SLURRY FORMULATION OPTIONS

CHALLENGES FOR DEFECT REDUCTION IN Cu,Ta/TaN AND Ru PLANARIZATION

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- My colleague Prof. Dip Roy
- Don Canaperi and his IBM team
Outline

- Introduction

- New Slurry options for Cu and Ta CMP
  - Defects during Cu/barrier polishing
  - Patterned wafer polish results
  - Post-polish surface analysis

- New barrier materials (Ru-based)
  - Slurry options
  - Galvanic corrosion

- Conclusions
Factors Affecting CMP

Chemical Mechanical Planarization

Tool Performance

Process Conditions

Consumable Performance

Slurry Performance

Pad Performance

A abrasive components

- Single abrasives
- Mixed or composite abrasives

Chemical components

- Oxidizing agents
- Passivating agents
- Surfactants
- Other additives
Slurry impact on Defects

- Particles → scratches and related defects, residues, etc.

- Chemicals → corrosion, etching, nonplanarity, non-or inadequate selectivity, residues, etc.

- Combined → Dishing (pad also plays a role), erosion, etc.
Defectivity vs. Slurry Design

More mechanical slurries

Higher Defects
  * scratches
  * slurry residues

Higher planarity

Higher friction

Higher down force to Maintain removal

More chemical slurries

* slurry residuals and precipitates
* chemically driven scratches
* clearing issues

Cu surface protection more critical

* corrosion risk
* Dendrites
* unstable process
* copper etching/corrosion pits, etc./
Barrier Slurry Requirements

- Barrier thickness is quite small → Rate not important
- Need to remove all the stop layer and perhaps some of the underlying dielectric
- Appropriate selectivity and achieving uniformity are critical
- Controlled dishing and erosion
- No galvanic corrosion
- Of course, no “damage” to the dielectric layer – pH has a strong influence
- ??
Cu loss due to galvanic corrosion

Barrier Slurry Selection


- C. Surisetty, PhD thesis, 2009 (Clarkson University)

- Sathish Janjam, PhD Thesis 2008 (Clarkson University)
Selection of slurry systems

Cu Slurries

- 0.021M Oxalic acid + 5wt% H₂O₂ + 4mM DBSA + 3wt% SiO₂ @ pH – 3 (Cu - I)

- 1wt% glycine + 0.021M Oxalic acid + 5wt% H₂O₂ + 3.5mM DBSA + 3wt% SiO₂ @ pH – 3 (Cu - II)

Barrier Slurries

- 0.065M K₂SO₄ + 1wt% H₂O₂ + 8wt% SiO₂ @ pH – 4 (Ta - I)

- 0.065M K₂SO₄ + 8wt% SiO₂ @ pH – 4 (Ta - II)
## Dishing – ITRS requirements vs results

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<tbody>
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<td>Technology Node</td>
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<td>hp</td>
<td>hp</td>
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<td>32</td>
<td>32</td>
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<td>32</td>
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<tr>
<td>Cu thinning</td>
<td>24</td>
<td>20</td>
<td>19</td>
<td>16</td>
<td>14</td>
<td>14</td>
<td>12</td>
<td>11</td>
<td>10</td>
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<tr>
<td>of global wiring</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>due to dishing</td>
<td></td>
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<td></td>
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<tr>
<td>(nm), 100 µm wide feature</td>
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</table>

<table>
<thead>
<tr>
<th>Dishing Performance</th>
<th>Commercially available Slurries</th>
<th>Obtained in this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 µm wide features</td>
<td>30-50 nm</td>
<td>10-15 nm</td>
</tr>
</tbody>
</table>
# Polishing Conditions

<table>
<thead>
<tr>
<th>Wafer size</th>
<th>300mm (12”)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tool</td>
<td>AMAT LK-Chamber</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>300 ml/min</td>
</tr>
<tr>
<td>Pressure</td>
<td>2.2 psi</td>
</tr>
<tr>
<td>Platen / Head speed</td>
<td>102 / 100 rpm</td>
</tr>
<tr>
<td>Silica</td>
<td>Colloidal silica (~ 35nm)</td>
</tr>
<tr>
<td>Pad</td>
<td>Hard / Soft</td>
</tr>
<tr>
<td>Hard pad Conditioning type</td>
<td>In-situ with 5lbf and head speed of 108 rpm</td>
</tr>
<tr>
<td>Soft pad Conditioning type</td>
<td>Ex-situ with 2lbf and platen/head speed of 101/108 rpm</td>
</tr>
</tbody>
</table>
**Pattern Description**

<table>
<thead>
<tr>
<th>Box</th>
<th>Pattern Description</th>
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<tbody>
<tr>
<td>1</td>
<td>Cu Plate</td>
</tr>
<tr>
<td></td>
<td>100% pattern factor</td>
</tr>
<tr>
<td>2</td>
<td>1 um line, 10 um space</td>
</tr>
<tr>
<td></td>
<td>9% pattern factor</td>
</tr>
<tr>
<td>3</td>
<td>0.8 um line, 0.2 um space</td>
</tr>
<tr>
<td></td>
<td>80% pattern factor</td>
</tr>
<tr>
<td>4</td>
<td>0.1 um line, 0.2 um space</td>
</tr>
<tr>
<td></td>
<td>33% pattern factor</td>
</tr>
<tr>
<td>5</td>
<td>1.8 um line, 0.2 um space</td>
</tr>
<tr>
<td></td>
<td>90% pattern factor</td>
</tr>
<tr>
<td>6</td>
<td>Minimum line, minimum space</td>
</tr>
<tr>
<td></td>
<td>50nm line/space; 50% pattern factor</td>
</tr>
</tbody>
</table>
Dishing comparison – Profilometry

**Comparison - Step 1 (center)**
- Commercial Cu slurry with Hard pad and Ta slurry with Soft pad
- Cu II with Hard pad and Ta I with Soft Pad
- Cu II + Ta I with Hard pad only
- Commercial Slurry with Hard pad only

**Comparison - Step 2 (108mm left from center)**
- Commercial Cu slurry with Hard pad and Ta slurry with Soft pad
- Cu II with Hard pad and Ta I with Soft Pad
- Cu II + Ta I with Hard pad only
- Commercial Slurry with Hard pad only

**Comparison - Step 3 (122mm right from center)**
- Commercial Cu slurry with Hard pad and Ta slurry with Soft pad
- Cu II with Hard pad and Ta I with Soft Pad
- Cu II + Ta I with Hard pad only
- Commercial Slurry with Hard pad only
SEM Inspection of wafers polished with various slurries

Commercial Cu slurry

Cu – I slurry

Cu – II slurry

Ta – I slurry

Tool: Brightfield Defect Detector
## Performance comparison of 2nd step slurries

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ta – I slurry (K$_2$SO$_4$-H$_2$O$_2$)</th>
<th>Ta – II slurry (K$_2$SO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dishing Improvement for 200 x 200 µm features</td>
<td>20 – 30 nm</td>
<td>Not measurable</td>
</tr>
<tr>
<td>Optical Profilometry</td>
<td>Good</td>
<td>Cu was damaged</td>
</tr>
<tr>
<td>SEM Inspection</td>
<td>Lower defects compared to commercial slurry</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Bulk Cu for these wafers was polished with commercial Cu slurry.
New Barrier materials (Ru-based)
-Slurry options
Challenges with Ta/TaN

- Barrier thickness is \(~ 5 \text{ nm or less}\) for \(< 45 \text{ nm technology node}\)
- Higher resistivity
- A Cu seed layer is required for electroplating Cu on Ta/TaN
- It is increasingly difficult to deposit Cu seed/Ta/TaN trilayer within the spatial limits
Alternative barrier requirements

- Need diffusion barriers with stability over wide (300 – 700 C) temperature range
- Conductive platform for direct electroplating of Cu, eliminating the need for a seed layer
- Single layer to decrease the complexity in the process
Alternative to Ta/TaN

**Stack**

- **Cu**
- **Ru**
- **TaN**

**Advantage**

- No seed layer required due to Ru conductive platform

- **Cu**
- **RuC, RuN..**

- No seed layer and single barrier layer
Some Advantages of Ruthenium

- Lower (~7 μΩ cm) resistivity compared to Ta (~14 μΩ cm) and TaN (~200μΩ cm)
- Good adhesion to Cu – improves electromigration resistance
- High thermal stability
- Direct electrodeposition of Cu
Ru barrier

Drawback with only Ru barrier
- Ru due to its columnar structure, may not be a good diffusion barrier below 10 nm thickness

Incorporation of materials into Ru or Ru stack
- Ru/TaN was shown to have improved barrier properties
- Carbon incorporation into Ru stabilizes the amorphous structure and thereby improves barrier properties
- Similarly N, P, B.. incorporations have been investigated for improving barrier performance
Replacement of W contacts with Cu

Problems for < 32 nm technology node with W:

- Large resistance of W (5.28 µΩ cm)
- Large resistance due to poor gap fill

Alternative:

- Cu (1.6 µΩ cm); but needs a robust diffusion barrier to block Cu diffusion
- Possible options for barrier: Ru/TaN, RuC, RuN.....
Comparison of W and Cu contacts

Line -200 nm depth and width of 35 nm, Cu contact on CVD Ru/TaN

Comparison of resistance

Challenges for Ru CMP

- Ru, a noble metal, has a very low polish rate in typical barrier slurries (needs oxidizer for higher RR\(s\))
- Can induce galvanic corrosion in Cu due to difference in corrosion potentials
- Selective removal of Cu, hardmask (SiO\(_2\)), and low-\(k\) (SiCOH) is required
# Ru CMP - Early Work

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>pH</th>
<th>RR (nm/min)</th>
<th>Pressure (psi)</th>
<th>Problem</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceric ammonium nitrate (CAN) + HNO₃</td>
<td>1</td>
<td>40</td>
<td>1</td>
<td>Formation of RuO₄ and insolubility of CAN above pH 2</td>
<td>Lee et al (2004)</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>3 -10</td>
<td>10</td>
<td>3</td>
<td>High silica wt% (30)</td>
<td>Vishwas (2005)</td>
</tr>
<tr>
<td>Sodium periodate</td>
<td>4 -10</td>
<td>130 (pH 6)</td>
<td>4</td>
<td>Na contamination</td>
<td>Park et al (2009)</td>
</tr>
</tbody>
</table>
New $\text{KIO}_4$-based slurry for Ru CMP

Some targets

- Ru Removal rate > 50 nm/min
- Eliminate formation of $\text{RuO}_4$ (toxic)
- Adequate removal rate selectivities over $\text{Cu}$ and $\text{SiO}_2$
- Minimize defects and galvanic corrosion

Concentration and pH of $\text{KIO}_4$

- Solubility at 20°C is 0.018 M, increased by adding KOH
- 0.015 M concentration was chosen for an initial study
- Toxic $\text{RuO}_4$ is reported to form in the acidic region (pH $\leq 7$), therefore pH 9 was chosen
Effect of Abrasives

pH 9. 0.015M KIO₄

RR, nm/min

No removal was observed

no abrasives 1 wt% alumina 1 wt% silica
Enhancement in the Ru RR

5 wt% silica + ‘x’ M KIO₄ at pH 9

Effect of ionic strength

5 wt% silica + 0.05 M KIO$_4$ – pH 9
Proposed reaction mechanism

- **pH ≤ 7**

  \[ Ru + KIO_4 \rightarrow RuO_4^{\text{toxic}} + I^- + K^+ \]

- **pH ≥ 8**

  \[ Ru + KIO_4 + 2OH^- \rightarrow RuO_4^- + H_2O + \frac{1}{2}O_2 + I^- + K^+ \]
  \[ 4RuO_4^- + 4OH^- \rightarrow 4RuO_4^{2-} + 2H_2O + O_2 \]
Galvanic Corrosion Analysis
Galvanic corrosion issue with Cu

Solution:
0.03 M KIO4 at pH 9

Observation:
Corrosion potential difference of ~600 mV
Combination of inhibitors (7 mM AA + 5 mM BTA)

Combination of inhibitors decreased the corrosion potential significantly to a value of \(~20\) mV.
RRs with and without inhibitors

System I:
0.015 KIO₄ + 5% Silica

System II:
0.015 M KIO₄ + inhibitors

Summary

- Slurry selection can severely impact defect control
- Barrier Slurry is becoming more critical
- New barrier materials (Ru and alloys) impose additional challenges
- Additives that can minimize the possibility of galvanic corrosion of Cu during Ru polishing have been identified.
- Mixed oxidizer slurries without BTA and sulfate-based barrier slurries are attractive