SLURRY YOU USE AND THE LESS WASTE YOU HAVE TO DEAL WITH – Flucto-CMP® CAN OFFER ATTRACTIVE ENVIRONMENTAL BENEFITS!

N = 8 wafers
Polishing Pressure = 3.0 PSI
All slurries were diluted as per manufacturers’ specification Flucto-CMP® at 1 W/cm²

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Conventional</th>
<th>Flucto-CMP®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier A</td>
<td>∆ = 11%</td>
<td></td>
</tr>
<tr>
<td>Supplier C</td>
<td>∆ = 18%</td>
<td></td>
</tr>
<tr>
<td>Supplier D</td>
<td>∆ = 31%</td>
<td></td>
</tr>
</tbody>
</table>

REMINDER – THE FASTER YOU POLISH, THE LESS SLURRY YOU USE AND THE LESS WASTE YOU HAVE TO DEAL WITH – Flucto-CMP® CAN OFFER ATTRACTIVE ENVIRONMENTAL BENEFITS!
Our Rationale Regarding Defect Reduction

- We believe that defect reduction – one of the main attractions of our technology – is due to three separate effects as follows:
  
  ❖ Sonic waves break up agglomerates. Already proven and patented by Samsung and Micron more than 20 years ago with ultrasonic radiation. The next 2 slides demonstrate the effectiveness of Flucto-CMP® on a modern-day copper slurry under megasonic waves.

  ❖ Megasonic waves increase the concentration of the reactive oxidizing species and result in the formation of a softer passivation layer in which BTA and other molecules are non-covalently bonded on copper. This softer layer gets removed with greater ease compared to the dense covalently-bonded BTA-copper passivation layer in conventional CMP. Proven by AFM results on the penetration depth into the passivation layer under wet conditions. Dynamic electrochemical results also support our claim.

  ❖ Lateral and normal vibrations of the carrier-wafer assembly are dramatically reduced (at times by as much as 80X) with Flucto-CMP® as supported by our real-time shear force and normal force variance results.
Preliminary Results on Deagglomeration

• Effect of Flucto-CMP® technology on slurry nano-particle (NP) health in the case of Cu Slurry Supplier A is shown below. We used a Malvern Zetasizer Nano ZS® particle sizing system.

• Results show that:

  ❖ Our salt-induced NP aggregation method works as many large aggregates are generated in the copper slurry. An average size of 2 microns!

  ❖ Only after 1 minute of exposure to sound waves, Flucto-CMP® restores the highly-aggregated slurry to its original state.
Time Traces – 1.5 PSI – 1.5 m/s – 1% H2O2

POR

RR: 3,650 A/min
Avg. COF: 0.548
Variance of SF: 3,728 lbf²
Variance of NF: 185 lbf²

Flucto-CMP®

RR: 4,782 A/min
Avg. COF: 0.551
Variance of SF: 74 lbf²
Variance of NF: 40 lbf²
Time Traces – 1.5 PSI – 1.5 m/s – 1.5% H2O2 – Copper Supplier A
Interfacial Effects with Cu⁺ – Coordinated Dense BTA Passivation Film?
Development of Sono-Activated® Additives

- **DROP-IN** and **RE-FORMULATION** approaches will be employed to modulate passivation film density (i.e., nature, hardness, and chemical activity).

- While some PV and temperature response is likely, the chemical activity and film formation mechanism will be **initiated by the release of the additives from sonication**, and not from slurry heating or shear force at the pad-wafer interface.

- While controlling or modulating ROS is one factor, it is the synergy between the redox and complexation mechanisms that will alter the nature of the surface film resulting in **SOFTER** and more productive CMP processes.
Addition of Sono-Activated® Additives to Cu Supplier A Slurry

N = 8 wafers
Polishing Pressure= 3.0 PSI
Cu Supplier A
Flucto-CMP® at 1 W/cm²

Additive Solubility (g/L)

Removal Rate (Å/min)

Conventional
Flucto-CMP®
Effect of Sono-Activated® Additive on 3 Slurries

N = 8 wafers
Polishing Pressure = 3.0 PSI
All slurries were diluted as per manufacturer’s specification
Flucto-CMP® at 1 W/cm²

Removal Rate (Å/min)

- Supplier A Additive I: Δ = +48%
- Supplier D Additive I: Δ = +56%
- Supplier C Additive I: Δ = +54%

N = 8 wafers
Polishing Pressure = 3.0 PSI
All slurries were diluted as per manufacturer’s specification
Flucto-CMP® at 1 W/cm²
The Sono-Activation® Additive approach makes all 3 bulk copper slurries behave somewhat similarly – This is good news for toolmakers!
Flucto-CMP® Range of Applications – STI

O₂ → O₂

−O₂ + H⁺ → 2HO₂ → H₂O₂ + O₂

2H⁺ + O₂ + 2 e⁻ → Sono

Oxide Removal Rate (Å/min)

STI No Sono | STI Sono | STI No Sono + Additive | STI Sono + Additive
Flucto-CMP® Range of Applications – Non-KMnO₄ SiC CMP
Thank You!