Lecture 12
Thermal Oxidation, part 3

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Reading:
Chapter 4, Fabrication Engineering at the Micro- and Nanoscale, 4th edition, Campbell

Deal-Grove Model

Rate equation:
\[
\frac{dt_{ox}}{dt} = \frac{B}{2t_{ox} + A}
\]

Gives:
\[
t_{ox}^2 + At_{ox} = B(t + \tau)
\]

\[
A = 2D\left(\frac{1}{r} + \frac{1}{k_f}\right)
\]

\[
B = \frac{2D}{N_i T_0}
\]

\[
\tau = \frac{t_{ox}^2 + At_{ox}}{B}
\]

Deal-Grove Model Example

Initial Oxide Thickness (t₀)

Deal-Grove Model Regimes

Rate equation:
\[
\frac{dt_{ox}}{dt} = \frac{B}{2t_{ox} + A}
\]

Linear Regime:
For \(t_{ox} << A/2\), \(\frac{dt_{ox}}{dt} = \frac{B}{A}\) and \(t_{ox} = \frac{B}{A}(t + \tau)\)

Parabolic Regime:
For \(t_{ox} >> A/2\), \(\frac{dt_{ox}}{dt} = \frac{B}{2t_{ox}}\) and \(t_{ox}^2 = \frac{B}{A}(t + \tau)\)

Model vs. Data

- When comparing model versus data, we find excellent agreement for wet oxidation
- For dry O₂ oxidation, the data shows a faster growth rate for the first 20 – 30 nm
  - The Deal-Grove model is not good at predicting oxide growth for thicknesses less than 30 nm
  - For thicker dry oxidation, we can use \(\tau\) (or \(t_{ox}\)) to account for the faster initial growth rate

Deal-Grove Model

\[
\begin{align*}
C_i & \quad \text{gas} \\
C_g & \quad \text{SiO}_2 \\
C_s & \quad \text{Si} \\
\end{align*}
\]

Step 1: oxygen diffuses from the bulk (\(C_g\)) to the wafer surface (\(C_s\))

Step 2: oxygen diffuses from the wafer surface (\(C_s\)) to the silicon interface (\(C_i\))

Step 3: oxygen reacts with silicon at the interface
**Dry Oxidation Initial Growth Rate**

\[ \tau = \frac{t_0^2 + At_0}{B} \]

\[ t_0 = 23 \text{ nm} \]

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**Deal-Grove Parameters**

**Table 4.1: Oxidation Coefficients for Silicon**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dry A (μm)</th>
<th>Dry B (μm²/h)</th>
<th>Dry r (h)</th>
<th>Wet A (μm)</th>
<th>Wet B (μm²/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.370</td>
<td>0.0011</td>
<td>9</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>920</td>
<td>0.235</td>
<td>0.0049</td>
<td>1.4</td>
<td>0.50</td>
<td>0.283</td>
</tr>
<tr>
<td>1000</td>
<td>0.165</td>
<td>0.0117</td>
<td>0.37</td>
<td>0.226</td>
<td>0.287</td>
</tr>
<tr>
<td>1100</td>
<td>0.090</td>
<td>0.027</td>
<td>0.06</td>
<td>0.11</td>
<td>0.510</td>
</tr>
<tr>
<td>1200</td>
<td>0.040</td>
<td>0.045</td>
<td>0.027</td>
<td>0.05</td>
<td>0.720</td>
</tr>
</tbody>
</table>

The \( r \) parameter is used to compensate for the rapid growth regime for thick oxides (after Deal and Grove), precision of constants is about 12%.


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**Temperature Dependence**

\[ A = 2D \left( \frac{1}{R} + \frac{1}{k_s} \right) \quad \text{(typically} \quad h \gg k_s) \]

\[ B = \frac{2DH_p}{N_1} \]

Temperature behavior determined by \( D \)

\[ \frac{B}{A} \approx \frac{k_sH_p}{N_1} \]

Temperature behavior determined by \( k_s \)

(Note: \( H \) is much higher for \( H_2O \) than for \( O_2 \))

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**Pressure Dependence**

- The model says \( A \) is independent of pressure, and \( B \) and \( B/A \) are proportional to partial pressure of oxidant
  - The is true experimentally for wet oxidation
  - For Dry \( O_2 \), we find that
    \[ \frac{B}{A} \propto P_{O_2} \]
    \[ 0.5 < n < 1 \]

Why? If molecular oxygen diffuses and reacts, we would expect \( n = 0.5 \). If both \( O \) and \( O_2 \) are involved, \( 0.5 < n < 1 \).

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**Crystal Orientation**

- The number of silicon atoms per unit area on the wafer surface depends on the crystal orientation, but what matters is the number of Si-Si bonds per unit area
  - This affects \( k_s \)
  - (111) wafers have highest surface bond density

- The consequences:
  - \( B \) is independent of \( k_s \) and thus crystal orientation
  - For (100) wafers, \( B/A \) is 1.68X smaller (\( A \) is 1.68X higher) than for (111) wafers
Other Factors

- **Substrate Doping**
  - Higher doping levels cause an increase in B/A (but not B)
  - This is probably due to an increase in crystal defects that allows for faster volume expansion
- **Adding HCl to the gas**
  - Recall that HCl is added (1-3%) to remove metal ions
  - This addition also causes an increase in oxidation rate (probably because HCl reacts with O₂ to form water)

Oxide Growth Geometry

\[ \rho_{Si} = 2.33 \text{ g/cm}^3 \quad \rho_{SiO_2} = 2.27 \text{ g/cm}^3 \]
\[ AW_{Si} = 28.09 \text{ g/mol} \quad MW_{SiO_2} = 60.09 \text{ g/mol} \]
\[ \text{Molar Density}_{Si} = 0.0830 \text{ mol/cm}^3 \]
\[ \text{Molar Density}_{SiO_2} = 0.0378 \text{ mol/cm}^3 \]
\[ \frac{\text{Molar Density}_{SiO_2}}{\text{Molar Density}_{Si}} = 0.455 = \frac{\text{Thickness of Si consumed}}{\text{Thickness of SiO}_2 \text{ grown}} \]

Lecture 12: What have we learned?

- Be able to make calculations using the Deal-Grove model
- What are the linear and parabolic rate constants?
- Understand how to use \( \tau \) when an initial oxide film is on the wafer
- Understand why \( \tau \) is used for dry oxidation calculations for film thickness > 30 nm
- How does pressure affect oxidation rates?
- How does crystal orientation affect oxidation rates?