Structure-Property Relations in ALD-Grown HfO₂ Gate Dielectrics: Effects of Precursor Chemistry

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Outline

• Need for high-k dielectrics

• Atomic Layer Deposition

• Choice of Precursors

• Electrical Characteristics of HfO$_2$ films

• Si Surface Passivation prior to ALD

• Summary and Future Work
High-k Dielectrics

Gate leakage current increases exponentially with decrease in $t_{ox}$

$$C_{ox} = \frac{\kappa \varepsilon_0 A}{t_{ox}}$$

$$t_{high-\kappa} = \left( \frac{\kappa_{high-\kappa}}{\kappa_{SiO_2}} \right) \cdot t_{SiO_2}$$

High-k Candidates

<table>
<thead>
<tr>
<th>Dielectric</th>
<th>$\kappa$</th>
<th>Bandgap (eV)</th>
<th>$\Delta E_c$ to Si</th>
<th>$\Delta E_v$ to Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>3.9</td>
<td>9</td>
<td>3.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>7</td>
<td>5.3</td>
<td>2.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9</td>
<td>8.8</td>
<td>2.8</td>
<td>4.9</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>25</td>
<td>5.8</td>
<td>1.4</td>
<td>3.3</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>25</td>
<td>6.0</td>
<td>1.5</td>
<td>3.4</td>
</tr>
</tbody>
</table>

ZrO$_2$ and HfO$_2$
- Thermodynamically stable on Si
- Acceptable band offsets to Si
- High dielectric constant
Atomic Layer Deposition

Schematic of the ALD process

- Self-limiting growth
- Highly conformal, low defect thin films
- Very good step coverage
- Low temperature deposition
- Excellent control over film thickness
- Uniform thickness over large areas
- Good control of stoichiometry
- Abrupt interface to the substrate

(courtesy Hyoungsub Kim)
Choice of Precursors

**Chlorides**
1. HCl is a by-prod of the reaction and is very corrosive
2. Chlorine contamination of the films
3. Solid source: gas line clogging and particle contamination

**Alkylamides**
1. No harmful by-products
2. No chlorine contamination
3. Liquid or low melting solid at RT
4. High growth rates

\[
\text{HfCl}_4
\]

\[
(C_2H_5)_2N - \text{Hf} - N(C_2H_5)_2
\]

Tetrakis(diethylamino)Hafnium (TDEAH)
Stanford ALD Chamber

Remote plasma system

TDEAH
TDEAZ
IPTEMT

MFC
MFC
MFC

N₂ Ar O₂ He

Throttle Valve

Loadlock

Turbo Pump

Rotary Pump

Scrubber

Turbo Pump
## ALD Process Parameters

<table>
<thead>
<tr>
<th></th>
<th>HfCl₄</th>
<th>TDEAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temp</td>
<td>300 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>Bubbler temp</td>
<td>150 °C</td>
<td>65 °C</td>
</tr>
<tr>
<td>Pulsing</td>
<td>1-60-1-60</td>
<td>1-50-1-50</td>
</tr>
<tr>
<td>Dep rate</td>
<td>0.5Å/cycle</td>
<td>0.75Å/cycle</td>
</tr>
<tr>
<td>Chamber wall</td>
<td>R.T</td>
<td>75 °C</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>H₂O</td>
<td>H₂O</td>
</tr>
<tr>
<td>N₂(carrier gas)</td>
<td>20 sccm</td>
<td>2.5 sccm</td>
</tr>
<tr>
<td>Process Pr</td>
<td>0.5 Torr</td>
<td>0.5 Torr</td>
</tr>
</tbody>
</table>
Capacitor Structure

- Metal electrodes deposited by e-beam evaporation
- FGA performed at 400°C to reduce $D_{it}$
C-V Hysteresis

Chloride

$t_{\text{HfO2}} = 45\,\text{Å}, \text{I.L} = 15\,\text{Å}$
Cap derived EOT = 23.1Å
Hysteresis ~ 20 mV

Alkylamide

$t_{\text{HfO2}} = 50\,\text{Å}, \text{I.L} = 15\,\text{Å}$
Cap derived EOT = 23.2Å
Hysteresis ~ 5 mV
Comparable leakage currents were observed on MOSCAP structures on HfO₂ grown using HfCl₄ and TDEAH.

EOT = 23Å
x-section TEM image shows a uniform amorphous HfO$_2$ film deposited on chemical oxide.

HfO$_2$ thickness = 45Å
I.L (chem ox) = 15Å
Effect of Precursor on \( V_{FB} \)

\[ V_{FB} \text{ (alkylamide)} = 0.09V \]
\[ V_{FB} \text{ (chloride)} = 0.49V \]

\[ Q_F \text{ (alkylamide)} = +2.4E12 \]
\[ Q_F \text{ (chloride)} = -1.29E12 \]

( Yee-Chia Yeo, et. al. IEEE EDL, 2002 )

\[ \phi_{Pt} = 5.25 \text{ eV on HfO}_2 \]

“Ideal” \( V_{FB} = 0.35V \)
Carbon and nitrogen impurities were below the detection levels of the XPS. In comparison, 1-2 atomic % Cl was typically detected from as-grown HfCl₄-derived films.
Templates for ALD

Passivation

Ex-situ
- Wet chem oxide
- RTO, RTON

In-situ
- UV ozone oxide
- Remote plasma oxide
Electrical Characteristics

C-V Characteristics

Leakage Current

50Å HfO₂ was deposited on the Chem Ox (15Å), RTO (20Å) and RTON (20Å) samples.

The electrical results indicate an excellent quality HfO₂ with very low leakage current.
Summary and Future Work

Summary
• We have successfully grown high quality HfO$_2$ thin films on silicon substrates using the ALD process.

• The electrical characteristics of the HfO$_2$ films grown using TDEAH are far superior to those obtained using the chlorides.

• The carbon and nitrogen impurity levels in the films were below the detection limits of the XPS.

• The low substrate temperature for the alkylamide process will facilitate area selective ALD on patterned substrates.

Future Work
• Study the crystallization kinetics of ALD HfO$_2$ grown using TDEAH.

• Optimize the ALD TaN process for in-situ gate electrode deposition.