Oxidation of Si

Why spend a whole lecture on oxidation of Si?
Ge has high $\mu_e$, $\mu_h$, Ge stable… … but no oxide
GaAs has high $\mu_e$ and direct band… … no oxide

Why SiO$_2$?
SiO$_2$ is stable down to $10^{-8}$ Torr, $T > 900^\circ$C
SiO$_2$ can be etched with HF which leaves Si unaffected
SiO$_2$ is a diffusion barrier for B, P, As
SiO$_2$ is good insulator, $\rho > 10^{16}$ $\Omega$cm, $E_g = 8$ eV!
SiO$_2$ has high dielectric breakdown field, 500 V/$\mu$m
SiO$_2$ growth on Si $\Rightarrow$ clean Si / SiO$_2$ interface
because $D^\text{Si}$ through SiO$_2$ $<< D^\text{Oxy}$ through SiO$_2$

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SiO$_2$ growth occurs at inside surface

Si + O$_2$ $\rightarrow$ SiO$_2$
or

Si + 2H$_2$O = SiO$_2$ + 2H$_2$
(faster growth, more porous, lower quality)

Unsaturated bond
Extra free volume in dangling bonds of amorphous SiO$_2$ =>

Implications different for field vs. patterned oxide.

Only when oxide is patterned does it cause problems with planarity.

RCA cleaning station for removing organic contaminants, Na$^+$ and other ions as well as native oxide (by HF-dip) from Si wafers.

Oxidation furnaces for controlled growth of oxide layer on Si:
1050 C and steam for field oxide.
Probably safe to say that entire course of semiconductor industry would be different without good SiO$_2$ growth on Si wafer. Device fabrication, especially MOS, would be more difficult.

*Depositing* SiO$_2$ or Al$_2$O$_3$ is not clean.

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It’s no accident that the world leader in Si chip technology, Intel, has been led by the flamboyant Hungarian, Andy Grove.

As a young researcher at Fairchild Semiconductor, he “wrote the book” on SiO$_2$ growth: the *Deal-Grove model*. 
**Deal-Grove model of silicon oxidation**

Oxide growth rate

Ideal gas law: \( P V = N k T \)

\[
\frac{N}{V} = C_g = \frac{P_g}{kT}
\]

\[
J_1 \geq D \frac{(C_g - C_s)}{t_{dead\ layer}}
\]

Turbulence \( \Rightarrow \)

\[
J_1 = h_g(C_g - C_s)
\]

\[
C_g = HP_g = Hk_BT C_s
\]

Henry’s law

\[
J_2 = D^{Ox} (SiO_2) \frac{C_g - C_i}{x_{ox}}
\]

Diffusion (\( D \) cm²/s)

\[
J_3 = k_i C_i
\]

rate constant \( k_i \) (cm/s)

Equate ideal gas & \( J_1 \)

to \( J_2 \) & Henry

\[
C_i = f_n \left( P_g, h_g, H, D^{Ox}, x_{ox}, k_i \right)
\]

Equate \( J_2 \) & Henry to \( J_3 \)

**Deal-Grove model of silicon oxidation**

Growth Process limited by

1. \( P(O_2) = P_g \propto C_g \)

2. Transport \( O_2 \) to \( SiO_2 \) surface across dead layer \( J_1 \)

3. Adhesion of \( C_s(O_2) \) at \( SiO_2 \) surface \( C_g \)

4. Diffusion \( O_2 \) through \( SiO_2 \) \( J_2 \)

5. Chemical reaction rate \( J_3 \)

SiO₂ growth occurs at \( Si/SiO_2 \) interface because \( D^{Ox}(SiO_2) > D^{Ox}(SiO_2) \)

Deal-Grove model of silicon oxidation

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**Deal-Grove model of silicon oxidation**

\[ J_1 = J_2 = J_3 \]

\[ \Rightarrow C_i = f\left(P, h, H, D^{032}, x_{oxide}, k_i\right) \]

\[ C_i = \frac{HP^g / k_i}{h + \frac{x_{oxide}}{D^{032}}} \]

\[ h = \frac{h_g}{HkT} \]

Slowest process controls concentration of oxygen at interface...

**Limits:**

**Diffusion limited:**

\[ D^{032}/x_{oxide} < k_i, h, \]

**Reaction-rate limited:**

\[ k_i < h, D^{032}/x_{oxide} \]

Slower process controls concentration of oxygen at interface, which in turn controls growth rate...

Wed., Feb. 16, 2005
Oxide growth rate

Rate of growth:
\[
\frac{dx_{\text{ox}}}{dt} = \frac{J_s}{n_{\text{SO}_2}} = \frac{C_i}{n_{\text{SO}_2}}.
\]

\(\frac{dx_{\text{ox}}}{dt} = \frac{HP_x/n_{\text{SO}_2}}{1 + \frac{x_{\text{ox}}}{D} + \frac{1}{k_i}}\)

\(x_{\text{ox}} = \frac{HP_x/n_{\text{SO}_2}}{1 + \frac{x_{\text{ox}}}{D} + \frac{1}{k_i}}\)

\((n_{\text{SO}_2} = \# \text{O}_2 \text{molecules in oxide / cm}^3)\)
\(n_{\text{SO}_2} = 2.2 \times 10^{22} / \text{cm}^3, \text{dry}\)
\(4.4 \times 10^{22} / \text{cm}^3, \text{H}_2\text{O}\)

\(x_{\text{ox}} = \frac{HP_x/n_{\text{SO}_2}}{1 + \frac{x_{\text{ox}}}{D} + \frac{1}{k_i}}\)

\(|x_{\text{ox}}| > 0\)

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\(\tau \) is the time corresponding to growth of pre-existing oxide.

\(\tau = \frac{x_{\text{ox}}^{2} + Ax_{\text{ox}}}{B} / \text{time}\)

\(x_{\text{ox}} = \frac{HP_x/n_{\text{SO}_2}}{1 + \frac{x_{\text{ox}}}{D} + \frac{1}{k_i}}\)

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Parabolic and linear growth rates

**Thick** oxide \(\Rightarrow\) parabolic rate constant, \(B\)

\(x_{\text{ox}}^{2} \gg Ax_{\text{ox}}\) Quad. Eq.

\(x_{\text{ox}} = \sqrt{B(t + \tau)}\)

**Thin** oxide \(\Rightarrow\) linear rate constant, \(B/A\)

\(x_{\text{ox}}^{2} << Ax_{\text{ox}}\) Quad. Eq.

\(x_{\text{ox}} = \frac{B}{A}(t + \tau)\)

Rate constants \(A\) and \(B\) known experimentally; both \(\propto D = D_0 e^{-E_a/kT}\)
How thick is thick, how thin is thin??

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

\[ x_{ox}^2 > A x_{ox} \quad \text{or} \quad x_{ox} > A \implies \text{thick} \]

\[ x_{ox} > 0.165 \, \mu m, \text{dry}; > 0.226 \, \mu m, \text{wet} \implies \text{thick} \]

\[ D^{2O}(_{2}SiO_{2}) < D^{18O}(_{2}SiO_{2}) \]

\[ 700-1200^\circ C, 1 \text{ atm, } 0.1 \mu m / \text{hr} \implies \text{dry oxide, denser, use for gate oxide.} \]

\[ 750-1100^\circ C, 25 \text{ atm, } 1 \mu m / \text{hr} \implies \text{wet oxide, more porous, poorer diffusion barriers; use for etch oxide, field oxide.} \]

\[ \text{Dry } O_2 + 1-3\% \ Cl; \ Cl \text{ is a metal getter} \implies \text{cleaner oxide.} \]
Exercise: calculate $x_{ox}$ grown for 1 hr. in dry oxidation at 1100 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dry</th>
<th>Wet (640 torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$ (µm)</td>
<td>$B$ (µm²/hr)</td>
</tr>
<tr>
<td>800</td>
<td>0.370</td>
<td>0.0011</td>
</tr>
<tr>
<td>920</td>
<td>0.235</td>
<td>0.0049</td>
</tr>
<tr>
<td>1000</td>
<td>0.165</td>
<td>0.0117</td>
</tr>
<tr>
<td>1100</td>
<td>0.090</td>
<td>0.027</td>
</tr>
<tr>
<td>1200</td>
<td>0.040</td>
<td>0.045</td>
</tr>
</tbody>
</table>

From table, $A = 0.09$ µm, $B = 0.027$ µm²/hr, $t = 0.076$ hr.

$$x_{ox} = \frac{-A + \sqrt{A^2 + 4B(t + \tau)}}{2} = 0.14 \text{ µm}$$

(0.1 - 1.0 µm/hr is typical)

This is the oxide thickness grown over any thin native oxide present.

Now you calculate $x_{ox}$ for steam oxidation at same time and temp.

Why is wet oxidation faster?

SiO₂/Si interface, local charges

Oxygen gradient exists in SiOₓ. Oxide near the interface is a sub oxide, SiOₓ, $x < 2$. 

$e^{-}$ is often + charged. WHY?

SiO, which is often + charged. WHY?
**SiO$_2$/Si interface and dry vs. wet oxidation**

Which species diffuse quickly?

Large  small  
O$^-$, O, H, H$, H^+$, H$^+$  fast  
Slow

O$^-$, SiO$^-$ $\rightarrow$ SiO$_2$

Outside  in oxide

O$_2$ $\rightarrow$ O$^+$ + O$^-$ + $h^+$  
2H$_2$O $\rightarrow$ O$^-$ + O$^+$ + $h^+$ + $n$(H$^+$, H, H$^-$)

What does dipole layer do to ions?

Gases unstable at 100$^\circ$C, dissociate at surface.

**Initial oxidation regime.**

Deal - Grove: at small $x_{ox}$,

\[
x_{ox} = \frac{B}{A} (t + \tau)
\]

\[
\frac{dx_{ox}}{dt} = \frac{B}{A} = \text{const.}
\]

To explain this…

many models have been proposed.

It appears that SiO$_2$ / Si interface is not sharp.

Oxide grows not just at $x_{ox}$ but also at $x_{ox} = \frac{\delta x}{2}$
3.155J/6.152J

**Structure of SiO<sub>2</sub>**

![Diagram of SiO<sub>2</sub> structure with bridging oxygen and disorder]

- Amorphous tetrahedral network
- Fewer bridging O's, some non-bridging.
- Network modifiers B, P replace Si

**Effects of Dopants on Oxidation of Si → SiO<sub>2</sub>**

We will see segregation coefficient for crystal growth:

\[ k = \frac{c_{\text{solid}}^{\text{max}}}{c_{\text{liquid}}^{\text{max}}} \quad \text{generally} < 1 \]

Related parameter for segregation of impurity X on oxidation:

\[ m = \frac{C_X \text{ (in Si)}}{C_X \text{ (in SiO}_2\text{)}} \]

Impurity concentration profiles depend on \( m \), \( D^x \) in Si, \( D^x \) in SiO<sub>2</sub> and growth rate (not shown below):

- \( D'(\text{SiO}_2) < D'(\text{Si}) \) and \( m < 1 \) (oxide consumes X)
- \( D'(\text{SiO}_2) > D'(\text{Si}) \) and \( m > 1 \) (oxide rejects impurity, X)
Common dopants in Si enhance oxidation at higher concentration

Oxide thickness vs. wet oxidation time
For three different boron concentrations

Now, go grow some glass!