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

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**Copper Precursors**

- **Copper (I) N,N'-di-sec-butylacetamidinate**
  - Melting Point: ~75 °C
  - Bubbler Temperature: 130 °C
  - Vapor Pressure: ~0.25 mbar at 95 °C

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

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ALD of Copper

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

ALD System

- 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.

![Graph 1: Film Thickness vs. Cycles]

**Graph 1:**
- ALD-Al$_2$O$_3$, ALD-HfO$_2$, Thermal SiO$_2$
- Initially ~2Å/cycle, ~0.5Å/cycle when surface is fully covered by Cu

![Graph 2: Film Thickness vs. Cycles]

**Graph 2:**
- Ru Substrates
  - 0.11Å/cycle

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Growth per cycle (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$/SiO$_2$</td>
<td>1.90 (based on 100 cycles)</td>
</tr>
<tr>
<td>Si$_3$N$_4$</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 Al$_2$O$_3$ curve)</td>
</tr>
</tbody>
</table>
Copper Seed Layer Using ALD

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

![ALD Cu in AR = 35:1 Holes](image)

- 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>2²</td>
</tr>
<tr>
<td>Cu/SiO₂</td>
<td>Failed</td>
<td>6²</td>
</tr>
<tr>
<td>Cu/WN/SiO₂</td>
<td>Failed</td>
<td>&gt;31</td>
</tr>
<tr>
<td>TaN/SiO₂</td>
<td>Passed</td>
<td>&gt;31</td>
</tr>
<tr>
<td>WN/SiO₂</td>
<td>Passed</td>
<td>&gt;31</td>
</tr>
<tr>
<td>Co/WN/SiO₂</td>
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</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:

  - Cu precursor + H₂O → Cu₂O
  - Cu precursor + NH₃ → Cu₃N
  - Cu precursor + H₂O + NH₃ → CuON

  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

Remote Plasma Generator

Plasma System

Temperature: RT - 50°C  
Reduction Time: 30-180s

Composition of CVD-CuON Films  
(H$_2$O:NH$_3$=30:10)
Cu Seed Layer Using CVD-CuON and Plasma Reduction

Surface Morphology of 20nm of CVD-CuON Films
(H$_2$O:NH$_3$=30:10)

- (a) 140°C, RMS: 0.64 nm
- (b) 160°C, RMS: 0.54 nm
- (c) 180°C, RMS: 0.72 nm
- (d) 220°C, RMS: 1.04 nm

Step Coverage in High AR Holes
(H$_2$O:NH$_3$=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**

**Motivation**

- 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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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-Mn$_4$N Barrier/Adhesion Layer

- CVD-Mn$_4$N (ε phase, FCC structure) can be prepared by reacting manganese amidinate precursors with NH$_3$

![Image of CVD-Mn$_4$N layer](image)

- Mn$_4$N layer as thin as 2.5 nm (1) shows barrier properties against Cu diffusion, (2) significantly improve adhesion (debonding energy = 6.5 J/m$^2$) between Cu and SiO$_2$

- Release of iodine and catalytic effects are observed on Mn$_4$N underlayer

![Image of Dielectrics and RMS roughness](image)

- Excellent step coverage holes with AR = 52:1

- RMS roughness = 0.97 nm for a 13.5 nm film
Surfactant Catalyzed Bottom-up Filling of CVD-Cu

With CVD-Mn₄N liner layer and iodine catalyst, trenches with width ≤ 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

Trenches with width ≤ 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

![Graph showing adhesion energy and Mn/Si ratio](image)

Cu Diffusion Barrier Test

(a) Reference
- Cu: 250nm
- Thermal SiO$_2$: 300nm
- n-Si

(b) With MnSi$_x$O$_y$
- Cu: 250nm
- MnSi$_x$O$_y$: 8nm
- Thermal SiO$_2$: 300nm
- n-Si

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 Mn₄N 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 (MnSiₓOᵧ) interfacial layer shows excellent barrier properties against Cu diffusion and protects Cu from corrosion by H₂O and O₂.
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