Effect of $X_i$ on Wafer Topography

- Less oxide grown, less Si consumed
- More oxide grown, more Si consumed
Factors Influencing Thermal Oxidation

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

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

Dry oxidation, 900°C

B/A (µm/min)

B (µm²/min)

10^{-2}

10^{-3}

10^{-4}

10^{-5}

10^{-6}

10^{17}

10^{18}

10^{19}

10^{20}

10^{21}

C_B (cm^{-3})

SiO_2

Si

k_s

vacancies

n^+

n

n^+

n

Professor N. Cheung, U.C. Berkeley
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
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%$\text{H}_2$+90%$\text{N}_2$ 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

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

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

\[ X_{OX}^2(t) + A \frac{d X_{OX}}{d t}(t) = B (t + \tau) \]

The growth rate \( \frac{d X_{OX}}{d t} = \frac{B}{A+2X_{OX}} \) 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”

$\Delta \approx 1.1 - 1.5 X_{ox}$

$X_{ox}$
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

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

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

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

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

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

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

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

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

e. g. 
\( \text{B,} \) oxidize with presence of \( \text{H}_2 \)
(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) SiO\(_2\) grown in O\(_2\).

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

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

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

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

\(\propto t\)

=> For thick oxides grown in O\(_2\) 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$_2$

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**

\[ Si + O_2 \rightarrow SiO_2 \]

**Silicon Nitride**

\[ Si_3N_4 + 3 O_2 \rightarrow 3 SiO_2 + 2 N_2 \]

**Tantalum Silicide**

\[ TaSi_2 + S_i + O_2 \rightarrow SiO_2 + TaSi_2 \]
2-Dimensional oxidation effects

Mechanical stress created by SiO₂ volume expansion also affects oxide growth rate (if interested, see Kao et al, International Electron Devices Meeting Digest, 1985, p.388)