Section 4: Thermal Oxidation

Jaeger Chapter 3
Properties of SiO$_2$

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$^3$

(1) Excellent Electrical Insulator
   Resistivity $> 1E20$ 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) SiO₂ 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
Properties of $\text{SiO}_2$ (cont’d)

(6) Very good etching selectivity between Si and $\text{SiO}_2$. 

SiO$_2$       HF dip  Si
Thermal Oxidation of Silicon

Dry Oxidation

\[ Si + O_2 \rightarrow SiO_2 \]

Wet Oxidation

\[ Si + 2H_2O \rightarrow SiO_2 + 2H_2 \]

Growth Occurs 54% above and 46% below original surface as silicon is consumed.
Thermal Oxidation Equipment

Horizontal Furnace

Vertical Furnace
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
**Silicon consumption during oxidation**

1 μm Si oxidized \( \rightarrow \) 2.17 μm SiO₂

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

\[
= X_{ox} \cdot \frac{2.3 \times 10^{22} \text{ molecules} / \text{cm}^3}{5 \times 10^{22} \text{ atoms} / \text{cm}^3} = 0.46 X_{ox}
\]
The Deal-Grove Model of Oxidation

- **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

$\triangleright$ **F**: Oxygen flux – the number of oxygen molecules that crosses a plane of a certain area in a certain time
The Deal-Grove Model of Oxidation (cont’d)

\[ F_1 = h_G \left( C_G - C_S \right) \]

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

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

“Fick’s Law of Solid-state Diffusion”

\[ \approx D \cdot \frac{C_o - C_i}{X_{ox}} \]

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

\[ F_3 = k_s \cdot C_i \]

Oxidation reaction rate constant
Diffusivity: the diffusion coefficient

\[ D = D_0 \exp\left(-\frac{E_A}{kT}\right) \]

- \( E_A \) = activation energy
- \( k \) = Boltzmann's constant = 1.38 x 10^{-23} \text{ J/K}
- \( T \) = absolute temperature
The Deal-Grove Model of Oxidation (cont’d)

- $C_S$ 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:

$$F_1 = F_2 = F_3 \ (2 \text{ equations})$$
The Deal-Grove Model of Oxidation (cont’d)

\[ C_o = H \cdot P_s \quad \text{Henry’s Law} \]

Henry’s partial pressure of oxidant constant at surface [in gaseous form].

\[ = H \cdot (kT \cdot C_s) \quad \text{from ideal gas law } PV = NkT \]

\[ \therefore C_s = \frac{C_o}{HkT} \]
The Deal-Grove Model of Oxidation (cont’d)

Define \( C_A \equiv (HkT \cdot C_G) \)

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

Similarly, we can set up equations for \( F_2 \) and \( F_3 \)

Using the steady-state condition:

\[
F_1 = F_2 = F_3 \quad \text{We therefore can solve for } C_o \text{ and } C_i
\]
The Deal-Grove Model of Oxidation (cont’d)

We have:

\[ F_2 \approx D \cdot \left( \frac{C_o - C_i}{X_{ox}} \right) \quad F_3 = k_s \cdot C_i \quad F_1 = h(C_A - C_o) \]

At equilibrium: \( F_1 = F_2 = F_3 \)

Solving, we get:

\[
C_i = \frac{C_A}{1 + \frac{k_s}{h} + \frac{k_sX_{ox}}{D}} \quad C_o = C_i \cdot \left(1 + \frac{k_sX_{ox}}{D} \right)
\]

\[
F \left(= F_1 = F_2 = F_3 \right) = k_s \cdot C_i = \frac{k_s C_A}{1 + \frac{k_s}{h} + \frac{k_sX_{ox}}{D}}
\]

Where \( h = h_g / HkT \)
The Deal-Grove Model of Oxidation (cont’d)

We can convert flux into growth thickness from:

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

\( \Delta X_{ox} \) Oxidant molecules/unit volume required to form a unit volume of SiO₂.
The Deal-Grove Model of Oxidation (cont’d)

Initial Condition: At $t = 0$, $X_{ox} = X_i$

Solution

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

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

Note: $h_g >> k_s$ for typical oxidation condition

$$B \equiv \frac{2DC_A}{N_1}$$

$$\tau = \frac{X_i^2 + AX_i}{B}$$
Dry / Wet Oxidation

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: Deal-Grove Model

Oxide Growth Rate slows down with increase of oxide thickness
Solution: Oxide Thickness Regimes

\[
X_{ox} = \frac{A}{2} \left\{ \sqrt{1 + \left( \frac{t + \tau}{\frac{A^2}{4B}} \right)} - 1 \right\}
\]

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

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

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

\[
X_{ox} \rightarrow \frac{B}{A} t
\]
Thermal Oxidation on $<100>$ Silicon
Thermal Oxidation on <111> Silicon
A \(<100>\) silicon wafer has a 2000-Å oxide on its surface.

(a) How long did it take to grow this oxide at 1100\( ^\circ \text{C} \) in dry oxygen?

(b) The wafer is put back in the furnace in wet oxygen at 1000\( ^\circ \text{C} \). How long will it take to grow an additional 3000 Å of oxide?
Thermal Oxidation Example
Graphical Solution

(a) According to Fig. 3.6, it would take 2.8 hr to grow 0.2 μm oxide in dry oxygen at 1100° C.
(b) The total oxide thickness at the end of the oxidation would be 0.5 \( \mu \text{m} \) which would require 1.5 hr to grow if there was no oxide on the surface to begin with. However, the wafer “thinks” it has already been in the furnace 0.4 hr. Thus the additional time needed to grow the 0.3 \( \mu \text{m} \) oxide is 1.5-0.4 = 1.1 hr.
Thermal Oxidation Example
Mathematical Solution

(a) From Table 3.1,
\[ B = 7.72 \times 10^2 \exp\left(-1.23\right) \frac{\mu m^2}{hr} \quad \frac{B}{A} = 3.71 \times 10^6 \exp\left(-2.00\right) \frac{\mu m}{hr} \quad X_i = 25 nm \]

For \( T = 1373 \) K, \( B = 0.0236 \frac{\mu m^2}{hr} \) and \( \frac{B}{A} = 0.169 \frac{\mu m}{hr} \)

\[ \tau = \frac{(0.025\mu m)^2}{0.0236 \frac{\mu m^2}{hr}} + \frac{0.025\mu m}{0.169 \frac{\mu m}{hr}} = 0.174 \text{ hr} \]

\[ t = \frac{(0.2\mu m)^2}{0.0236 \frac{\mu m^2}{hr}} + \frac{0.2\mu m}{0.169 \frac{\mu m}{hr}} - 0.174 \text{ hr} = 2.70 \text{ hr} \]
Thermal Oxidation Example
Mathematical Solution

(b) From Table 3.1,

\[ B = 3.86 \times 10^2 \exp\left(\frac{-0.78}{kT}\right) \frac{\mu m^2}{hr} \]
\[ \frac{B}{A} = 9.70 \times 10^7 \exp\left(\frac{-2.05}{kT}\right) \frac{\mu m}{hr} \]
\[ X_i = 0 \]

For \( T = 1273 \, \text{K} \), \( B = 0.314 \frac{\mu m^2}{hr} \) and \( \frac{B}{A} = 0.742 \frac{\mu m}{hr} \)

\[ \tau = \frac{(0.2 \, \mu m)^2}{0.314 \frac{\mu m^2}{hr}} + \frac{0.2 \, \mu m}{0.742 \frac{\mu m}{hr}} = 0.398 \, \text{hr} \]

\[ t = \frac{(0.5 \, \mu m)^2}{0.314 \frac{\mu m^2}{hr}} + \frac{0.5 \, \mu m}{0.742 \frac{\mu m}{hr}} - 0.398 \, \text{hr} = 1.07 \, \text{hr} \]
Effect of Xi on Wafer Topography

SiO₂  SiO₂  Xi

Si

Xᵢ
Effect of Xi on Wafer Topography

- Less oxide grown, less Si consumed
- More oxide grown, more Si consumed

1. SiO₂
2. SiO₂
3. Xᵢ

EE143 - Ali Javey
Factors Influencing Thermal Oxidation

- Temperature
- Ambient Type (Dry $O_2$, Steam, HCl)
- Ambient Pressure
- Substrate Crystallographic Orientation
- Substrate Doping
High Doping Concentration Effect

Coefficients for dry oxidation at 900°C as function of surface Phosphorus concentration

Dry oxidation, 900°C

$B/A (\mu m/min)$

$B (\mu m^2/min)$

$C_B (cm^{-3})$

$10^{-6}$

$10^{-5}$

$10^{-4}$

$10^{-3}$

$10^{-2}$

$10^{17}$

$10^{18}$

$10^{19}$

$10^{20}$

$10^{21}$

$n^+$

$n$

$SiO_2$

EE143 - Ali Javey
Transmission Electron Micrograph of Si/SiO₂ Interface

Amorphous SiO₂

Crystalline Si

Interface plane

perturbed area

3.14 Å
Thermal Oxide Charges

- Potassium ($K^+$) mobile ionic charge ($Q_m$)
- Sodium ($Na^+$)
- Oxide trapped charge ($Q_{ot}$)
- Fixed oxide charge ($Q_f$)
- Interface trapped charge ($Q_{it}$)

SiO$_2$

SiO$_x$

Si
Oxide Quality Improvement

To minimize Interface Charges $Q_f$ and $Q_{it}$

• Use inert gas ambient (Ar or N2) when cooling down at end of oxidation step

• A final annealing step at 400-450°C is performed with 10%H₂+90%N₂ ambient ("forming gas") after the IC metallization step.
Oxidation with Chlorine-containing Gas

- Introduction of halogen species during oxidation e.g. add \( \sim 1\%-5\% \) HCl or TCE (trichloroethylene) to \( O_2 \)
  - \( \rightarrow \) reduction in metallic contamination
  - \( \rightarrow \) improved SiO\(_2\)/Si interface properties

\[ M + Cl \rightarrow MCl \]

Na\(^+\) or K\(^+\) in SiO\(_2\) are mobile!
Effect of HCl on Oxidation Rate

\[ \text{HCl} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 \]
**Local Oxidation of Si [LOCOS]**

~100 Å SiO$_2$ (thermal) - pad oxide to release mechanical stress between nitride and Si.
Local Oxidation of Silicon (LOCOS)

Standard process suffers for significant bird’s beak

Fully recessed process attempts to minimize bird’s beak

Si₃N₄

SiO₂ pad

Silicon wafer

Oxidation

"Bird's beak"

Nitride removal

SiO₂

Silicon wafer

Silicon etch

Oxidation

"Bird's beak"

Nitride removal

SiO₂
Dopant Redistribution during Thermal Oxidation

Segregation Coefficient

\[ m \equiv \frac{\text{equilibrium dopant conc. in Si}}{\text{equilibrium dopant conc. in SiO}_2} = \frac{C_1}{C_2} \]

(\text{can be } >1 \text{ or } <1)

Fixed ratio

conc. \quad Si \quad e. \text{ g. B, P, As, Sb.}

\[ C_B \text{ (uniform)} \]

\[ x \]

\[ SiO_2 \quad Si \]

\[ C_1 \quad C_2 \quad C_B \]
Four Cases of Interest

(A) $m < 1$ and dopant diffuses slowly in $\text{SiO}_2$

\[ D \quad C_1 \quad C_2 \quad C_B \]

$\text{SiO}_2$ \quad $\text{Si}$

- flux loss through $\text{SiO}_2$ surface not considered here.

$\Rightarrow$ B will be depleted near Si interface.
Four Cases of Interest

(B) $m > 1$, slow diffusion in SiO$_2$.

e.g. P, As, Sb

⇒ dopant piling up near Si interface for P, As & Sb
Four Cases of Interest

(C) \( m < 1 \), fast diffusion in \( \text{SiO}_2 \)

- \( C_1 \), oxidize with presence of \( \text{H}_2 \)
Four Cases of Interest

(D) $m > 1$, fast diffusion in SiO$_2$

![Diagram](image_url)
Polycrystalline Si Oxidation

poly-Si

grain boundaries (have lots of defects).

SiO₂

roughness with $X_{ox}$

fast

slower

Overall growth rate is higher than single-crystal Si
2-Dimensional oxidation effects

Mechanical stress created by SiO₂ volume expansion also affects oxide growth rate