

Using Ideal Gas Laws

$$C_G = \frac{p_G}{kT} \quad \text{and} \quad C_S = \frac{p_S}{kT} \quad \text{(ii)}$$

where  $p_G$  and  $p_S$  are partial pressure of the Oxidant <sup>at</sup> Gas ambient and Oxide surface

$$\therefore F_1 = h_a \left( \frac{p_G}{kT} - \frac{p_S}{kT} \right) = \frac{h_a}{kT} (p_G - p_S) \quad \text{--- (iii)}$$

We invoke Henry's Law of Gases / Fluids.

Accordingly  $C^*$  and  $C_0$  are the Oxidant Conc. in equilibrium in Solid state with Bulk Gas Ambient ( $C_a$ ) and Surface ( $C_s$ ). Henry's law states that

$$C^* \propto p_G \quad \text{and} \quad C_0 \propto p_S \quad \text{--- (iv)}$$

or  $C^* = H p_G$  and  $C_0 = H \cdot p_S$  where  $H$  is Henry's Const



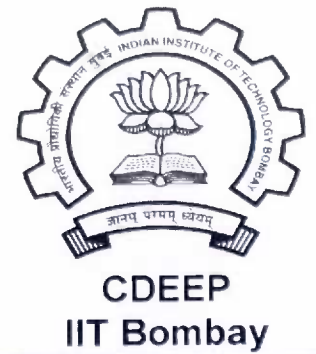
CDEEP  
IIT Bombay

EE 669 L 12 / Slide 01



$$\text{or } F_2 = -D_{\text{eff}} \left[ \frac{C_i - C_o}{x_o} \right] \quad \text{--- (vi)}$$

where  $D_{\text{eff}}$  is the Diffusion Coefficient of Oxidant in Oxide.



[3] The oxidant reaches at  $\text{SiO}_2$ -Si interface and then reacts with Si with Flux  $F_3$ . Then

$$F_3 \propto C_i$$

or  $F_3 = k_s \cdot C_i$  --- (vii) where  $k_s$  is called Reaction Rate Constant.

In Steady State

$$F = F_1 = F_2 = F_3 \quad \text{--- (viii)}$$

First we take  $F_1 = F_2$ , then

$$h(c^* - c_0) = -D_{eff} \left( \frac{c_i - c_0}{x_0} \right) \quad - (ix)$$

Then  $F_2 = F_3$  can also be used to give

$$-D_{eff} \left( \frac{c_i - c_0}{x_0} \right) = k_s c_i \quad - (x)$$

Solving equs. (ix) and (x), we get

$$c_i = \frac{c^*}{\left[ 1 + \frac{k_s}{h} + \frac{k_s x_0}{D_{eff}} \right]} \quad - (xi)$$

$$c_0 = \frac{\left[ 1 + \frac{k_s x_0}{D_{eff}} \right] c^*}{\left[ 1 + \frac{k_s x_0}{D_{eff}} + \frac{k_s}{h} \right]} \quad - (xii)$$



CDEEP  
IIT Bombay

EE 669 L 12 / Slide 04

This Deal-Grove Model can then be used to get  $x_0$  as function of Temperature of oxidation and time of Oxidation.



CDEEP  
IIT Bombay

If  $N_1$  is conc. of Oxidant molecules, then

EE 669 L 12 / Slide 05

$$\frac{dx_0}{dt} = \frac{F}{N_1} = \frac{F_3}{N_1} = \frac{k_s C_i}{N_1} \quad - (xiii)$$

Substituting  $C_i$  from (xi) into (xiii), we get

$$\frac{dx_0}{dt} = \frac{k_s C^*}{N_1} \frac{1}{\left[1 + \frac{k_s}{h} + \frac{k_s x_0}{D_{eff}}\right]} \quad - (xiv)$$

We know

$$N_{1O_2} = 2.22 \times 10^{22} / \text{cc} \quad \text{and} \quad N_{1H_2O} = 4.44 \times 10^{22} / \text{cc}$$

From eq. (xiv)

$$\frac{dx_0}{dt} = \frac{2c^* D_{eff}}{N_1} \cdot \frac{1}{\frac{2D_{eff}}{k_s} \left(1 + \frac{k_s}{h} + \frac{k_s}{D_{eff}} x_0\right)}$$

$$= \frac{2c^* D_{eff}}{N_1} \cdot \frac{1}{2D_{eff} \left(\frac{1}{k_s} + \frac{1}{h}\right) + 2x_0} \quad \dots (xv)$$

We define

$$A = 2D_{eff} \left(\frac{1}{k_s} + \frac{1}{h}\right)$$

and  $B = \frac{2D_{eff} c^*}{N_1}$

Then  $\frac{dx_0}{dt} = \frac{B}{A + 2x_0} \quad \dots (xvi) a$



CDEEP  
IIT Bombay

EE 669 L 12 / Slide 06



$$\text{or } A \frac{dx_0}{dt} + 2x_0 \frac{dx_0}{dt} = B \quad \text{--- (xvi)}$$

Initial Condition

$$\text{At } t=0 \quad x_0 = x_i \quad (\text{By assumption})$$

$$\text{or } (A + 2x_0) dx_0 = B dt$$

Integrating

$$Ax_0 + \frac{2x_0^2}{2} = Bt + B\tau \quad \text{--- (xvii)}$$

where  $\tau$  is time taken to grow oxide thickness  $x_i$

$$\text{or we can say } \tau = \frac{x_i^2 + Ax_i}{B} \quad \text{--- (xviii)}$$



CDEEP  
IIT Bombay





Two Limiting Cases :

(i) Case - 1 : Time of Oxidation 't' is small,  
Such that  $(t + \tau) \ll A^2/4B$

$$\text{Then } x_0 = \frac{A}{2} \left[ 1 + \frac{1}{2} \frac{(t + \tau)}{(A^2/4B)} - 1 \right]$$

$$\text{or } x_0 = \frac{B}{A} (t + \tau) \quad \text{--- (xxii)}$$

Since for a process condition (Gas Flow, Temp. etc)

$\left(\frac{B}{A}\right)$  is constant

$$\therefore x_0 \propto (t + \tau)$$

or  $x_0 \propto t$   $x_0$  has linear Growth with Time



CDEEP  
IIT Bombay

EE 669 L 12 / Slide 09

We find

$$\left(\frac{B}{A}\right) = \frac{2 D_{\text{eff}} C^* / N_1}{2 D_{\text{eff}} \left(\frac{1}{k_s} + \frac{1}{h}\right)} = \frac{C^*}{N_1} \left(\frac{k_s h}{k_s + h}\right)$$

In General  $h \gg k_s$

$$\therefore \left(\frac{B}{A}\right) = \frac{C^*}{N_1} k_s \quad \text{since } k_s \text{ is Reaction Rate Coefficient}$$

$\therefore (B/A)$  is called Linear Rate Constant

$$\therefore x_0 = \frac{C^*}{N_1} \cdot k_s (t + \tau)$$

Hence initial Oxide growth is controlled by Reaction Rate of Oxidant and Silicon, as amount of Oxidant reaching  $\text{SiO}_2$ -Si interface is large amount.



CDEEP  
IIT Bombay

EE 669 L 12 / Slide 10

(ii) Case-II :

When oxidation time is large enough,  
We have

$$t \gg \tau \quad \text{and} \quad t \gg A^2/4B$$

$$\text{Then } x_0 = \frac{2\sqrt{t} \sqrt{B}}{A} \cdot \frac{A}{2} = \frac{A}{2}$$

$$\text{or } x_0 = \sqrt{Bt} \quad \text{or } x_0^2 = B \cdot t$$

Clearly  $x_0$  is increasing parabolically with Time.

$\therefore B$  is called Parabolic Rate Constant



CDEEP  
IIT Bombay

EE 669 L 12 / Slide 11