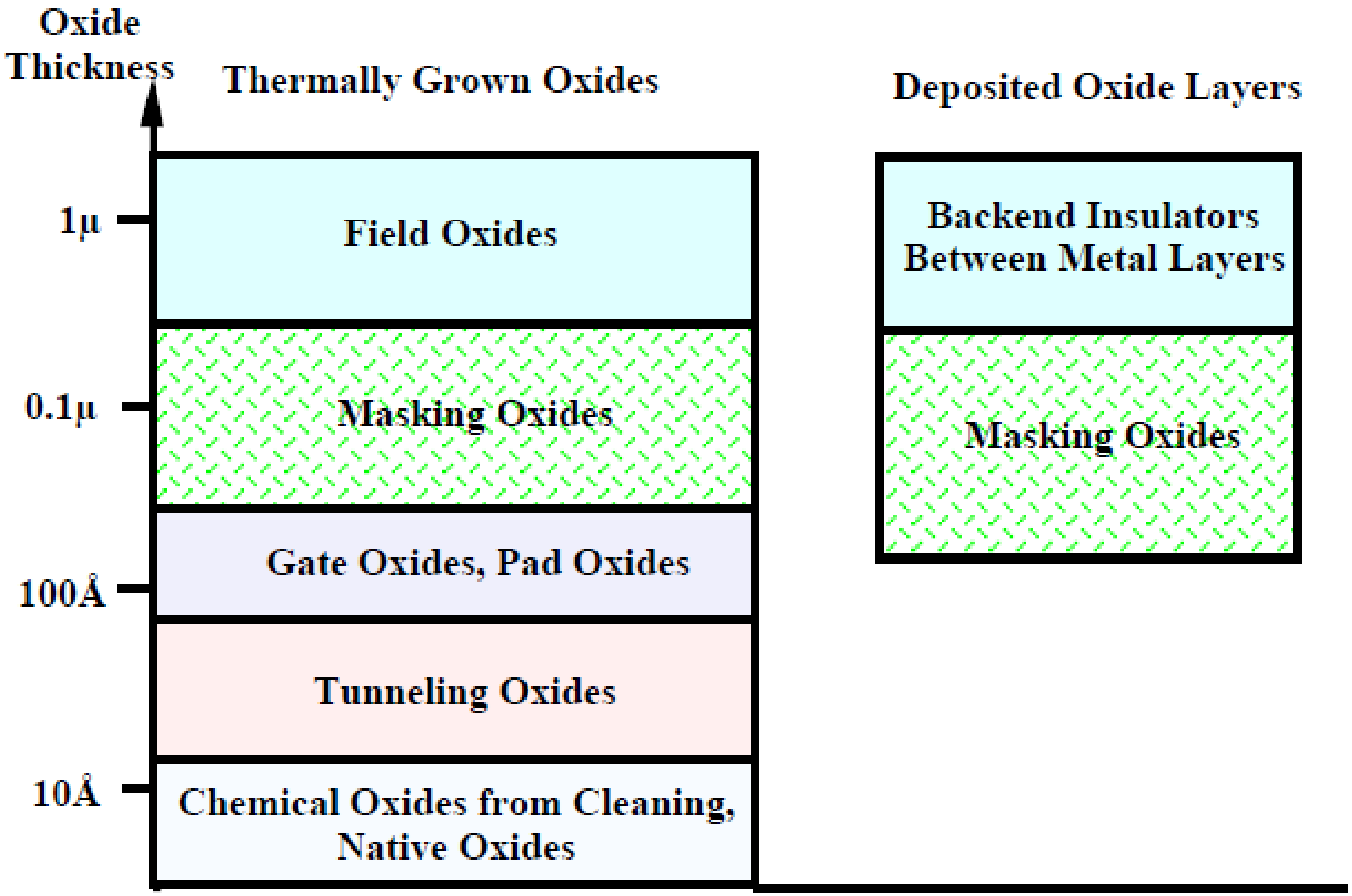
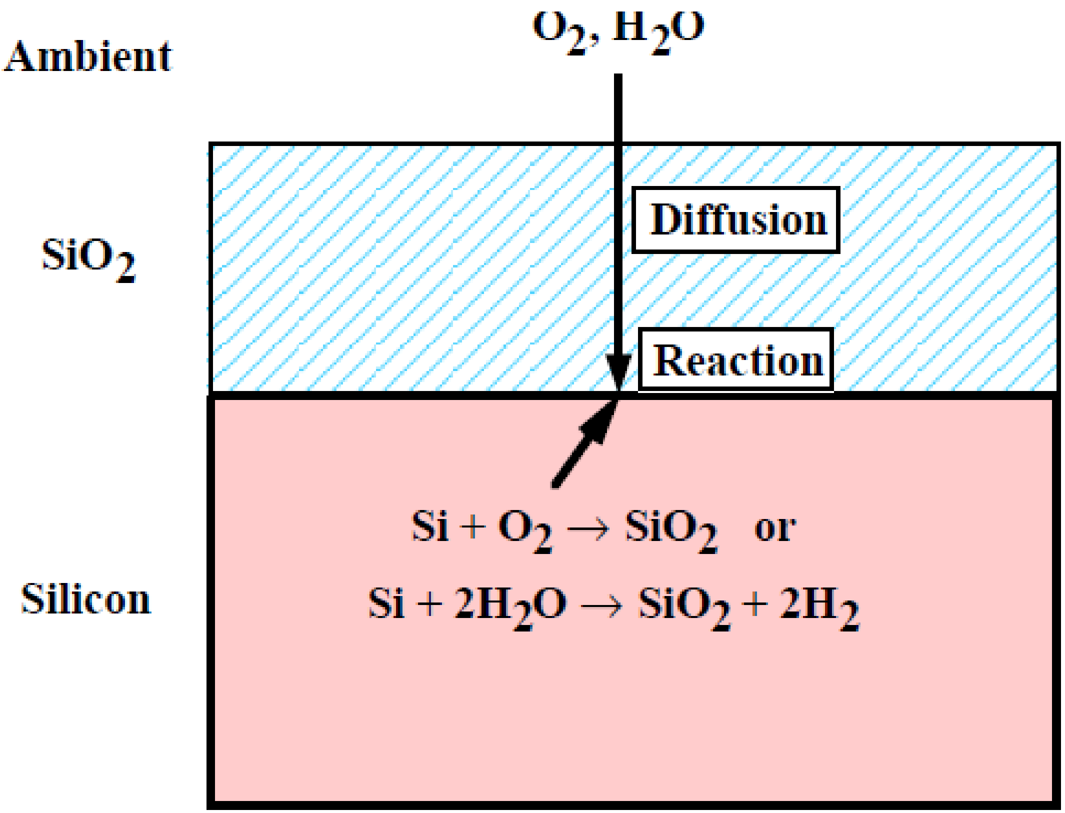
Basic Concepts

- SiO_2 and the Si/SiO_2 interface are the principal reasons for silicon's dominance in the IC industry.
- SiO_2:
  - Easily selectively etched using lithography.
  - Masks most common impurities (B, P, As, Sb).
  - Excellent insulator ($\rho > 10^{16}$ Ωcm, $E_g > 9$ eV).
  - High breakdown field (10^7 Vcm^{-1})
  - Excellent junction passivation.
  - Stable bulk electrical properties.
  - Stable and reproducible interface with Si.


Oxide Thickness
Thermally Grown Oxides
Deposited Oxide Layers
1µ
0.1µ
100Å
10Å
Field Oxides
Masking Oxides
Gate Oxides, Pad Oxides
Tunneling Oxides
Chemical Oxides from Cleaning, Native Oxides
Backend Insulators Between Metal Layers
Masking Oxides



Ambient

O_2, H_2O

SiO_2

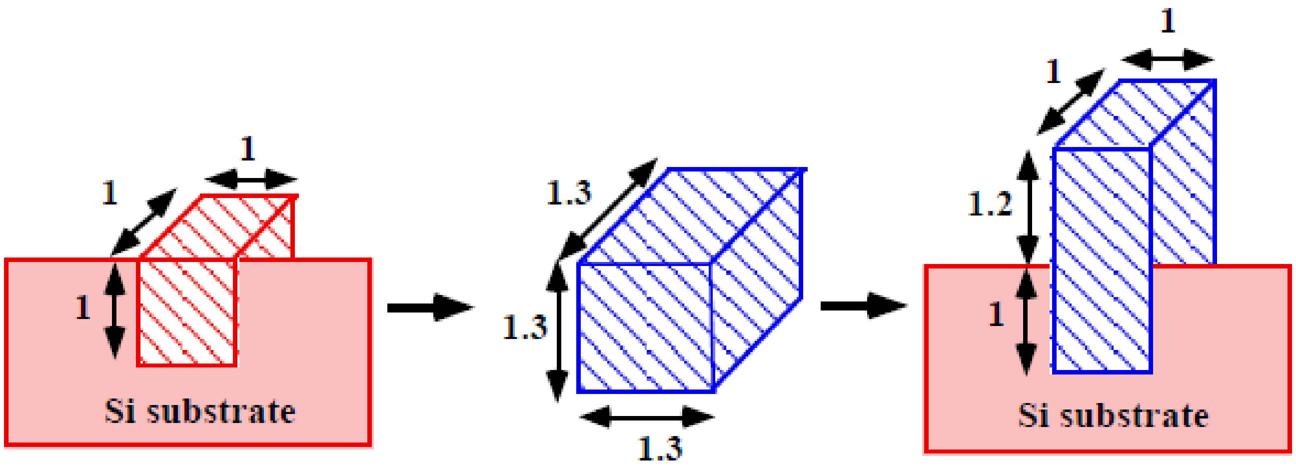
Diffusion

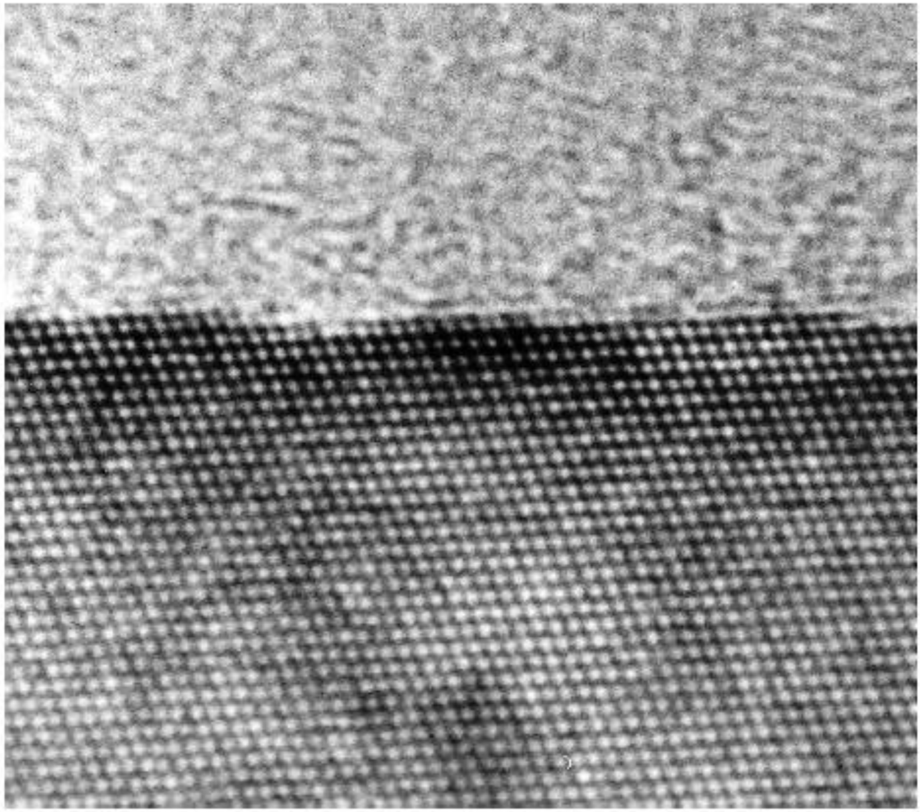
Reaction

Silicon

$Si + O_2 \rightarrow SiO_2$ or

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

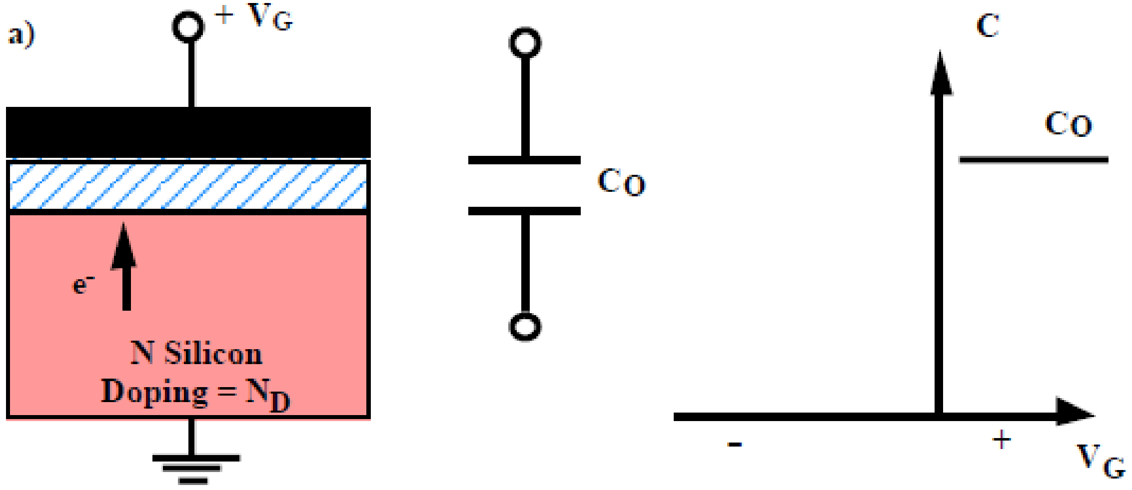


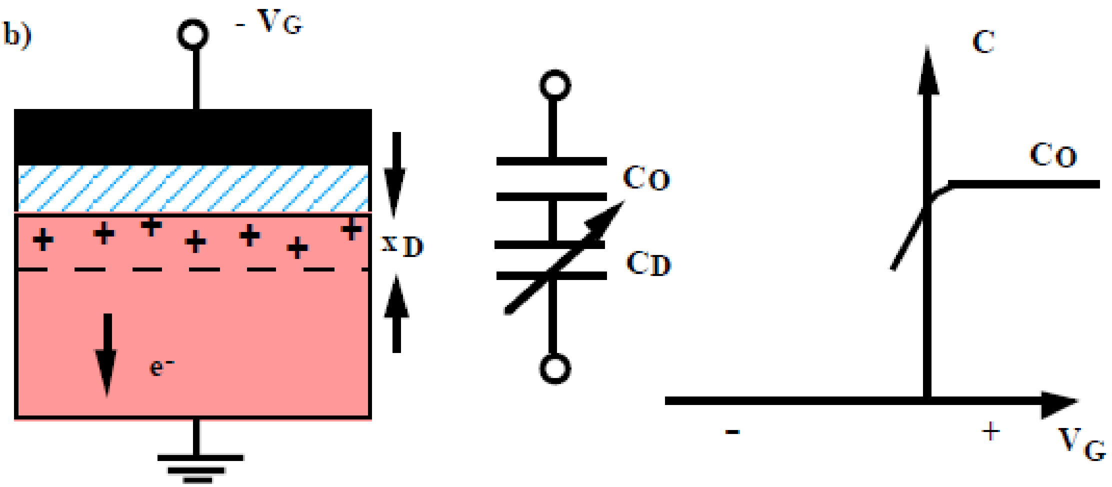


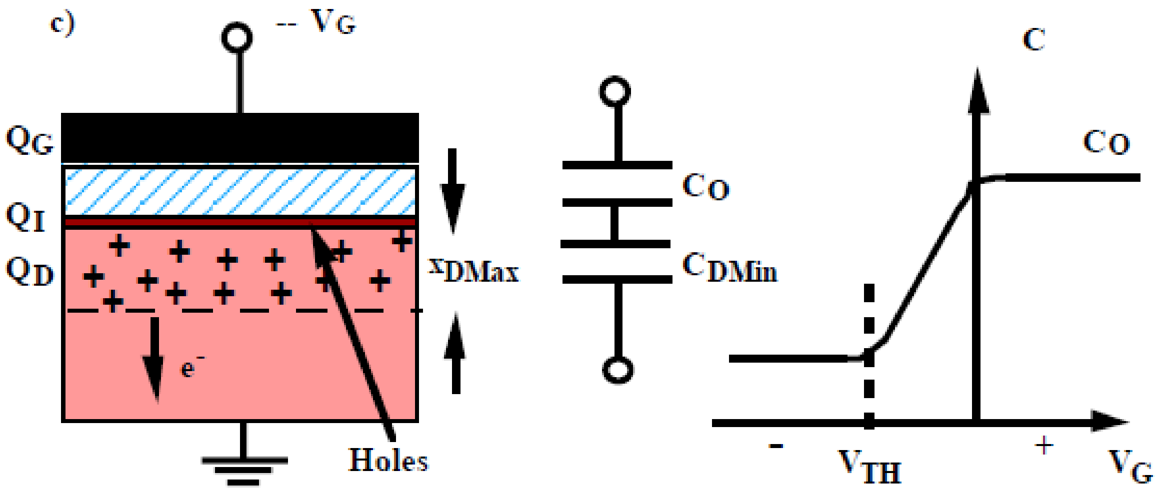
- SiO_2 is amorphous even though it grows on a crystalline substrate.

C-V Measurements

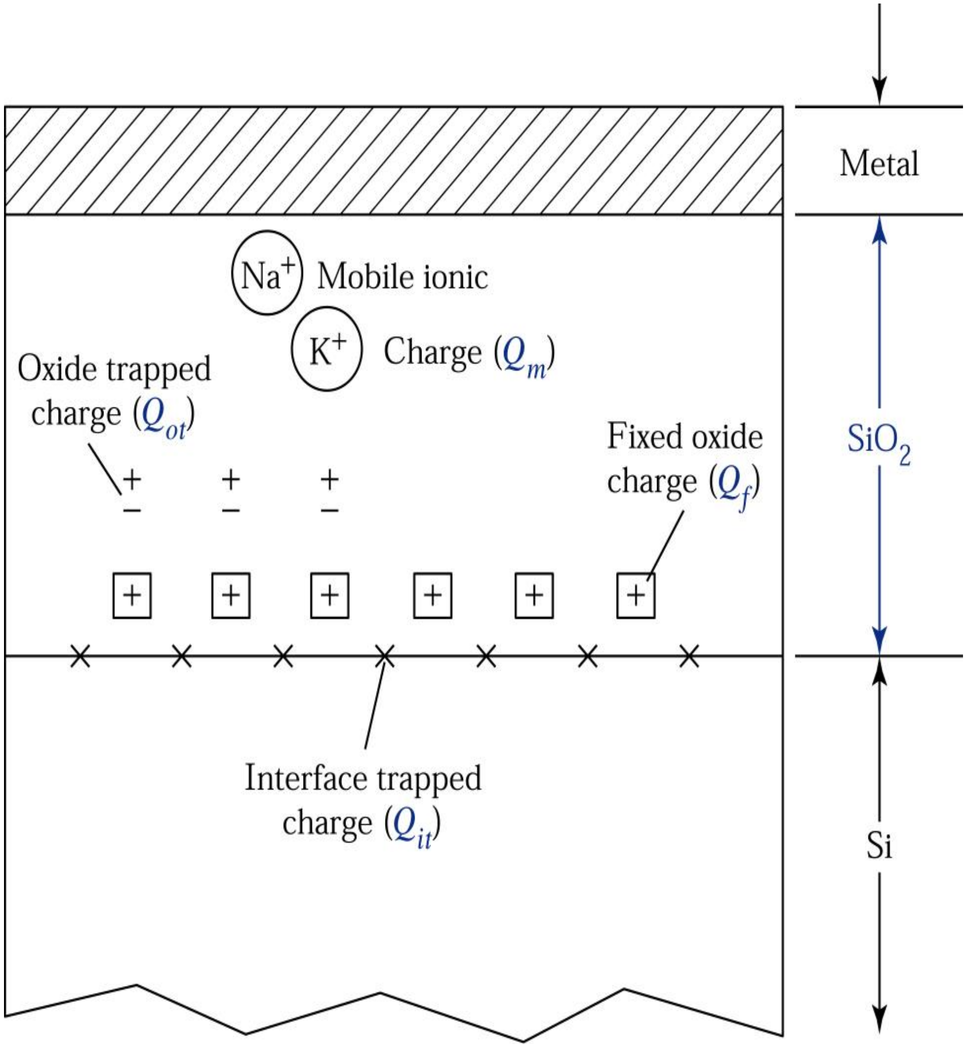
- There are a number of measurement techniques used to characterize SiO_2 and the Si/SiO_2 interface.
- The most powerful of these is the C-V method which is described in the text in detail.




b)
- VG
xD
e-
CO
CD
C
CO
-
+
VG


c)
-- VG
QG
QI
QD
xDMax
e-
Holes
CO
CDMin
C
CO
-
VTH
+
VG

ΕΠΙΔΡΑΣΗ ΦΟΡΤΙΩΝ ΕΝΤΟΣ ΟΞΕΙΔΙΟΥ



Σχήμα . Τα **διάφορα φορτία** που σχετίζονται με το θερμικό οξείδιο του πυριτίου.

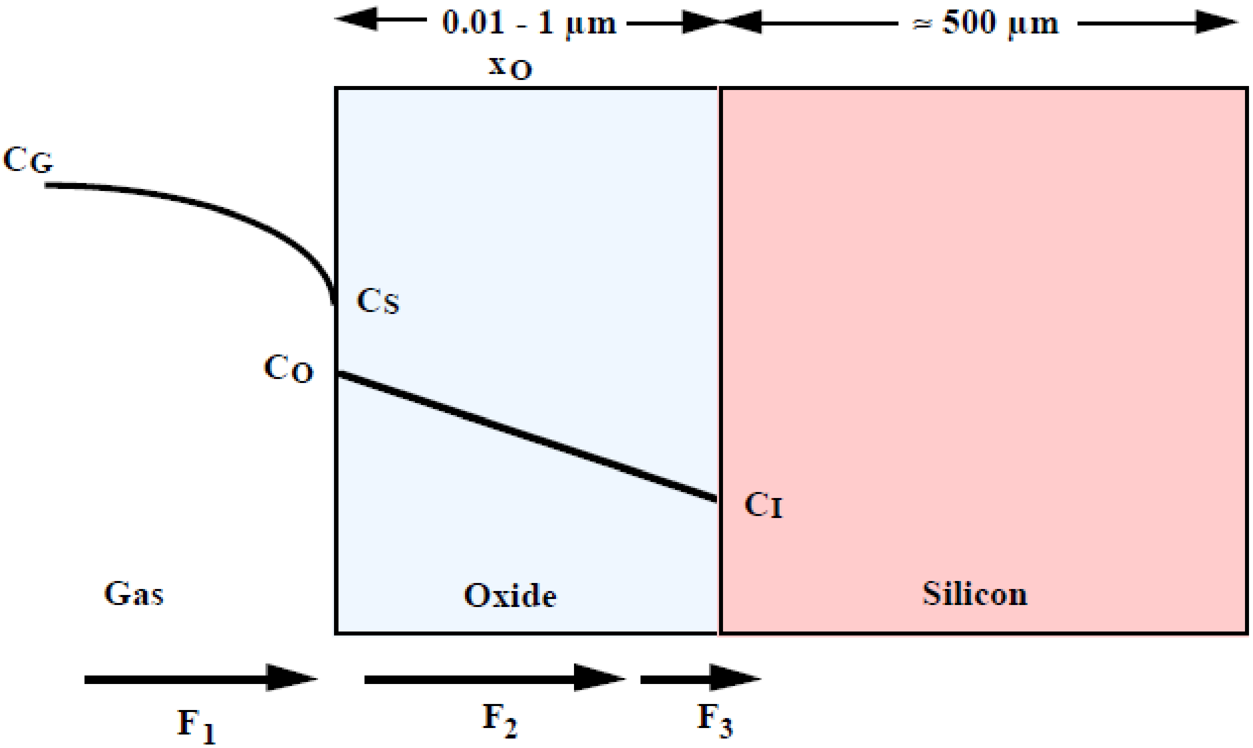
1) Παγίδες διεπιφάνειας SiO_2/Si (Q_{it}) οι οποίες έχουν ενεργειακές καταστάσεις μέσα στο ενεργειακό χάσμα του Si. Η συγκέντρωσή τους είναι της τάξης του 10^{10} cm^{-2} για Si <100> και συμβολίζεται ($\frac{Q_{it}}{q}$), (δηλαδή ανά 10^5 άτομα που βρίσκονται στη διεπιφάνεια SiO_2/Si αναλογεί μια παγίδα). Οι παγίδες μπορούν να φορτίζονται και να εκφορτίζονται μεταβάλλοντας το δυναμικό στην επαφή του μετάλλου.

2) Σε απόσταση 30-40 Å από τη διεπιφάνεια και στο εσωτερικό του οξειδίου υπάρχει θετικό φορτίο το οποίο είναι σταθερό (δεν φορτίζεται – αποφορτίζεται) από τη τάση στη πύλη και δεν μετακινείται. Η πυκνότητά του είναι της τάξης του 10^{10} cm^{-2} (οφείλεται σε ιόντα Si).

3) Κινητό φορτίο εντός του οξειδίου οφειλόμενο σε ιόντα Na ή άλλα αλκαλικά ιόντα το οποίο είναι δυνατόν να αποφευχθεί με κατάλληλο χημικό καθαρισμό της επιφάνειας και παρουσία HCl κατά την οξείδωση.

Συνήθως τα παραπάνω φορτία που οφείλονται σε διαφορετικές αιτίες τα αντιμετωπίζουμε σαν ένα συνολικό φορτίο (C/cm^2) και διερευνούμε την επίδρασή τους στη τάση επιπέδων ζωνών flat-band voltage για την οποία μιλήσαμε προηγουμένως.

SiO_2 Growth Kinetics Models
A. Deal Grove Model



- The basic model for oxidation was developed in 1965 by Deal and Grove.

$$Si + O_2 \rightarrow SiO_2 \qquad (2)$$

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2 \qquad (3)$$

- **Three first order flux equations describe the three series parts of the process.**

$$F_1 = h_G(C_G - C_S) \qquad (4)$$

$$F_1 = h\,(C^* - C_o)$$

$$F_2 = D\frac{\partial N}{\partial x} = D\left(\frac{C_O - C_I}{x_O}\right) \qquad (5)$$

$$F_3 = k_S C_I \qquad (6)$$

C^* : solubility of O_2 or H_2O in SiO_2

- Under steady state conditions, $F_1 = F_2 = F_3$, so

$$C_I = \frac{C^*}{1 + \frac{k_S}{h} + \frac{k_S x_O}{D}} \cong \frac{C^*}{1 + \frac{k_S x_O}{D}} \qquad (7)$$

$$C_O = \frac{C^*\left(1 + \frac{k_S x_O}{D}\right)}{1 + \frac{k_S}{h} + \frac{k_S x_O}{D}} \cong C^* \qquad (8)$$

- Note that the simplifications are made by neglecting F_1 which is a very good approximation.

LIMIT CASES

$K_s\ x_o/D << 1$, $C_I = C^*$

$K_s\ x_o/D >> 1$, $C_I = 0^*$

- Combining (6) and (7), we have

$$\frac{dx}{dt} = \frac{F}{N_1} = \frac{k_S C^*}{1 + \frac{k_S}{h} + \frac{k_S x_O}{D}} \qquad (9)$$

Number of O_2 in unit oxide volume: $N_1 = 2.2\ 10^{22}\ \text{cm}^{-3}$

- Integrating this equation (see text), results in the linear parabolic model.

$$\frac{x_O^2 - x_i^2}{B} + \frac{x_O - x_i}{B/A} = t \qquad (10)$$

where $B = \frac{2DC^*}{N_1}$ (parabolic rate constant) (11)

$$\frac{B}{A} = \frac{C^*}{N_1\left(\frac{1}{k_S} + \frac{1}{h}\right)} \cong \frac{C^* k_S}{N_1}$$ (linear rate constant) (12)

- (10) can also be written with oxide thickness as a function of time.

$$x_O = \frac{A}{2}\left\{\sqrt{1+\frac{t+\tau}{A^2/4B}}-1\right\} \qquad (13)$$

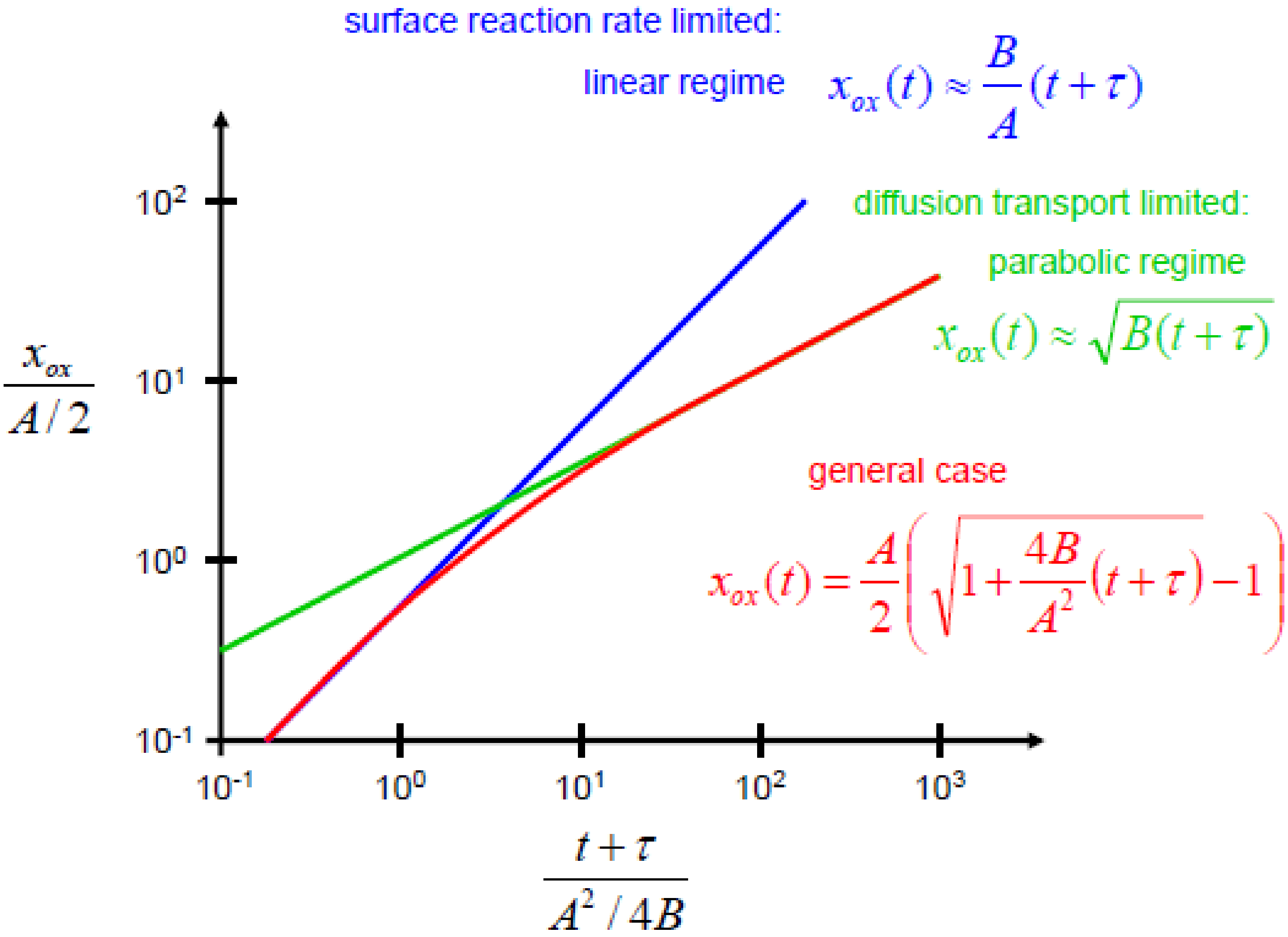
where

$$\tau = \frac{x_i^2 + Ax_i}{B} \qquad (14)$$

- The rate constants B and B/A have physical meaning (oxidant diffusion and interface reaction rate respectively).

$$B = C_1 \exp\left(-E_1/kT\right) \qquad (15)$$

$$\frac{B}{A} = C_2 \exp\left(-E_2/kT\right) \qquad (16)$$



surface reaction rate limited:

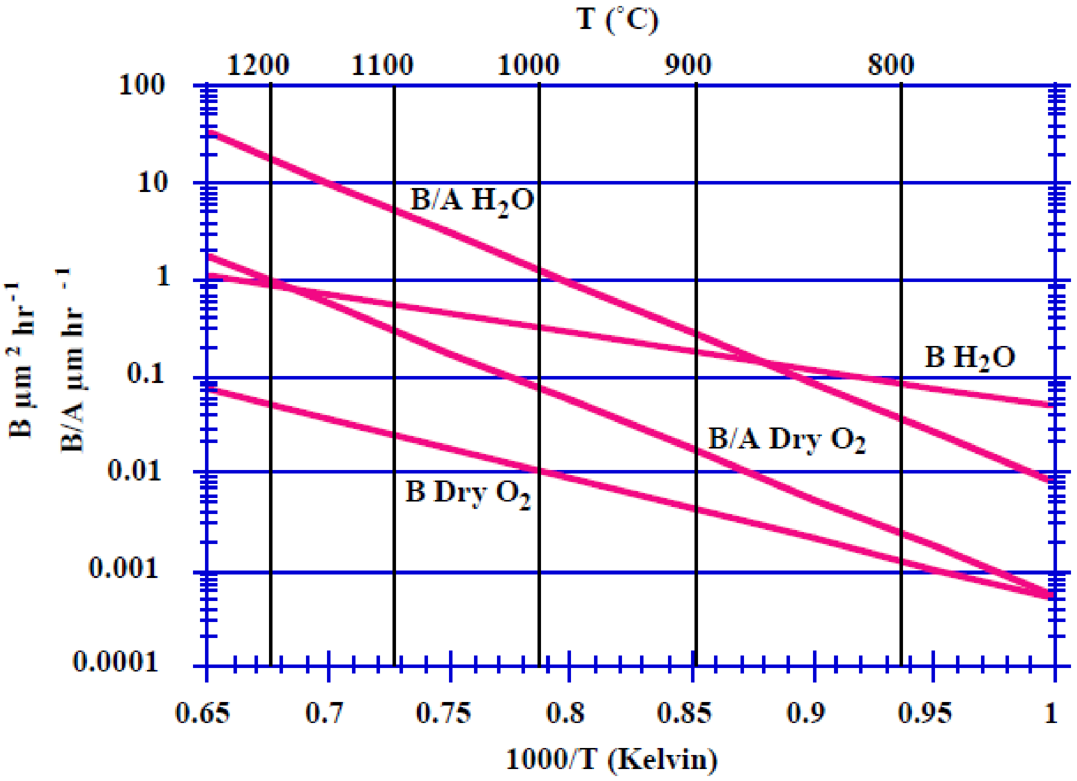
linear regime $x_{ox}(t) \approx \frac{B}{A}(t+\tau)$

diffusion transport limited:

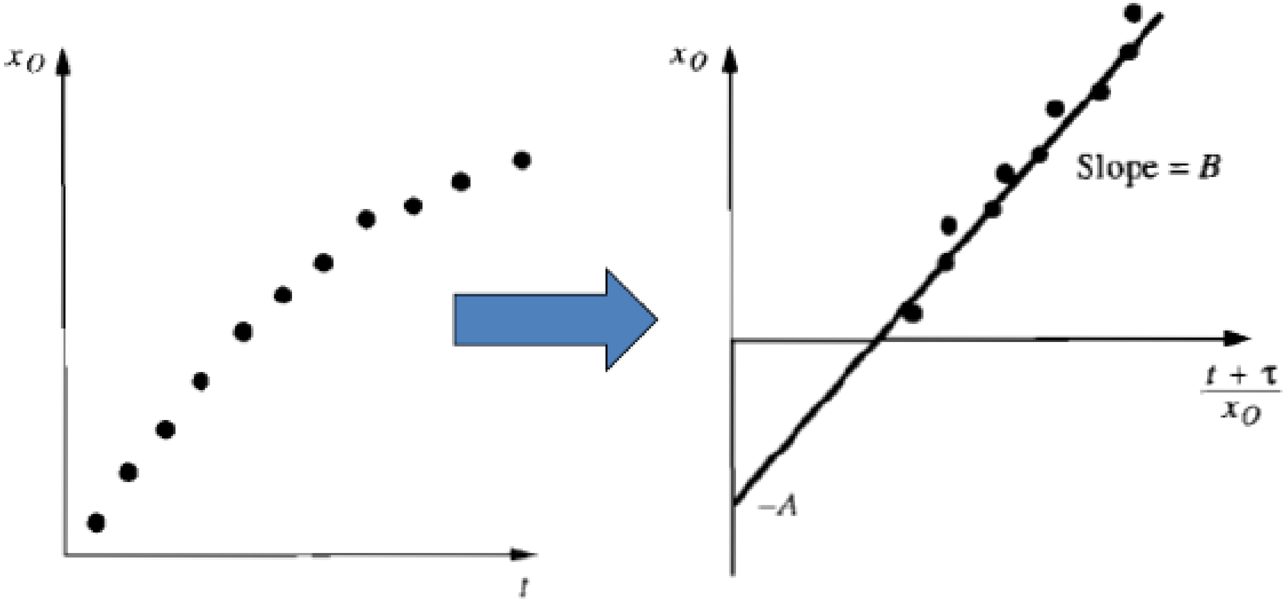
parabolic regime $x_{ox}(t) \approx \sqrt{B(t+\tau)}$

general case $x_{ox}(t) = \frac{A}{2}\left(\sqrt{1+\frac{4B}{A^2}(t+\tau)}-1\right)$

Ambient	B	B/A
Dry O_2	$C_1 = 7.72 \text{ x } 10^2\ \mu^2\ \text{hr}^{-1}$ $E_1 = 1.23$ eV	$C_2 = 6.23 \text{ x } 10^6\ \mu\ \text{hr}^{-1}$ $E_1 = 2.0$ eV
Wet O_2	$C_1 = 2.14 \text{ x } 10^2\ \mu^2\ \text{hr}^{-1}$ $E_1 = 0.71$ eV	$C_2 = 8.95 \text{ x } 10^7\ \mu\ \text{hr}^{-1}$ $E_1 = 2.05$ eV
H_2O	$C_1 = 3.86 \text{ x } 10^2\ \mu^2\ \text{hr}^{-1}$ $E_1 = 0.78$ eV	$C_2 = 1.63 \text{ x } 10^8\ \mu\ \text{hr}^{-1}$ $E_1 = 2.05$ eV

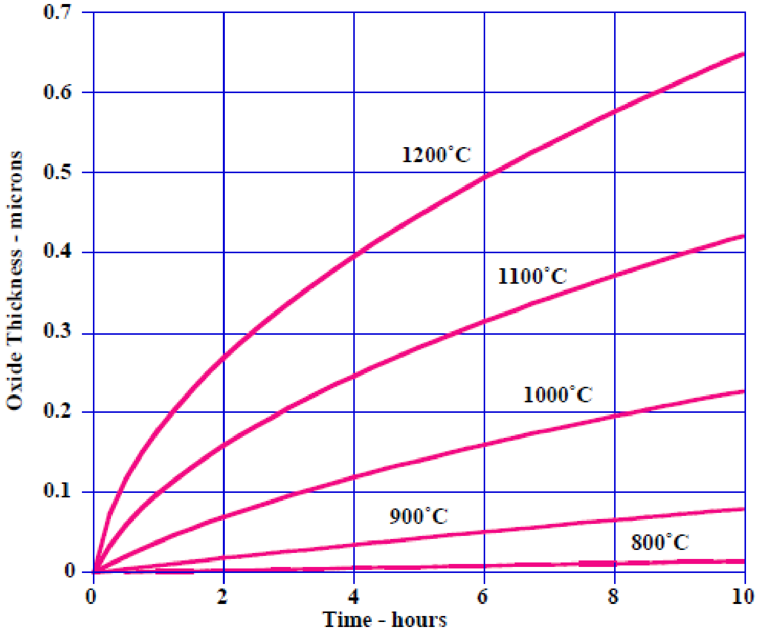


Extraction of B and B/A from experimental data

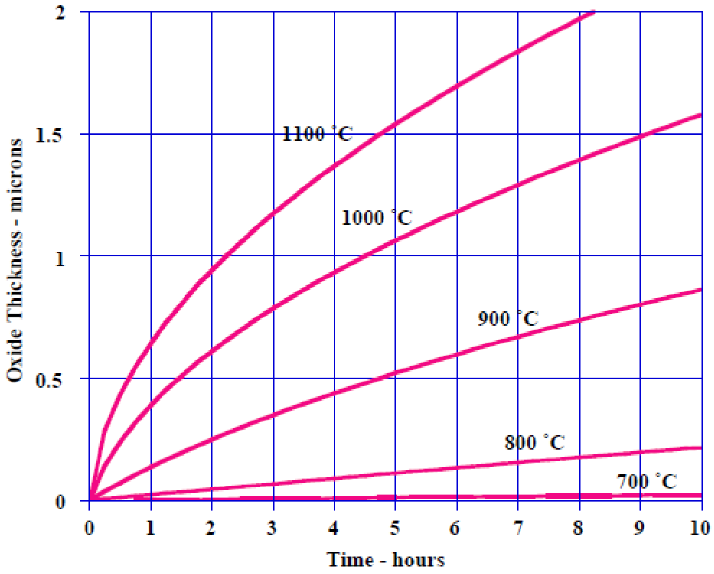


$$\frac{x_0^2}{B}+\frac{x_0}{B/A}=t+\tau \quad\Rightarrow\quad x_0 = B\frac{t+\tau}{x_0}-A$$

τ is provided by experiments



- **Calculated dry O_2 oxidation rates using Deal Grove.**



- **Calculated H_2O oxidation rates using Deal Grove.**

6.7. Why is steam oxidation more rapid than dry O_2 oxidation?

Answer:

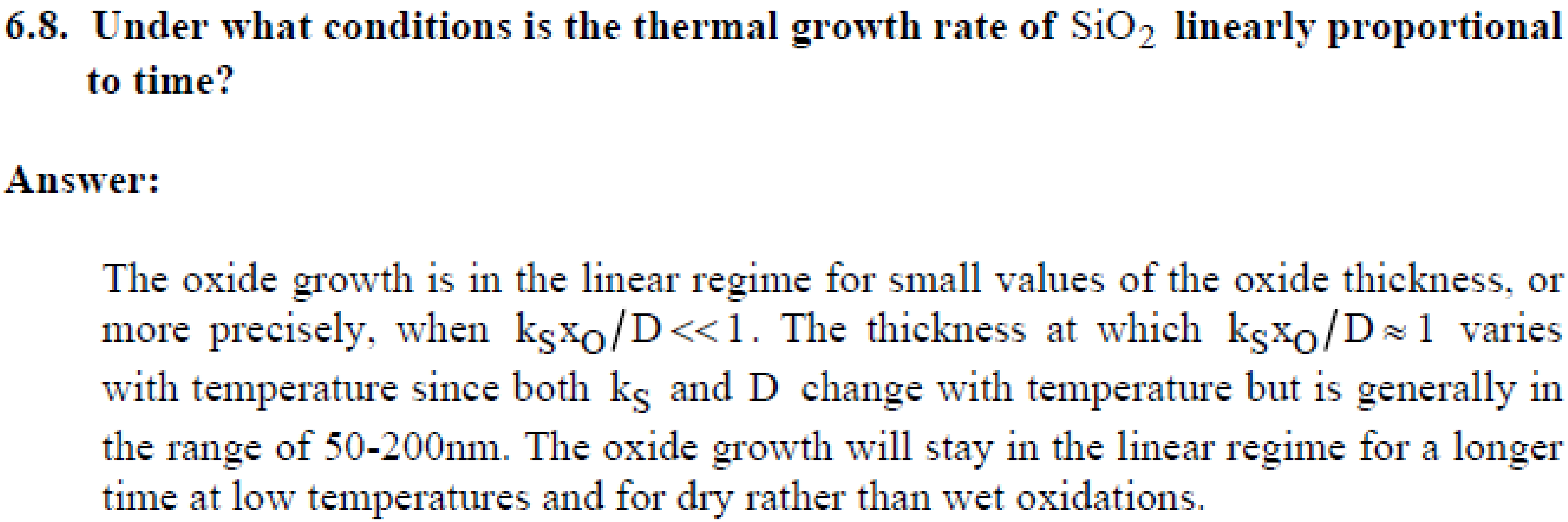
The effective diffusivities of both O_2 and H_2O are on the same order (about 5 x 10^3 μm^2 hr^{-1} at 1100°C).

At 1100°C, typical values for C^* are $\approx 5 \times 10^{16}$ cm^{-3} for dry O_2 and $\approx 3 \times 10^{19}$ cm^{-3} for H_2O. As a result, both rate constants, B and B/A are much larger for H_2O than for O_2.

Thus, the main reason that steam oxidation is faster than dry oxidation is becaus the solubility of the oxidant species is higher by three orders of magnitude.

$$\mathbf{B = \frac{2DC^*}{N_1}} \text{ (parabolic rate constant)}$$

$$\mathbf{\frac{B}{A} = \frac{C^*}{N_1\left(\frac{1}{k_S}+\frac{1}{h}\right)} \cong \frac{C^* k_S}{N_1}} \text{ (linear rate constant)}$$



6.8. Under what conditions is the thermal growth rate of SiO_2 linearly proportional to time?

Answer:

The oxide growth is in the linear regime for small values of the oxide thickness, or more precisely, when $k_S x_O / D << 1$. The thickness at which $k_S x_O / D \approx 1$ varies with temperature since both k_S and D change with temperature but is generally in the range of 50-200nm. The oxide growth will stay in the linear regime for a longer time at low temperatures and for dry rather than wet oxidations.

$$\frac{x_O^2 - x_i^2}{B} + \frac{x_O - x_i}{B/A} = t$$

$x_o N_1/C^* (x_o/2D + 1/k_s) = t$, linear for $x_o/2D << 1/k_s$

6.12 A silicon wafer is covered by an SiO_2 film 0.3 µm thick.

a. What is the time required to increase the thickness by 0.5 µm by oxidation in H_2O at 1200°C?

b. Repeat for oxidation in dry O_2 at 1200°C.

Answer:

We will perform the calculation for <111> silicon wafers. For <100> wafers, the linear rate constant should be divided by 1.68.

a. At 1200°C, in H_2O

$$B = 3.86 \times 10^{2} \exp\left(-\frac{0.78}{kT}\right) = 0.829\ \mu m^{2} / hr$$

$$\frac{B}{A} = 1.63 \times 10^{8} \exp\left(-\frac{2.05}{kT}\right) = 15.86\ \mu m / hr$$

$$A = 0.052\ \mu m$$

The initial oxide, if grown at 1200°C would have taken this long to grow

$$\tau = \frac{x_i^2 + Ax_i}{B} = \frac{(0.3)^2 + (0.052)(0.3)}{0.829} = 0.127 \text{ hr}$$

$$\frac{x_O^2 - x_i^2}{B} + \frac{x_O - x_i}{B/A} = t$$

The time required to grow $0.8\ \mu\text{m}$ at 1200°C is

$$\tau + t = \frac{x_o^2 + Ax_o}{B} = \frac{(0.8)^2 + (0.052)(0.8)}{0.829} = 0.822 \text{ hr}$$

Thus, the time required to add $0.5\ \mu\text{m}$ to an existing $0.3\ \mu\text{m}$ film is $0.822 - 0.127 = 0.695$ hr or 41.7 minutes.

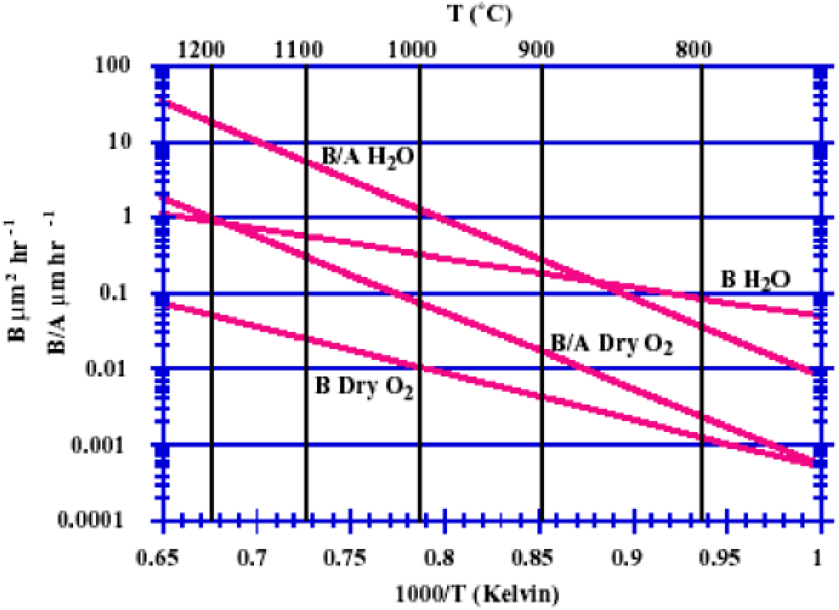
b. At 1200°C, in dry oxygen

$$B = 7.72 \times 10^2 \exp\left(-\frac{1.23}{k(1200 + 273)} \right) = 0.048\ \mu\text{m}^2/\text{hr}$$

$$\frac{B}{A} = 6.23 \times 10^{6} \exp\left(-\frac{2.0}{kT}\right) = 0.899\ \mu m / hr$$

$$A = 0.053\ \mu m$$

The initial oxide would have taken 2.206 hours to grow in dry oxygen, it would require 14.217 hours to grow $0.8\ \mu m$, thus would require an additional 12 hours to add $0.5\ \mu m$ to an existing $0.3\ \mu m$ film.



Σταθερές οξείδωσης

What is the approximate oxide thickness after a 100 minute dry O2 oxidation followed by a 35 minute H2O oxidation at 900°C?

We will perform the calculation for <111> silicon wafers. For <100> wafers, the linear rate constant should be divided by 1.68.

At 900°C, in dry oxygen

$$B = 7.72 \times 10^2 \exp\left(-\frac{1.23}{k(900+273)}\right) = 0.004\ \mu m^2/hr$$

$$\frac{B}{A} = 6.23 \times 10^6 \exp\left(-\frac{2.0}{kT}\right) = 0.016\ \mu m/hr$$

$$A = 0.251\ \mu m$$

At 900°C, in H_2O

$$B = 3.86 \times 10^2 \exp\left(-\frac{0.78}{kT}\right) = 0.172\ \mu m^2/hr$$

$$\frac{B}{A} = 1.63 \times 10^8 \exp\left(-\frac{2.05}{kT}\right) = 0.255\ \mu m/hr$$

$$A = 0.674\ \mu m$$

$$\frac{\mathbf{x_O^2 - x_i^2}}{\mathbf{B}} + \frac{\mathbf{x_O - x_i}}{\mathbf{B/A}} = \mathbf{t}$$

The thickness after 100 minutes in dry oxygen at 900˚C is

$$x_O = \frac{A}{2}\left\{\sqrt{1+\frac{t+\tau}{A^2/4B}}-1\right\} = \frac{0.251}{2}\left\{\sqrt{1+\frac{100/60}{(0.251)^2/4(0.004)}}-1\right\} = 0.024\ \mu\text{m}$$

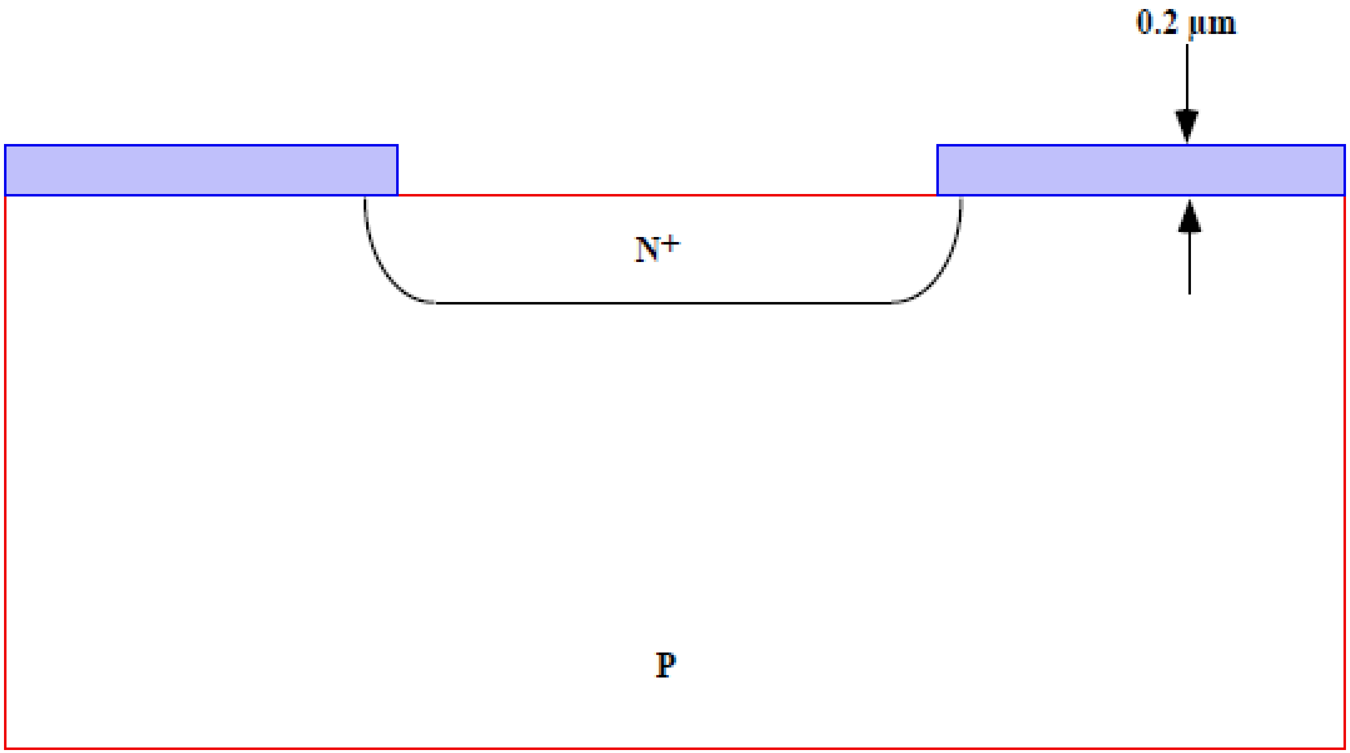
This thickness corresponds to a time of

$$\tau = \frac{x_i^2 + Ax_i}{B} = \frac{(0.024)^2 + (0.674)(0.024)}{0.172} = 0.097\ \text{hr}$$

in H_2O at 900˚C. This corresponds to the "initial time" that should be used for the wet oxidation step, giving the thickness after an additional 35 minutes in wet oxide as

$$x_O = \frac{A}{2}\left\{\sqrt{1+\frac{t+\tau}{A^2/4B}}-1\right\} = \frac{0.674}{2}\left\{\sqrt{1+\frac{35/60+0.097}{(0.674)^2/4(0.172)}}-1\right\} = 0.143\ \mu\text{m}$$

The structure shown below is formed by oxidizing a silicon wafer (x0 = 200 nm), and then using standard masking and etching techniques to remove the SiO_2 in the center region. An N+ doping step is then used to produce the structure shown. The structure is next placed in an oxidation furnace and oxidized at 900°C in H_2O. The oxide will grow faster over the N+ region than it will over the lightly doped substrate. Assume that B/A is enhanced by 4X over the N+ region. Will the growing oxide over the N+ region ever catch up in thickness to the other oxide? If so, when and at what thickness.



Using the Deal Grove model for oxidation, the growth is described by

$$\frac{X_O^2 - X_i^2}{B} + \frac{X_O - X_i}{B/A} = t$$

If the oxide over the N^+ region catches up with the oxide over the P region at some time t, then at that time we will have

$$\frac{X_O^2 - X_i^2}{B} + \frac{X_O - X_i}{B/A} = \frac{X_O^2}{B} + \frac{X_O}{4B/A}$$

where $x_i = 0.2\ \mu m$. This gives

$$x_0 = \frac{4}{3}\left(\frac{x_i^2}{A} + x_i\right)$$

At 900°C, in H_2O

$$B = 3.86 \times 10^2 \exp\left(-\frac{0.78}{kT}\right) = 0.172\ \mu m^2 / hr$$

$$\frac{B}{A} = 1.63 \times 10^{8} \exp\left(-\frac{2.05}{kT}\right) = 0.255\ \mu m / hr$$

$$A = 0.674\ \mu m$$

These values apply to (111) silicon. For (100) silicon, B/A is 1.68 times smaller. Thus we have,

$$A_{(111)} = 0.674\ \mu m$$

$$A_{(100)} = 1.13\ \mu m$$

Finally, the N^{+} oxide catches up with the P oxide at an oxide thickness of

$$X_{(111)} = 0.346\ \mu m$$

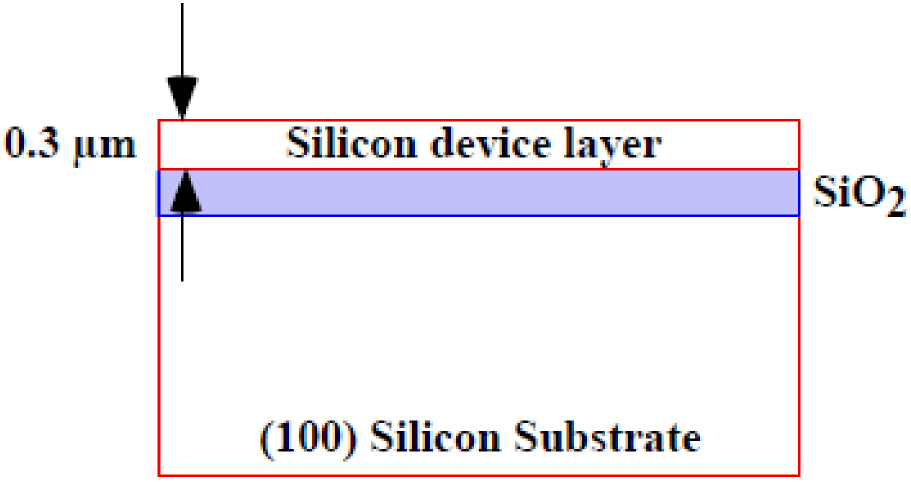
$$X_{(100)} = 0.314\ \mu m$$

This occurs at a time given by

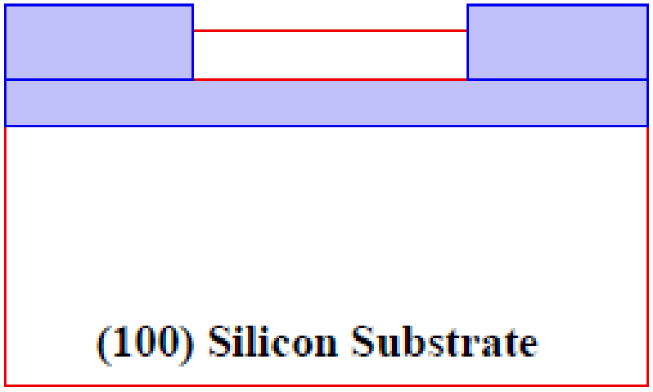
$$t_{(111)} = \frac{(0.346)^2 - (0.2)^2}{.172} + \frac{0.346 - 0.2}{0.255} = 1.04\ \text{hrs}$$

$$t_{(100)} = \frac{(0.314)^2 - (0.2)^2}{.172} + \frac{0.314 - 0.2}{0.152} = 1.09\ \text{hrs}$$

Silicon on Insulator or SOI is a new substrate material that is being considered for future integrated circuits. The structure, shown below, consists of a thin single crystal silicon layer on an insulating (SiO2) substrate. The silicon below the SiO2 provides mechanical support for the structure. One of the reasons this type of material is being considered, is because junctions can be diffused completely through the thin silicon layer to the underlying SiO2. This reduces junction capacitances and produces faster circuits. Isolation is also easy to achieve in this material, because the thin Si layer can be completely oxidized, resulting in devices completely surrounded by SiO2. A LOCOS process is used to locally oxidize through the silicon as shown on the right below. Assuming the LOCOS oxidation is done in H2O at 1000°C, how long will it take to oxidize through the 0.3 µm silicon layer? Calculate a numerical answer using the Deal Grove model.



Starting Material



After LOCOS Isolation

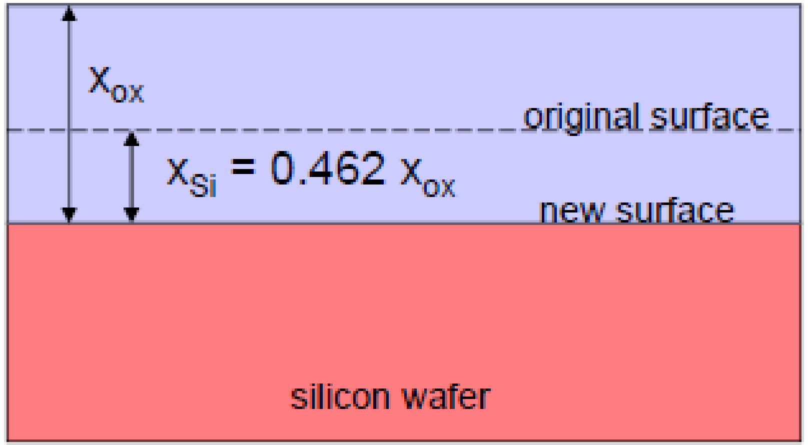
To oxidize completely through a 0.3 μm silicon layer, we will need to grow (2.2)(0.3 μm) = 0.66 μm of SiO_2. At 1000°C in H_2O, the Deal Grove rate constants are given by (Table 6-2):

$$B = 3.86x10^2 \exp\left(-\frac{0.78\text{eV}}{kT}\right) = 0.316\mu m^2 hr^{-1}$$

$$\frac{B}{A} = \frac{1.63x10^8}{1.68}\exp\left(-\frac{2.05\text{eV}}{kT}\right) = 0.747\mu m hr^{-1}$$

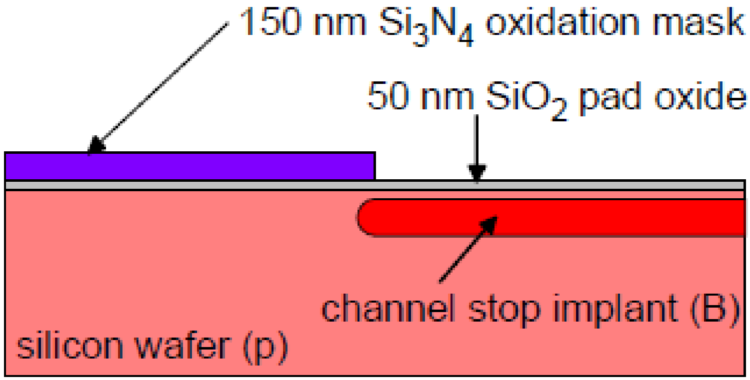
$$\therefore t = \frac{(0.66)^2}{0.316} + \frac{0.66}{0.747} \cong 2.25 \text{ hours}$$

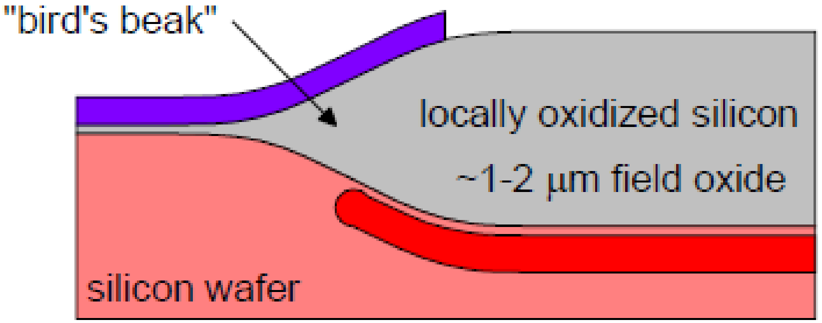
$$\frac{\mathbf{x_O^2 - x_i^2}}{\mathbf{B}} + \frac{\mathbf{x_O - x_i}}{\mathbf{B/A}} = \mathbf{t}$$

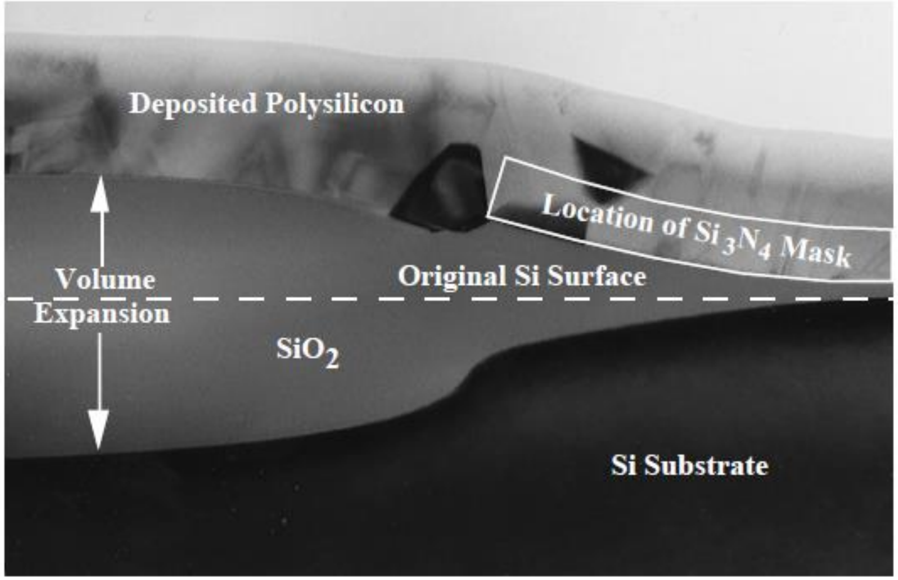


Local Oxidation of Silicon (LOCOS) - 2

- LOCOS process steps:
  - 50 nm pad oxide
  - 150 nm CVD nitride layer
  - Pattern and etch nitride
  - Channel stop implant
  - Wet oxidation of field oxide
    - Typ. 1000°C for 4-10 hours.
    - HIPOX often used for this.
  - Strip nitride
  - Strip pad oxide







A uniform oxide layer of 0.4µm thickness is selectively etched to expose the silicon surface in some locations on a wafer surface. A second oxidation at 1000°C in H2O grows 0.2µm on the bare silicon. Sketch a cross-section of the SiO2 in all locations on the wafer and the position of the Si/SiO2 interface.

We will perform the calculation for <111> silicon wafers. For <100> wafers, the linear rate constant should be divided by 1.68.

$$\frac{x_O^2 - x_i^2}{B} + \frac{x_O - x_i}{B/A} = t$$

The time to grow 0.2 µm is then

$$t = \frac{x_o^2 + Ax_o}{B} = \frac{(0.2)^2 + (0.252)(0.2)}{0.316} = 0.286 \text{ hr}$$

The time to grow the initial 0.4 µm was

$$\tau = \frac{x_i^2 + Ax_i}{B} = \frac{(0.4)^2 + (0.252)(0.4)}{0.316} = 0.825 \text{ hr}$$

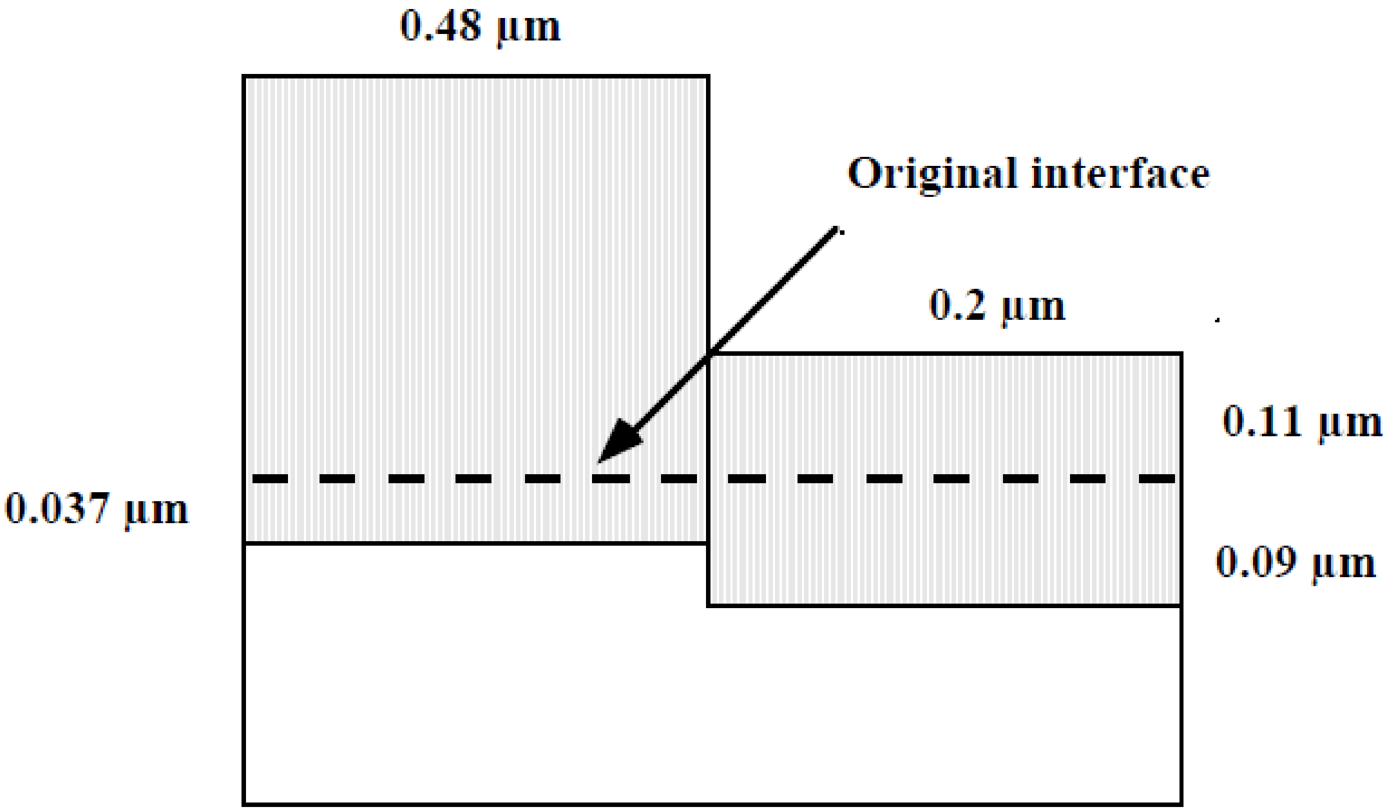
The extra time to grow 0.2 µm in the bare areas will grow some extra oxide where the initial 0.4 µm oxide existed

$$x_O = \frac{A}{2}\left\{\sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1\right\} = \frac{0.252}{2}\left\{\sqrt{1 + \frac{0.286 + 0.825}{(0.252)^2/4(0.316)}} - 1\right\} = 0.480 \text{ µm}$$

The growth of the extra $0.080\ \mu m$ will consume $0.46 \times 0.080 = 0.037\ \mu m$ of silicon under the thick oxide.

The growth of $0.2\ \mu m$ of oxide will consume $0.46 \times 0.2 = 0.092\ \mu m$ of silicon.

Thus, a sketch of the old and new oxide-silicon interface is shown below:



As part of an IC process flow, a CVD SiO2 layer 1.0 µm thick is deposited on a <100> silicon substrate. This structure is then oxidized at 900°C for 60 minutes in an H2O ambient. What is the final SiO2 thickness after this oxidation? Calculate an answer, do not use the oxidation charts in the text.

At 900°C in H_2O, the oxidation rate constants are given by:

$$\frac{x_O^2 - x_i^2}{B} + \frac{x_O - x_i}{B/A} = t$$

$$B = 3.86\text{x}10^2 \exp\left(-\frac{0.78}{(8.62\text{x}10^{-5})(1173)}\right) \mu\text{m}^2\ \text{hr}^{-1} = 0.17\ \mu\text{m}^2\ \text{hr}^{-1}$$

$$\frac{B}{A} = \frac{1.63\text{x}10^8}{1.68} \exp\left(-\frac{2.05}{(8.62\text{x}10^{-5})(1173)}\right) \mu\text{m hr}^{-1} = 0.152\ \mu\text{m hr}^{-1}$$

The initial oxide on the wafer is 1.0 µm thick. This corresponds to a τ of

$$\tau = \frac{(1)^2 + (1)\left(\frac{0.17}{0.152}\right)}{0.17} = 12.46 \text{ hours}$$

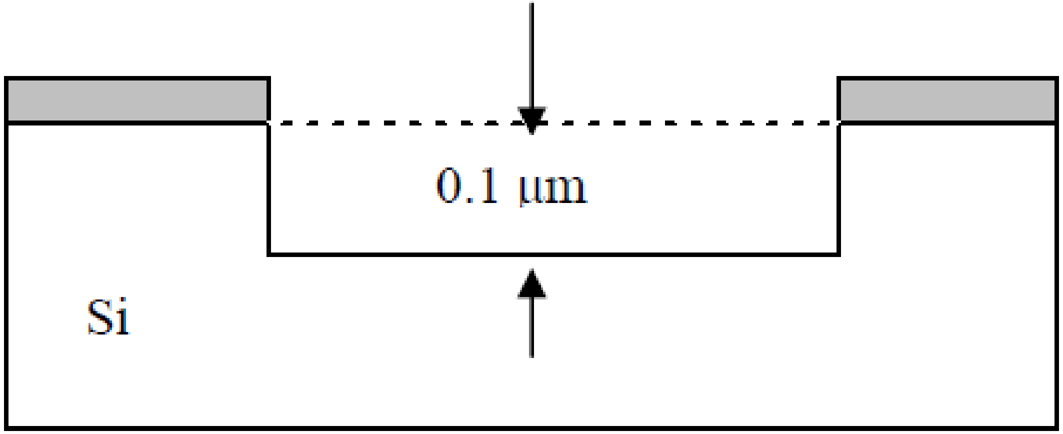
$$\tau = \frac{x_i^2 + Ax_i}{B}$$

Thus the final oxide thickness is given by

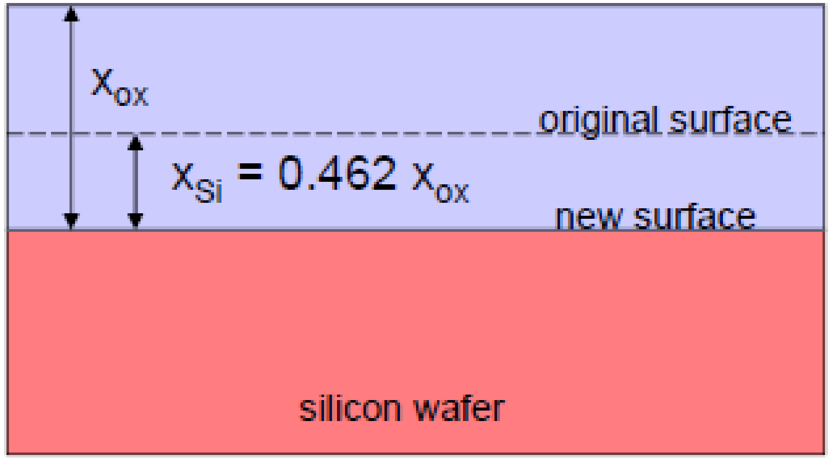
$$x_O = \frac{A}{2}\left\{\sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1\right\}$$

$$x_o = \frac{0.17}{(2)(0.152)}\left\{\sqrt{1 + \frac{13.46}{\frac{(1.11)^2}{(4)(0.17)}}} - 1\right\} = 1.064\ \mu\text{m}$$

Όπως φαίνεται στο παρακάτω σχήμα έχει σχηματισθεί άνοιγμα βάθους 0.1 μm εντός του πυριτίου. Η υπόλοιπη επιφάνεια προστατεύεται με νιτρίδιο πυριτίου (γκρι χρώμα).



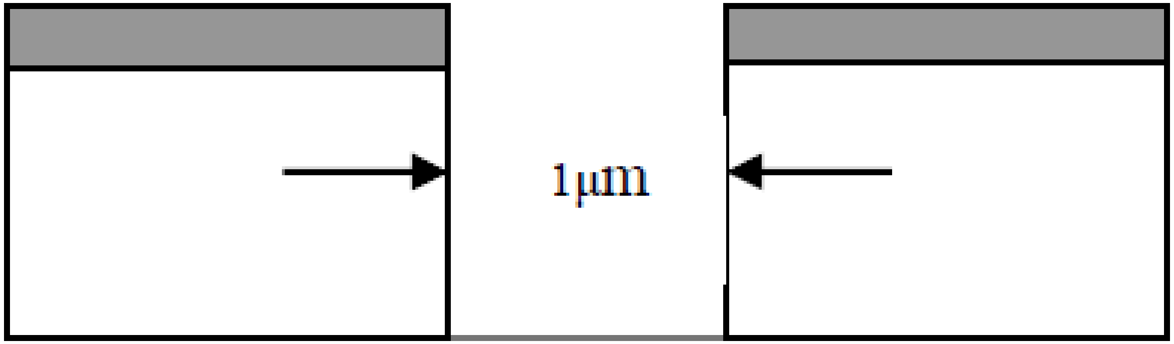
Υποθέτοντας ότι η οριζόντια διάσταση του ανοίγματος είναι πολύ μεγαλύτερη από 0.1 μm να βρείτε το πάχος του οξειδίου που απαιτείται να σχηματισθεί με θερμική οξείδωση ώστε το άνοιγμα να γεμίσει με οξείδιο μέχρι την αρχική επιφάνεια του πυριτίου.



0.1 um = 0.54 Xox

Xox = 0.185 um

Πυρίτιο εγχαράσσεται σε βάθος αρκετών δεκάδων μικρομέτρων και πλάτος 1 μm όπως στο σχήμα. Βρείτε τον χρόνο που απαιτείται ώστε να κλείσει το κενό του 1 μm οξειδώνοντας στους 1100 ºC και υγρό περιβάλλον. Το στρώμα του νιτριδίου (με σκούρο χρώμα) προστατεύει το πυρίτιο απο οξείδωση στην επιφάνεια.



0.5 um = 0.54 Xox

Xox = 0.9 um