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 ~ 9 eV

2. High Breakdown Electric Field
   > 10MV/cm

3. Stable and Reproducible Si/SiO$_2$ Interface
Properties of $\text{SiO}_2$ (cont’d)

(4) Conformal oxide growth on exposed Si surface

(5) $\text{SiO}_2$ 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
Properties of $SiO_2$ (cont’d)

(6) Very good etching selectivity between Si and $SiO_2$. 

Diagram:
- $SiO_2$
- Si
- HF dip
- Si
Thermal Oxidation of Silicon

Dry Oxidation

\[ S_i + O_2 \rightarrow S_iO_2 \]

Wet Oxidation

\[ S_i + 2H_2O \rightarrow S_iO_2 + 2H_2 \]

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 Flow Stagnant Layer

Oxidant Flow ($O_2$ or $H_2O$)

Gas Diffusion

Solid-state Diffusion

$SiO_2$ Formation

Si-Substrate
Silicon consumption during oxidation

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

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

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

- **Gas transport flux**
- **Diffusion flux through SiO\(_2\)**
- **Reaction flux at interface**

\[ F: \text{oxygen flux} = \text{the number of oxygen molecules that crosses a plane of a certain area in a certain time} \]
The Deal-Grove Model of Oxidation (cont’d)

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

Mass transfer coefficient [cm/sec].

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

“Fick’s Law of Solid-state Diffusion”

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

Diffusivity [cm^2/sec]

\[ F_3 = k_i \cdot C_i \]

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 = \( 1.38 \times 10^{-23} \) 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:

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

\[ C_o = H \cdot P_s \]

Henry’s Law

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

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

from ideal gas law \( PV = NkT \)

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

We have:

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

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

Solving, we get:

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

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

Where \( h = h_g / H_k T \)
The Deal-Grove Model of Oxidation (cont’d)

We can convert flux into growth thickness from:

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

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

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

\[
A = 2D \left( \frac{1}{k_s} + \frac{1}{h_g} \right)
\]

\[
B = \frac{2DC}{N_1} A
\]

Note: \( h_g \gg k_s \) for typical oxidation condition

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

Note: “dry” and “wet” oxidation have different $N_1$ factors

$N_1 = 2.3 \times 10^{22} / \text{cm}^3$ \hspace{1cm} for $O_2$ as oxidant

$Si + O_2 \rightarrow SiO_2$

$N_1 = 4.6 \times 10^{22} / \text{cm}^3$ \hspace{1cm} 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

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

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

\[ \therefore \frac{dx_{ox}}{dt} = \frac{B}{A + 2X_{ox}} \]
Solution: Oxide Thickness Regimes

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

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

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

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

\[ X_{ox} \rightarrow \frac{B}{A} t \]
Thermal Oxidation on $<100>$ Silicon
Thermal Oxidation on <111> Silicon
Thermal Oxidation Example

A <100> silicon wafer has a 2000-Å oxide on its surface

(a) How long did it take to grow this oxide at 1100° C in dry oxygen?

(b) The wafer is put back in the furnace in wet oxygen at 1000° C. How long will it take to grow an additional 3000 Å of oxide?
(a) According to Fig. 3.6, it would take 2.8 hr to grow 0.2 μm oxide in dry oxygen at 1100°C.
Thermal Oxidation Example
Graphical Solution

(b) The total oxide thickness at the end of the oxidation would be 0.5 μm 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 μm oxide is 1.5-0.4 = 1.1 hr.
**Thermal Oxidation Example**

**Mathematical Solution**

(a) From Table 3.1,

$$B = 7.72 \times 10^2 \exp \left( \frac{-1.23}{kT} \right) \frac{\mu m^2}{hr} \quad B = 3.71 \times 10^6 \exp \left( \frac{-2.00}{kT} \right) \frac{\mu m}{hr} \quad X_i = 25nm$$

For $T = 1273$ K, $B = 0.0236 \frac{\mu m^2}{hr}$ and $B/A = 0.169 \frac{\mu m}{hr}$

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

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

(b) From Table 3.1,

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

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

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

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

- SiO$_2$ grown:
  - Less oxide grown
  - Less Si consumed
  - More oxide grown
  - More Si consumed

Figures 1, 2, and 3 show the topography changes with $X_i$. Figure 1 shows less oxide grown and less Si consumed. Figure 2 illustrates more oxide grown and more Si consumed.
Factors Influencing Thermal Oxidation

- Temperature
- Ambient Type (Dry O₂, 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

* highly doped Si has more vacancies

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

- Amorphous SiO₂
- Crystalline Si

**Interface Plane**

**Perturbed Area**

**5.14 Å**

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Thermal Oxide Charges

- **K⁺**: Mobile ionic charge ($Q_m$)
- **Na⁺**: Oxide trapped charge ($Q_{ot}$)
- Fixed oxide charge ($Q_f$)
- Interface trapped charge ($Q_{it}$)

Materials:
- **SiO₂**
- **SiOₓ**
- **Si**

Keywords: potassium, sodium, Thermal Oxide Charges
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%$H_2$+90%$N_2$ ambient ("forming gas") after the IC metallization step.
**Oxidation with Chlorine-containing Gas**

- Introduction of halogen species during oxidation
e.g. add ~1-5% HCl or TCE (trichloroethylene) to O₂
  → reduction in metallic contamination
  → improved SiO₂/Si interface properties

\[ M + Cl \rightarrow MCl \]

Na⁺ or K⁺ in SiO₂ are mobile!
Effect of HCl on Oxidation Rate

\[ \text{HCl} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 \]

Graphs showing the parabolic rate constant and linear rate constant as a function of HCl concentration at different temperatures.
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

- Si$_3$N$_4$
- Oxidation
- ”Bird’s beak”
- Nitride removal
- SiO$_2$

Fully recessed process attempts to minimize bird’s beak

- Si$_3$N$_4$
- SiO$_2$ pad
- Silicon etch
- Oxidation
- ”Bird’s beak”
- Nitride removal
- SiO$_2$
**Segregation Coefficient**

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

Fixed ratio

\[ m = \frac{C_1}{C_2} \quad \text{(can be >1 or <1)} \]
Four Cases of Interest

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

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

$\text{C}_1 \quad C_2 \quad C_B$

$\text{D}$

$\Rightarrow \text{B will be depleted near Si interface.}$

*e. g. B ($m = 0.3$)*

*flux loss through $\text{SiO}_2$ surface not considered here.*
(B) $m > 1$, slow diffusion in SiO$_2$.

e.g. P, As, Sb

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

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

e. g. $B$, oxidize with presence of $H_2$
Four Cases of Interest

(D) $m > 1$, fast diffusion in $\text{SiO}_2$

e. g. Ga ($m=20$)
Thin Oxide Growth

The Deal-Grove model provides excellent agreement with experimental data except for thin (<20 nm) SiO₂ grown in O₂

When \( X_{ox} \) becomes large, additional term becomes zero

\[
\frac{dX_{ox}}{dt} = \frac{B}{A+2X_{ox}} + Ce^{\frac{X_{ox}}{L}}
\]

\( L \sim 7\text{nm} \)

=> For thick oxides grown in O₂ on bare Si, assume \( X_i = 25\text{ nm} \) when using the D-G equations

25 nm

\( X_{ox} \)

\( t \)
Polycrystalline Si Oxidation

Poly-Si grain boundaries (have lots of defects).

SiO$_2$

Overall growth rate is higher than single-crystal Si
Mechanical stress created by SiO₂ volume expansion also affects oxide growth rate.