Thermal Oxidation of Silicon

(i) SiO_2 Structure & Properties

(ii) Kinetics of Thermal Growth of Silicon

(iii) $Si-SiO_2$ interface

(iv) Characterisation of Quality of SiO_2

(v) Growth Technology

MOS Technology is used in creation of Silicon ICs, owe most of it's credit to $Si-SiO_2$ system.

In fact more than calling ICs as Silicon ICs, we should really call ICs as SiO_2 ICs.

SiO_2 is used in VLSI Technology as

(i) Field Oxide (4000 Å to 1.4 μm)

(ii) Masking Oxide (600 Å to 4000 Å)

(iii) Gate Oxide (Gate Dielectric) [1 nm to 1000 Å]

(iv) Pad Oxide (100 to 400 Å)

(v) Chemical oxide ; During RCA Cleaning

Technologies used for creation of SiO_2

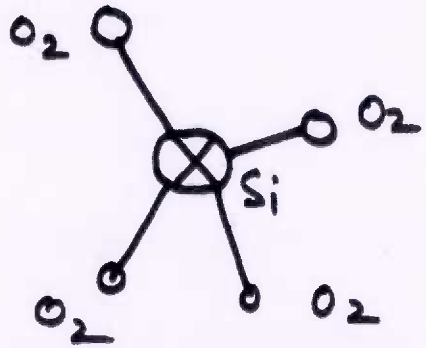
1. Thermal Oxidation
   (a) Dry Oxidation
   (b) Wet Oxidation

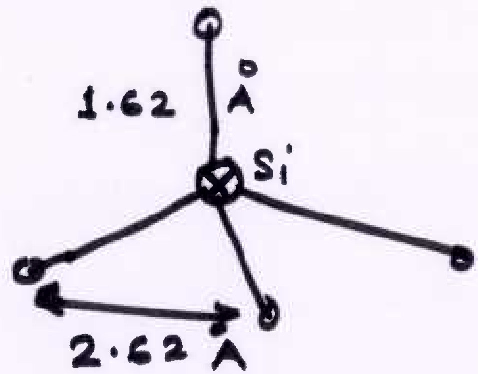
2. Deposition techniques
   (a) Chemical Vapour Deposition
   (b) Physical Vapour Deposition
   (c) Rapid Thermal Oxidation
   (d) Sol.-gel Process
   (e) Plasma Oxidation

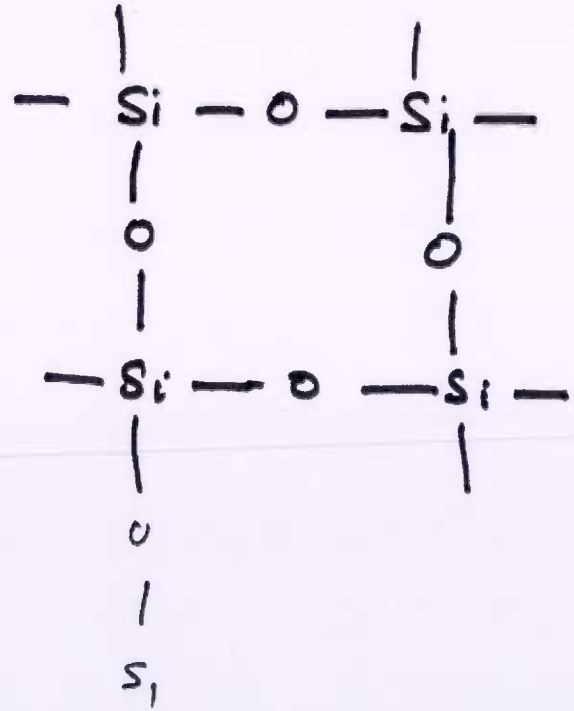
Thermal Oxidation is most basic oxidation technique and is most important step in creation of Gate - Oxide in a MOS Transistor.

Properties of Silicon Dioxide

(i) Bonding : Si – O – Si is a natural bond in SiO_2.







O – O Bond length → 2.62 Å

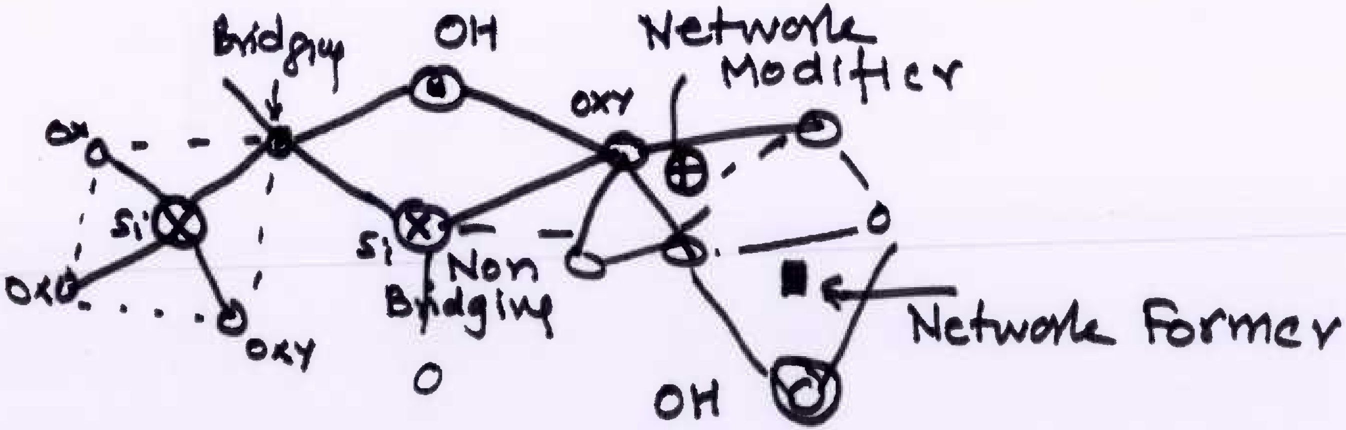
Si – O Bond Length → 1.62 Å

Si – Si Bond Length → 3 Å

SiO_2 is a Dielectric Material and is available in (i) Amorphous Phase

(ii) Crystalline Phase → Quartz

Thermally grown oxides are Amorphous in nature. Typical atomic structure of SiO_2 with some impurities or ions is as below:



Some observations:

(i) From the Lattice structures of SiO_2, we observe that if Si has to leave SiO_2 lattice, it must break 4 Si-O bonds.

While if Oxygen atom has to leave SiO_2 lattice, it [redacted] needs to break only One bond.

(ii) SiO_2 with no Impurities like Diffusing Impurities, or Sodium, Lead, Borium etc, is called Intrinsic Silica.

While SiO_2 with Impurities is called Extrinsic Silica.

(iii) Boron, Phosphorous & Arsenic (etc.) replace Silicon and hence create bond between Oxygen & them. Such Impurities are called Network former.

However if Impurities sit in Interstitial Sites, then they modify the Network of SiO_2, and hence called Network Modifier. Na_2O, Pb_2O_3, Ba_2O_3 are such Modifier.

(iv) If SiO_2 is put into water, we can have reaction as

$$Si-O-Si + \begin{matrix} H \\ | \\ OH \end{matrix} \longrightarrow \begin{matrix} SiOH \\ | \\ SiOH \end{matrix}$$

It is also to be noted that SiO_2 is strong Hydrophilic in nature.

(v) Physical Properties of SiO_2

1. $\sigma \leq 10^{-16}$ mhos/cm
2. Bandgap $E_g \geq 9$ eV
3. Refractory Index $\eta = 1.45$
4. Density = 2.22
5. No. of atoms/cc = 2.3×10^{22}/cc
6. Dielectric Constant $K_{SiO_2} = 3.9$
7. Dielectric Strength = 10^7 V/cm.

(vi) SiO_2 has strong Utility in IC processing as

(a) Easy to Etch $SiO_2 + 4HF \rightarrow 4SiF + 2H_2O$

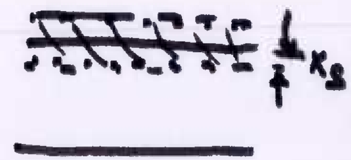
(b) Excellent Insulator with High Dielectric Strength

(c) Most Impurities (in Silicon) have poor Diffusion Constant in SiO_2.

(d) It is extremely Stable.

(e) Interface is quite Stable ($Si - SiO_2$) and very much reproducible as is desired in IC fabrication.

(vii) When Si is Oxidised, there is volume expansion. If x_s is Silicon Thickness and after oxidation it creates oxide Thickness X_{ox}. Then we use Law of Mass-action to say



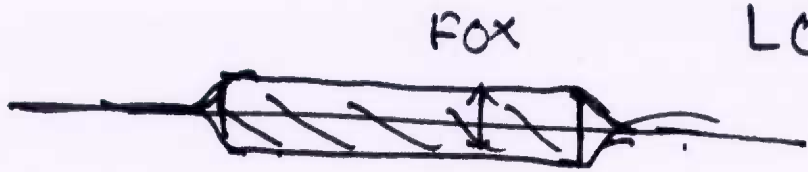
$$N_s \cdot x_s = N_{ox} x_{ox}$$

where N_s is Si Conc $= 5 \times 10^{22}$/cc and N_{ox} is SiO_2 Conc. $= 2.3 \times 10^{22}$/cc

$$\therefore X_s = \frac{N_{ox}}{N_s} \cdot X_{ox} = 0.46 X_{ox}$$

Local Oxidation Silicon.

LOCOS



"Kinetics of Thermal Oxidation of Silicon"

Silicon dioxide (SiO_2) is generally grown by Oxidation of Silicon at high temperatures (800°c to 1200°c) in Oxygen rich ambient. It could be pure O_2 or H_2O. Oxygen reacts with Silicon to form SiO_2.

$$Si + O_2 \xrightarrow{\text{High T}} SiO_2 \Rightarrow \text{Dry Oxidation}$$

SiO_2 formation by oxidation of Silicon in Water Vapour may have a bit complicated reaction. Overall however it may be like:

$$Si + 2H_2O \xrightarrow{\text{High T}} SiO_2 + 2H_2 \Rightarrow \text{Wet Oxidation}$$

The detailed reaction could be as :

$$H_2O + Si-O-Si \rightarrow \begin{array}{l} Si-OH \\ \ \ | \\ Si-OH \end{array} \qquad -(i)$$

$$\begin{array}{l} Si-OH \\ \ \ | \\ Si-OH \end{array} + Si-Si \rightarrow \begin{array}{l} Si-O-Si \\ \\ Si-O-Si \end{array} + H_2 \qquad -(ii)$$

$$(SiO_2 \text{ structure})$$

$$\frac{1}{2} H_2 + O-Si \rightleftharpoons OH-Si \qquad -(iii)$$

(i) H_2O attacks Bridging O_2 and Creates Non-Bridging (bond). This weaken the Network

(ii) At $Si-SiO_2$ interface, OH group reacts with Silicon to form Si–O–Si bond Structure which is essentially SiO_2.

(iii) H_2 diffuses through SiO_2 layer and reacts with Bridging O_2. Loosening of Network.

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.

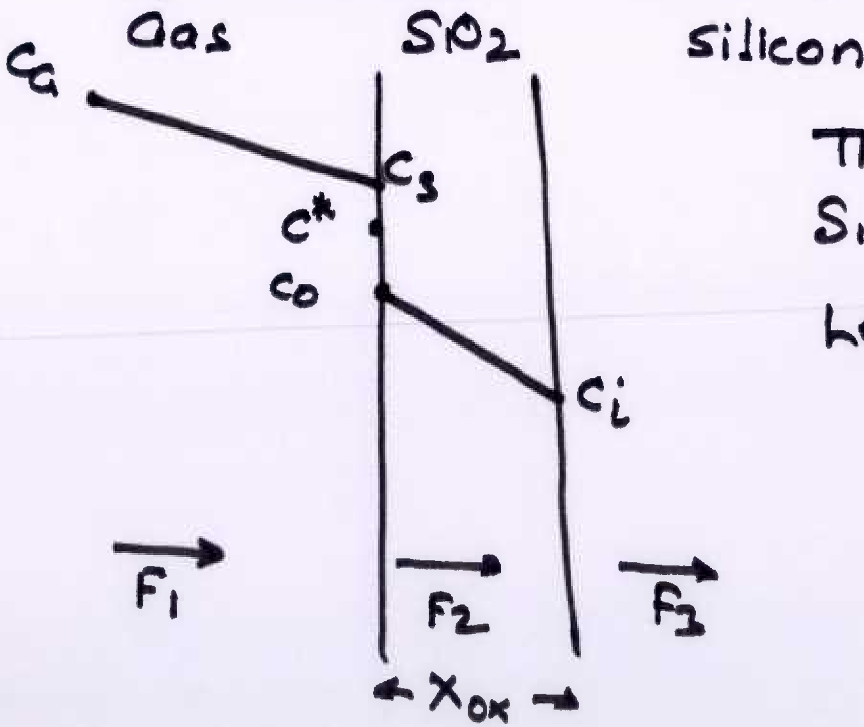
Model Assumptions

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

ⓑ 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.

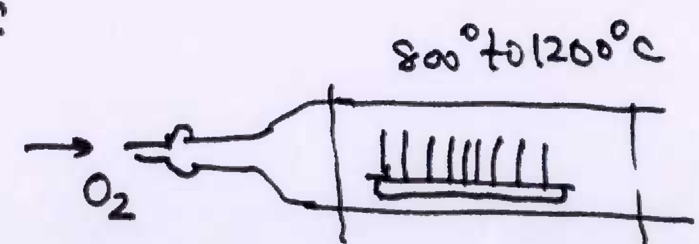
(A) Transport of Oxidant from the Furnace ambient to the Oxide surface takes place with Flux F_1.

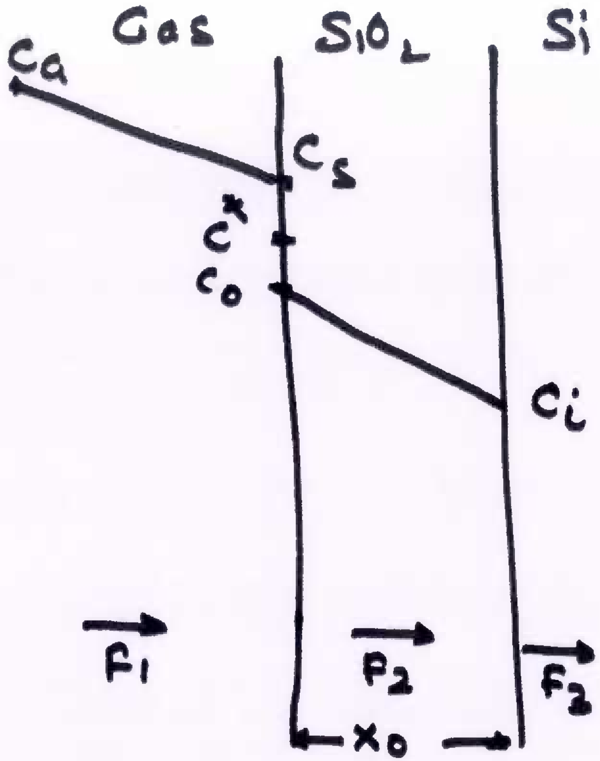
(B) Oxidant specie Diffuses through SiO_2 layer with a flux F_2.

(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