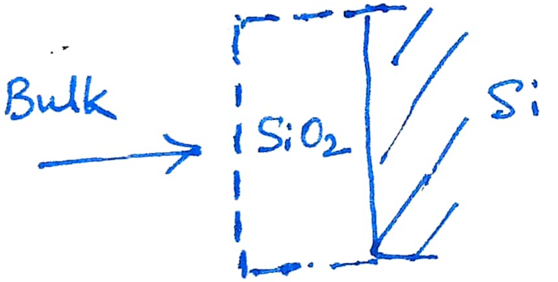
DEAL - GROVE MODEL

Growth of oxide layer on the surface of a material
(Thermal oxidation of silicon to SiO_2)



(i) Diffusion from bulk to the surface
(ii) Diffusion through the existing oxide layer
(iii) Reaction with the substrate (Si in this case)

Reaction is first order
or pseudo-first order as Si is in excess.

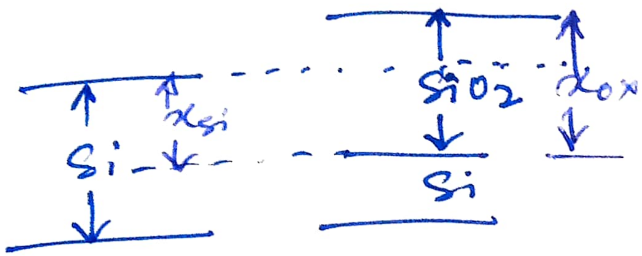
$$\left.\begin{aligned} J_{(i)} &= k_g (C_g - C_s) \\ J_{(ii)} &= D_{ox} \frac{(C_s - C_i)}{x} \\ J_{(iii)} &= k_i C_i \end{aligned}\right\} \Rightarrow (C_g - C_s) + (C_s - C_i) + C_i = \frac{J_{(i)}}{k_g} + \frac{J_{(ii)}x}{D_{ox}} + \frac{J_{(iii)}}{k_i}$$

At steady state $J_{(i)} = J_{(ii)} = J_{(iii)} = J$

$$C_g = J\left[\frac{1}{k_g} + \frac{x}{D_{ox}} + \frac{1}{k_i}\right]$$

$$\Leftarrow \boxed{\frac{C_g}{\frac{1}{k_g} + \frac{x}{D_{ox}} + \frac{1}{k_i}} = J \propto N_i \frac{dx}{dt}}$$

Thickness of Si consumed, and SiO_2 formed are not same



$$A\, x_{Si} \left\{ \begin{array}{c} \text{Atomic Density} \\ \text{of Si} \end{array} \right\} = A\, x_{ox} \left\{ \begin{array}{c} \text{Molecular} \\ \text{density of} \\ SiO_2 \end{array} \right\}$$

Since ~~the~~ stoichiometrically
$$Si + O_2 \rightarrow SiO_2$$

Atomic density of Si

$$= \left(\begin{array}{c} \text{Bulk density} \\ \text{of Si} \end{array} \right) \times \frac{6.023 \times 10^{23}}{\text{Atomic wt. of Si}}$$

$$= 2.3296 \frac{gm}{cc} \times \frac{6.023 \times 10^{23} \text{ atoms/mole}}{28 \frac{gm}{mole}}$$

$$= 5 \times 10^{22} \frac{\text{atoms}}{cc}$$

$$x_{Si} = x_{ox} \frac{2.3 \times 10^{22} \text{ molecules/cc}}{5 \times 10^{22} \text{ atoms/cc}}$$

$$= 0.46\, x_{ox}$$

$\Rightarrow$ 1 μm Si oxidized
$\equiv$ 2.17 μm SiO_2 produced

For a Si sphere with 1 μm diameter, the converted SiO_2 sphere will have a diameter of 1.3 μm.

Considering gas phase outside oxide layer as well-mixed,

$$k_i C_i = \frac{D}{x}(C_s - C_i)$$

$$\Rightarrow \quad C_i = \frac{C_s}{1 + \frac{k_i}{D} x}$$

And

If M = No. of oxidant molecules incorporated per unit volume of oxide grown,

$$= \left(\frac{\text{Mass of } SiO_2}{\text{Vol.}}\right) \times \frac{6.023 \times 10^{23}}{\text{mol. wt. of } SiO_2}$$

$$= \frac{2.2 \text{ gm/cc}}{60 \text{ gm/mole}} \times 6.023 \times 10^{23} \frac{\text{molecules}}{\text{mole}}$$

$$= 2.3 \times 10^{22} \frac{\text{molecules}}{\text{cc}}$$

Growth Rate

$$\frac{dx}{dt} = \frac{k_i C_i}{M}$$

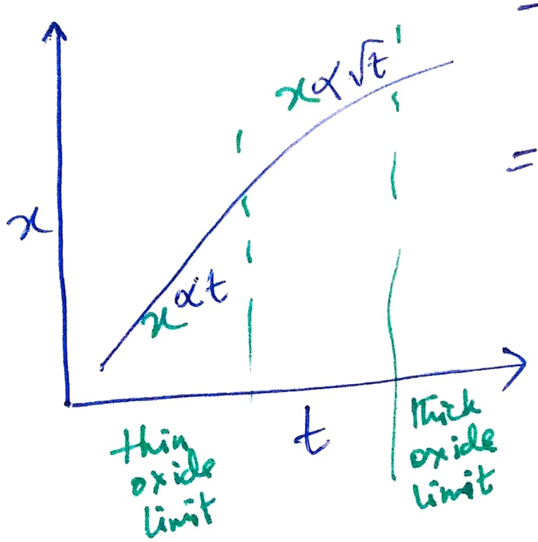
$$= \frac{k_i C_s}{M\left(1 + \frac{k_i}{D} x\right)}$$

$$= \frac{B/2}{A/2 + x}$$

$$\Rightarrow \left(\frac{A}{2} + x\right) dx = \frac{B}{2} dt$$

Upon integration, with initial condition $x = x_i$ at $t = 0$

$$\Rightarrow \frac{A}{2} x + \frac{x^2}{2} - A\frac{x_i}{2} - \frac{x_i^2}{2} = B\frac{t}{2}$$



when $x << \frac{A}{2}$ (Thin ~~Thick~~ oxide limit)

$$\frac{dx}{dt} = \frac{B}{A} \Rightarrow x = \frac{B}{A} t \Rightarrow x \propto t$$

when $x >> \frac{A}{2}$ (thick oxide limit)

$$\frac{dx}{dt} = \frac{B}{2x} \Rightarrow x = \sqrt{2Bt} \Rightarrow x \propto \sqrt{t}$$