Thermal Oxidation of Si

- General Properties of SiO₂
- Applications of thermal SiO₂
- Deal-Grove Model of Oxidation

Thermal SiO₂ is amorphous.
Weight Density = 2.20 gm/cm³
Molecular Density = 2.3E22 molecules/cm³

Crystalline SiO₂ [Quartz] = 2.65 gm/cm³
Thermal SiO$_2$ 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/SiO$_2$ Interface

(4) Conformal oxide growth on exposed Si surface
(5) SiO₂ is a good diffusion mask for common dopants

\[ D_{\text{SiO}_2} << D_{\text{Si}} \]
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 SiO₂.
Steam generation for wet oxidation

Thermal Oxidation Equipment
Thickness of Si consumed during oxidation

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

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

Suggested calculation exercise:

1 µm Si sphere completely oxidized to 1.3 µm SiO₂ sphere

1 µm Si oxidized to 2.17 µm SiO₂
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

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Deal-Grove Model

- Stagnant layer
- Note: $C_s \neq C_0$

Fluxes:
- $F_1$: Gas transport flux
- $F_2$: Diffusion flux through SiO$_2$
- $F_3$: Reaction flux at interface
\[
F_1 = h_G \left( C_G - C_S \right)
\]

Mass transfer coefficient [cm/sec].

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

“Fick’s Law of Solid-state Diffusion”

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

Diffusivity [cm²/sec]

\[
F_3 = k_s \cdot C_i
\]

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:

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

\[ C_o = H \cdot P_s \]

Henry's Law

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

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

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

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

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

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

Oxidant molecules/unit volume required to form a unit volume of SiO$_2$.

Therefore, we have the oxide growth rate eqn:

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

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

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

\[
N_1 = \frac{2.3 \times 10^{22} \text{ } / \text{cm}^3}{\text{for O}_2 \text{ as oxidant}}
\]

\[
Si + O_2 \rightarrow SiO_2
\]

\[
N_1 = \frac{4.6 \times 10^{22} \text{ } / \text{cm}^3}{\text{for H}_2\text{O as oxidant}}
\]

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

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

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

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

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

(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

\( B \equiv \frac{2D C_A}{N_1} \propto D \)  

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

\( \frac{B}{A} = \frac{1}{\left( \frac{1}{h} + \frac{1}{k_s} \right)} \frac{C_A}{N_{1}} \)

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

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)
\[ B = \text{Parabolic Constant} \]
\[ \frac{B}{A} = \text{Linear Constant} \]
Oxidation Charts

Wet and dry silicon dioxide growth for (100) silicon

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

SiO₂  4000°A

Si

(2) Grown at 1100°C, 24min

SiO₂  4000°A

Si

(3) CVD Oxide

SiO₂  4000°A

CVD Oxide

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