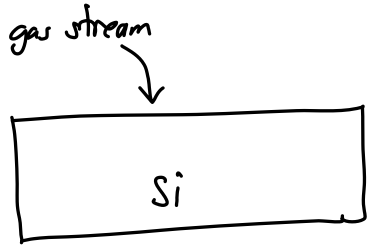
Lecture 10: Oxidation Theory

- Announcements:
  - Correction to HW#3 broadcast by email
  - HW#3 now due on Friday, at 5 p.m.
- ------------------------------------
- Lecture Topics:
  - Oxidation
  - Oxidation Theory
  - Oxidation Graphs
  - Dopant Redistribution During Oxidation
- ------------------------------------
- Last Time:

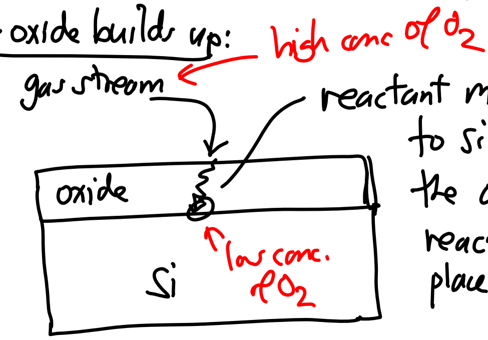
Modeling: Deal-Grove or "Linear-Parabolic" Model

① Initially: (no oxide @ surface)

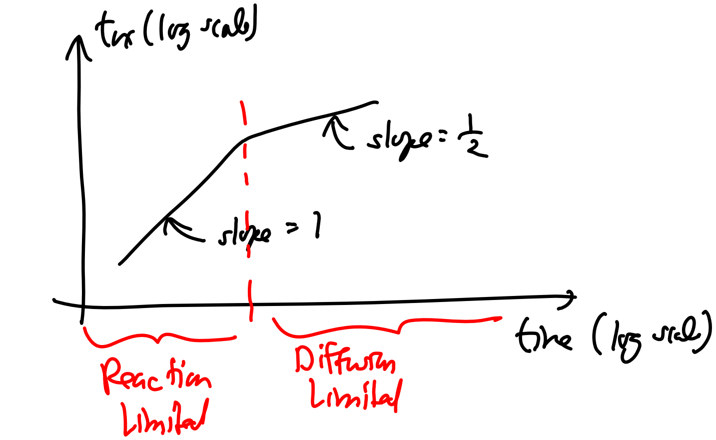


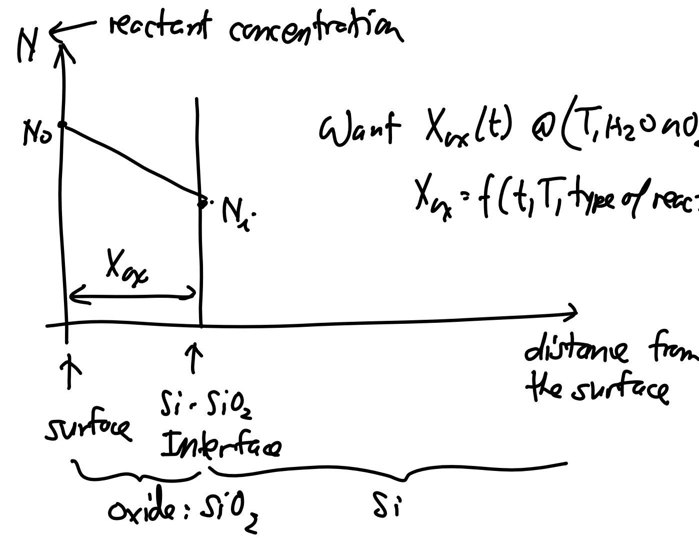
growth rate is determined by the reaction rate → largely linear

② As oxide builds up:



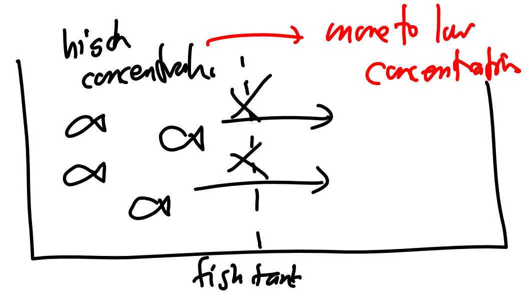
reactant must diffuse to Si surface where the oxidation reaction takes place





Want $X_{ox}(t)$ @ $(T, H_2O \text{ or } O_2)$

$X_{ox} = f(t, T, \text{type of reactant}, \ldots)$



N_o = reactant conc. @ oxide surface [in cm^{-2}]

N_i = reactant " " Si-SiO_2 interface

J = reactant flux = $-D \frac{\partial N(x,t)}{\partial x}$ [Fick's 1st Law of Diffusion]

diffusion coeff. [in $\mu m/hr$ or m/s]

In the SiO_2:

$$\boxed{J = D\frac{(N_o - N_i)}{X_{ox}}} = \text{constant} \qquad (1)$$

[in # particles/($cm^2 \cdot s$)]

assumption that the reactant does not accumulate in the oxide

At the Si-SiO_2 interface:

oxidation rate $\propto N_i$ $\therefore$ $J \propto N_i$

$$\boxed{J = k_s N_i} \qquad (2)$$

reaction rate const. @ Si-SiO_2 interface

Combining (1) & (2):

$$\left[N_i = \frac{J}{k_s}\right] \Rightarrow J = D\left(\frac{N_o - \frac{J}{k_s}}{X_{ox}}\right)$$

$$\therefore \boxed{J = \frac{DN_o}{X_{ox} + \frac{D}{k_s}} = \text{flux of reactants}}$$

Find an expression for $X_{ox}(t)$:

Rate of change of oxide layer thickness w/ time $\Big\} = \frac{dX_{ox}}{dt} = \frac{J}{M} = \frac{(DN_o/M)}{(X_{ox} + D/k_s)}$

oxidizing flux

(3)

M = # molecules of oxidizing species incorporated into a unit volume of oxide

$= 2.2\times10^{22}\ cm^{-3}$ for O_2

$= 4.4\times10^{22}\ cm^{-3}$ for H_2O

Solve (3) for $X_{ox}(t)$: [Initial Cond.: $X_{ox}(t=0) = X_i$]

$$\frac{dX_{ox}}{dt} = \frac{DN_o/M}{X_{ox} + D/k_s}$$

$$\int_{X_i}^{X_{ox}(t)} \left(X_{ox} + \frac{D}{k_s}\right) dX_{ox} = \int_0^t \frac{DN_o}{M} dt$$

$$\frac{1}{2}X_{ox}^2 + \frac{D}{k_s}X_{ox} - \frac{1}{2}X_i^2 - \frac{D}{k_s}X_i = \frac{DN_o}{M}t$$

$$t = \frac{1}{2}\frac{M}{DN_o}X_{ox}^2 + \frac{M}{DN_o}\frac{D}{k_s}X_{ox} - \frac{1}{2}\frac{M}{DN_o}X_i^2 - \frac{M}{DN_o}\frac{D}{k_s}X_i$$

$$t = \frac{X_{ox}^2}{B} + \frac{X_{ox}}{(B/A)} - \tau$$

where $B = \frac{2DN_o}{M} \triangleq$ parabolic rate constant

$\frac{B}{A} = \frac{N_o k_s}{M} \triangleq$ linear rate constant

τ

$$* \quad A = B\left(\frac{M}{N_0 k_s}\right) = \left(\frac{2D\cancel{N_0}}{\cancel{M}}\right)\left(\frac{\cancel{M}}{\cancel{N_0} k_s}\right) \Rightarrow A = \frac{2D}{k_s}$$

$$\tau = \frac{X_i^2}{B} + \frac{X_i}{(B/A)}$$

Solve for $X_{ox}(t)$:

$$\frac{X_{ox}^2}{B} + \frac{X_{ox}}{(B/A)} - \tau - t = 0$$

Quadratic Formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$X_{ox}(t) = \frac{B}{2}\left\{\frac{1}{-(B/A)} \pm \frac{1}{(B/A)}\left(1 + \frac{4B}{A^2}(t+\tau)\right)^{1/2}\right\}$$

choose (+), because this cannot physically be (−)!

additional time req'd to get from $X_i \rightarrow X_{ox}$

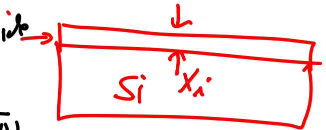
time req'd to grow X_i

$$\boxed{X_{ox}(t) = \frac{A}{2}\left\{\left[1 + \frac{4B}{A^2}(t+\tau)\right]^{1/2} - 1\right\}}$$

where $A = \frac{2D}{k_s}$

$B = \frac{2DN_0}{M}$

$\tau = \frac{X_i^2}{B} + \frac{X_i}{(B/A)}$



X_i: initial oxide thickness

$D = D_0 \exp\left(-\frac{E_A}{kT}\right) \Rightarrow$ governed by an Arrhenius relationship

↳ heavily temp. dep.

For short times:

$\left[(t+\tau) \ll \frac{A^2}{4B}\right] \Rightarrow \boxed{X_{ox}(t) = \underbrace{\left(\frac{B}{A}\right)}_{\text{linear growth rate constant}}(t+\tau)}$

use Taylor expansion (first term after 1's cancel)

↳ oxidation growth limited by the reaction @ the Si-SiO_2 interface (and not by diffusion)

For long oxidation times:

$$\left[(t+\tau) \gg \frac{A^2}{4B}\right] \Rightarrow \boxed{x_{ox}(t) = \sqrt{B(t+\tau)} \approx \sqrt{Bt}}$$

$t \gg \tau$

parabolic rate const.

→ oxide growth diffusion limited

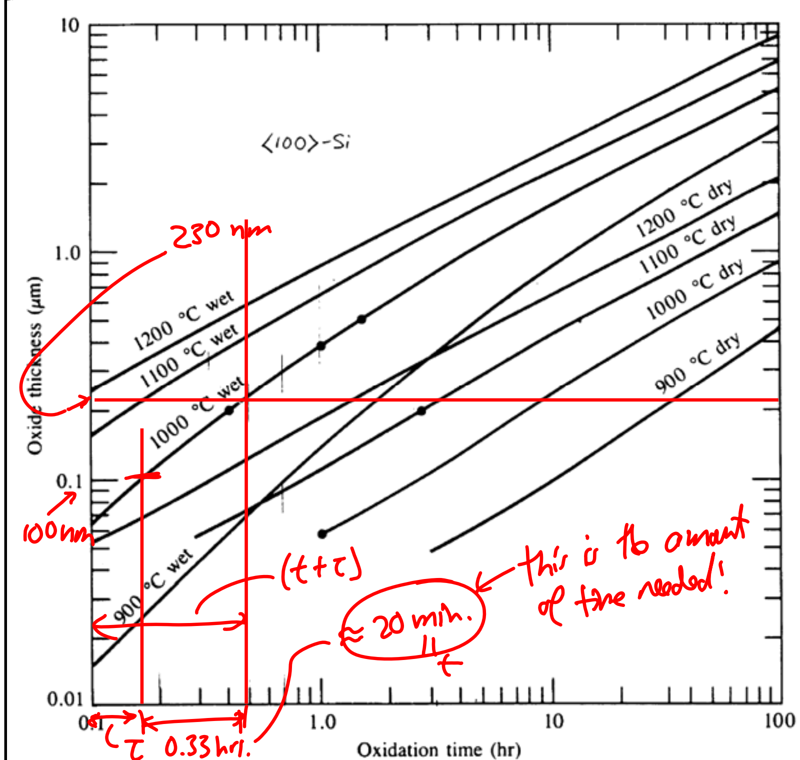
In summary, oxide thickness is dependent on:

1. time
2. temperature (thru D)
3. partial pressure of oxidizing species ($\propto N_0$)

Also dependent on:

4. reactant: dry O_2
   water → faster oxidation, since it has a higher solubility in SiO_2 than O_2 → manifested in D
5. crystal orientation:
   <111> ← faster, because there are more bonds available @ the Si-surface
   <100> ← less interface traps
   → smaller # of unsatisfied Si-bonds @ the Si-SiO_2 interface
6. Impurity Doping
   P: increases linear rate const.; no effect on parabolic " } faster initial growth ↓ surface reaction rate increased
   B: no effect on linear rate const.; increases the parabolic } faster growth even on initial oxide ↳ diffusion faster

Oxidation Graph

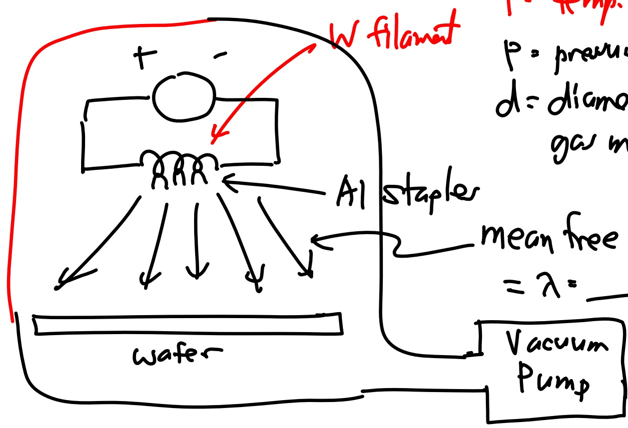


Ex: Starting oxide thickness: $X_i = 100\,nm$
Want to do wet oxidation @ 1000°C to achieve $X_{ox} = 230\,nm$.
What is the time t required for this?

Film Deposition

- Physical Deposition
  - Evaporation
  - Sputtering
- Chemical Deposition
  - LPCVD
  - PECVD
- Epitaxy

Filament Evaporation System



mean free path $= \lambda = \dfrac{kT}{\sqrt{2}\pi P d^2}$

k: Boltzmann const.
T: temp.
P = pressure
d = diameter of gas molecule