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 SiO₂ Properties

(1) Excellent Electrical Insulator
   Resistivity > 1E20 ohm-cm
   Energy Gap ~ 9 eV
(2) High Breakdown Electric Field
   > 10MV/cm
(3) Stable and Reproducible Si/SiO₂ Interface
(4) Conformal oxide growth on exposed Si surface
(5) SiO$_2$ is a good diffusion mask for common dopants

\[ D_{SiO_2} << D_{si} \]

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
Thickness of Si consumed during oxidation

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

molecular density of SiO_2
atomic density of Si

\[ = X_{ox} \cdot \frac{2.3 \times 10^{22} \text{ molecules / cm}^3}{5 \times 10^{22} \text{ atoms / cm}^3} = 0.46 X_{ox} \]
For 1-dimensional planar oxide growth

1 μm Si oxidized

2.17 μm SiO$_2$

Suggested calculation exercise:

1 μm diameter Si sphere completely oxidized

1.3 μm diameter SiO$_2$ sphere
Kinetics of SiO$_2$ Growth

- Gas Diffusion
- Solid-state Diffusion
- SiO$_2$ Formation

Oxidant Flow (O$_2$ or H$_2$O)

Gas Flow
Stagnant Layer

SiO$_2$

Si-Substrate
Deal-Grove Model

- Stagnant layer
- Note: $C_S \neq C_O$

- Fluxes:
  - $F_1$: gas transport flux
  - $F_2$: diffusion flux through SiO$_2$
  - $F_3$: reaction flux at interface

- Concentrations:
  - $C_G$
  - $C_S$
  - $C_O$
  - $C_i$

- Regions:
  - SiO$_2$
  - Si
\[ F_1 = h_G (C_G - C_S) \]

Mass transfer coefficient [cm/sec].

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

“Fick’s Law of Solid-state Diffusion”

\[ F_3 = k_s \cdot C_i \]

Surface reaction rate constant [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 CVD growth rate 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:

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

**Henry's Law**

\[ C_o = H \cdot P_s \]

Henry's constant

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: \( C_o \) & \( C_i \)
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 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 SiO₂.

Therefore, we have the oxide growth rate eqn:

\[ N_1 \cdot \frac{dX_{ox}}{dt} = \left[ \frac{k_s C_A}{1 + \frac{k_s}{h} + \frac{k_s X_{ox}}{D}} \right] \]
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: $h >> k_s$ 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

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

$Si + O_2 \rightarrow SiO_2$

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

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

\[ X_{ox}^2 + AX_{0x} = B(t + \tau) \]

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

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

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 \( X_{ox} \)]

\[ X_{ox} \rightarrow \sqrt{Bt} \]

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

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

\[(1)\quad B \equiv \frac{2 \ D \ C_A}{N_1} \propto D\]

\[D \propto e^{-\frac{Q}{kT}}\]

\[Q = \text{activation energy for diffusion}\]

\[(2)\quad \frac{B}{A} = \frac{1}{\left( \frac{1}{h} + \frac{1}{k_s} \right)} \frac{C_A}{N_1}\]

\[k_s \propto e^{-\frac{Q'}{kT}}\]

\[Q' = \text{activation energy for interface reaction}\]

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 = Parabolic Constant
B/A = Linear Constant
Oxidation Charts

The charts are based on $X_i = 0$!

Wet and dry silicon dioxide growth for (100) silicon
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

$X_i = 4000\ A \Rightarrow \tau = 24\ min\ at\ 1100^\circ C\ from\ chart$

$\therefore\ Total\ effective\ oxidation\ time$

$(24 + 33)\ min = 57\ min\ \ if\ start\ with\ X_i = 0$
(1) Grown at 1000°C, 5hrs

\[
\begin{array}{|c|c|}
\hline
\text{SiO}_2 & 4000°A \\
\hline
\text{Si} & \text{Si} \\
\hline
\end{array}
\]

(2) Grown at 1100°C, 24min

\[
\begin{array}{|c|c|}
\hline
\text{SiO}_2 & 4000°A \\
\hline
\text{Si} & \text{Si} \\
\hline
\end{array}
\]

(3) CVD Oxide

\[
\begin{array}{|c|c|}
\hline
\text{SiO}_2 & 4000°A \\
\hline
\text{Si} & \text{Si} \\
\hline
\end{array}
\]

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