Using Ideal Gas Laws

$$C_G = \frac{p_G}{kT} \quad \text{and} \quad C_s = \frac{p_s}{kT} \qquad \text{(ii)}$$

where p_G and p_s are partial pressure of the Oxidant at Gas ambient and Oxide surface

$$\therefore \; F_1 = h_G\left(\frac{p_G}{kT} - \frac{p_s}{kT}\right) = \frac{h_G}{kT}(p_G - p_s) \quad \text{— (iii)}$$

We invoke Henry's Law of Gases / Fluids.

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

$$C^* \propto p_G \quad \text{and} \quad C_o \propto p_s \quad \text{— (iv)}$$

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

From equation (iii)

$$F_1 = \frac{h_G}{kT}\left(\frac{C^*}{H} - \frac{C_0}{H}\right)$$

or $$F_1 = \frac{h_G}{HkT}(C^* - C_0) \qquad \text{— (V) a}$$

where we can further define $h = \frac{h_G}{HkT}$ & then

$$F_1 = h(C^* - C_0) \qquad \text{— (V)}$$

[2] Once the Oxidant reaches Oxide surface with concentration of C_0, It diffuses into Oxide (x_0).

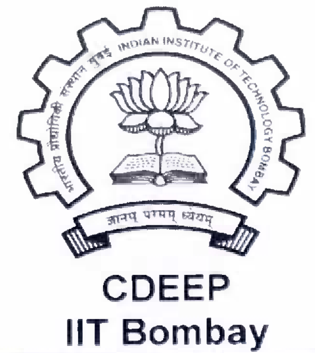
By Ficks law

$$F_2 \propto \frac{C_0 - C_i}{x_0}$$

where C_i is the Oxidant Conc at SiO_2-Si interface.

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

where Deff is the Diffusion Coefficient of Oxidant in Oxide.



[3] The oxidant reaches at SiO_2-Si interface and then reacts with Si with Flux F_3. Then

$$F_3 \propto C_i$$

or $$F_3 = k_s \cdot C_i \quad \text{— (vii)}$$ 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

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

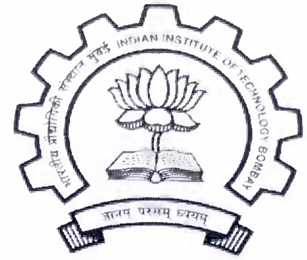
Then $F_2 = F_3$ can also be used to give

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

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

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

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



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

If N_1 is conc. of Oxidant molecules, then

$$\frac{dx_o}{dt} = \frac{F}{N_1} = \frac{F_3}{N_1} = \frac{k_s C_i}{N_1} \quad \text{— (xiii)}$$

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

$$\frac{dx_o}{dt} = \frac{k_s C^*}{N_1} \frac{1}{\left[1 + \frac{k_s}{h} + \frac{k_s x_o}{D_{eff}}\right]} \quad \text{— (xiv)}$$

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

From eq. (XIV)

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

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

We define

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

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

Then $$\frac{dx_0}{dt} = \frac{B}{A + 2x_0} \quad \text{———} \quad (XVI)a$$

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

Initial Condition

At $t=0^-$ $\quad x_0 = x_i$ (By assumption)

or $(A+2x_0)\,dx_0 = B\,dt$

Integrating

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

where τ is time taken to grow oxide thickness x_i

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

Then $x_0^2 + Ax_0 = B(t+\tau)$ — (XIX)

Solution is :

$$x_0 = \frac{-A \pm \sqrt{A^2 + 4(B)(t+\tau)}}{2}$$

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

−ve Solution is Discarded as x_0 cannot be Negative.

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

We define

k_p B as Parabolic Rate Constant

and k_L $\frac{B}{A}$ as Linear Rate Constant] (XXi)

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Two Limiting Cases :

(i) Case - 1 : Time of Oxidation 't' is Small,

Such that $(t+\tau) << A^2/4B$

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

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

Since for a Process Condition (Gas Flow, Temp. etc)

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

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

or $x_0 \propto t$ $\quad$ x_0 has Linear Growth with Time

We find

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

In General $h \gg k_s$

$$\therefore \left(\frac{B}{A}\right) = \frac{C^*}{N_1} k_s$$

Since k_s 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 SiO_2-Si interface is large amount.

(ii) Case-II :

When oxidation time is large enough, we have

$t >> \tau$ and $t >> A^2/4B$

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

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

Clearly x_0 is increasing Parabolically with Time.

$\therefore$ B is called Parabolic Rate Constant

Experiment - 1

oxidation is performed at $T = 920^\circ C$.
Given $\tau = 50$ sec, we monitor x_0 at different times and the result is

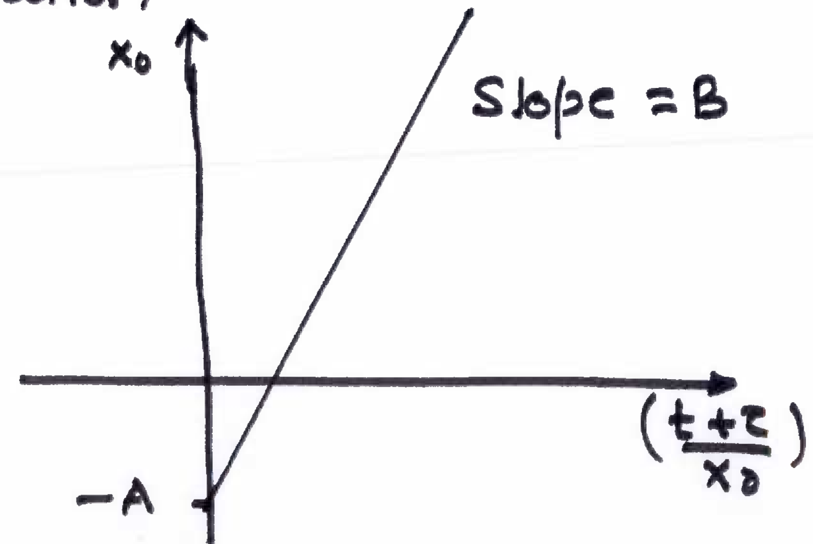
Time (Hours) →	0.11	0.3	0.4	0.5	0.6
x_0 (μm) →	0.041	0.10	0.128	0.153	0.177

We have oxide thickness equation

$$x_0^2 = B(t+\tau) - A x_0$$

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

We plot x_0 vs $\frac{t+\tau}{x_0}$ as shown



From experimental data $x_0 - t$ as above, our plot of x_0 Vs. $\frac{t+\tau}{x_0}$ gives

$$B = 0.2\ \mu^2/\text{Hour} \quad \text{— (i)}$$

and $A = 0.5\ \mu$

or $$\frac{B}{A} = 0.4\ \mu m/\text{Hour} \quad \text{— (ii)}$$

Experiment-II We repeat the above oxidations at same times for Temperatures $1000^\circ c$, $1100^\circ c$ & $1200^\circ c$ and evaluate B and $\frac{B}{A}$ at various temperatures. We then Plot B and B/A versus $(1/T)$

Data :

T	B (μ^2/H)	B/A ($\mu m/H$)
920°C	0.203	0.406
1000°C	0.287	01.27
1100°C	0.510	4.64
1200°C	0.720	14.4

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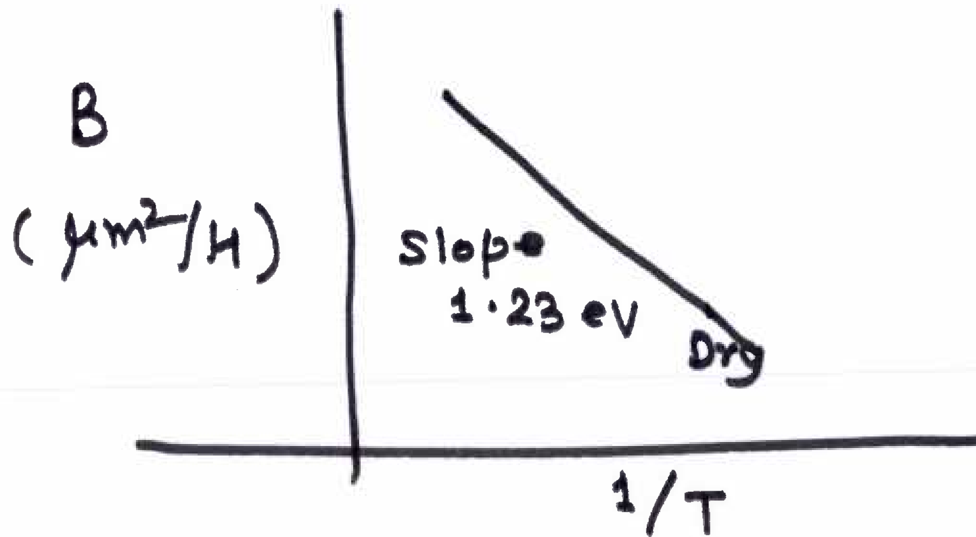
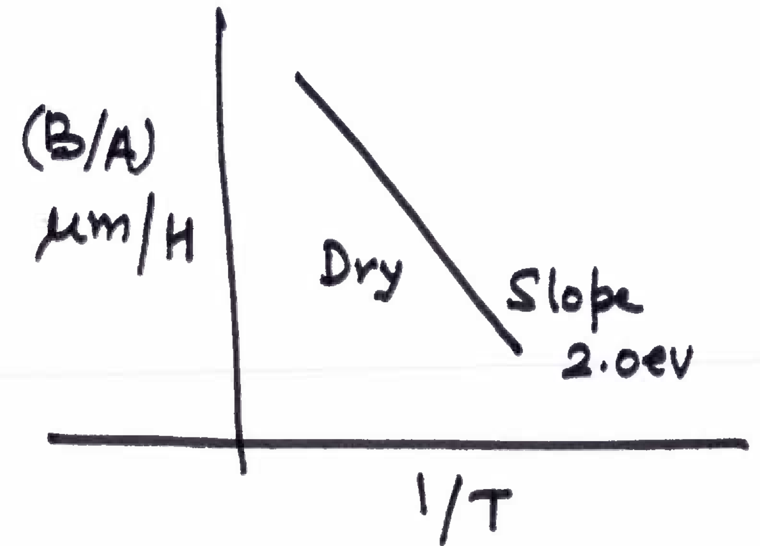
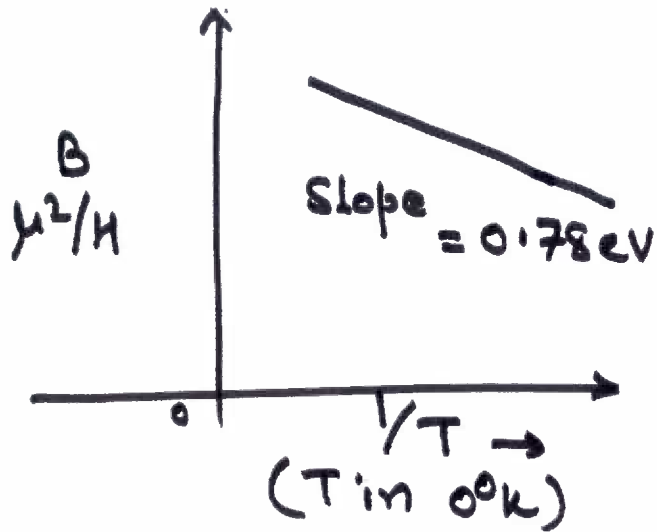
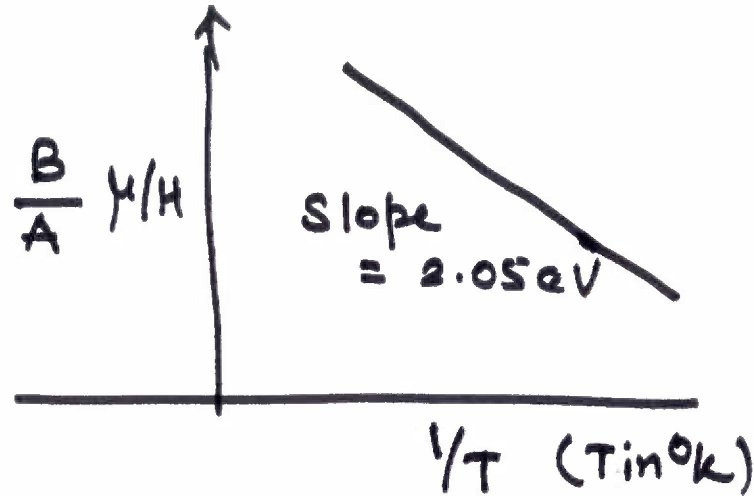




Wet Oxidation





From the experimental data, we can empirically write expressions for B and B/A as

$$\frac{B}{A} = K_L = C_1 \exp\left[-E_1/kT\right] = \frac{C^* k_s}{N_1}$$

$$B = K_p = C_2 \exp\left[-E_2/kT\right] = \frac{2 D_{eff} C^*}{N_1}$$

E_1 and E_2 are activation energies and C_1 & C_2 are Pre exponent.

For K_p and K_L, we have :

Orientation	Parameters	Dry Oxidation	Wet Oxidation
<100>	C_1	6.23×10^6 μ/H	1.63×10^8 μ/H
	E_1	2.0 eV	2.05 eV
	C_2	7.72×10^2 μ^2/H	3.86×10^2 μ^2/H
	E_2	1.23 eV	0.78 eV
<111>	C_1	3.66 μ/H	0.96 μ/H

E_1, E_2 and C_2 are same for <111> as for <100> case

– [C.H4]

From $\frac{B}{A}$ and B expressions

$$\left(\frac{B}{A}\right) = C_1 \exp(-E_1/kT) = \frac{C^*}{N_1} k_s$$

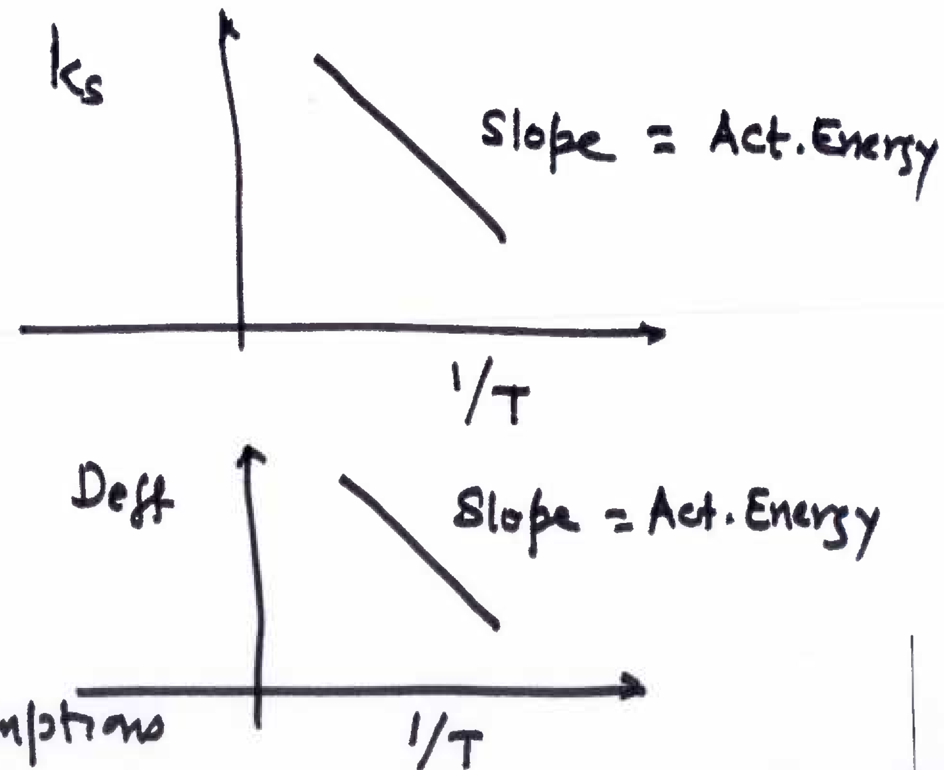
& $$B = C_2 \exp(-E_2/kT) = \frac{2D_{eff}}{N_1} C^*$$

Since C^* and N_1 are constant, then

$$\left(\frac{B}{A}\right) = K_L \propto k_s$$

and $$(B) = K_p \propto D_{eff}$$

Since activation energy of k_s and E_1 are similar and so also D_{eff} and E_2 are also same, we conclude that Deal - Grove Model based on assumptions is VALID.



Various Effects on SiO_2 Growth Rate

[1] Orientation :—

It is observed that

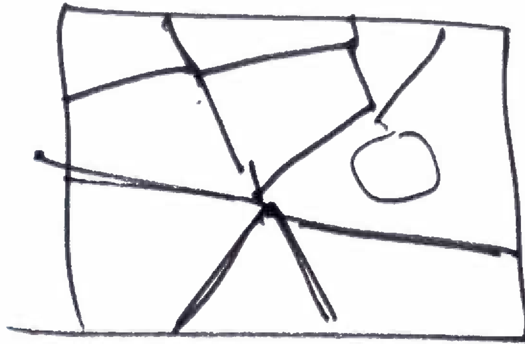
$$(B/A)_{<111>} = 1.7\,(B/A)_{<100>}$$

Hence for Linear growth regime for same time

$$x_{o(111)} = 1.7\; x_{o(100)}$$

This is due to the fact that no of atomic bonds available on Surface of Si at SiO_2-Si interface are 1.7 times larger for (111) case than (100) case.

[2] Poly Oxide : Poly Silicon has many Crystallites and hence many Grain Boundaries. Oxidant diffuses faster through Grain Boundaries leading to enhanced oxidation rate. $x_o = at^n \quad (n > 0.5)$



Grain Boundaries

[3] Pressure Effect

Under Pressure, the crystals are stressed leading to enhanced defects. (Jayraman et al 1970)

This creats more bonds available for oxidant atoms. Hence oxidation rate is enhanced for Linear Growth regime.

$$(B/A)_P = (B/A)_{Atm\,P} \; P^n \qquad n = 0.7 \text{ to } 0.8$$

P = 1 to 3 Atm.

[4] Doped Silicon Oxidation: For dopings of $> 10^{19}/cc$

$(B/A)_{doped} = 20\,(B/A)_{undoped} \rightarrow$ n-Type

$= 2\,(B/A)_{undoped} \rightarrow$ P-Type

$(B)_{doped} = 2\,(B)_{undoped} \rightarrow$ n type

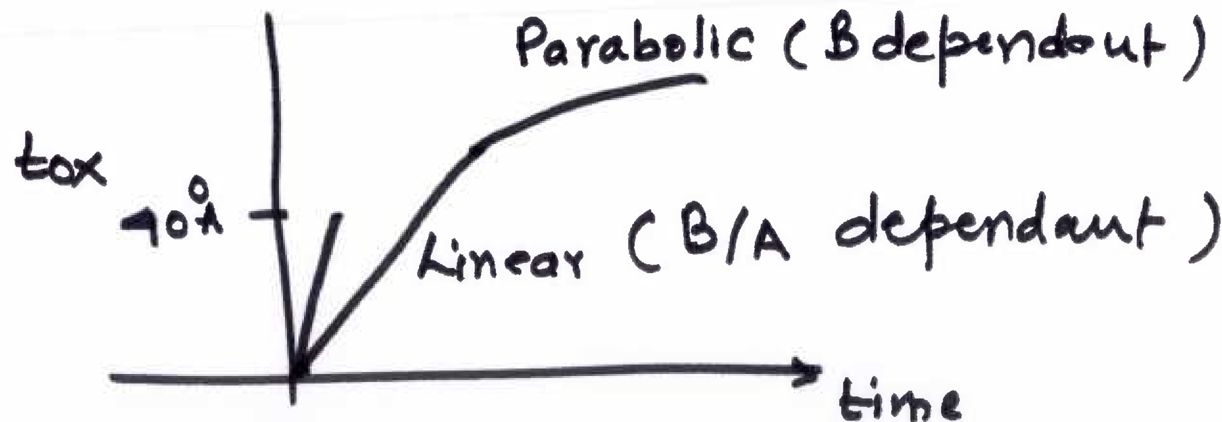
$(B)_{doped} = 0.04\,(B)_{undoped} \rightarrow$ P-Type

Thin Oxide Growth Models.

In Scaled down devices, one needs to reduce (Insulator) Gate oxide thickness.

Till 90 nm node (Even 65 node too), the Gate oxide was SiO_2 and it's thickness was below 4 nm (40 Å).

The kinetics of Thin oxide Growth, was not exactly as predicted by Deal-Grove Model.



The thin oxide needs to be grown at Lower Temperature around 800°c. — There are various models for Thin-Oxide Growth Regime.

(i) Reisman's Model :

$$x_0 = a(t+t_{in})^b$$

or $$x_0 = a\left\{t + \left(\frac{x_i}{a}\right)^{1/b}\right\}^b$$

x_i is Initial oxide at t0 —

a & b are used as fit parameters

(ii) Han and Helms Model :

$$\frac{dx_0}{dt} = \frac{B_1}{2x_0 + A_1} + \frac{B_2}{2x_0 + A_2}$$

Second term signifies parallel reaction, to fit the data, this term was introduced

(iii) Massoud & Plummer model :

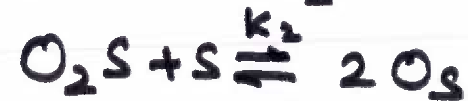
$$\frac{dx_0}{dt} = \frac{B}{2x_0 + A} + C \exp\left(-\frac{x_0}{L}\right)$$

Second term is added for fitting data.

Here, for $L < 70\,\mathring{A}$, the above model is good.

(iv) Moharir, Vasi, Chandorkar Model : (JAP-1989)

$$\frac{dx_0}{dt} = \frac{P\,C_i^{1/2}}{1 + QC_i + RC_i^{1/2}}$$



where $P = \Omega[Si-Si]n\,k_3\,(K_1 K_2)^{1/2}$

$Q = K_1$

$R = (K_1 K_2)^{1/2}$

O = Atomic oxygen

O_2 = Molecular Oxygen

S = Available Site at SiO_2-Si interface

For 800°C & 900°C Cases, this Model fits to Massoud's data, when Pressure used ≤ 0.1 Atm

Bruce Deal and Andy Grove were first to model the process of Thermal Oxidation. (Ref: J. Appl. Phys., Vol. 36, p 3770, 1965) Hence the Model is called 'Deal – Grove' Model.

This model provides kinetics of growth of SiO_2 (X_{ox}) as a function of temperature and time.

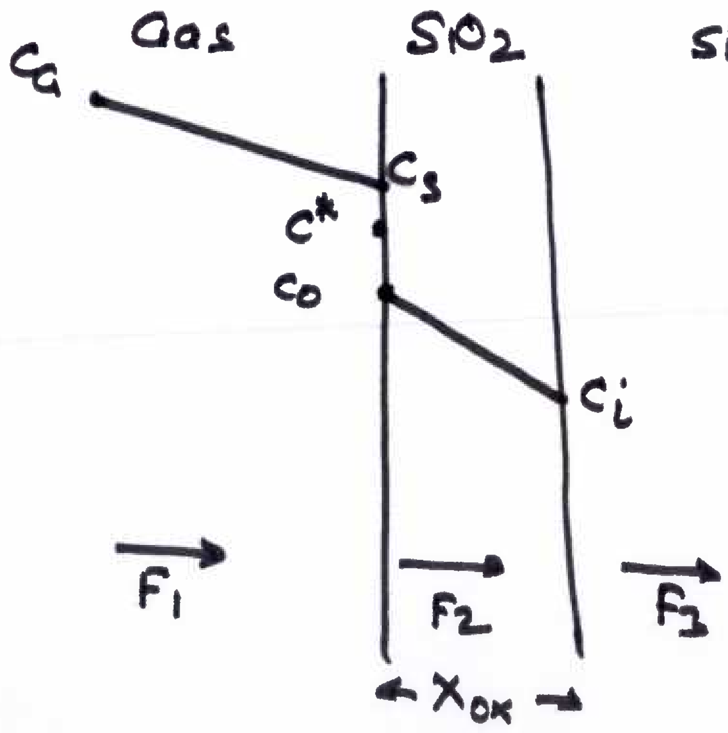
Model Assumptions

(a) Initially there is a finite (Thin) oxide layer, before oxidation ($t = 0^-$) Starts

(b) The Oxidant Gas specie impiges on this SiO_2 layer and diffuses through the Oxide-layer and reaches $Si - SiO_2$ interface.

(c) The Oxidant specie then reacts with Silicon atoms at the Interface and creates newer oxide layer.

This process continues and Sidioxide layer keeps growing to a thickness by end of time of Oxidation. This process is depicted in the Fig. below:



There are Three Fluxes in Gas, SiO_2 and Silicon regions.

Let F_1 be oxidant flux in Gas phase

F_2 be oxidant flux in SiO_2

F_3 be oxidant flux for reaction at Silicon.

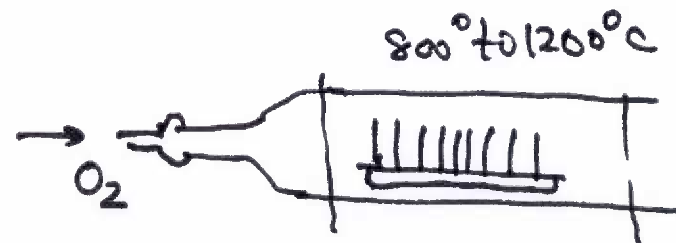
(A) Transport of Oxidant from the Furnace ambient to the Oxide surface takes place with Flux F_1.

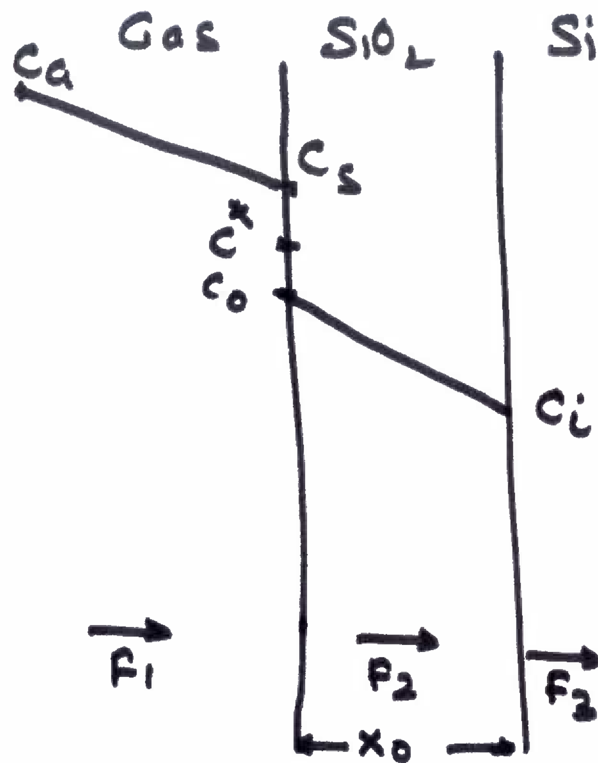
(B) Oxidant specie Diffuses through SiO_2 layer with a flux F_2.

(C) Oxidant reacts with Silicon with Flux F_3.

However in Steady State we can say that

$$F_1 = F_2 = F_3 = F$$





Deal – Grove Model

Here:

C_a – Oxidant Conc. in Bulk-Gas.

C_s – Oxidant Conc. at Oxide Interface in Gas-Phase.

C^* – Equilibrium oxidant conc. in Solid – related to C_a

C_o – Equilibrium Oxidant conc. in Solid – related to C_s

C_i – Oxidant Conc. at SiO_2–Si Interface.

[1] Flux F_1 in Gas ambient is essentially governed by Mass-Transfer, which can written as

$$F_1 \propto (C_a - C_s) \quad \text{or} \quad F_1 = h_a (C_a - C_s) \qquad \text{— [1]}$$

where h_a is called Mass Transfer Coefficient