Thermal Oxidation of Si

- General Properties of SiO$_2$
- Applications of thermal SiO$_2$
- Deal-Grove Model of Oxidation

Thermal SiO$_2$ is **amorphous**.
Weight Density $= 2.20$ gm/cm$^3$
Molecular Density $= 2.3E22$ molecules/cm$^3$

Crystalline SiO$_2$ [Quartz] $= 2.65$ gm/cm$^3$
Thermal SiO$_2$ Properties

(1) Excellent Electrical Insulator
   Resistivity $> 1 \times 10^{20}$ ohm-cm   Energy Gap $\sim 9$ eV

(2) High Breakdown Electric Field
   $> 10$ MV/cm

(3) Stable and Reproducible Si/SiO$_2$ Interface

(4) Conformal oxide growth on exposed Si surface
(5) SiO$_2$ is a good diffusion mask for common dopants

\[ D_{\text{SiO}_2} \ll D_{\text{Si}} \]

e.g. B, P, As, Sb.

*exceptions are Ga (a p-type dopant) and some metals, e.g. Cu, Au

(6) Very good etching selectivity between Si and SiO$_2$. 
Steam generation for wet oxidation
Volume change due to thermal oxidation

**Molecular Density of SiO$_2$ = 2.3E22 molecules / cm$^3$**

**Atomic Density of Si = 5.0E22 atoms / cm$^3$**

$\therefore$ Volume of SiO$_2$ = 2.16 $\times$ Volume of Si consumed

**Mechanical stress will be generated with confined oxidation**
One-dimensional planar oxide growth

Suggested exercise:

1 \( \mu \text{m} \) diameter Si sphere

\[ \xrightarrow{\text{completely oxidized}} \]

1.3 \( \mu \text{m} \) diameter SiO\(_2\) sphere
Thickness of Si consumed (planar oxidation)

\[ X_{si} = X_{ox} \cdot \frac{N_{ox}}{N_{si}} \]

molecular density of SiO\(_2\)

atomic density of Si

\[ = X_{ox} \cdot \frac{2.3 \times 10^{22} \text{ molecules} \ / \ cm^3}{5 \times 10^{22} \text{ atoms} \ / \ cm^3} = 0.46 \cdot X_{ox} \]
Kinetics of SiO₂ Growth

- Oxidant Flow (O₂ or H₂O)
- Gas Diffusion
- Solid-state Diffusion
- SiO₂ Formation
- Si-Substrate
Deal-Grove Model

\[ C_G \]  
\[ C_S \]  
\[ C_o \]  
\[ C_i \]  
\[ X_{0x} \]

- Stagnant layer
- Note: \( C_s \neq C_o \)

**Stages:**
- \( F_1 \): Gas transport flux
- \( F_2 \): Diffusion flux through \( \text{SiO}_2 \)
- \( F_3 \): Reaction flux at interface
\[ F_1 = h_G (C_G - C_S) \]

Mass transfer coefficient \([\text{cm/sec}].\)

\[ F_2 = -D \frac{\partial C}{\partial x} \]

“Fick’s Law of Solid-state Diffusion”

\[ \equiv D \cdot \left( \frac{C_o - C_i}{X_{ox}} \right) \]

Diffusivity \([\text{cm}^2/\text{sec}]\)

\[ F_3 = k_s \cdot C_i \]

Surface reaction rate constant \([\text{cm/sec}]\)

**Comment:** The derivation used in Jaeger textbook assumes \(F1\) is large (not a rate-limiting factor for growth rate). Hence, the algebra looks simpler. However, the lecture notes derivation includes gas transport effect and can be directly applied to the CVD growth rate model which will be discussed in later weeks.
How to solve the oxidant concentrations?

• $C_S$ and $C_o$ are related by Henry’s Law

• $C_G$ is a controlled process variable (proportional to the input oxidant gas pressure)

Only $C_o$ and $C_i$ are the 2 unknown variables which can be solved from the steady-state condition:

$$F_1 = F_2 = F_3 \quad (2 \text{ equations})$$
Derivation of Oxidation Growth Rate

\[ C_o = H \cdot P_s \]

Henry's Law

partial pressure of oxidant at surface [in gaseous form].

\[ = H \cdot (kT \cdot C_s) \]

from ideal gas law PV = NkT

\[ \therefore C_s = \frac{C_o}{HkT} \]
Define \( C_A \equiv (HkT \cdot C_G) \)

F\(_1\) can be re-written as:

\[
F_1 = \frac{h_G}{HkT} (C_A - C_o)
\]

\[\equiv h\]

Using the steady-state condition:

Conservation of mass flux: \( F_1 = F_2 = F_3 \)

2 equations to solve the 2 unknowns: \( C_o \) & \( C_i \)

This is a control process variable. For a given oxidant pressure, \( C_A \) is known.
Derivation of Oxidation Growth Rate – cont.

Therefore

\[ C_i = \frac{C_A}{1 + \frac{k_s}{h} + \frac{k_s X_{ox}}{D}} \]

\[ C_o = C_i \cdot \left(1 + \frac{k_s X_{ox}}{D}\right) \]

\[ F = F_1 = F_2 = F_3 = k_s \cdot C_i = \frac{k_s C_A}{1 + \frac{k_s}{h} + \frac{k_s X_{ox}}{D}} \]
Now, convert Flux $F$ into Oxide Thickness Growth Rate

\[ F = N_1 \cdot \left( \frac{dX_{ox}}{dt} \right) \]

Oxidant molecules/unit volume required to form a unit volume of $\text{SiO}_2$.

Therefore, we have the oxide growth rate eqn:

\[ N_1 \cdot \frac{dX_{ox}}{dt} = \left[ \frac{k_s C_A}{1 + \frac{k_s D}{h} + \frac{k_s X_{ox}}{D}} \right] \]
Initial Condition: At $t = 0$, $X_{ox} = X_i$

Solution

$X_{ox}^2 + AX_{ox} = B(t + \tau)$

$$A \equiv 2D\left(\frac{1}{k_s} + \frac{1}{h}\right)$$

Note: $h \gg k_s$ for typical oxidation condition

$$B \equiv \frac{2DC}{N_1}A$$

$$\tau = \frac{X_i^2 + AX_i}{B}$$
Note: “dry” and “wet” oxidation have different $N_1$ factors

$N_1 = 2.3 \times 10^{22} / cm^3$ for $O_2$ as oxidant

$Si + O_2 \rightarrow SiO_2$

$N_1 = 4.6 \times 10^{22} / cm^3$ for $H_2O$ as oxidant

$Si + 2H_2O \rightarrow SiO_2 + 2H_2 \uparrow$
Summary of Deal-Grove Model

\[
X_{ox}^2 + AX_{ox} = B(t + \tau)
\]

\[
2X_{ox} \frac{dx_{ox}}{dt} + A \frac{dx_{ox}}{dt} = B
\]

\[
\frac{dx_{ox}}{dt} = \frac{B}{A + 2X_{ox}}
\]

Oxide Growth Rate slows down with increase of oxide thickness
\[ X_{ox} = \frac{A}{2} \left\{ \sqrt{1 + \left( \frac{t + \tau}{A^2/4B} \right)} - 1 \right\} \]

(Case 1) Large \( t \) [large \( X_{ox} \)]

\[ X_{ox} \rightarrow \sqrt{B}t \]

(Case 2) Small \( t \) [Small \( X_{ox} \)]

\[ X_{ox} \rightarrow \frac{B}{A}t \]
### Deal-Grove Model Parameters

#### Equation (1)

\[
B \equiv \frac{2 \, D \, C^A}{N_1} \propto D
\]

#### Equation (2)

\[
\frac{B}{A} = \frac{1}{\left( \frac{1}{h} + \frac{1}{k_s} \right) N_1} \frac{C^A}{N_1}
\]

- \(D \propto e^{-\frac{Q}{kT}}\)
- \(Q = \text{activation energy for diffusion}\)

- \(k_s \propto e^{-\frac{Q'}{kT}}\)
- \(Q' = \text{activation energy for interface reaction}\)

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For thermal oxidation of Si, \(h\) is typically \(>> k_s\).

\(B/A\) is \(\propto k_s\) (i.e. \(F_1\) is rarely the rate-limiting step).
\[ B = \text{Parabolic Constant} \]
\[ B/A = \text{Linear Constant} \]
Oxidation Charts

The charts are based on $X_i = 0$!
Two Ways to Calculate Oxide Thickness Grown by Thermal Oxidation

E.g.

Method 1: Find B & B/A from Charts

Solve \( X_{ox}^2 + AX_{ox} = B(t + \tau) \)
Two Ways to Calculate Oxide Thickness Grown by Thermal Oxidation

Method 2: Use Oxidation Charts

\[ X_i = 4000 \, \text{A} \Rightarrow \tau = 24 \, \text{min} \text{ at } 1100^\circ \text{C from chart} \]

\[ \therefore \text{Total effective oxidation time} \]

\[ (24+33) \, \text{min} = 57 \, \text{min} \text{ if start with } X_i = 0 \]
(1) Grown at 1000°C, 5hrs

\[
\begin{align*}
\text{SiO}_2 & \quad 4000\text{oA} \\
\text{Si} & 
\end{align*}
\]

(2) Grown at 1100°C, 24min

\[
\begin{align*}
\text{SiO}_2 & \quad 4000\text{oA} \\
\text{Si} & 
\end{align*}
\]

(3) CVD Oxide

\[
\begin{align*}
X_i & \quad \text{SiO}_2 \quad 4000\text{oA} \\
& \quad \text{Si} 
\end{align*}
\]

CVD Oxide

For same \(X_i\), \(\tau\) is the same for all three cases shown here.