

Oxidation of Si

Why spend a whole lecture on oxidation of Si?

Ge has high μ_e , μ_h , Ge stable... ... but no oxide

GaAs has high μ_e and direct band... ... no oxide

Why SiO₂?

SiO₂ is **stable** down to 10⁻⁹ Torr, $T > 900^\circ\text{C}$

SiO₂ can be **etched** with HF which leaves Si unaffected

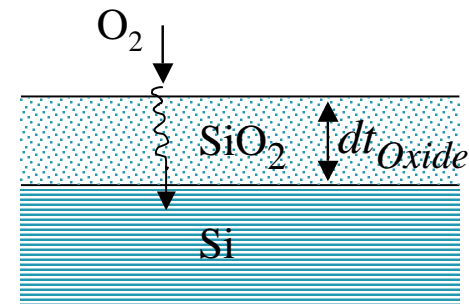
SiO₂ is a **diffusion barrier** for B, P, As

SiO₂ is good **insulator**, $\rho > 10^{16} \Omega\text{cm}$, $E_g = 8 \text{ eV}$!

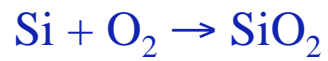
SiO₂ has high **dielectric breakdown** field, 500 V/ μm

SiO₂ growth on Si \Rightarrow **clean Si / SiO₂ interface**

because D^{Si} through SiO₂ $\ll D^{\text{Oxy}}$ through SiO₂



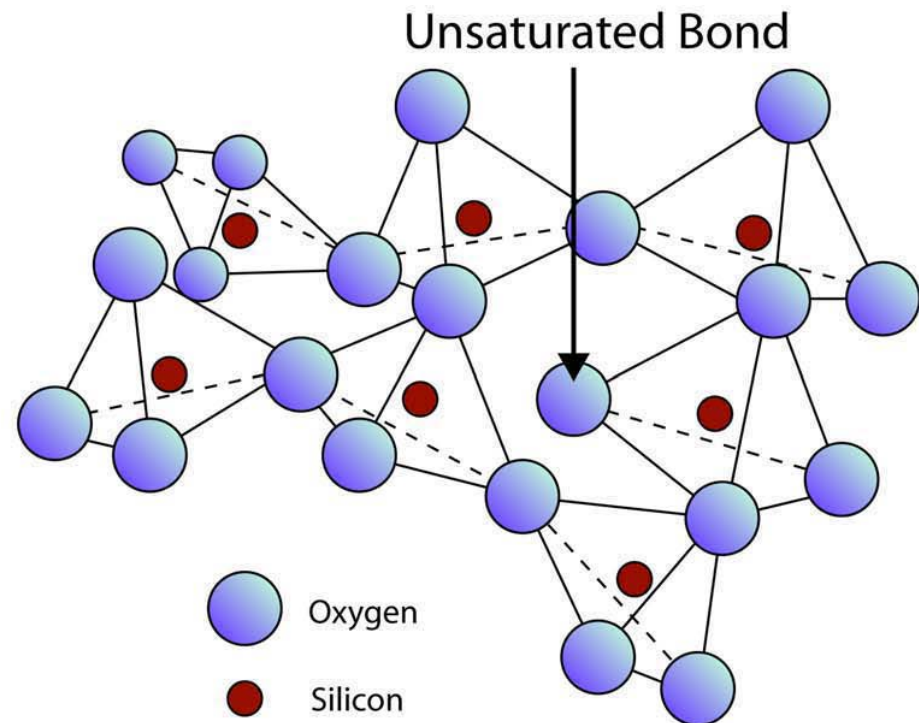
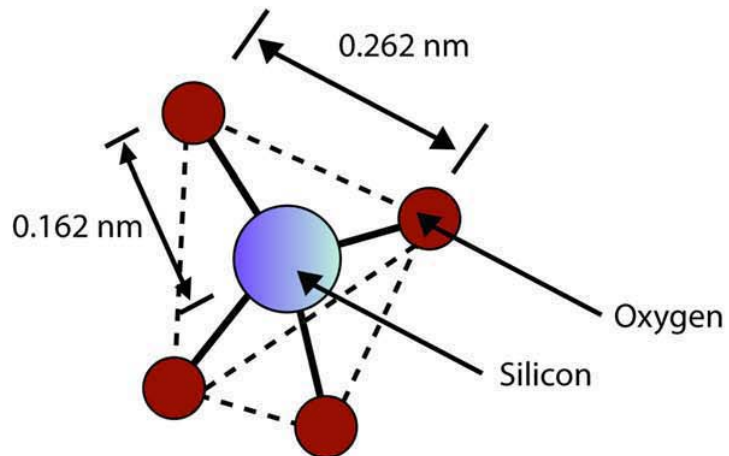
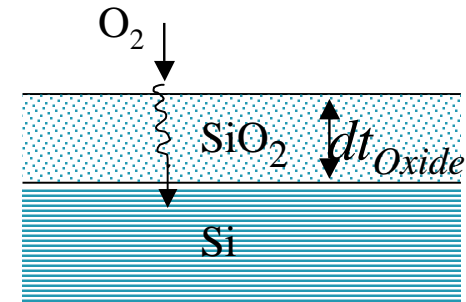
So SiO_2 growth occurs at *inside* surface

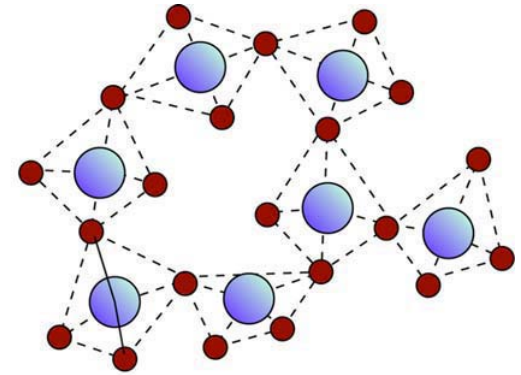
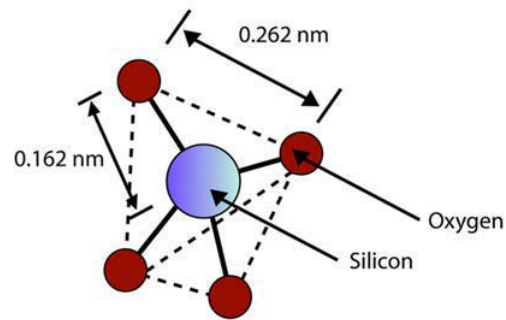
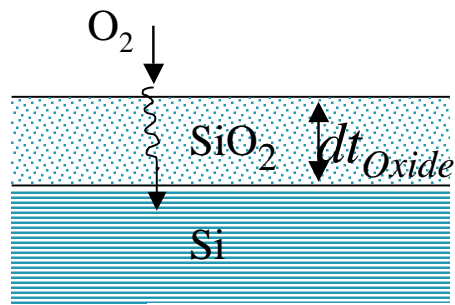


or

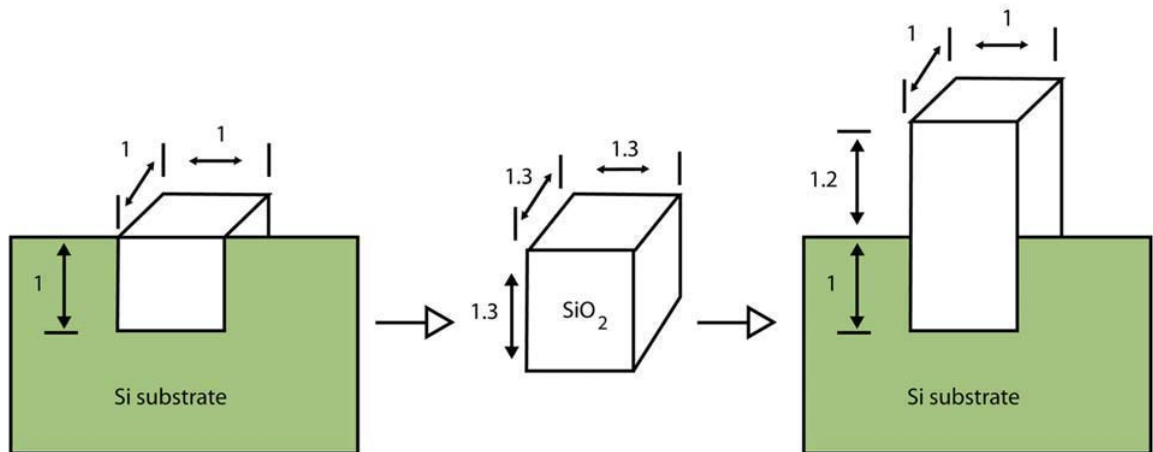


(faster growth,
more porous,
lower quality)





Extra free volume
in dangling bonds of
amorphous $SiO_2 \Rightarrow$



Implications different for field vs. patterned oxide.



Cleaning station for removing organic contaminants and 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 SiO_2 .

Device fabrication, especially MOS,
more difficult.

Depositing SiO_2 or Al_2O_3 is not clean.

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

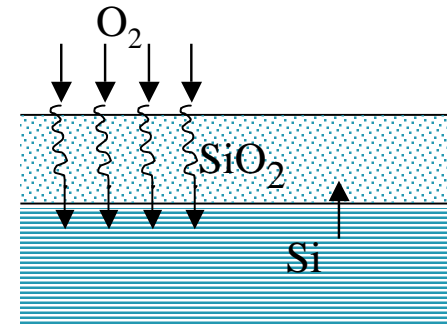
As a young researcher at Fairchild Semiconductor, he wrote the book on SiO₂ growth: the *Deal-Grove model*.

Deal-Grove model of silicon oxidation

SiO₂ growth occurs

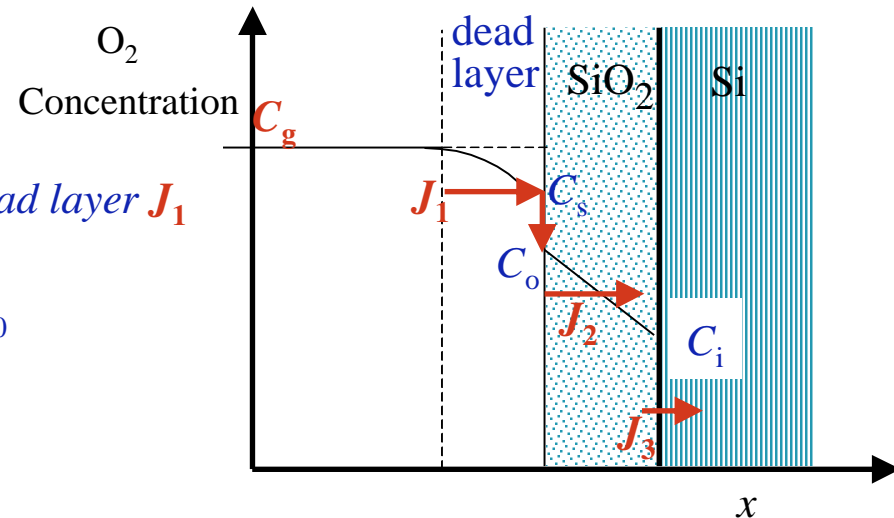
at Si / SiO₂ interface

because $D^{O_2}(SiO_2) \gg D^{Si}(SiO_2)$



Growth Process limited by

1. $P(O_2) = P_g \propto C_g$
2. Transport O₂ to SiO₂ surface across *dead layer* J_1
3. Adhesion of $C_s(O_2)$ at SiO₂ surface C_0
4. Diffusion O₂ through SiO₂ J_2
5. Chemical reaction rate J_3



Deal-Grove model of silicon oxidation

Oxide growth rate

Ideal gas law: $P_g V = NkT$

$$\frac{N}{V} = C_g = \frac{P_g}{kT}$$

$$J_1 > D \frac{(C_g - C_s)}{t_{\text{dead layer}}}$$

Turbulence =>

$$J_1 = h_g(C_g - C_s)$$

$$C_0 = HP_s = Hk_B T C_s$$

Henry's law

$$J_2 = D^{O_2}(\text{SiO}_2) \frac{C_s - C_0}{x_{\text{ox}}}$$

Diffusion ($D \text{ cm}^2/\text{s}$)

$$J_3 = k_i C_i$$

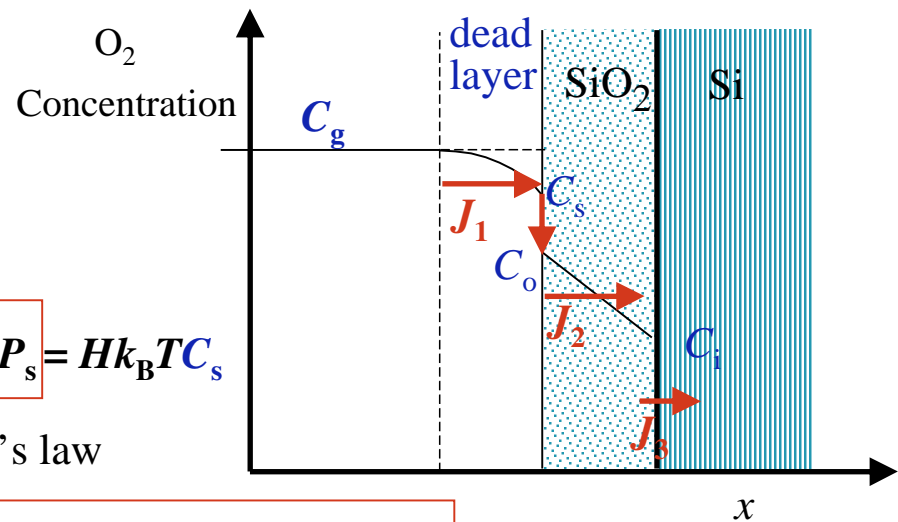
rate constant
 $k_i \text{ (cm/s)}$

Equate ideal gas + J_1
to J_2 + Henry

Equate J_2 + Henry to J_3

$$\Rightarrow C_i = f_n(P_g, h_g, H, D^{O_2}, x_{\text{oxide}}, k_i)$$

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Deal-Grove model of silicon oxidation

$$J_1 = J_2 = J_3$$

$$\Rightarrow C_i = f_n(P_g, h_g, H, D^{O_2}, x_{oxide}, k_i)$$

$$C_i = \frac{HP_g / k_i}{\frac{1}{h} + \frac{x_{ox}}{D^{O_2}} + \frac{1}{k_i}}$$

mass
transport

J_1

Diffusion

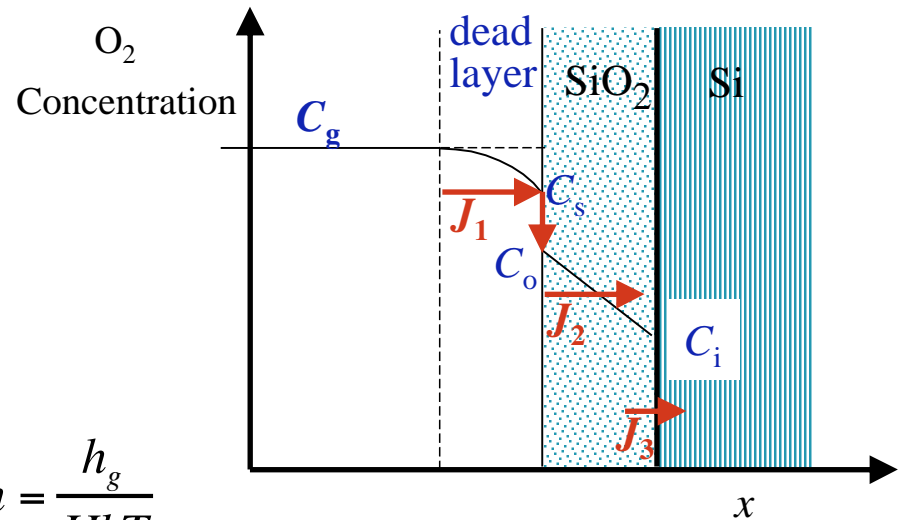
J_2

Reaction

J_3

$$h = \frac{h_g}{HkT}$$

($k_i = k_s$ in text)



Slowest process controls concentration of oxygen at interface...

$$C_i = \frac{HP_g / k_i}{\frac{1}{h} + \frac{x_{ox}}{D^{O_2}} + \frac{1}{k_i}}$$

$$h = \frac{h_g}{HkT} \text{ very large}$$

Limits:

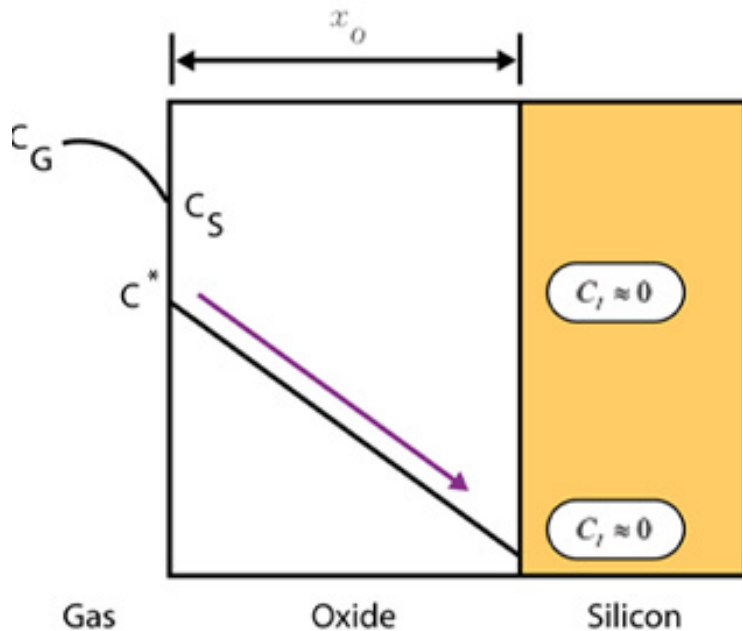
Growth limited by: mass transport, diffusion, reaction

Diffusion limited:

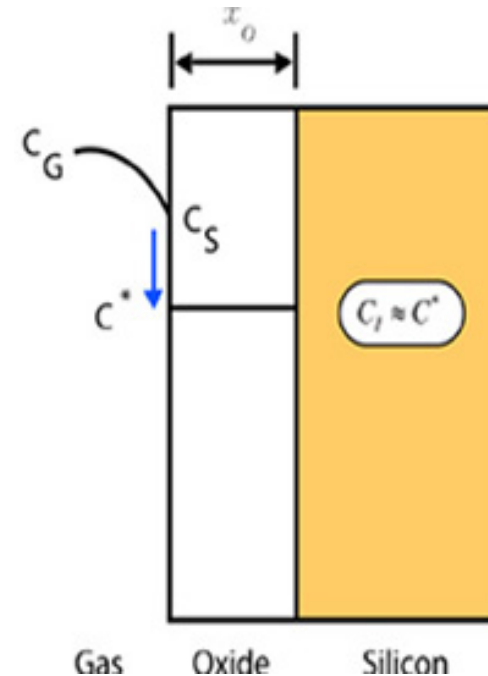
$$D^{O_2}/x_{ox} < k_i, h_g,$$

Reaction-rate limited:

$$k_i < h_g, D^{O_2}/x_{ox}$$



$$C_i = \frac{HP_g D^{O_2}}{k_i x_{ox}}$$



$$C_i = HP_g$$

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

Oxide growth rate

$$\text{Rate of growth} = \frac{dx_{\text{ox}}}{dt} = \frac{J_3}{N} = \frac{C_i k_i}{N},$$

$$C_i = \frac{HP_g / k_i}{\frac{1}{h} + \frac{x_{\text{ox}}}{D^{O_2}} + \frac{1}{k_i}}$$

(N = # O_2 molecules incorporated / cm^3)

$N = 2.2 \times 10^{22} / \text{cm}^3$, dry
 $4.4 \times 10^{22} / \text{cm}^3$, H_2O

$$\frac{dx_{\text{ox}}}{dt} = \frac{HP_g / N}{\frac{1}{h} + \frac{x_{\text{ox}}}{D} + \frac{1}{k_i}}$$

rate depends on x_{oxide}

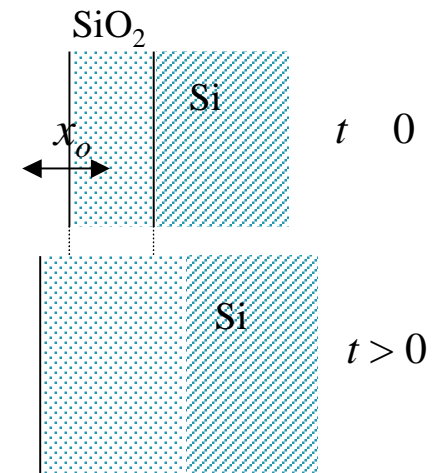
$$\int_{x_0}^{x_{\text{ox}}} \left(\frac{1}{h} + \frac{x_{\text{ox}}}{D} + \frac{1}{k_i} \right) dx_{\text{ox}} = \int_0^t \frac{HP_g}{N} dt$$

$$x_{\text{ox}}^2 + Ax_{\text{ox}} = B(t + \tau)$$

$$A = 2D \left(\frac{1}{h} + \frac{1}{k_i} \right) \quad (\text{length})$$

$$B = 2DHP_g / N \quad \left(\frac{\text{length}^2}{\text{time}} \right)$$

$$\tau = (x_0^2 + Ax_0) / B \quad (\text{time})$$



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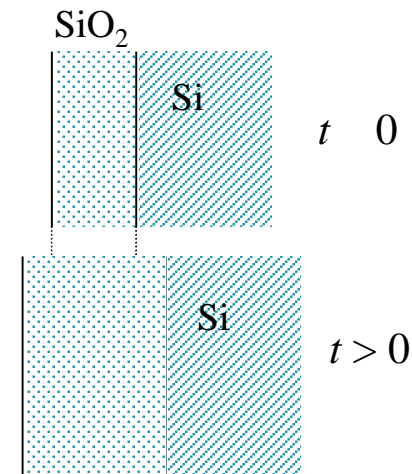
$$x_{\text{ox}}^2 + Ax_{\text{ox}} = B(t + \tau)$$

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

$$A = 2D \left(\frac{1}{h} + \frac{1}{k_i} \right)$$

$$B = 2DH P_g / N$$

$$\tau = (x_0^2 + Ax_0) / B$$



Rate constants A and B known experimentally;
both $\propto D = D_0 e^{-E_a/kT}$

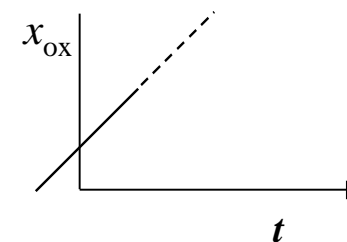
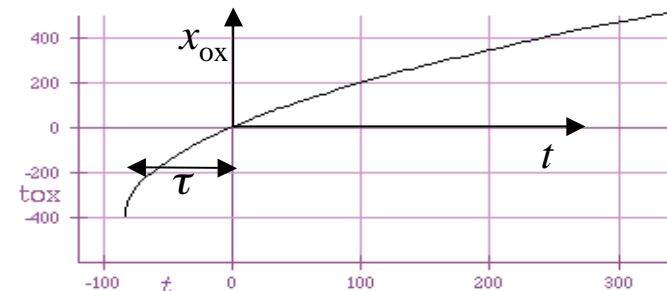
Parabolic and linear growth rates

Thick oxide \Rightarrow parabolic rate constant, B

$$x_{\text{ox}}^2 \gg Ax_{\text{ox}} \xrightarrow{\text{Quad.Eq}} x_{\text{ox}} = \sqrt{B(t + \tau)}$$

Thin oxide \Rightarrow linear rate constant, B/A

$$x_{\text{ox}}^2 \ll Ax_{\text{ox}} \xrightarrow{\text{Quad.Eq}} x_{\text{ox}} \cong \frac{B}{A}(t + \tau)$$



Oxidation coefficients for silicon

Temperature (°C)	Dry			Wet (640 torr)	
	A (μm)	B (μm ² /hr)	τ (hr)	A (μm)	B (μm ² /hr)
800	0.370	0.0011	9	—	—
920	0.235	0.0049	1.4	0.50	0.203
1000	0.165	0.0117	0.37	0.226	0.287
1100	0.090	0.027	0.076	0.11	0.510
1200	0.040	0.045	0.027	0.05	0.720

$$D^{\text{O}_2}(\text{SiO}_2) <$$

$$D^{\text{H}_2\text{O}}(\text{SiO}_2)$$

700-1200°C, 1 atm, 0.1 μm / hr
 ⇒ **dry oxide**, denser,
 use for **gate oxide**.

750-1100°C, 25 atm, 1 μm / hr
 ⇒ **wet oxide**,
 more porous, poorer diffusion barriers;
 use for **etch oxide, field oxide**.

Dry O₂ + 1-3% Cl; Cl is a metal getter ➡ cleaner oxide.

Exercise: calculate x_{ox} grown for 1 hr. in *dry* oxidation at 1100 °C.

Oxidation coefficients for silicon					
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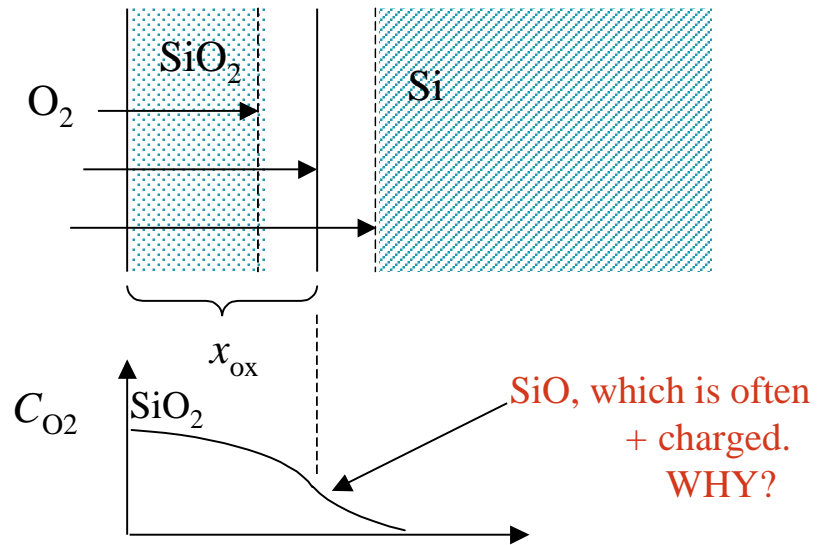
From table, $A = 0.09 \mu\text{m}$, $B = 0.027 \mu\text{m}^2/\text{hr}$, $\tau = 0.076 \text{ hr}$.

$$x_{\text{ox}} = \frac{-A + \sqrt{A^2 + 4B(t + \tau)}}{2} = 0.14 \mu\text{m} \quad (0.1 - 1.0 \mu\text{m} / \text{hr} \text{ is typical})$$

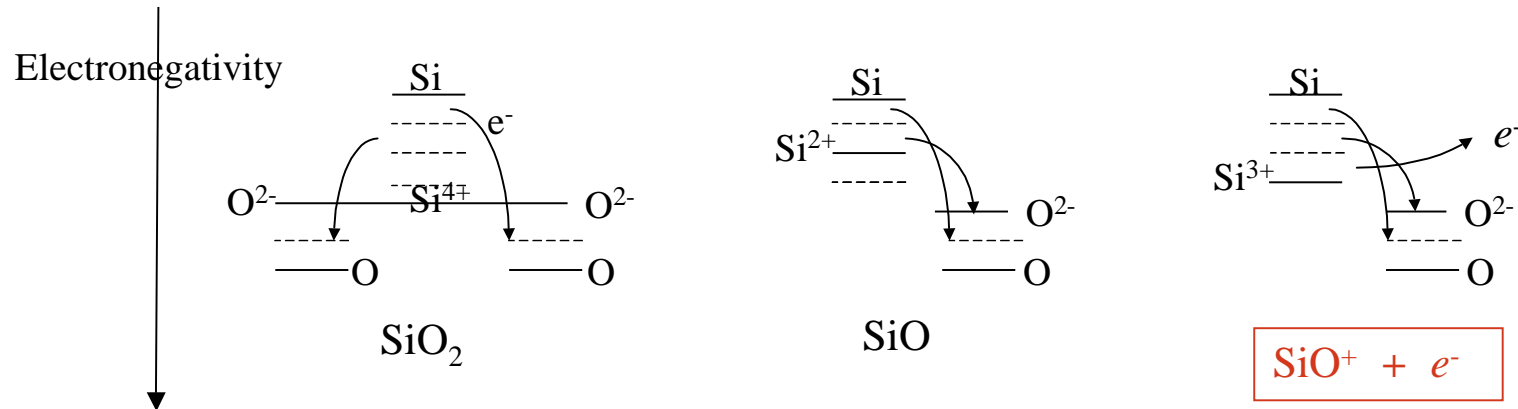
This is the oxide thickness grown over any thin native oxide present.

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

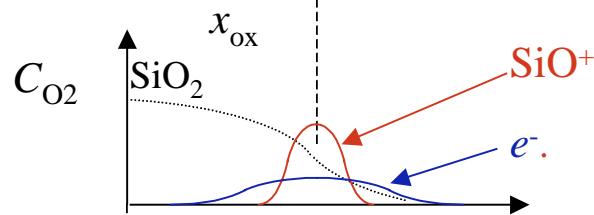
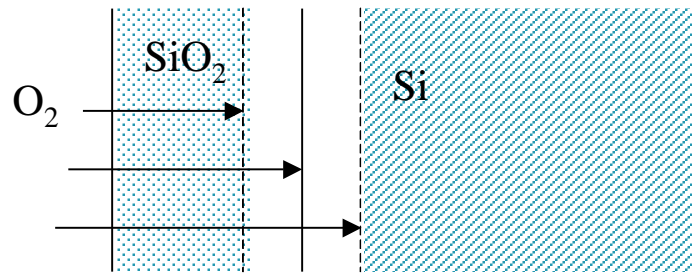
SiO₂/Si interface, local charges



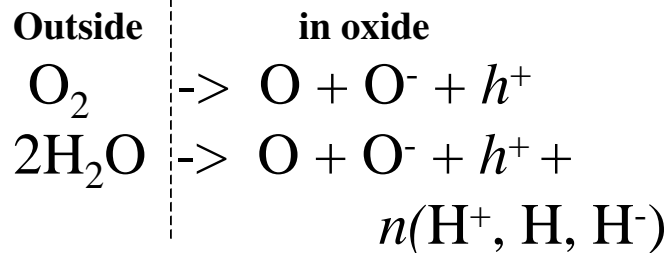
**Oxide near the interface
is a sub oxide, SiO_x, $x < 2$.**



SiO₂/Si interface and dry vs. wet oxidation



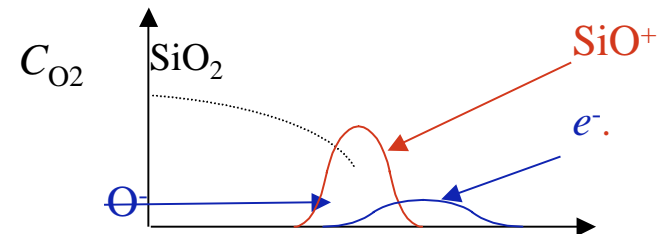
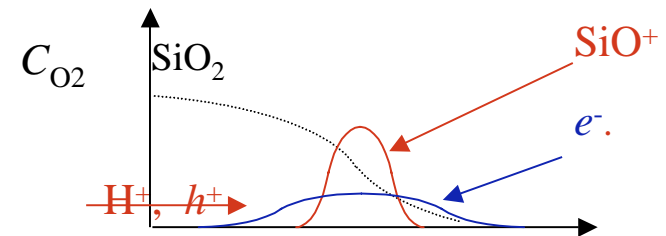
Gases unstable at 100°C, dissociate at surface.



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Which species diffuse quickly?

Large	small
O ⁻ , O, H ⁻ , H, H ⁺ , h ⁺	
Slow	fast



3.155J/6.152J

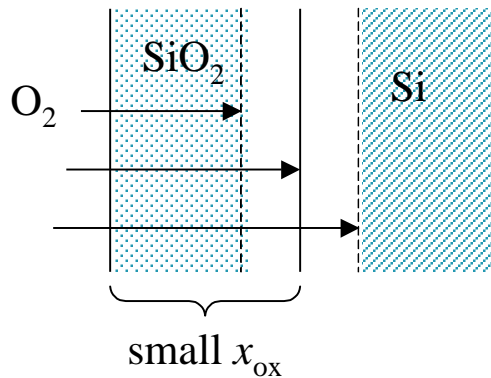
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Initial oxidation regime.

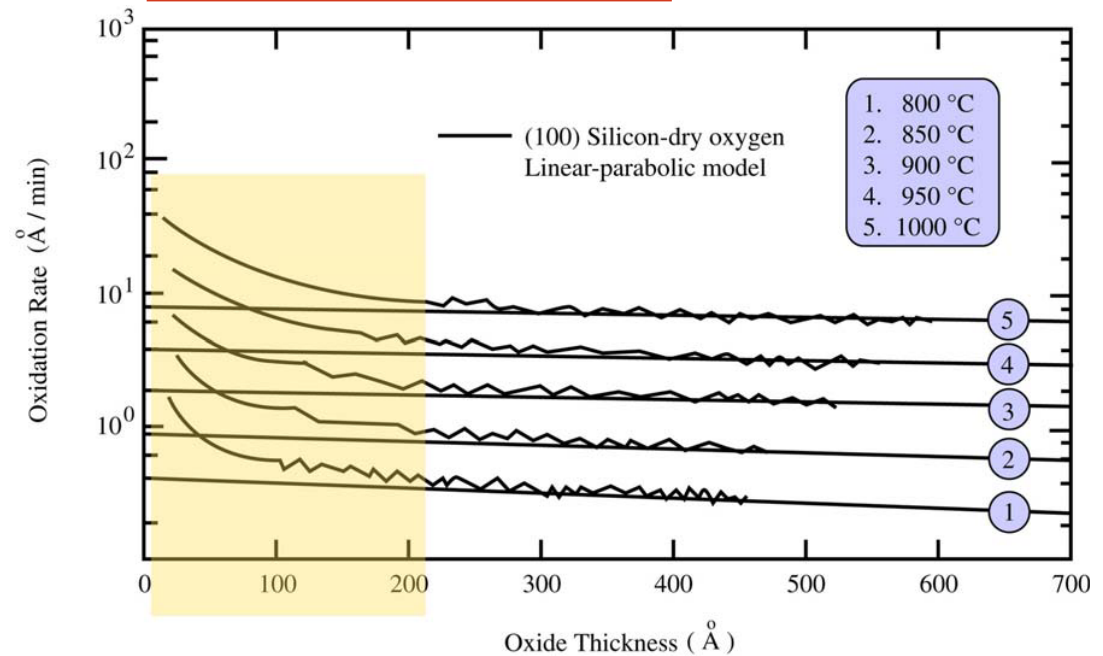
Deal - Grove: at small x_{ox} ,

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

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



$$x_{\text{ox}}^2 + Ax_{\text{ox}} = B(t + \tau)$$



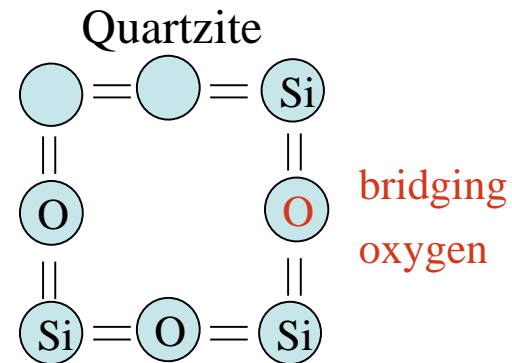
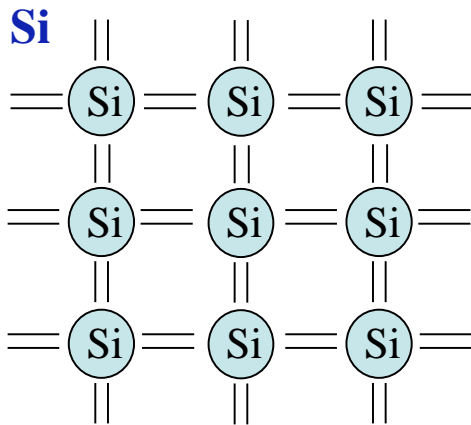
To explain this...

many models proposed.

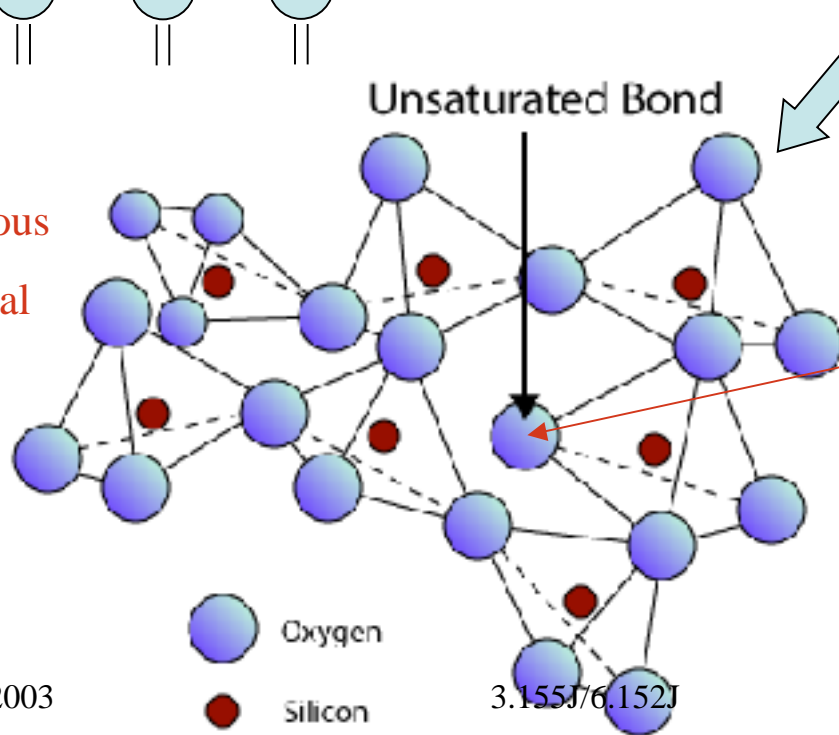
It appears that SiO₂ / Si interface is not sharp.

Oxide grows not just at x_{ox} but also at $x_{\text{ox}} - \frac{\delta x}{2}$

Structure of SiO₂



Amorphous
tetrahedral
network



disorder

fewer bridging O's,
some non-bridging.

Network modifiers B, P
replace Si

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3.155/6.152J

Effects of Dopants on Oxidation of Si \rightarrow SiO₂

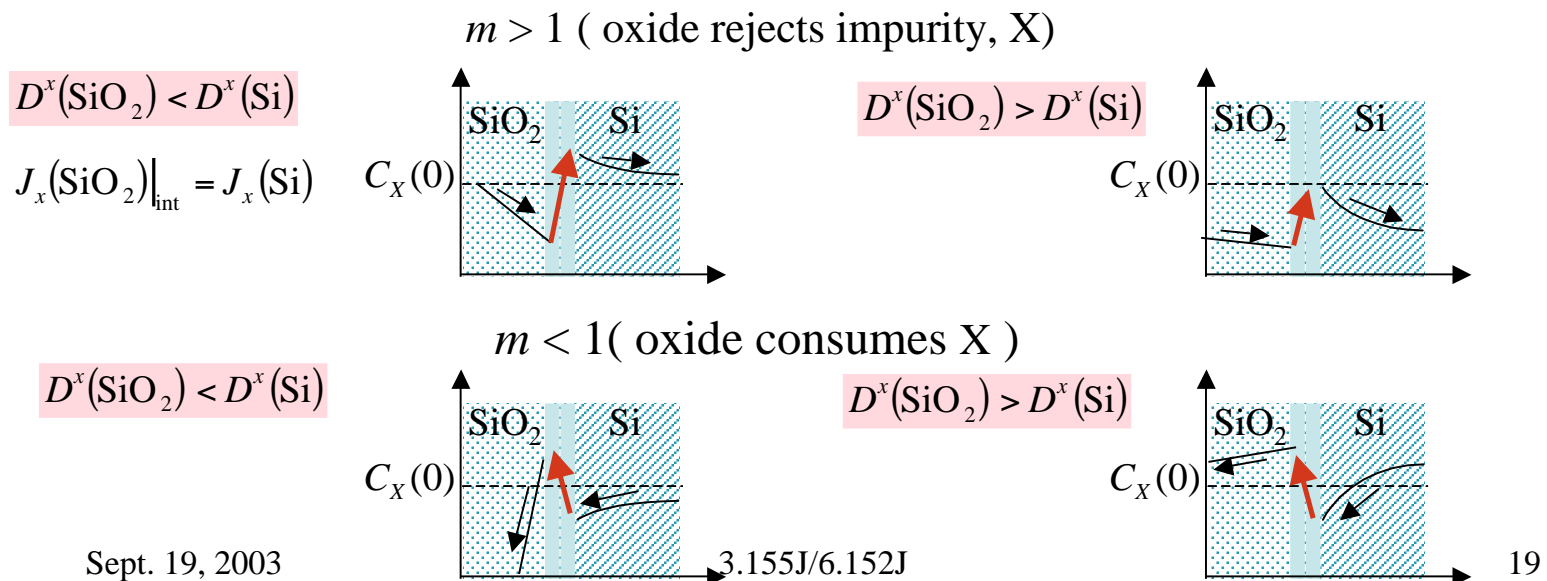
We will see segregation coefficient for crystal growth: $k = \frac{C_S}{C_L}$ generally < 1

Related parameter

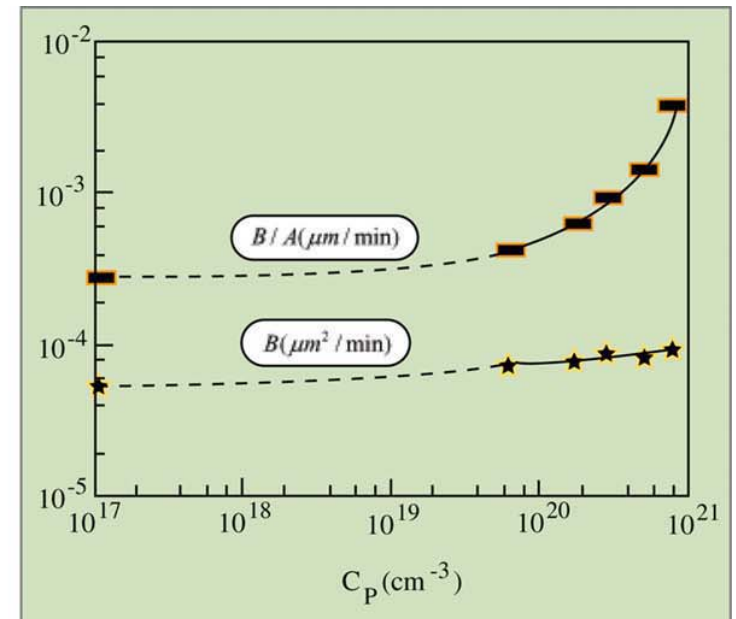
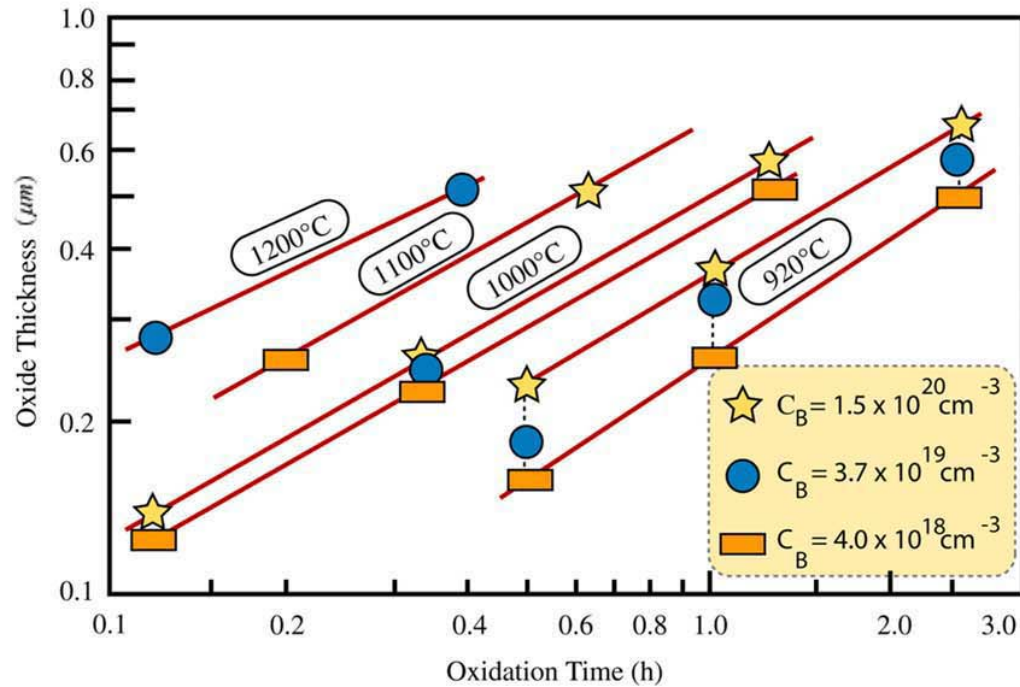
for segregation of impurity X on oxidation:

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

Impurity concentration profiles depend on m , D^x in Si, D^x in SiO₂ and growth rate
(not shown below):



Common dopants in Si enhance oxidation at higher concentration



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

Linear, B/A , and parabolic, B , rate constants
vs. **phosphorus** concentration.