Cu-SiO$_2$ films for 3D filling in microelectronic applications by an organometallic chemical liquid deposition (OMCLD) route

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Mobile Multimedia Communication
Consumer
Multimedia
Wireless and wireline products

Computer Peripheral Group
Chips for computer peripherals (hard disk controllers, printers...)

Memory Product Group
Stand-alone memory chips
Non-volatile memory chips

Micro, Power and Analog Group
Analog and power circuits for microcontrollers
Discrete semiconductor products

Automotive Product Group
Analog and digital chips
Broadcasting integrated circuits
Microcontrollers (automotive, power trains, safety)

Semiconductor sales leader in 2009

<table>
<thead>
<tr>
<th>Rank</th>
<th>Company</th>
<th>Continent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Intel Corporation</td>
<td>USA</td>
</tr>
<tr>
<td>2</td>
<td>Samsung</td>
<td>South Korea</td>
</tr>
<tr>
<td>3</td>
<td>Toshiba</td>
<td>Japan</td>
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<tr>
<td>4</td>
<td>Texas Instruments</td>
<td>USA</td>
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<td>5</td>
<td>STMicroelectronics</td>
<td>France/Italy</td>
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<tr>
<td>6</td>
<td>Qualcomm</td>
<td>USA</td>
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<tr>
<td>7</td>
<td>Hynix</td>
<td>South Korea</td>
</tr>
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<td>8</td>
<td>Renesas Technology</td>
<td>Japan</td>
</tr>
<tr>
<td>9</td>
<td>AMD</td>
<td>USA</td>
</tr>
<tr>
<td>10</td>
<td>Sony</td>
<td>Japan</td>
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</tbody>
</table>
Introduction

- Copper is widely used in microelectronics.
- Techniques to deposit copper in microelectronics:
  - Chemical Vapor Deposition (CVD) (i.e. Atomic Layer Deposition (ALD)*)
  - Physical Vapor Deposition (PVD)
- Integrated circuit’s power
  - downsizing device
  - stacking of function 3D
- Common device
  - up to 20 different layers of metal are present in small chips.
- Numerous deposition systems → high cost

Organometallic deposit of Cu and located metallisation in solution

**Aim:** to develop a method of deposit in liquid phase from organometallic solutions in order to form either thin or thick conductive layers on planar and 3D-structured (vias or trenches) substrates.

- **Nobles:** (Pt, Au)
- **Oxidables:** (Cu, Ni, Ir…)

**First step:** deposition of a Cu-SiO$_2$ layer

*Scheme of a Cu-SiO$_2$ deposit in a crossing via*
1. Copper Nanoparticles synthesis

Organometallic precursors:

Cu^1(Mesityl)

Cu^1(amidinate)

Solvent: Toluene  T=110°C

Reducing agent: H₂

Transmission electron microscopy pictures

Organic stabilizing agent: Dodecylamine C12 (DDA)

NH₂

Copper Nanoparticles deposition: Cu(mes)

Presence of ligand

Cu(mes) + DDA $\xrightarrow{T^\circ C, P_{H_2}}$ Cu NPs

Toluene

Drop deposition $\xrightarrow{+ \text{annealing}}$

Resistivity: $10 \cdot 10^{-6} \Omega \cdot \text{cm}$

Absence of ligand

Cu(mes) $\xrightarrow{T^\circ C, P_{H_2}}$ Cu NPs

Toluene

Direct deposition $\xrightarrow{+ \text{annealing}}$

Resistivity: $50 \cdot 10^{-6} \Omega \cdot \text{cm}$

Copper Nanoparticles deposition: Cu(am)

Presence of ligand

Cu(am) + DDA $\xrightarrow{T^\circ C, P_H_2}$ Cu NPs
Toluene

Drop deposition + annealing

Absence of ligand

Cu(am) $\xrightarrow{T^\circ C, P_H_2}$ Cu NPs
Toluene

Drop deposition + annealing

Film
Nanoparticles
Large aggregates precipitation

silica substrate

100 nm
2. Cu-SiO₂ deposit

General reaction:

\[
\begin{align*}
\text{Cu(amidinate)} & + \text{EtO-Si-OEt} \\
& \xrightarrow{110 \, ^\circ\text{C, 3 bar H}_2} \text{substrate, 15 hours}
\end{align*}
\]

Annealing steps: 300°C (increments of 1°C/min) under air (1h)
300°C (increments of 1°C/min) under reducing gas H₂(10%)/Ar(90%) (1h).

Deposits are made on Si/SiO₂ substrates that has first undergone plasma O₂.

Barriere, C.; Fau, P.; Chaudret, B.; Margeat, O.; Patent: WO 2009125143
Control of $\text{H}_2\text{O}$ content

**Variation of $\text{H}_2\text{O}$ quantity (reaction time: 15 hours)**

<table>
<thead>
<tr>
<th>$\text{H}_2\text{O}$ content</th>
<th>200 ppm $\text{H}_2\text{O}$</th>
<th>500 ppm $\text{H}_2\text{O}$</th>
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<td>65% Cu(am) consumed</td>
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For a 15h reaction with control of the water at the beginning of the reaction:
- **total consumption of the copper precursor**
- **poor adherence on SiO$_2$ substrate**
Data after 2 hours of reaction
500 ppm H₂O

Approximately 5% of the copper precursor is consumed
Data after 4 hours of reaction
500 ppm H₂O

Approximately 6% of the copper precursor is consumed

SEM picture of the deposit

1H NMR after 4h
Data after 6 hours of reaction
500 ppm H₂O

Approximately 7.5% of the copper precursor is consumed

SEM picture of the deposit

$^1$H NMR after 6h
Data after 8 hours of reaction
500 ppm H₂O

Approximately 11% of the copper precursor is consumed
\[ ^1\text{H} \text{NMR of the reaction} \]

**H\textsubscript{2}O content in TEOS: 500 ppm**

\[ ^1\text{H} \text{NMR after 15h: 95\% of the precursor is consumed} \]

Between 8 and 15h, significant increase of the consumption of the copper precursor.
SEM pictures

After 15 hours of reaction

Effect of the annealing on the morphology of the deposit.

Annealing steps: 300°C (increments of 1°C/min) under air (1h)
300°C (increments of 1°C/min) under reducing gas $\text{H}_2(10%)/\text{Ar}(90%)$ (1h).
Focused Ion Beam (FIB) pictures

1. 44 μm (cs)
2. 44 μm (cs)
3. 38.27 μm (cs)
4. 695.5 nm (cs)
5. 209.8 nm
6. 175.4 nm
7. 102.7 nm
8. 162.5 nm
9. 97.2 nm
10. 78.2 nm
11. 695.5 nm (cs)
**Electroless copper bath**

**Principle:**
- Reduction of a Cu$^{2+}$ salt by reducing agent
- Autocatalytic reaction: deposit of copper *only* on metallic parts

**Redox reaction (example):**
\[ \text{Cu(EDTA)}^{2-} + 2 \text{HCHO} + 4 \text{OH}^- \rightarrow \text{Cu} + 2 \text{HCOO}^- + \text{H}_2 + 2 \text{H}_2\text{O} + \text{EDTA}^{4-} \]

**Characteristics:**
- Catalytic surface increases reaction rate: deposit on the catalyst
- Electron provided by the catalytic oxidation of a reducing agent

**Advantages:**
- Very good distribution in thickness (homogeneous layer)
- No need of a conductive substrate (≠ electrodeposition)

**Limitations:**
- Low deposit rate
- Instability of the bath
- Needs a metallic seed layer adherent to the substrate
- Seed layer has to be conductive to catalyse the reaction
Second step: deposition of a Cu layer by electroless bath.

Main problems encountered is the superfilling of the via, or the presence of a hollow part in the end of the via.
Electroless bath copper deposition

Copper electroless deposition on a glass substrate
Conclusion

• Deposition in 3D-structures can be achieved with a good « step coverage »

• Comprehension of the mechanism for the Cu-SiO₂ deposit will lead to the control of all parameters that are operating during the reaction.

• Electroless bath is under investigation. Copper deposit has been observed but the technique has to be mastered.
Aknowledgments

Yannick COPPEL (NMR), Vincent COLLIERE (SEM), Dominique GENARD (FIB)

Pôle de compétitivité CAPI, CIFRE, STMicroelectronics

L team
Thank you for your attention!

¡Gracias por su atención!

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