A Study of Dilute Cu Alloys for Dual-Damascene Interconnect Applications

Cara Hutchison, Anil Bhanap, Mike Pinter, Wuwen Yi, Karen Scholer, Nicole Truong, Bob Prater, Eal Lee

Honeywell Electronic Materials

November 19, 2003
TFUG Meeting
eal.lee@honeywell.com
**Objectives**

Cu integration research is presently focused on the reduction of electromigration, stress migration and associated void formation along with inhibiting corrosion. As part of this effort, a set of Cu alloys is characterized to assess their performance.

**Evaluated Alloys**
- 6N Cu
- Cu-0.5at%Ag
- Cu-0.5at%Al
- Cu-0.5at%Sn
- Cu-0.5at%Ti

**Target Properties**
- Target hardness
- Target grain recovery
- Electrical resistivity
- Thermal conductivity
- CTE
- IV characteristics
- Deposition yield

**PVD ECD Film Properties**
- Electrical resistivity
- Reflectivity
- Stress
- Adhesion
- XRD orientation
- SIMS diffusion profile
- AFM microstructure
- Corrosion
- Leakage current, line resistance

Due to the memory constraints, only highlights are presented here. For details, please contact eal.lee@honeywell.com
Target Characterization Summary

• Alloying addition increases hardness of forged alloys, but the increase becomes insignificant once exposed to elevated temperature (>350 C) after recrystallization.

• Ti increases electrical resistivity most and resistance to grain growth.

• Alloying addition increases electrical resistivity and decreases thermal conductivity.

• Ag produces the least increase in electrical resistivity and the lowest CTE.

• V vs. Power and I vs. Power show no significant difference in response regardless of alloy composition.

• Alloying addition refines grain size and improves deposition yield.
Al addition increased the grain size slightly.

**Ra** (surface roughness): Average of absolute values of the delta of all the height values from the mean (not rms)
AFM Microstructure of PVD Cu-Seed Film

Cu-Ti (Ra=1.7 nm)

Cu-Sn (Ra=1.01 nm)

Grain size 86 nm

Grain size 57 nm

Ti and Sn addition produced finer grain sizes.
AFM Microstructure of PVD Cu-Seed Film

Cu-Ag (Ra=1.05 nm)

Grain size 25 nm

Angled View of Cu-Ag

Ag addition produced the finest grain sizes.
High power deposition produces finer grain size and smoother surface due to enhanced nucleation rate.
<table>
<thead>
<tr>
<th>Film (350°C/30 min)</th>
<th>XRD Integrated Peak Intensity (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;111&gt;</td>
<td>&lt;200&gt;</td>
<td>&lt;220&gt;</td>
<td>&lt;113&gt;</td>
</tr>
<tr>
<td>6N Cu-Seed</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6N Cu + ECD</td>
<td>85.1</td>
<td>4.8</td>
<td>3.1</td>
<td>6.9</td>
</tr>
<tr>
<td>CuSn-Seed</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuSn + ECD</td>
<td>82.2</td>
<td>8.2</td>
<td>4.0</td>
<td>5.6</td>
</tr>
<tr>
<td>CuAl-Seed</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuAl + ECD</td>
<td>64.8</td>
<td>18.0</td>
<td>7.3</td>
<td>10.0</td>
</tr>
<tr>
<td>CuAg-Seed</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuAg + ECD</td>
<td>56.0</td>
<td>21.9</td>
<td>10.2</td>
<td>11.9</td>
</tr>
<tr>
<td>CuTi-Seed</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuTi + ECD</td>
<td>80.7</td>
<td>6.8</td>
<td>3.5</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Cu-seed showed predominantly <111> orientation for all alloying additions, but ECD Cu orientation varied with seed composition, 69Cu seed extending <111> orientation most.
Annealed @ 400 °C for 1 hour

Cu 2kÅ Alloy  ECD 5kÅ Cu  Cu 2kÅ Alloy  TaN/Ta Barrier

Oxide layer at this interface remains and may suppress the diffusion. This can cause non-symmetric SIMS profile.

Oxide layer at this interface dissolves away during ECD.
Ag diffuses fastest followed by Sn.
Film Characterization Summary

• Reflectivity of Cu-seed layer varies strongly with annealing temperature, whereas that of ECD Cu shows little variation.

• Alloying addition imparts little effect on the grain size and electrical resistivity of ECD copper.

• Stress of seed layer is generally higher than those of ECD Cu, but imparts little effect on the stress of ECD film.

• All alloyed Cu-seed films show good adhesion to TaN/Ta barrier.

• All Cu-seed showed predominantly <111> orientation regardless of composition.

• SIMS analysis shows complete homogenization of Ag through ECD Cu, whereas Mg shows limited diffusion. Non-symmetric diffusion of Ti and Al SIMS indicates surface oxidation effect. Potential advantage or disadvantage of this diffusional behavior should be evaluated.
**Electrical Testing Flow**

**Process flow**

1. **ILD deposition:** SiN\SiO₂
2. **Trench patterning:** Litho, Etch, Ash
3. **Degas:** 415°C, 100 s
   - **Barrier dep.:** TaN\Ta
   - **Cu seed dep.**
4. **ECP Cu (10kA)**
5. **Cu Anneal**
   - 200°C/60min
6. **CMP**
7. **E-TEST**

**Test structure**

- **Snake**
- **Comb**

- **Line-to-line leakage (also called comb leakage):**
  - Apply voltage between Pads (1,2 shorted) and Pad (3)

- **Snake resistance (also called Serpentine resistance):**
  - Apply voltage between Pad 1 and Pad 2
• Cu alloy composition did not significantly affect comb leakage current
• Cu-Ag and Cu-Al show 10-15% higher serpentine resistance than 69Cu
• Cu-Ti and Cu-Sn show % higher serpentine resistance than 69Cu
Serpentine resistance in the 0.24 – 0.38 micron line width range:

Line resistance decreases with line width because of reduced liner contribution

Alloying Effect: 69Cu < Cu-Al ~ Cu-Ag < Cu-Ti ~ Cu-Sn
Water Box Corrosion Test

Process flow

Si wafer

Oxide ILD deposition

M1 trench patterning

Degas/Barrier/Cu Seed dep

Cu plating

Anneal: 200C, 1 hr

M1 CMP

Optical inspection

ETEST

Alloys
69Cu
Cu-Al
Cu-Ag
Cu-Sn
Cu-Ti
Cu-Mg

At serpentine-comb structures from 9 dies near wafer center

Water box exposure

Optical inspection

ETEST

Store in sealed wafer box with DI water at bottom. Room Temp. 24 hr
Optical Inspection of 69Cu
Optical Inspection of Cu-Al

Corrosion
Optical Inspection of Cu-Ag

Corrosion
Optical Inspection of Cu-Sn

Corrosion
Optical Inspection of Cu-Mg

Profuse Corrosion
Summary of Optical Inspection

• Significant corrosion was seen after water box test in case of seed layer formed by 69Cu, Cu-Ag, Cu-Sn, and Cu-Mg alloys

• Very little corrosion was observed in case of Cu-Al, whereas Cu-Ti seed layer showed no corrosion.

• Preferred corrosion sites are edges and corners of Cu features, especially those adjacent to large field regions.
Serpentine Resistance before and after exposure to water vapor

L/S = 0.32/0.32 µm

Before water-box exposure

After water-box exposure

Water box exposure caused the highest increase in serpentine resistance for 69Cu and Cu-Ag, followed by Cu-Sn.

No change in serpentine resistance was noticed in case of Cu-Al and Cu-Ti seed layers.
Summary of E-Test

- ECD Cu with 69Cu seed rendered the lowest line resistance and the highest with CuTi seed.

- Alloying elements imparted no significant impact on line leakage current.

- Excellent corrosion resistance was seen in single level metal structures formed using Cu-Al and Cu-Ti alloys as seed layer. This is likely due to a possible formation of a protective oxide film on Cu surface (e.g., Al₂O₃, TiO₂).

- While Ag and Sn diffuse easily throughout Cu during annealing, it doesn’t seem to form a protective layer.

- Cu-Sn alloy needs to be studied further. While the optical images showed significant corrosion, the serpentine resistance was affected less than in case of 69Cu and Cu-Ag.
Final Remarks

• Ag is considered to be the best candidate for improving electromigration resistance in consideration of its fast homogenization, low electrical resistivity, and high atomic mass. However, actual EM data is still needed.

• Ti shows the best corrosion resistance but increases electrical resistivity in both seed and ECD Cu.

• Al shows excellent corrosion resistance and produces negligible increase in electrical resistivity for ECD Cu.

• Sn is the highest atomic mass element tested and considered to be good for electromigration resistance.