Atomic Layer Deposition (ALD) and Chemical Vapor Deposition (CVD) of Copper-based Metallization for Microelectronic Fabrication

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ALD and CVD of Copper-Based Metallization for Microelectronic Fabrication

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Introduction

- Periodic improvements in performance of microelectronic devices have been achieved through device-scaling.

- Copper was selected because of its (1) abundance, (2) low resistivity, and (3) better electromigration reliability.

- Damascene process (EP and CMP) is commonly adopted for patterning copper.
Outline

In today’s presentation:

- ALD and CVD of Cu films from a Cu(I) amidinate precursor
- Formation of Cu seed layer by ALD of Cu and by CVD of CuON
- Bottom-up filling of CVD-Cu and CuMn alloy in nanoscale features
- Summary
Copper Precursors

- Requirements for good ALD Cu precursors: (1) thermally stable, (2) volatile, and (3) minimal contaminations

![Chemical structures of Cu precursors]

**Advantages of metal amidinates precursors:**
- Bidentate chelating effect enhances thermal stability
- Tunable reactivity and volatility
- Minimal carbon and oxygen contamination

Copper films could be deposited by ALD using molecular hydrogen as reducing agent.

Copper deposited on ALD-Al₂O₃ substrate at low temperatures (150-190 °C):

ALD of Copper

- Growth behavior can be affected by many factors: surface chemistry, precursor exposure, deposition temperature, etc.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Growth per cycle (Å/cycle)</th>
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</thead>
<tbody>
<tr>
<td>Al₂O₃/SiO₂</td>
<td>1.90 (based on 100 cycles)</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>1.50 (based on 60 cycles)</td>
</tr>
<tr>
<td>WN</td>
<td>0.54 (based on 30 cycles)</td>
</tr>
<tr>
<td>Ru</td>
<td>0.11 (based on 100 cycles)</td>
</tr>
<tr>
<td>Co</td>
<td>0.40 (based on 30 cycles)</td>
</tr>
<tr>
<td>Cu</td>
<td>~0.5 (from Al₂O₃ curve)</td>
</tr>
</tbody>
</table>

ALD-Al₂O₃, ALD-HfO₂, Thermal SiO₂
Initially ~2Å/cycle, ~0.5Å/cycle when surface is fully covered by Cu

Ru Substrates
0.11Å/cycle
Copper Seed Layer Using ALD

- ALD has the ability to grow films conformally and uniformly over high aspect ratio holes and trenches

Four-point bend experiment showed high adhesion energies for Cu/Co/WN/SiO₂

<table>
<thead>
<tr>
<th>Structure</th>
<th>Scotch tape test</th>
<th>Adhesion energy (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/SiO₂</td>
<td>Failed</td>
<td>2ᵃ</td>
</tr>
<tr>
<td>Cu/SiO₂</td>
<td>Failed</td>
<td></td>
</tr>
<tr>
<td>Cu/WN/SiO₂</td>
<td>Failed</td>
<td></td>
</tr>
<tr>
<td>TaN/SiO₂</td>
<td>Passed</td>
<td>6ᵃ</td>
</tr>
<tr>
<td>WN/SiO₂</td>
<td>Passed</td>
<td>&gt;31</td>
</tr>
<tr>
<td>Co/WN/SiO₂</td>
<td>Passed</td>
<td>&gt;31</td>
</tr>
<tr>
<td>Cu/Co/WN/SiO₂</td>
<td>Passed</td>
<td>&gt;31</td>
</tr>
</tbody>
</table>

In-situ Resistance Measurement
ALD Cu on Glass (185 °C)

Cu Seed Layer Using CVD-CuON and Plasma Reduction

- Copper seed layers must have conformal step coverage, strong adhesion and smooth surface morphology

- Island growth of CVD-Cu on Ta underlayer
- Cu has fairly high wettability on Ru, but requires >20nm to form a continuous film due to island growth

- New approach:
  
  \[
  \begin{align*}
  \text{Cu precursor} + \text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{O} \\
  \text{Cu precursor} + \text{NH}_3 & \rightarrow \text{Cu}_3\text{N} \\
  \text{Cu precursor} + \text{H}_2\text{O} + \text{NH}_3 & \rightarrow \text{CuON}
  \end{align*}
  \]

  Low Surface Energy (22-26 mJ/m² for Cu₂O and Cu₃N, compared to 1700-1900 mJ/m² for Cu)

  Remote Hydrogen Plasma Reduction near RT

  Thin (<10 nm), Smooth (RMS ~1 nm), High Density (95%) CVD Cu Seed Layer

Cu Seed Layer Using CVD-CuON and Plasma Reduction

**CVD System**

- **Temperature:** 140-220°C
- **Pressure:** 8 Torr

**Plasma System**

- **Remote Plasma Generator**
- **Temperature:** RT - 50°C
- **Reduction Time:** 30-180s

![Graph](chart.png)

**Composition of CVD-CuON Films**

(H₂O:NH₃=30:10)
Cu Seed Layer Using CVD-CuON and Plasma Reduction

Surface Morphology of 20nm of CVD-CuON Films  
(H₂O:NH₃=30:10)

- 140°C, RMS: 0.64 nm
- 160°C, RMS: 0.54 nm
- 180°C, RMS: 0.72 nm
- 220°C, RMS: 1.04 nm

Step Coverage in High AR Holes  
(H₂O:NH₃=30:10, 140°C)

100 nm
Filling Narrow Features with CVD of Copper

- Conventional techniques lead to formation of voids and seams in very narrow features
- Iodine is a catalytic surfactant that promotes smoother morphology and higher deposit rate
- Bottom-up filling of sub-micrometer features could be achieved by CVD

This process requires a conformal Cu seed layer on top of the diffusion barrier and adhesion layer

**Surfactant Catalyzed CVD Cu and CuMn in Narrow Trenches**

**Key Points**

- Conformally deposited manganese nitride serves as a barrier/adhesion layer.
- Iodine acts as a surfactant catalyst to promote Cu and Mn growth.
- Void-free, bottom-up filling of Cu or Cu-Mn alloy in narrow trenches with AR up to at least 5:1.
- Mn diffuses out from Cu during post-annealing to further improve adhesion and barrier properties at Cu/insulator interface.

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**Motivation**

Chemical Vapor Deposition of Copper

CVD System

Temperature
130°C for Mn₄N
180°C for Cu and CuMn
Pressure: 5 Torr

Precursors

Bis (N,N'-diisopropylpentylamidinato)manganese(II)
Melting Point: ~60°C
Bubbler Temperature: 90°C
Vapor Pressure: ~0.1 mbar at 90°C

Copper (I) N,N'-di-sec-butylacetamidinate
Melting Point: ~75°C
Bubbler Temperature: 130°C
Vapor Pressure: ~0.25 mbar at 95°C
CVD-Mn₄N Barrier/Adhesion Layer

- CVD-Mn₄N (ε phase, FCC structure) can be prepared by reacting manganese amidinate precursors with NH₃

- Mn₄N layer as thin as 2.5 nm (1) shows barrier properties against Cu diffusion, (2) significantly improve adhesion (debonding energy = 6.5 J/m²) between Cu and SiO₂

- Release of iodine and catalytic effects are observed on Mn₄N underlayer
Surfactant Catalyzed Bottom-up Filling of CVD-Cu

With CVD-Mn$_4$N liner layer and iodine catalyst, trenches with width $\leq 20$ nm and aspect ratio over 5:1 can be completely filled with CVD-Cu.
Surfactant Catalyzed Bottom-up Filling of CVD-CuMn Alloy

- Cu-Mn alloy can be formed by (1) alternating CVD-Cu and Mn or (2) co-depositing Cu and Mn

**Diagram:**
- CVD-Mn$_4$N Deposition
- Iodine Exposure
- CVD-CuMn Alloy

**Image:**
- Trenches with width $\leq 30$ nm can be completely filled with CuMn alloy
- Manganese concentration: 0.5-2.0 atomic %
Enhancement by Diffusion of Mn from Cu to Interface

- Insulators encourages diffusion of Mn through Cu grain boundaries to interface
- Mn improves both adhesion and barrier properties at the interface

Summary

- Copper can be deposited by ALD or CVD using a Cu(I) amidinate precursor

- Conformal and uniform seed layers can be prepared by ALD-Cu or by CVD-CuON followed by remote hydrogen plasma reduction

- Nanoscale trenches can be superconformally filled by CVD-Cu and CVD-CuMn alloy with an iodine surfactant on Mn$_4$N liner layer

- Manganese in Cu-Mn alloy diffuses out to strengthen the interface between Cu and insulators without increasing the resistivity of Cu

- Manganese silicate (MnSi$_x$O$_y$) interfacial layer shows excellent barrier properties against Cu diffusion and protects Cu from corrosion by H$_2$O and O$_2$
Acknowledgements

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