THERMAL OXIDATION - Chapter 6

Basic Concepts

• SiO₂ and the Si/SiO₂ interface are the principal reasons for silicon’s dominance in the IC industry.

SiO₂:
• Easily selectively etched using lithography.
• Masks most common impurities (B, P, As, Sb).
• Excellent insulator ($\rho > 10^{16} \ \Omega\text{cm}, \ E_g > 9 \text{ eV}$).
• High breakdown field ($10^7 \ \text{Vcm}^{-1}$)
• Excellent junction passivation.
• Stable bulk electrical properties.
• Stable and reproducible interface with Si.

• No other known semiconductor/insulator combination has properties that approach the Si/SiO₂ interface.
• Oxidation involves a volume expansion ($\approx 2.2X$).
• Especially in 2D and 3D structures, stress effects play a dominant role.
SiO\textsubscript{2} is amorphous even though it grows on a crystalline substrate.

Four charges are associated with insulators and insulator/ semiconductor interfaces.

- \( Q_f \) - fixed oxide charge
- \( Q_{it} \) - interface trapped charge
- \( Q_m \) - mobile oxide charge
- \( Q_{ot} \) - oxide trapped charge
• Oxidation systems are conceptually very simple.
• In practice today, vertical furnaces, RTO systems and fast ramp furnaces all find use.

Thermal oxidation can potentially be used in many places in chip fabrication. In practice, deposited SiO₂ layers are increasingly being used (lower Dt).
C-V Measurements

- Powerful technique for characterizing semiconductor/insulator structures.

a) Accumulation

b) Depletion

c) Inversion

- DC bias + small AC high frequency signal applied.
- Electric field lines pass through the “perfect” insulator and Si/SiO$_2$ interface, into the substrate where they control charge carriers.
- Accumulation, depletion and inversion result.
- HF curve - inversion layer carriers cannot be generated fast enough to follow the AC signal so $C_{inv}$ is $C_{ox} + C_D$.
- LF curve - inversion layer carriers can be created and recombine at AC signal frequency so $C_{inv}$ is just $C_{ox}$.
- Deep depletion - “DC” voltage is applied fast enough that inversion layer carriers cannot follow it, so $C_D$ must expand to balance the charge on the gate.
- C-V measurements can be used to extract quantitative values for:
  - $t_{ox}$ - oxide thickness
  - $N_A$ - the substrate doping profile
  - $Q_f$, $Q_{it}$, $Q_m$, $Q_{ot}$ - oxide, interface charges
SiO₂ Growth Kinetics Models

A. Deal Grove Model

- The basic model for oxidation was developed in 1965 by Deal and Grove.

\[
\begin{align*}
\text{Si} + \text{O}_2 & \rightarrow \text{SiO}_2 \quad (2) \\
\text{Si} + 2\text{H}_2\text{O} & \rightarrow \text{SiO}_2 + 2\text{H}_2 \quad (3)
\end{align*}
\]

\[
\begin{align*}
F_1 &= h_G(C_G - C_S) \\
F_2 &= D \frac{\partial N}{\partial x} = D \left( \frac{C_O - C_I}{x_O} \right) \\
F_3 &= k_S C_I
\end{align*}
\]
• Under steady state conditions, \( F_1 = F_2 = F_3 \) so

\[
C_1 = \frac{C^*}{1 + \frac{k_s}{h} + \frac{k_s x_O}{D}} \approx \frac{C^*}{1 + \frac{k_s x_O}{D}} \quad (7)
\]

\[
C_O = \frac{C^* \left(1 + \frac{k_s x_O}{D}\right)}{1 + \frac{k_s}{h} + \frac{k_s x_O}{D}} \approx C^* \quad (8)
\]

• Note that the simplifications are made by neglecting \( F_1 \) which is a very good approximation.

• Combining (6) and (7), we have

\[
\frac{dx}{dt} = \frac{F}{N_1} = \frac{k_s C^*}{N_1 \left(1 + \frac{k_s}{h} + \frac{k_s x_O}{D}\right)} \quad (9)
\]

• Integrating this equation (see text), results in the linear parabolic model.
\[ \frac{x_0^2 - x_i^2}{B} + \frac{x_0 - x_i}{B/A} = t \]  \hspace{1cm} (10)

where \( B = \frac{2DC^*}{N_1} \) \hspace{1cm} (parabolic rate constant) \hspace{1cm} (11)

and \[ \frac{B}{A} = \frac{C^*}{N_1 \left( \frac{1}{k_S} + \frac{1}{h} \right)} \equiv \frac{C^* k_S}{N_1} \] \hspace{1cm} (linear rate constant) \hspace{1cm} (12)

- (10) can also be written with oxide thickness as a function of time.

\[ x_O = \frac{A}{2} \left\{ \sqrt{1 + \frac{t + \tau}{A^2 / 4B}} - 1 \right\} \]  \hspace{1cm} (13)

where \[ \tau = \frac{x_i^2 + Ax_i}{B} \]  \hspace{1cm} (14)
- The rate constants $B$ and $B/A$ have physical meaning (oxidant diffusion and interface reaction rate respectively).

$$B = C_1 \exp\left(-\frac{E_1}{kT}\right) \quad (15)$$

$$\frac{B}{A} = C_2 \exp\left(-\frac{E_2}{kT}\right) \quad (16)$$

- Numbers are for (111) silicon, for (100) divide $C_2$ by 1.68.

- Plots of $B$, $B/A$ using the values in the above Table.
Calculated (100) silicon dry O$_2$ oxidation rates using Deal Grove.

Calculated (100) silicon H$_2$O oxidation rates using Deal Grove.

Example: Problem 6.13 in the text: a) 3 hrs in O$_2$ @ 1100 °C = 0.21 μm + b) 2 hrs in H$_2$O @ 900 °C = 0.4 μm + c) 2 hrs in O$_2$ @ 1200 °C = 0.5 μm total oxide thickness.
B. Thin Oxide Growth Kinetics

- A major problem with the Deal Grove model was recognized when it was first proposed - it does not correctly model thin O₂ growth kinetics.
- Experimentally O₂ oxides grow much faster for ≈ 20 nm than Deal Grove predicts.
- MANY models have been suggested in the literature.

1. Reisman et. al. Model

\[ x_O = a(t + t_i)^b \quad \text{or} \quad x_O = a \left( t + \left( \frac{x_i}{a} \right)^{\frac{1}{b}} \right)^b \]  

(17)

- Power law “fits the data” for all oxide thicknesses.
- a and b are experimentally extracted parameters.
- Physically - interface reaction controlled, volume expansion and viscous flow of SiO₂ control growth.

2. Han and Helms Model

\[ \frac{dx_O}{dt} = \frac{B_1}{2x_O + A_1} + \frac{B_2}{2x_O + A_2} \]  

(18)

- Second parallel reaction added - “fits the data” ” for all oxide thicknesses.
- Three parameters (one of the A values is 0).
- Second process may be outdiffusion of O₉ and reaction at the gas/SiO₂ interface.
3. Massoud et. al. Model

\[
\frac{dx_O}{dt} = \frac{B}{2x_O + A} + C \exp\left(-\frac{x_O}{L}\right)
\]  

(19)

- Second term added to Deal Grove model - higher \(\frac{dx}{dt}\) during initial growth.
- \(L \approx 7\) nm, second term disappears for thicker oxides.
- Easy to implement along with the DG model, \(\mathcal{Y}\) used in process simulators.
- Data agrees with the Reisman, Han and Massoud models. (800°C dry \(O_2\) model comparison below.)
C. 2D SiO\textsubscript{2} Growth Kinetics

- These effects were investigated in detail experimentally by Kao et. al. about 15 years ago.
- Typical experimental results below.

(Kao et.al)
Several physical mechanisms seem to be important:

- Crystal orientation
- 2D oxidant diffusion
- Stress due to volume expansion

To model the stress effects, Kao et al. suggested modifying the Deal Grove parameters.

\[ k_\text{S (stress)} = k_\text{S} \exp \left( -\frac{\sigma_n V_R}{kT} \right) \exp \left( -\frac{\sigma_t V_T}{kT} \right) \] (20)

\[ D(\text{stress}) = D \exp \left( -\frac{(P)(V_D)}{kT} \right) \] (21)

\[ C^*(\text{stress}) = C^* \exp \left( -\frac{(P)(V_S)}{kT} \right) \] (22)

where \( \sigma_n \) and \( \sigma_t \) are the normal and tangential stresses at the interface. 

\( V_R, V_T \) and \( V_S \) are reaction volumes and are fitting parameters.
In addition, the flow properties of the SiO$_2$ need to be described by a stress dependent viscosity

$$\eta(\text{stress}) = \eta(T) \frac{\sigma_s V_C / 2kT}{\sinh(\sigma_s V_C / 2kT)}$$

Where $\sigma_s$ is the shear stress in the oxide and $V_C$ is again a fitting parameter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_R$</td>
<td>0.0125 nm$^3$</td>
</tr>
<tr>
<td>$V_D$</td>
<td>0.0065 nm$^3$</td>
</tr>
<tr>
<td>$V_S$, $V_T$</td>
<td>0</td>
</tr>
</tbody>
</table>
| $V_C$     | 0.3 nm$^3$ @ 850$^\circ$C  
0.72 nm$^3$ @ 1050$^\circ$C |
| $\eta(T)$ - SiO$_2$ | $3.13 \times 10^{10} \exp(2.19 \text{ eV/kT})$ poise |
| $\eta(T)$ - Si$_3$N$_4$ | $4.77 \times 10^{10} \exp(1.12 \text{ eV/kT})$ poise |

• These models have been implemented in modern process simulators and allow them to predict shapes and stress levels for VLSI structures (above right).
• ATHENA simulation: Left - no stress dependent parameters, Right - including stress dependence.
D. Point Defect Based Models

• The oxidation models we have considered to this point are macroscopic models (diffusion coefficients, chemical reactions etc.).

• There is also an atomistic picture of oxidation that has emerged in recent years.

• Most of these ideas are driven by the volume expansion occurring during oxidation and the need for “free volume”.

• In Chapter 3 we described internal oxidation in the following way:

\[ (1 + 2\gamma)\text{Si}_{\text{Si}} + 2\text{O}_1 + 2\beta\text{V} \leftrightarrow \text{SiO}_2 + 2\gamma\text{I} + \text{stress} \]  

(24)

• Surface oxidation can be thought of in the same way.
• The connection between oxidation and other processes can then be modeled as shown below.

Example - ATHENA simulation of OED.

• Oxidation injects interstitials to create “free volume” for the oxidation process.
• Oxidation can also consume vacancies for the same reason.
• These processes increase I concentrations and decrease V concentrations in nearby silicon regions.
• Any process (diffusion etc) which occurs via I and V will be affected.
E. Complete Process Simulation of Oxidation

• Many of these models (and others in Chapter 6), have been implemented in programs like SUPREM.

• Simulation of an advanced isolation structure (the SWAMI process originally developed by Hewlett-Packard), using SSUPREM IV. The structure prior to oxidation is on the top left. A 450 min H$_2$O oxidation at 1000 °C is then performed which results in the structure on the top right. An experimental structure fabricated with a similar process flow is shown on the bottom right. The stress levels in the growing SiO$_2$ are shown at the end of the oxidation on the bottom left.
Summary of Key Ideas

- Thermal oxidation has been a key element of silicon technology since its inception.

- Thermally, chemically, mechanically and electrically stable SiO$_2$ layers on silicon distinguish silicon from other possible semiconductors.

- The basic growth kinetics of SiO$_2$ on silicon are controlled by oxidant diffusion and Si/SiO$_2$ interface chemical reaction.

- This simple Deal-Grove model has been extended to include 2D effects, high dopant concentrations, mixed ambients and thin oxides.

- Oxidation can also have long range effects on dopant diffusion (OED or ORD) which are modeled through point defect interactions.

- Process simulators today include all these physical effects (and more) and are quite powerful in predicting oxidation geometry and properties.