Protecting Against Cobalt Corrosion in Advanced CMP Slurries

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Motivation

- Increasingly, Co is attracting interest from chipmakers for use in IC’s, especially due to:
  - Favorable adhesion of Co to Cu seed layers
  - Ease of conformal Co deposition
  - Most importantly, as Cu line sizes continue to shrink, trenches can be harder to fill without voids/keyholes. Co ensures conductive linings inside trenches even if Cu voids are present

- Novel stacking structures present new challenges for CMP slurries. Slurry interactions with Co becoming increasingly significant!

![Diagram of Co and copper structure]

NOT TO SCALE

Copper
Copper Seed
Cobalt
Barrier
Oxide
Challenges

• Co does not self passivate and is susceptible to corrosion
  – Pitting corrosion problems on blankets
  – Galvanic corrosion on patterns
  – Co ions quite reactive

• Thus, a solution is the essentially provide a protective layer on Co via additives
  – Additives should be selective for Co over Cu, so as not to compromise slurry performance
  – Only takes a small concentration of additive for large effect
**Fundamental Electrochemistry**

<table>
<thead>
<tr>
<th>Oxidation Potential vs SHE</th>
<th>Oxidation Reaction</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>-0.46</td>
<td>Ru $\leftrightarrow$ Ru$^{2+} + 2e^-$</td>
</tr>
<tr>
<td>Cu</td>
<td>-0.34/-0.52</td>
<td>Cu$^+/Cu^{2+}$</td>
</tr>
<tr>
<td>Co</td>
<td>0.28</td>
<td>Co $\leftrightarrow$ Co$^{2+} + 2e^-$</td>
</tr>
<tr>
<td>Ta</td>
<td>0.75</td>
<td>2Ta + 5H$_2$O $\leftrightarrow$ Ta$_2$O$_5$ + 10H$^+$</td>
</tr>
<tr>
<td>Ti</td>
<td>1.63</td>
<td>Ti $\leftrightarrow$ Ti$^{2+} + 2e^-$</td>
</tr>
</tbody>
</table>

- Co thermodynamically oxidizes and does not self passivate. Corrosion continues unless Co is protected.
• If Co corrosion can be suppressed and/or the Co RR can be decreased, Co on the trench walls can be protected
POU Droplets on Co Wafer (Initial)

DiW/Higher Oxidizer Conc ONLY
DiW/Lower Oxidizer Conc ONLY

Cu Slurry with Co suppressor
Legacy Cu Slurry
POU Droplets on Co Wafer (After Drying)

- DIW/Higher Oxidizer Conc ONLY
- Cu Slurry with Co suppressor

- DIW/Lower Oxidizer Conc ONLY
- Legacy Cu Slurry
Cobalt is easily corroded by slurry oxidizer in DIW, regardless of concentration. Brown byproduct is observed.

Oxidizer concentrations slightly above and below POU oxidizer concentrations
Legacy Cu with **higher** oxidizer concentration

Legacy Cu with **lower** oxidizer concentration

Brown byproducts of cobalt corrosion are observed, although the byproducts are suppressed compared to DIW/oxidizer solution only.

Protection against Co corrosion unchanged with oxidizer concentration.
POU Droplets on Co Wafer (After Drying)

Cu Slurry with Co suppressor, higher oxidizer concentration

Cu Slurry with Co suppressor, lower oxidizer concentration

Reduction in brown byproducts of cobalt corrosion at both oxidizer levels
Current exchange density ~2 orders of magnitude lower for the case with the Co corrosion suppressor, meaning that corrosion happens less rapidly (kinetics).

Corrosion potential higher for case with suppressor, meaning more energetically difficult (thermodynamics).
Co Static Etch Tests

- Compare static etch rates for legacy Cu slurry vs Cu slurry with Co corrosion suppressor

20C Normalized Co Static Etch Rates

- Legacy Cu Slurry
- Co Suppressor Slurry V.1
- Co Suppressor Slurry V.2

40C Normalized Co Static Etch Rates

- Legacy Cu Slurry
- Co Suppressor Slurry V.1
- Co Suppressor Slurry V.2
20C Co Static Etch Tests

- Pitting corrosion mollified by Co corrosion suppressor
40C Co Static Etch Tests

- Pitting corrosion mollified by Co corrosion suppressor
Polishing Tests of Co Blanket Wafers

- Co wafers had same initial thicknesses, Co wafers cleared for legacy slurries between 1-3 psi.
POU Droplets on Cu Wafer (After Drying)

Legacy Cu Slurry  Cu Slurry with Co suppressor

Similar Cu behavior, no added undesirable Cu interactions
Conclusions

• The addition of novel components to Cu CMP slurries can improve compatibility with Co, which is becoming a growing need for the industry
  – Lower static etch rates
  – Lower polishing rates
  – Higher corrosion potential and lower exchange current density
  – Copper polishing performance not compromised