Lecture 10: Oxidation II (Theory)

- Announcements:
  - HW#4 due tomorrow (Wednesday) morning
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- Lecture Topics:
  - Oxidation
  - Oxidation Theory
  - Oxidation Graphs
  - Dopant Redistribution During Oxidation
- ---
- Last Time:

Thermal Oxidation of Silicon

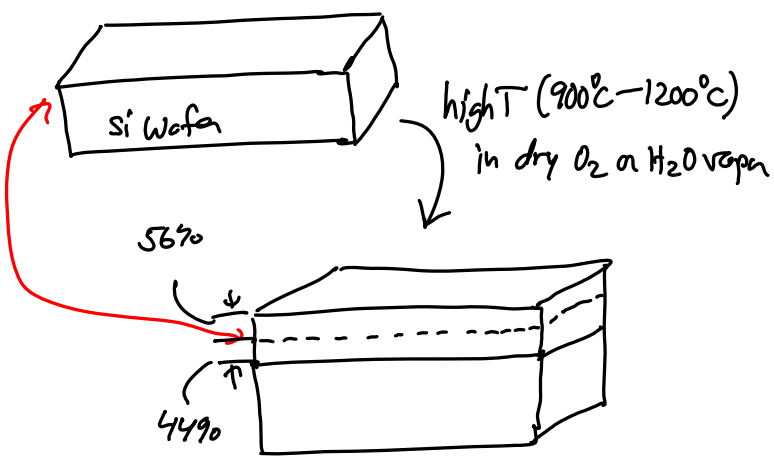
For dry O_2:

$$Si + O_2 \rightarrow SiO_2$$

For Water Vapor:

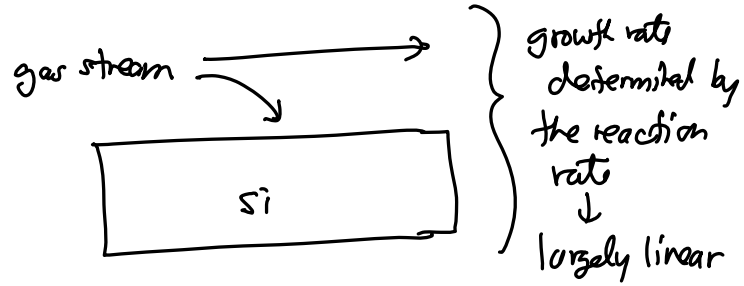
$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

Schematically:

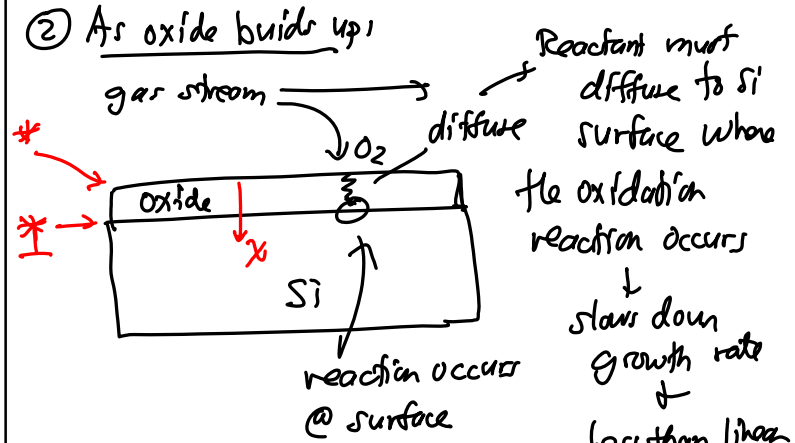


Modeling: Deal-Grove or "Linear-Parabolic" Model

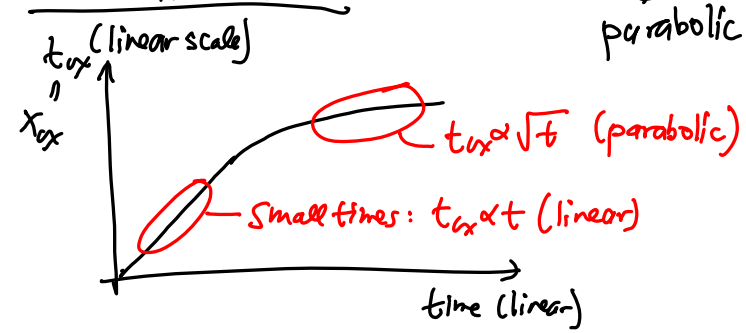
① Initially: (no oxide on the surface)

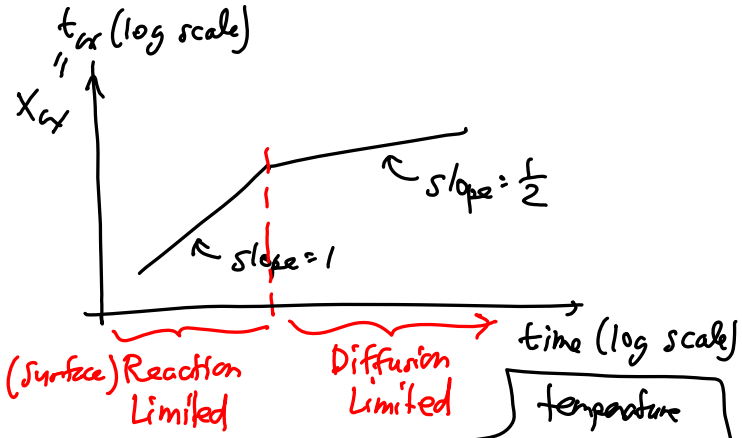


② As oxide builds up:



The Qualitative Result:

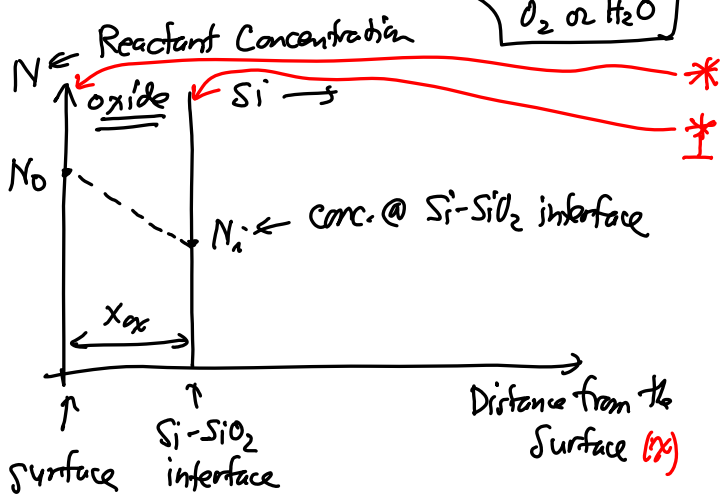


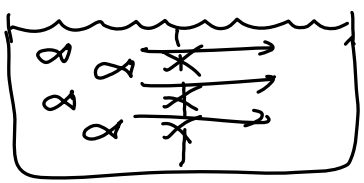


Derive Expressions for $X_{ox} = f(t, T, \text{reactant})$

temperature

O_2 or H_2O





N_o = reactant conc. @ oxide surface [in cm^{-3}]

N_i = reactant conc. @ Si-SiO_2 interface

$$J = \text{reactant flux} = -D \frac{\partial N(x,t)}{\partial x}$$

diffusion coeff. [in $\mu m^2/hr$ or cm^2/s]

[Fick's 1st Law of Diffusion]

In the SiO_2:

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

assumption that the reactant does not accumulate in the oxide

At the Si-SiO_2 interface:

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

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

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 $X_{ox}(t)$:

oxidizing flux

Rate of Change of oxide layer thickness w/ time $\left\}\ \dfrac{dX_{ox}}{dt} = \dfrac{J}{M} = \dfrac{(DN_o/M)}{(X_{ox} + D/k_s)}\right.$ (3)

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: $X_{ox}(t=0) = X_i$]

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

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

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

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

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

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

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

$$A = B\left(\frac{M}{N_o k_s}\right) = \left(\frac{2D\cancel{N_o}}{\cancel{M}}\right)\left(\frac{\cancel{M}}{\cancel{N_o}k_s}\right) \rightarrow A = \frac{2D}{k_s}$$

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

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

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

Quadratic Formula:

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

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

Choose (+), because this cannot physically be (−).

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

time required to grow X_i

additional time (beyond t) req'd to get from $X_i \to X_{ox}$

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

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

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

X_i: initial oxide thickness

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

activation energy

thermal energy

↳ heavily temp. dep.

Take some cases to simplify:

Case ①: Short Times → oxidation growth rate limited by surface reaction @ Si-SiO_2 interface (not by diffusion)

$$\left[(t+\tau) \ll \frac{A^2}{4B}\right] \Rightarrow$$

Taylor expansion $\left[1 + \frac{4B}{A^2}(t+\tau)\right]^{1/2}$ (small)

Binomial Thm: $1 + \frac{1}{2}\left(\frac{4B}{A^2}\right)(t+\tau)$

$$\boxed{X_{ox}(t) = \left(\frac{B}{A}\right)(t+\tau)}$$

linear growth rate constant

Case ②: Long oxidation time

↳ built up oxide → diffusion limit

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

$t \gg \tau$

Parabolic Rate Const.

In summary, oxide thickness is dependent upon:

① time
② temperature (thru D)
③ partial pressure of oxidizing species (∝ N_0)

Also, dependent upon:

④ reactant: dry O_2

water → faster oxidation rate, 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 (Si's) available @ Si surface

⟨100⟩ ← slower, but has the advantage of fewer interface traps → charging ✗

↳ smaller # of unsatisfied Si-bonds @ the Si-SiO_2 interface

⑥ Impurity Dopings

P: increases the linear rate const. } faster initial growth
no effect on parabolic " " }
↓
surface reaction rate increased!

B: no effect on linear rate const. } faster growth over an initial oxide
increase the parabolic " " }
↳ diffusion faster

$\boxed{\text{Graphs}}$

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 needed for this?