Effect of $X_i$ on Wafer Topography

1. Less oxide grown, less Si consumed
2. More oxide grown, more Si consumed
Factors Influencing Thermal Oxidation

– Temperature
– Ambient Type (Dry O$_2$, Steam, HCl)
– Ambient Pressure
– Substrate Crystallographic Orientation
– Substrate Doping
High Pressure Oxidation

\[
\frac{B}{A} = \frac{C_A}{[N_1(1/k_s+1/h)]} \propto C_A \propto P_G
\]

\[
B = \frac{2DC_A}{N_1} \propto C_A \propto P_G
\]

When \( P_G \) increases, both \( B \) and \( B/A \) will increase. Therefore oxidation rate increases.

1) The oxidation temperature can be reduced if the pressure is increased, to achieve a given oxidation rate
2) To grow a given oxide thickness at same temperature, time can be reduced
High Doping Concentration Effect

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

* highly doped Si has more vacancies
Substrate Orientation Effect

**Reason:**
(111) surface has more Si bonds than (100) Surface

* difference more obvious for thin oxides

most IC’s made with (100) Si

\[ k_s(111) > (k_s(100)) \]
Transmission Electron Micrograph of Si/SiO2 Interface

Amorphous SiO2

Crystalline Si
Thermal Oxide Charges

Figure 4.14  Silicon–silicon dioxide structure with mobile, fixed charge, and interface states (© 1980, IEEE, after Deal).
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 O_2
  → reduction in metallic contamination
  → improved SiO_2/Si interface properties

\[ \text{M} + \text{Cl} \rightarrow \text{MCl} \]

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

\[ \text{HCl} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 \]
SUMMARY of Deal Grove Model

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

The growth rate \( \frac{dX_{ox}}{dt} = \frac{B}{A+2X_{ox}} \) slows down as \( X_{ox} \) increases

### Dependence of B/A and B on Processing Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Linear Constant B/A</th>
<th>Parabolic Constant B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Pressure</td>
<td>linear with oxygen pressure (actually ( \propto P^{0.8} ))</td>
<td>linear with oxygen pressure</td>
</tr>
<tr>
<td>Steam versus O(_2)</td>
<td>larger for steam oxidation</td>
<td>larger for steam oxidation</td>
</tr>
<tr>
<td>Si crystal orientation</td>
<td>( B/A(111):B/A(100) = 1.68:1 )</td>
<td>independent of orientation</td>
</tr>
<tr>
<td>Dopant type and concentration in Si</td>
<td>increases with dopant concentration</td>
<td>insensitive</td>
</tr>
<tr>
<td>Addition of Cl-containing gas in oxidation ambient</td>
<td>insensitive</td>
<td>increases</td>
</tr>
</tbody>
</table>
Local Oxidation of Si [LOCOS]

- Si$_3$N$_4$ (CVD)
- ~100 Å SiO$_2$ (thermal) - pad oxide to release mechanical stress between nitride and Si.

"bird’s beak"

$\Delta \approx 1.1 - 1.5 \, X_{ox}$
Si substrate is etched to a depth of ~1/2 the intended grown oxide thickness.

Grown oxide surface is approximately planar with substrate surface.
Dopant Redistribution during Thermal Oxidation

Segregation Coefficient

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

Fixed ratio

\[ m = \frac{C_1}{C_2} \]

(can be >1 or <1)
Four Cases of Interest

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

\[
\begin{array}{c}
\text{SiO}_2 \\
\includegraphics[width=0.5\textwidth]{diagram.png} \\
\text{Si}
\end{array}
\]

\( C_2 \) \quad \text{e. g. } B \ (m = 0.3)

\( C_B \)

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

\[\Rightarrow \quad \text{B will be depleted near Si interface.}\]
(B) $m > 1$, slow diffusion in $\text{SiO}_2$.

$\Rightarrow$ dopant piling up near Si interface for P, As & Sb
(C) \( m < 1 \), fast diffusion in \( \text{SiO}_2 \)

\[ \begin{align*}
\text{SiO}_2 & \quad \text{Si} \\
C_2 & \quad C_B
\end{align*} \]

\text{e.g.} \quad B, \  \text{oxidize with presence of } H_2
(D) $m > 1$, fast diffusion in $\text{SiO}_2$

\[ \text{SiO}_2 \quad \text{Si} \]

$C_1$, $C_2$, $C_B$

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.

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

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

\( \propto t^{1/2} \)

\( \propto t \)

\( \propto t \)

25 nm

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

Poly-Si

grain boundaries (have lots of defects).

Overall growth rate is higher than single-crystal Si

fast

slower

roughness with $X_{ox}$

SiO$_2$
Schematic Illustration of Thermal Oxidation of Si-containing materials in which SiO2 is the final reaction product.
2-Dimensional oxidation effects

Mechanical stress created by SiO$_2$ volume expansion also affects oxide growth rate (if interested, see Kao et al, International Electron Devices Meeting Digest, 1985, p.388)