Effect of $X_i$ on Wafer Topography

- More oxide grown ($X_i$) → More Si consumed
- Less oxide grown ($X_i$) → Less Si consumed
Factors Influencing Thermal Oxidation

– Temperature
– Ambient Type (Dry O₂, 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

\[ \text{Dry oxidation, 900°C} \]

\[ B/A (\mu\text{m/min}) \quad B (\mu\text{m}^2/\text{min}) \]

\[ 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \]

\[ 10^{17} \quad 10^{18} \quad 10^{19} \quad 10^{20} \quad 10^{21} \]

* highly doped Si has more vacancies

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

\[ \text{vacancies} \]
Origin of Substrate Orientation Effect

(111) Surface density of Si bonds > (100) Surface density of Si bonds

(100): □ □ □
(111): □ □ □

\[ k_{S(111)} > k_{S(100)} \]

\[ \log X_{ox} \]

* difference more obvious for thin oxides

most IC’s made with (100) Si
Thermal Oxide Charges

To minimize $Q_{it}$,
A final annealing step at 400-450$^\circ$C is performed with 10%$H_2 + 90%N_2$ ambient (“forming gas”) after the metallization step.

To minimize $Q_f$,
Use inert gas ambient (Ar or N2) when cooling down at end of oxidation step.

Figure 4.14 Silicon–silicon dioxide structure with mobile, fixed charge, and interface states (© 1980, IEEE, after Deal).

Professor N. Cheung, U.C. Berkeley
Oxidation with Cl-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

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

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

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 ( (\text{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]

\[ \Delta \approx 1.1 - 1.5 X_{ox} \]

Si\textsubscript{3}N\textsubscript{4} (CVD)

~100 A SiO\textsubscript{2} (thermal) - pad oxide to release mechanical stress between nitride and Si.

“bird’s beak”

SiO\textsubscript{2}

Si
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

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

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

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

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

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

\[
\begin{array}{c}
\text{SiO}_2 \\
\uparrow
\end{array}
\hspace{1cm}
\begin{array}{c}
\text{Si} \\
\downarrow
\end{array}
\]

\( C_1 \quad C_2 \quad C_B \)

\text{e.g. } P, \text{ As, Sb}

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

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

\[C_2 \quad C_B \]

\[C_1 \]

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

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

$L \sim 7nm$

$\propto t$  \hspace{1cm}  $\propto t^{1/2}$

$X_{ox}$

25 nm

$X_i = 25 \text{ nm}$ when using the D-G equations.

$=>$ 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).

SiO$_2$

Roughness with $X_{ox}$

Overall growth rate is higher than single-crystal Si
Schematic Illustration of Thermal Oxidation of Si-containing materials in which SiO2 is the final reaction product

 POLYCRYSTALLINE SILICON

$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$

 SILICON NITRIDE

$\text{Si}_3\text{N}_4 + 3 \text{O}_2 \rightarrow 3 \text{SiO}_2 + 2 \text{N}_2$

 TANTALUM SILICIDE

$\text{TaSi}_2 + \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 + \text{TaSi}_2$
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)