ECE 418/518
Semiconductor Device Processing
Thermal Oxidation
Thermal Oxidation of Silicon

- In this chapter we will study the following topics.
  - General introduction to SiO$_2$
  - Dry and wet oxidation processes
  - Kinetic model of oxide growth
  - Dopant redistribution during oxide growth.
  - Selective oxidation.

- SiO$_2$ is used in the processing industry in a variety of roles:
  - as an insulator
  - as a diffusion mask
  - for p-n junction passivation
  - as a gate dielectric in MOS devices
Crystalline SiO$_2$ occurs naturally in the form of mineral quartz. Amorphous SiO$_2$ obtained by melting and cooling of crystalline silica is called vitreous silica, or fused silica or fused quartz. In the laboratory amorphous SiO$_2$ is obtained by the chemical reaction of SiH$_4$ or SiCl$_4$ with oxygen (chemical vapor deposition of SiO$_2$) or by the thermal oxidation of Si.

Si wafer surface readily reacts with the atmospheric oxygen even at room temperature to form SiO$_2$. This oxide is called the native oxide. Its thickness is typically in the range of 20 - 30 Å depending upon the process conditions.

Thermally grown Si-SiO$_2$ is one of the cleanest interfaces known to mankind. The industry routinely achieves interface defect density of the order of $10^9$ cm$^{-2}$ (i.e for approximately $10^6$ Si atoms on the surface there is only one defect). This is a crucial reason for the success of Si in the semiconductor industry.
# Comparison of properties of Si and SiO$_2$

<table>
<thead>
<tr>
<th>Property</th>
<th>SiO$_2$</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gm/cc)</td>
<td>2.22</td>
<td>2.33</td>
</tr>
<tr>
<td>Linear expansion coefficient</td>
<td>0.5x10$^{-6}$</td>
<td>2.3x10$^{-6}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>60</td>
<td>28</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>3.9</td>
<td>11.7</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.46</td>
<td>3.42</td>
</tr>
<tr>
<td>Breakdown strength</td>
<td>3x10$^7$ V/cm</td>
<td>~ 10$^7$ V/cm</td>
</tr>
<tr>
<td>Bandgap (at 300 K)</td>
<td>9 eV</td>
<td>1.12 eV</td>
</tr>
<tr>
<td>Resistivity</td>
<td>10$^{12}$ - 10$^{16}$ ohm-cm</td>
<td>10$^{-2}$ - 10$^{4}$ ohm-cm</td>
</tr>
</tbody>
</table>
Stress in the oxide film

- The difference in the linear expansion coefficients of Si and its oxide gives rise to a stress in the oxide film. The oxide experiences a compressive stress of \( \sim 3 \times 10^9 \) dynes/cm\(^2\). There is a corresponding tensile stress in Si too, but its magnitude is small since Si thickness (\( \sim 500 \mu m \)) is large as compared to the oxide thickness (\( \sim 1 \mu m \)).

- When there is oxide on both sides of the wafer there is no bowing of the wafer. However, when the oxide layer is removed from the backside, bowing of the wafer may occur (particularly for large diameter wafers).
Thermal Oxidation of Silicon

- Growth of SiO₂ on silicon surface at high temperature.

**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 Si surface

**Single crystal SiO₂ (quartz)**

- Density 2.65g/cm³

**Amorphous SiO₂**

- Density 2.21g/cm³
Diffusion of Oxygen through SiO$_2$

- **Fick’s Law**
  \[ J = -D \frac{\partial N}{\partial x} \]

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

**Arrhenius Relationship**

\[ E_A = \text{activation energy} \]

\[ k = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J/K} \]

\[ T = \text{absolute temperature} \]
Reaction at Si Surface

\[ J(X_0) = k_s N_i \]

\[ k_s = k_0 \exp\left(\frac{-E_A}{kT}\right) \quad \text{Arrhenius Relationship} \]

- \( E_A \) = activation energy
- \( k_0 \) = Boltzmann's constant = \( 1.38 \times 10^{-23} \) J/K
- \( T \) = absolute temperature
Deal-Grove model (steady state)

\[ J = -D \frac{\partial N(x,t)}{\partial x} = -D \frac{(N_i - N_0)}{X_o} \]

\[ J(X_o) = k_s N_i \]

\[ t = \frac{X_o^2}{B} + \frac{X_i}{(B/A)} - \tau \]

\[ \tau = \frac{X_i^2}{B} + \frac{X_i}{(B/A)} \]

\[ A = \frac{2D}{k_s} \quad B = \frac{2DN_0}{M} \]

\[ X_o(t) = 0.5A \left[ 1 + 4 \frac{B}{A^2} (t + \tau) \right]^{0.5} - 1 \]

Oxide growth occurs at \( X_o \)

\[ \frac{\partial X_o}{\partial t} = \frac{J}{M} \]

- \( X_o \) = final oxide thickness
- \( D \) = diffusion coefficient
- \( X_i \) = initial oxide thickness
- \( N \) = concentration of oxygen
- \( \tau \) = time required to grow initial oxide
- \( k_s \) = rate constant at Si-SiO₂ interface
- \( M \) = oxygen molecules per unit volume of oxide
Parabolic Regime

For Long Times \(- (t + \tau) \gg \frac{A^2}{4B}\)

\[ X_o(t) = \sqrt{Bt} \]

B = parabolic rate constant
Linear Regime

For Short Times - \((t + \tau) \ll \frac{A^2}{4B}\)

\[ X_o(t) \cong \left( \frac{B}{A} \right) (t + \tau) \]

\left( \frac{B}{A} \right) = \text{linear rate constant}
# Rate Constants

<table>
<thead>
<tr>
<th></th>
<th>Wet $O_2(X_i = 0 \text{ nm})$</th>
<th>Dry $O_2(X_i = 25 \text{ nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_0$</td>
<td>$E_A$</td>
</tr>
<tr>
<td>$&lt;100&gt;$ Silicon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear (B/A)</td>
<td>$9.70 \times 10^7 \mu\text{m/hr}$</td>
<td>2.05 eV</td>
</tr>
<tr>
<td>Parabolic (B)</td>
<td>$386 \mu\text{m}^2$/hr</td>
<td>0.78 eV</td>
</tr>
<tr>
<td>$&lt;111&gt;$ Silicon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear (B/A)</td>
<td>$1.63 \times 10^8 \mu\text{m/hr}$</td>
<td>2.05 eV</td>
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</table>

*Data from Ref.[9]*

\[
\text{Rate Constant} = D_0 \exp\left(-\frac{E_A}{k_B T}\right)
\]
Rate Tables
Dopant redistribution during oxide growth

- The dopants in the Si wafer (e.g. P, B, etc.) redistribute during the thermal oxidation process.
  - The ratio of the dopant concentration in Si to that in the oxide near the interface is known as the distribution coefficient (m).
  - For the n-type dopants (P, As, Sb), \( m > 1 \). The oxide rejects the dopants into Si. There is a pile of impurity concentration in Si near the interface after oxidation.
  - On the other hand, in the case of B, the oxide takes up impurity from Si. Distribution coefficient \( m < 1 \). There is a depletion of B in Si near the interface.
  - Process models should take into account these dopant redistribution effects sufficient accurately to predict the correct working conditions of the device.
Impurity Redistribution

FIGURE 3.9
The effects of oxidation on impurity profiles.
(a) Slow diffusion in oxide (boron); (b) fast diffusion in oxide (boron with hydrogen ambient); (c) slow diffusion in oxide (phosphorus); (d) fast diffusion in oxide (gallium). $C_B$ is the bulk concentration in the silicon. Copyright John Wiley & Sons, Inc. Reprinted with permission from Ref. [5].
Masking of Diffusion with SiO2

- Required oxide thickness depends upon dopant species and temperature
- Hydrogen greatly enhances diffusion of boron - wet oxidation release hydrogen

**FIGURE 3.10**

Thickness of silicon dioxide needed to mask boron and phosphorus diffusions as a function of diffusion time and temperature.
Selective Oxidation

- In Si MOS technology, selective oxidation is used to get leakage-free junctions at the source-substrate and drain-substrate junctions.
- Selective oxidation is realized by using nitride as a masking layer during oxidation:
  - A nitride layer is first deposited on the wafer.
  - The wafer is then patterned to expose the areas of Si where the oxidation needs to take place.
  - The nitride patterned wafer is then oxidized (wet or dry). Oxidation takes place only in those areas where the bare Si wafer is exposed to the oxidizing ambient.
  - Finally, the nitride layer is removed for further processing of the selectively oxidized wafer.
Selective oxidation using nitride mask

Fig. 3.12 Cross section depicting process sequence for (a) semirecessed and (b) fully recessed oxidations of silicon.
Oxidation Furnace
Oxide Thickness Characterization: Profilometer
Oxide Thickness Characterization: Ellipsometer

[Diagram of ellipsometer setup]

[Diagram illustrating linearly polarized and elliptically polarized light]

[Image of an ellipsometer instrument]
Ellipsometry

Snell's Law: \[ n_i \sin \theta_i = n_t \sin \theta_t \]

Fresnel Reflection:

\[ r_p = \frac{E_{rp}}{E_{ip}} = \frac{n_t \cos \theta_i - n_i \cos \theta_t}{n_t \cos \theta_i + n_i \cos \theta_t} \]
\[ t_p = \frac{E_{tp}}{E_{ip}} = \frac{2n_i \cos \theta_i}{n_t \cos \theta_i + n_i \cos \theta_t} \]
\[ r_s = \frac{E_{rs}}{E_{is}} = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} \]
\[ t_s = \frac{E_{ts}}{E_{is}} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t} \]