Chemical Vapor Deposition of Organosilicon Composite Films for Porous Low-k Dielectrics

April D. Ross and Karen K. Gleason
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA  02139

ERC TeleSeminar
12 June 2003
Motivation

Near Term: 2001-2007

<table>
<thead>
<tr>
<th>Year of Production</th>
<th>2001</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlevel metal insulator (effective dielectric constant ($\kappa$))</td>
<td>3.0–3.6</td>
<td>3.0–3.6</td>
<td>3.0–3.6</td>
<td>2.6–3.1</td>
<td>2.6–3.1</td>
<td>2.6–3.1</td>
<td>2.3–2.7</td>
</tr>
<tr>
<td>Interlevel metal insulator (minimum expected bulk dielectric constant ($\kappa$))</td>
<td>&lt;2.7</td>
<td>&lt;2.7</td>
<td>&lt;2.7</td>
<td>&lt;2.4</td>
<td>&lt;2.4</td>
<td>&lt;2.4</td>
<td>&lt;2.1</td>
</tr>
</tbody>
</table>


- **Manufacturable solutions exist**
- **Manufacturable solutions are known**
- **Manufacturable solutions are NOT known**
**Motivation**

- The widely used ILD material for 0.13µm and older technologies are PECVD SiO₂ and SiOF

<table>
<thead>
<tr>
<th>Materials/Technology</th>
<th>0.13µm or 0.09µm</th>
<th>0.07µm</th>
<th>0.05µm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organic</strong></td>
<td>SiLκ™, Flare™, Paralyne-F(N), αFC, PAE, etc.</td>
<td>Porous SiLκ™, Porous Flare™, OXD, etc</td>
<td>Partial Air Gap, Complete Air Gap</td>
</tr>
<tr>
<td><strong>Organosilicates</strong></td>
<td>Carbon Doped Oxide, SOG, etc.</td>
<td>Porous CVD CDO, Porous SOD, CDO, etc.</td>
<td>Partial Air Gap, Complete Air Gap</td>
</tr>
<tr>
<td><strong>Range of κ</strong></td>
<td>2.8 to 3.0</td>
<td>1.9 to 2.6</td>
<td>1.0 T to 1.5</td>
</tr>
</tbody>
</table>

Dr. Eb Andideh, Intel Corporation  
(2003, MIT hosted ERC teleconference)
Goals

- Create a Porous, Low-\( \kappa \) Film by CVD
  - Rigid Organosilicon Matrix
  - Thermally Labile Porogen
  - Deposition by Pulsed Plasma Enhanced CVD

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fully dense ( \kappa )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>4.0</td>
</tr>
<tr>
<td>Si:O:C:H (Organosilicate Glass - OSG)</td>
<td>2.7 - 3.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% Porosity</th>
<th>( \kappa )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.7</td>
</tr>
<tr>
<td>20</td>
<td>2.3</td>
</tr>
<tr>
<td>50</td>
<td>1.75</td>
</tr>
<tr>
<td>90</td>
<td>1.15</td>
</tr>
</tbody>
</table>
A. Manufacturing Metrics (Effect on Performance, Yield, and Cost)

Replacing the silicon dioxide (SiO$_2$) interlevel dielectric layers in microprocessors with films of lower dielectric constant, $\kappa$, increases the speed, reduces the power consumption, and decreases the crosstalk between adjacent metal lines. The lowest dielectric constant leads to the fewest levels of interconnect, resulting in an economic and environmental “win-win”. Spin-on process for low $\kappa$ dielectrics such as SIlk (Dow) have the potential for high waste and solvent-related ESH concerns. Plasma CVD process are another possible candidate for the manufacture of low $\kappa$ dielectrics.

B. ESH Metrics

<table>
<thead>
<tr>
<th>Goals / Possibilities</th>
<th>Energy</th>
<th>Water</th>
<th>Chemicals</th>
<th>PFCs</th>
<th>VOCs</th>
<th>HAPs</th>
<th>Other Hazardous Wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Filament CVD for $\kappa &lt; 2.2$</td>
<td>HFCVD uses 5-60% less power than plasma CVD</td>
<td>NA</td>
<td>2.2% utilization for HFCVD $&gt;\rightarrow$ plasma CVD or spin on</td>
<td>TBD ${\text{Reduction compared to plasma CVD (fewer chamber cleans may be required)}}$</td>
<td>Great reduction vs spin-on $\sim$ same as plasma CVD</td>
<td>Some reduction in acid vapors</td>
<td>NA</td>
</tr>
</tbody>
</table>
Pulsed Plasma Enhanced CVD

Typical Operating Parameters

- pressure: 300 mTorr
- peak power: 100-300 W
- duty cycle: 10-25%
- substrate temp: cooling water
- precursor flow rate: 0 - 20 sccm
Composite Materials

Co-deposition of Porogen and Matrix Materials

Polystyrene Beads as Porogen–Matrix Deposition Independent

Decouple Processing Windows
Porogen: Polystyrene Beads

- Controlled Pore Size & Distribution
- Distributed Over Large Area
- Bead Diameters: 15nm (std = 3), 96nm (std = 9)
- No Covalent Bonding
- Decompose under 400°C
- Health=0, Flammability=1, Reactivity=0
- 1% Styrene in Air: Health=1, Flammability=0, Reactivity=1

\[
\left(\begin{array}{c}
\text{CH} \\
\text{CH}_2
\end{array}\right)_n
\]
Proof of Concept

- Non-collapsing Structure
- Variable Porosity
- Manufacturable Process

Dielectric constant 1.4
Refractive index 1.067

(Qingguo Wu)
Alternating Bead-Matrix Deposition

- Non-collapsing Structure
- Variable Porosity
- Manufacturable Process

FTIR

Polystyrene

Polystyrene + OSG

Polystyrene + OSG Annealed

Wavenumber (cm\(^{-1}\))

Phenyl Stretch 700 cm\(^{-1}\)

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
Sequential Vacuum Deposition

- ✔ Non-collapsing Structure
- ✔ Variable Porosity
- ❌ Manufacturable Process
Sequential Vacuum Deposition

Ultrasonic Atomizer

• Uses low ultrasonic vibrational energy for atomization
• Dispenses microliters/min
• Continuous or intermittent spray
• Pressureless atomization
• Can handle up to 30% solids
Sequential Vacuum Deposition

- Non-collapsing Structure
- Variable Porosity
- Manufacturable Process
Processing Conditions

- Gas flowrate (20-100 sccm)
- Liquid flowrate (100-5000 µL/min)
- Chamber pressure (3 – 5 torr)
- Temperature (20 – 30°C)
- Bead Concentration (0.0005 – 0.05% solids)
Bead Distribution

- Effect of Gas Flowrate

Low Gas Flowrate

High Gas Flowrate
Bead Distribution

Optical Microscopy
Magnification: 500x
~4% beads by area

SEM
Conclusions

- Polystyrene beads viable porogen
  - Spherical voids created in CVD films
  - Dielectric constant $= 1.4$

- Sequential Vacuum Deposition
  - Ultrasonic Atomization
  - Compatible with current CVD process
  - Controlled Degree of Porosity
Acknowledgments

- NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing
- MIT MRSEC Shared Facilities supported by the NSF
- Semiconductor Research Corporation/TI
- Gleason Research Group