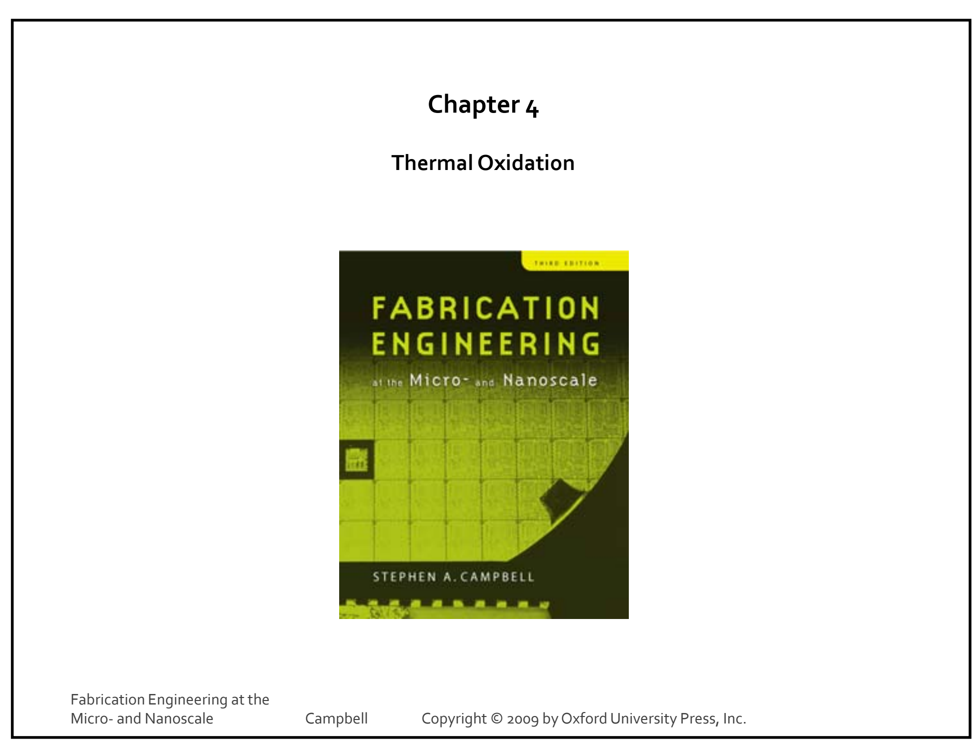
ECE 416/516 IC Technologies

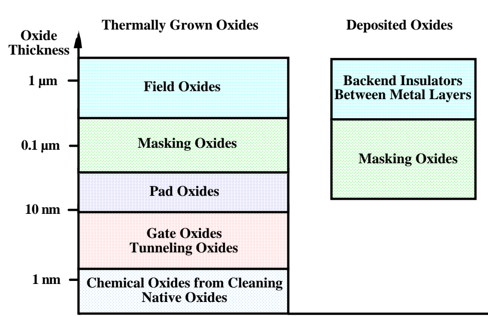
Lecture 4: Oxidation

Professor James E. Morris
Spring 2012



THERMAL OXIDATION
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 ($\rho > 10^{16}\ \Omega\text{cm},\ E_g > 9\ \text{eV}$).
- High breakdown field ($10^7\ \text{Vcm}^{-1}$)
- Excellent junction passivation.
- Stable bulk electrical properties.
- Stable and reproducible interface with Si.

- No other known semiconductor/insulator combination has properties that approach the Si/SiO_2 interface.

3

Figure 4.24 Horizontal tube oxidation/diffusion system includes computer controller, load station, and four tubes *(photo courtesy of ASM International).*

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Figure 4.26 Vertical oxidation system showing carousel, robot arm, and wafers about to be raised into the furnace *(photo courtesy of ASM International).*

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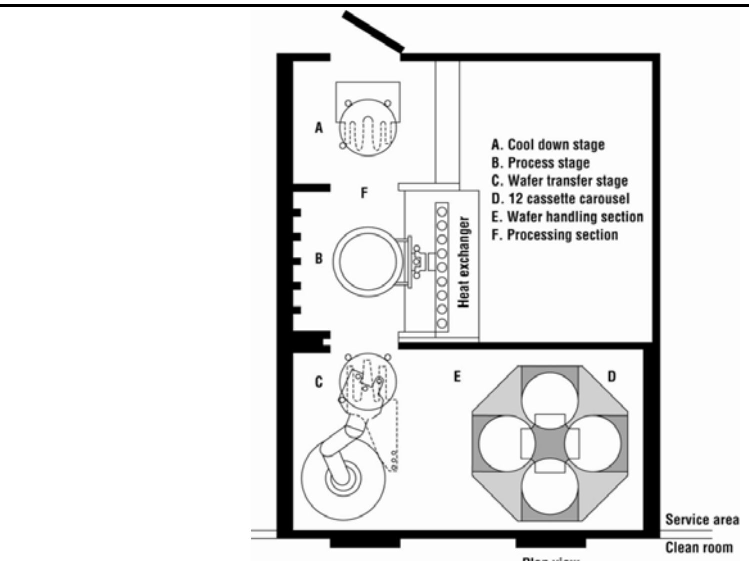

Figure 4.25 Plan view of vertical furnace. Cassettes with 25 wafers are loaded into the carousel and transferred to the process stage, where they are raised into the furnace *(courtesy of ASM International).*

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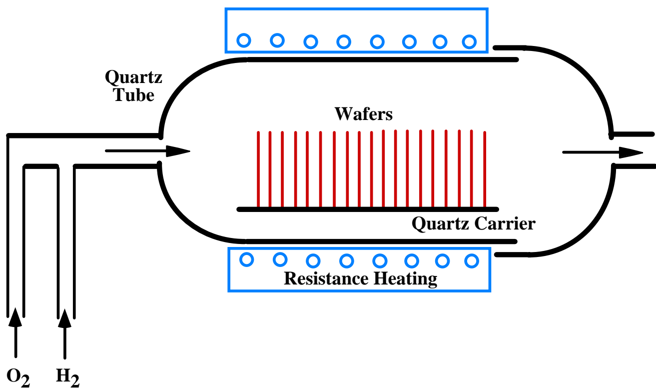
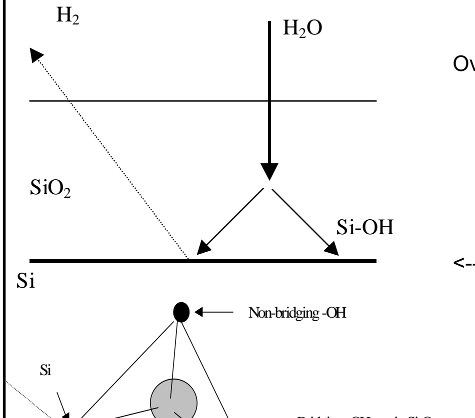
- **Oxidation systems are conceptually very simple.**
- **In practice today, vertical furnaces, RTO systems and fast ramp furnaces all find use.**



- **Thermal oxidation can potentially be used in many places in chip fabrication. In practice, deposited SiO_2 layers are increasingly being used (lower Dt).**

7

Thermal Oxidation of Si in steam



Overall Reaction is:

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

In SiO_2:

$$H_20 + Si\text{-}0\text{-}Si \rightarrow 2Si\text{-}OH$$

$$2Si\text{-}OH + Si\text{-}Si \rightarrow 2Si\text{-}O\text{-}Si + 2H_2$$

<---- Reaction builds SiO_2 at Si surface

Final Si/SiO2 interface inside original Si
∴ Interface clean & well characterized

Diffusion process important

$D = D_0 \exp - E_a/kT$

Si(solid) + O_2(gas) → SiO_2 OR: Si (solid) + $2H_2O$ (steam) → SiO_2 + $2H_2$

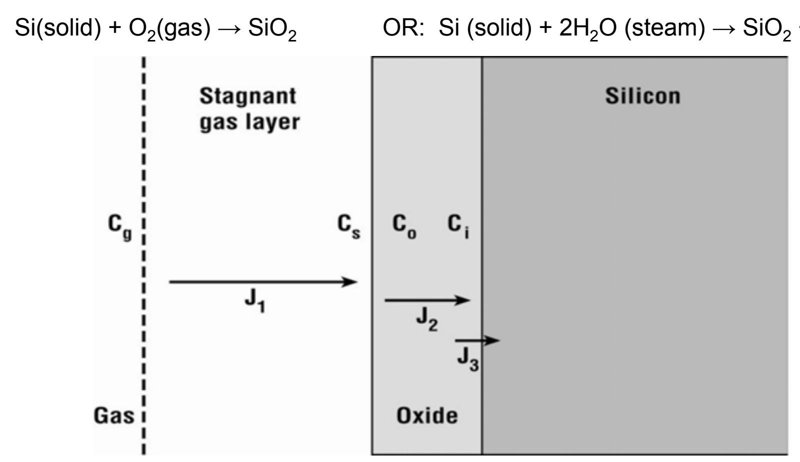


Figure 4.1 Schematic diagram of the oxidant flows during oxidation.

Could write $J_1 = J_{gas} = D_{O_2}\dfrac{C_g - C_s}{t_{sgl}}$, where $C_g = \dfrac{n}{V} = \dfrac{P_g}{kT}$

but more commonly $J_1 = h_g(C_g - C_s)$, where h_g = mass transport coefficient

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So $J_1 = h_g(C_g - C_s)$, $J_2 = \mathrm{D_{O_2}}\dfrac{\mathrm{C_o} - C_i}{\mathrm{t_{ox}}}$, & $J_3 = k_s C_i$, where k_s = chemical rate constant

Continuity : $J = J_1 = J_2 = J_3$ gives 2 equations in 3 unknowns : $\mathrm{C_s}$, $\mathrm{C_o}$, $\mathrm{C_i}$

$$h_g(C_g - C_s) = \mathrm{D_{O_2}}\frac{\mathrm{C_o} - C_i}{\mathrm{t_{ox}}} = k_s C_i$$

Add Henry's Law : $C_o = Hp_g = HkTC_s$, where H is a segregation coefficient,

then solving gives $C_i = \dfrac{Hp_g}{1 + \dfrac{k_s}{h} + \dfrac{k_s t_{ox}}{D_{O_2}}}$ where $h = \dfrac{h_g}{HkT}$

and growth rate $R = \dfrac{J}{N_1} = \dfrac{k_s C_i}{N_1} = \dfrac{dt_{ox}}{dt} = \dfrac{Hk_s p_g}{N_1\left[1 + \dfrac{k_s}{h} + \dfrac{k_s t_{ox}}{D_{O_2}}\right]}$

where N_1 = oxidant molecule density in grown oxide

$= 2.2\text{x}10^{22}$/cc for O_2 and $4.4\text{x}10^{22}$/cc for H_2O

$$\frac{dt_{ox}}{dt}=\frac{Hk_s p_g}{N_1\left[1+\frac{k_s}{h}+\frac{k_s t_{ox}}{D_{O_2}}\right]} \text{ gives } N_1\int_{t_i}^{t_{ox}}\left[1+\frac{k_s}{h}+\frac{k_s t_{ox}}{D_{O_2}}\right]dt_{ox}=Hk_s p_g\int_0^t dt$$

$$\text{with solution } \frac{N_1}{Hk_s p_g}\left[\left(1+\frac{k_s}{h}\right)[t_{ox}-t_i]+\left(\frac{k_s}{2D_{O_2}}\right)[t_{ox}{}^2-t_i{}^2]\right]=t$$

$$\frac{[t_{ox}-t_i]}{B/A}+\frac{[t_{ox}{}^2-t_i{}^2]}{B}=t \rightarrow \frac{t_{ox}{}^2}{B}+\frac{t_{ox}}{B/A}=t+\tau$$

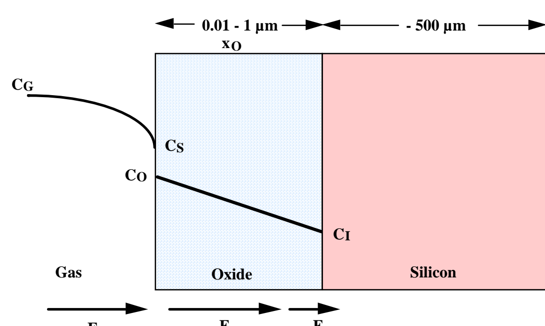
where t_i and $\tau=\frac{t_i^2+At_i}{B}$ acount for any initial oxide thickness.

The quadratic solution is $t_{ox}=\frac{A}{2}\left[\sqrt{1+\frac{t+\tau}{A^2/4B}}-1\right]$ with two limiting solutions:

$t_{ox}\approx\frac{B}{A}(t+\tau)$ for small t_{ox}, and $t_{ox}^2\approx B(t+\tau)$ for large t_{ox}

B/A and B are referred to as the linear and parabolic rate constants

SiO_2 Growth Kinetics Models
A. Deal Grove Model



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

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

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

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

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

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

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

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

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

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

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

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

- Integrating this equation, results in the linear parabolic model.

13

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

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

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

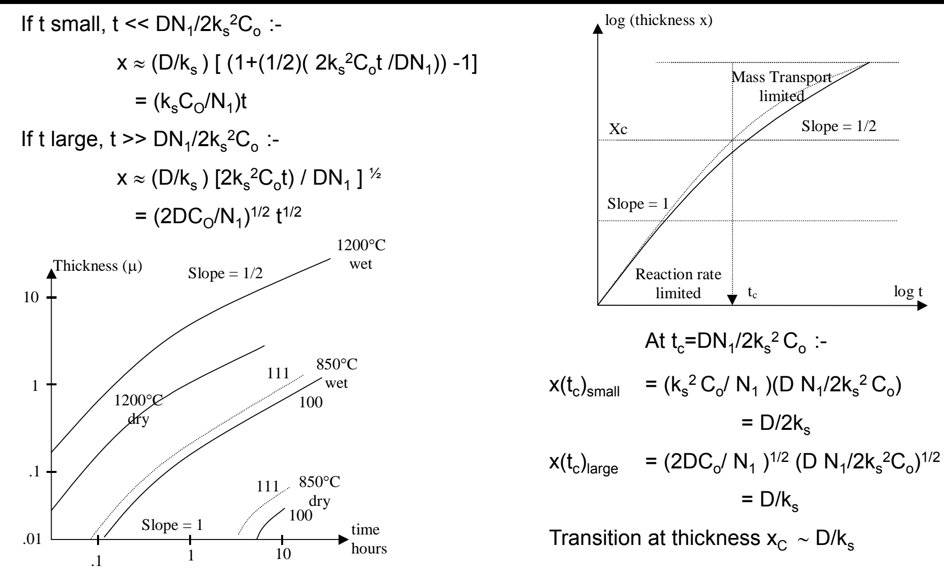
- (10) can also be written with oxide thickness as a function of time.

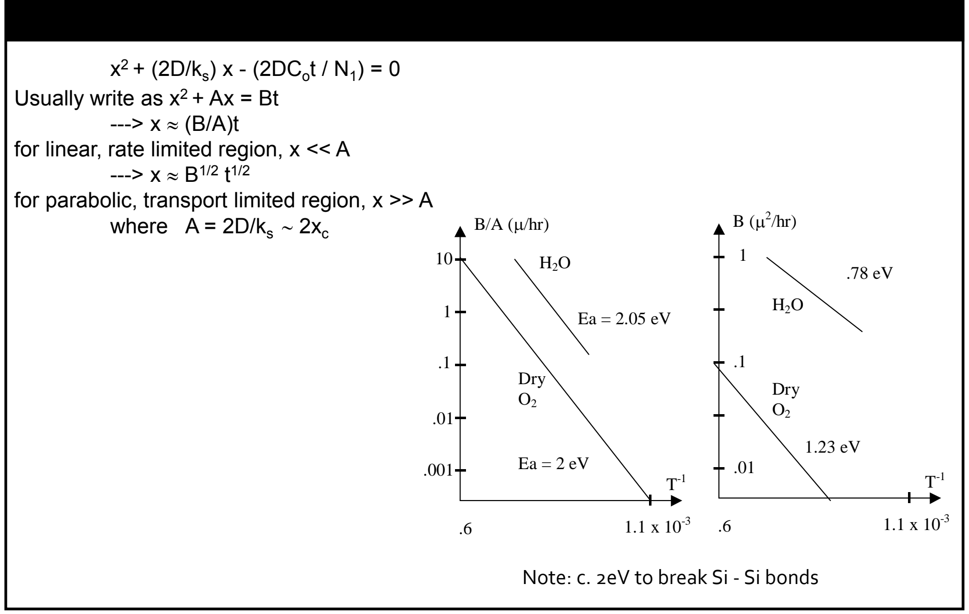
$$x_O = \frac{A}{2}\left\{\sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1\right\} \quad (13)$$

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

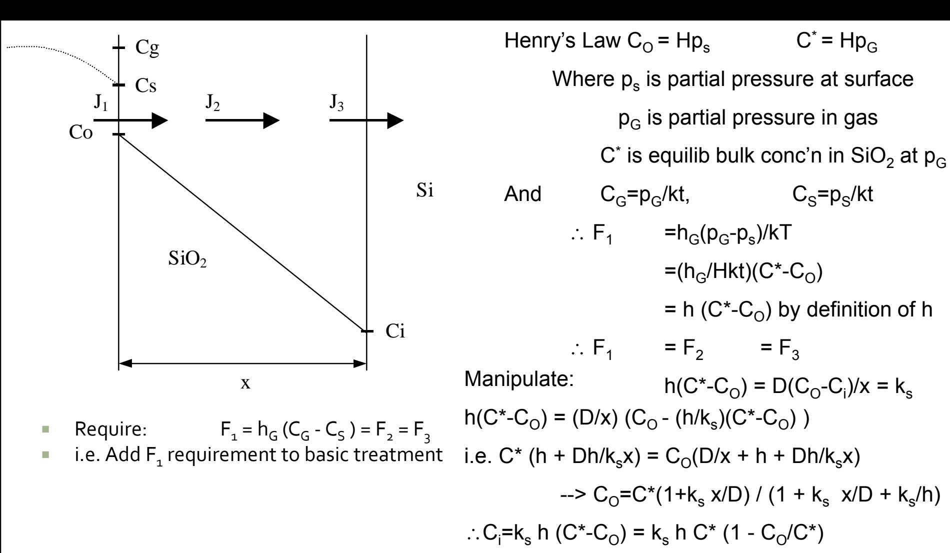
and $\frac{dx}{dt} = \frac{B}{A + 2x_0} \rightarrow \frac{B}{A + 2x_0} + Ce^{-x_o/L}$ for simulations (Massoud et al)

14


Oxide Growth: Sketch Plots
If t small, $t << DN_1/2k_s^2C_o$:-
$x \approx (D/k_s)\,[\,(1+(1/2)(\,2k_s^2C_ot\,/DN_1))\,-1]$
$= (k_sC_O/N_1)t$
If t large, $t >> DN_1/2k_s^2C_o$:-
$x \approx (D/k_s)\,[2k_s^2C_ot)\,/\,DN_1\,]^{½}$
$= (2DC_O/N_1)^{1/2}\,t^{1/2}$
Thickness (μ)
Slope = 1/2
1200°C wet
10
1
.1
.01
1200°C dry
111
850°C wet
100
111
850°C dry
100
Slope = 1
time hours
.1
1
10
log (thickness x)
Mass Transport limited
Xc
Slope = 1/2
Slope = 1
Reaction rate limited
t_c
log t
At $t_c=DN_1/2k_s^2\,C_o$:-
$x(t_c)_{small}$ $= (k_s^2\,C_o/\,N_1\,)(D\,N_1/2k_s^2\,C_o)$
$= D/2k_s$
$x(t_c)_{large}$ $= (2DC_o/\,N_1\,)^{1/2}\,(D\,N_1/2k_s^2C_o)^{1/2}$
$= D/k_s$
Transition at thickness $x_C \sim D/k_s$


Oxide Growth: Linear/Parabolic Rates
$x^2 + (2D/k_s)\,x - (2DC_ot\,/\,N_1) = 0$
Usually write as $x^2 + Ax = Bt$
---> $x \approx (B/A)t$
for linear, rate limited region, x << A
---> $x \approx B^{1/2}\,t^{1/2}$
for parabolic, transport limited region, x >> A
where $A = 2D/k_s \sim 2x_c$
B/A (μ/hr)
10
1
.1
.01
.001
H_2O
Ea = 2.05 eV
Dry O_2
Ea = 2 eV
T^{-1}
.6
1.1 x 10^{-3}
B ($μ^2$/hr)
1
.78 eV
H_2O
.1
Dry O_2
1.23 eV
.01
T^{-1}
.6
1.1 x 10^{-3}
Note: c. 2eV to break Si - Si bonds

Stagnation Layer #1



Stagnation Layer #2

It is more useful to have constants A & B in terms of C^* than C_O, i.e. related to p_G
Also C_0 not constant - depends on x

∴Redo basic theory: $dx/dt = F_3/N_1 = (DC_O/N_1) /(x+D/k_s)$

$(= k_s C_i/N_1)$

$=(D/N_1)(1+k_s x/D)C^*/(D/k_s)(1+k_s x/D)(1+k_s x/D+k_s/h)$

$= k_s (C^*/N_1) / (1+k_s x/D +k_s/h)$

$\therefore (k_s/D)\, x\,dx + (1+k_s/h)\, dx = (k_s C^*/N_1)\, dt$

$(k_s/2D)x^2 + (1+k_s/h)x = (k_s C^*/N_1)t + \text{constant}$

Boundary condition at t=0:

$\text{constant} = (k_s x_i^2 / 2D) + (1 + k_s/h)x_i$

$= k_s C^* \tau /N_1$ as definition of τ

i.e. $\tau = (N_1/C^*) [x_i^2/2D + x_i(1/k_s + 1/h)]$

$\therefore x^2 + 2D(1/k_s + 1/h)x - (2DC^*/N_1)(t+ \tau) = 0$

giving $x= D (1/k_s + 1/h) \times [\{1+2C^*(t+ \tau) / N_1 D (1/k_s + 1/h)^2\}^{1/2} -1]$

Stagnation Layer #3

If t small:

$x=D(1/k_s+1/h)\,[C^*(t+\tau)/N_1D(1/k_s + 1/h)^2]$

$= C^*(t+\tau) / N_1\,(1/k_s + 1/h)$

$= (B/A)(t+\tau)$ defining B/A

If t large:

$x \approx [2DC^*(t+\tau)/N_1]^{1/2}$

$= B^{1/2}\,(t+\tau)^{1/2}$ defining B

where $B=2DC^*/N_1$ (compare $2DC_O/N_1$)

and $A=2DC^*/N_1 / C^*/N_1(1/k_s + 1/h)$

$= 2D(1/k_s + 1/h)$ (compare $2D/k_s$)

and $\tau = (x_i^2+Ax_i) / B$

Very Thin Films

- Theory above assumes diffusion through oxide
  - •What if there is no oxide??

•If extrapolate experimental data based on theory above to t=0, get initial film intercept at c.20nm

•Early growth processes not clear

•Initial accelerated growth:

- •to 23±3nm in dry O_2
- •negligible effect in wet O_2/steam

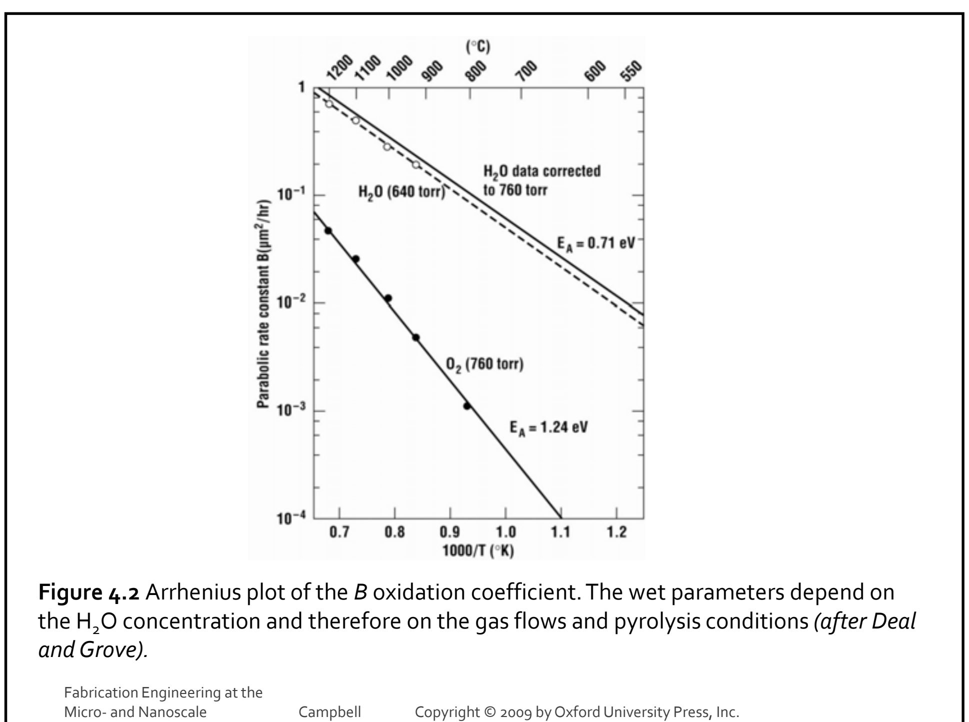


Figure 4.2 Arrhenius plot of the *B* oxidation coefficient. The wet parameters depend on the H_2O concentration and therefore on the gas flows and pyrolysis conditions *(after Deal and Grove).*

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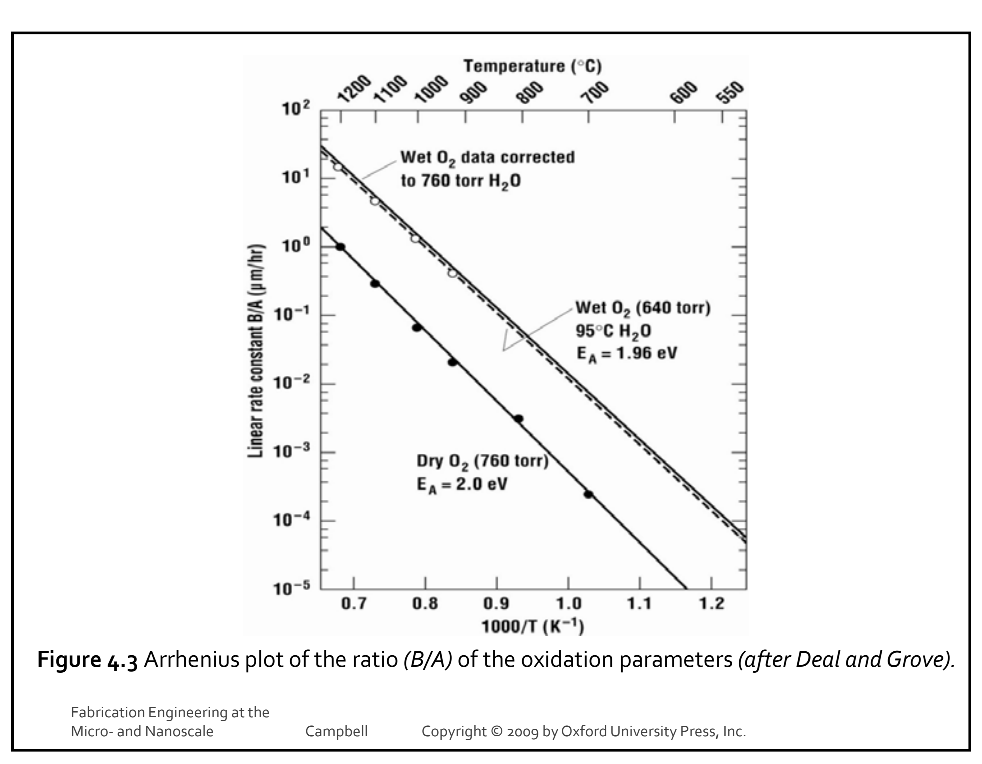

Figure 4.3 Arrhenius plot of the ratio *(B/A)* of the oxidation parameters *(after Deal and Grove).*

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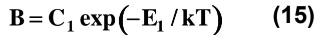
- The rate constants B and B/A have physical meaning (oxidant diffusion and interface reaction rate respectively).

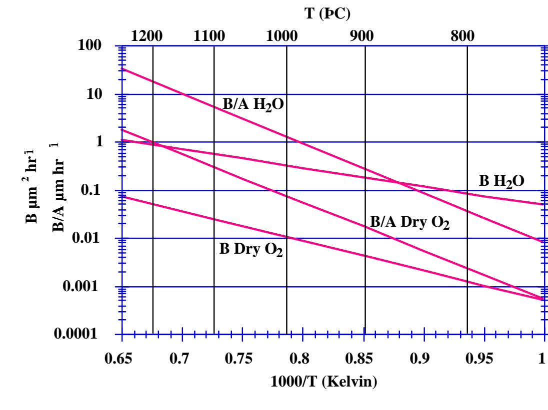
Ambient	B	B/A
Dry O_2	$C_1 = 7.72 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 1.23$ eV	$C_2 = 6.23 \times 10^6\ \mu\ hr^{-1}$ $E_2 = 2.0$ eV
Wet O_2	$C_1 = 2.14 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 0.71$ eV	$C_2 = 8.95 \times 10^7\ \mu\ hr^{-1}$ $E_2 = 2.05$ eV
H_2O	$C_1 = 3.86 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 0.78$ eV	$C_2 = 1.63 \times 10^8\ \mu\ hr^{-1}$ $E_2 = 2.05$ eV



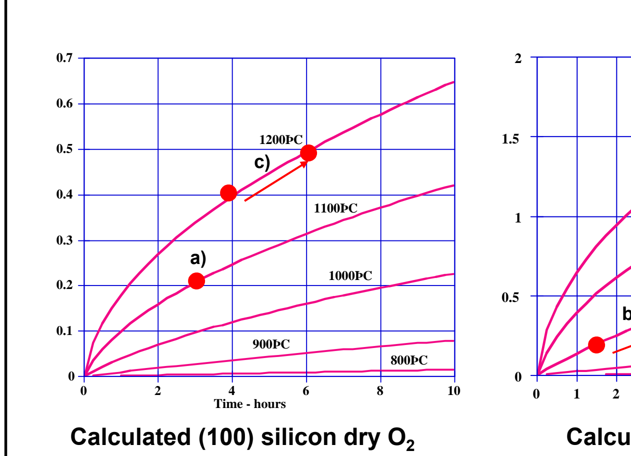
$$B = C_1 \exp(-E_1 / kT) \quad (15)$$

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

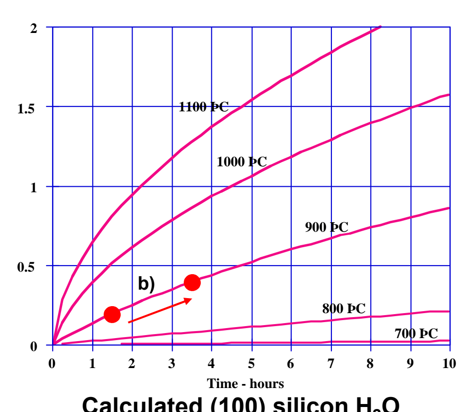
- Numbers are for (111) silicon, for (100) divide C_2 by 1.68.



- Plots of B, B/A using the values in the above Table.



Calculated (100) silicon dry O_2 oxidation rates using Deal Grove.



Calculated (100) silicon H_2O oxidation rates using Deal Grove.

Example: Problem 6.13 in the text: a) 3 hrs in O_2 @ 1100 ˚C = 0.21 µm + b) 2 hrs in H_2O @ 900 ˚C = 0.4 µm + c) 2 hrs in O_2 @ 1200 ˚C = 0.5 µm total oxide thickness.

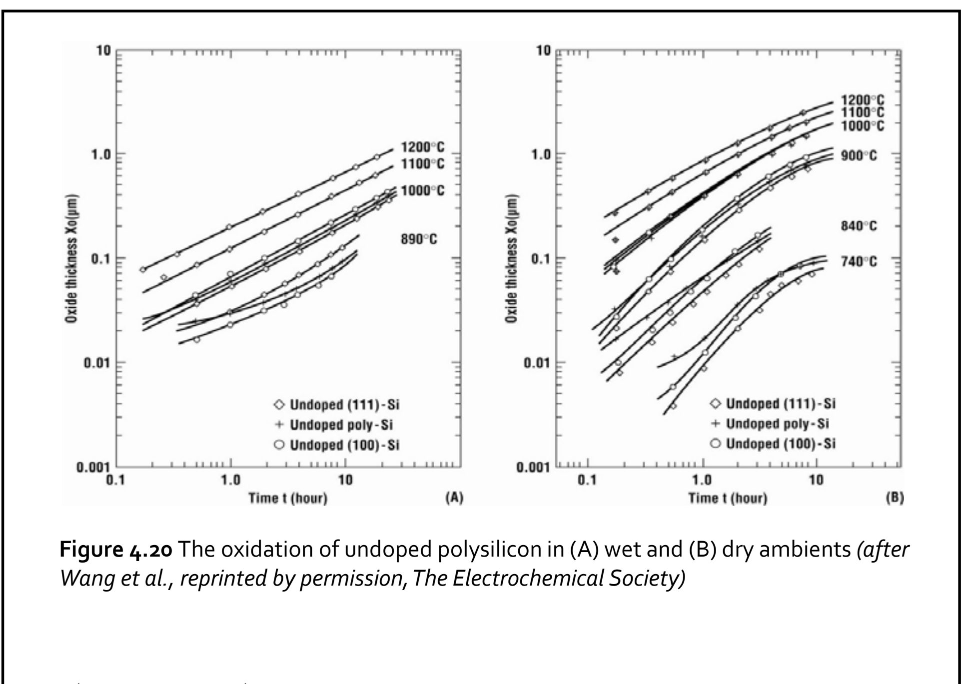


Figure 4.20 The oxidation of undoped polysilicon in (A) wet and (B) dry ambients *(after Wang et al., reprinted by permission, The Electrochemical Society)*

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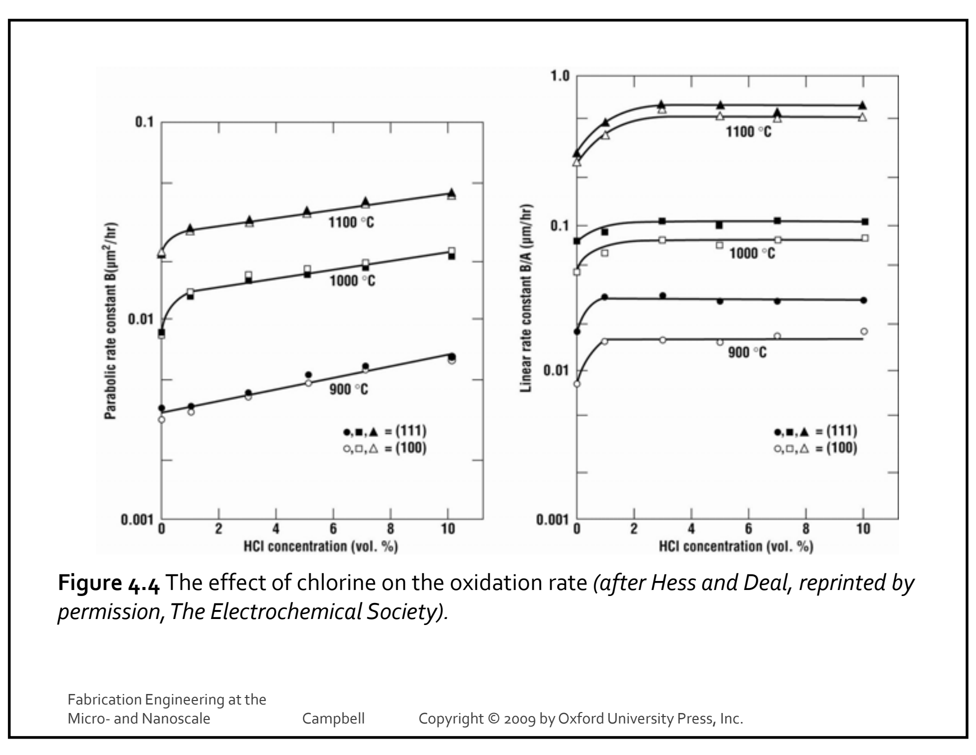

Figure 4.4 The effect of chlorine on the oxidation rate *(after Hess and Deal, reprinted by permission, The Electrochemical Society).*

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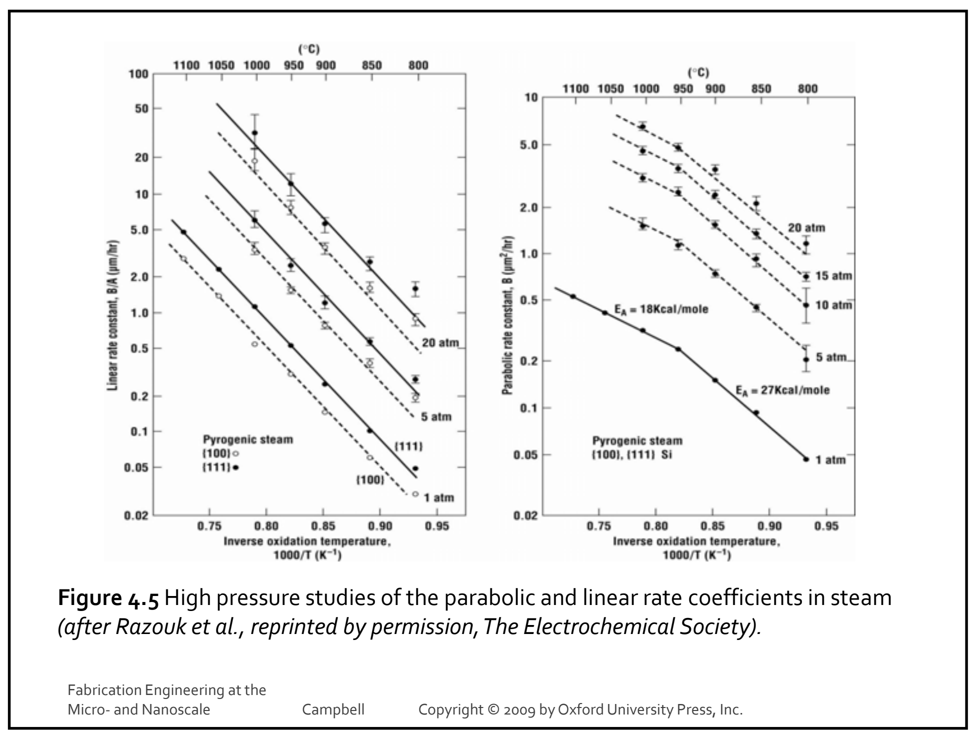

Figure 4.5 High pressure studies of the parabolic and linear rate coefficients in steam *(after Razouk et al., reprinted by permission, The Electrochemical Society).*

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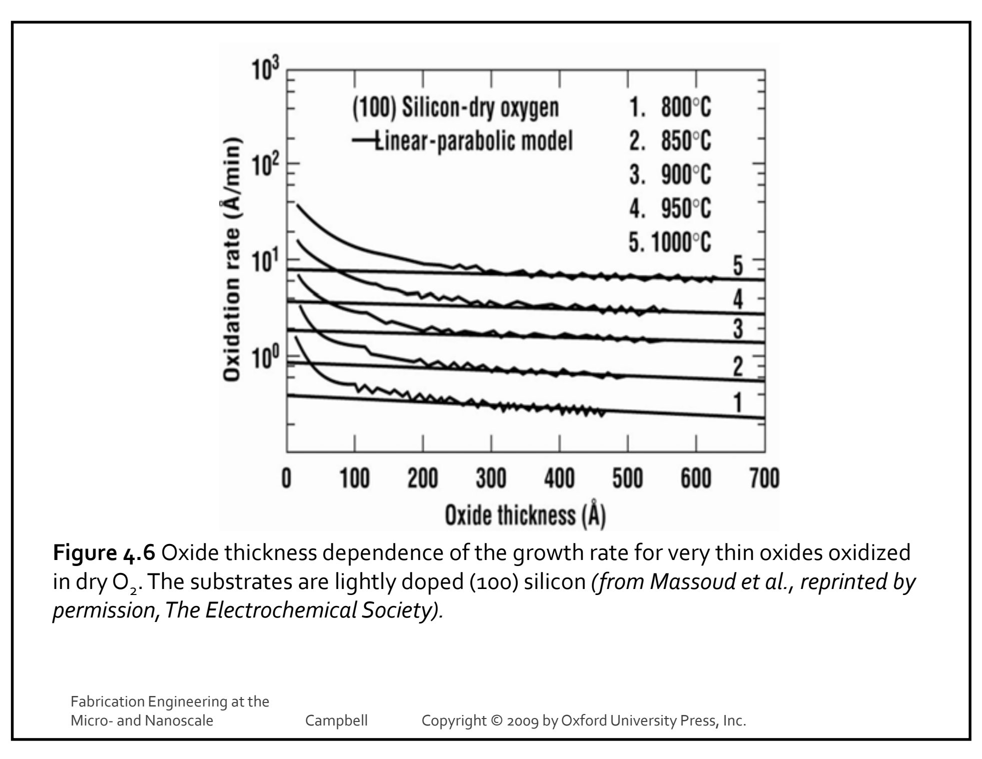

Figure 4.6 Oxide thickness dependence of the growth rate for very thin oxides oxidized in dry O_2. The substrates are lightly doped (100) silicon *(from Massoud et al., reprinted by permission, The Electrochemical Society).*

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B. Thin Oxide Growth Kinetics

- A major problem with the Deal Grove model was recognized when it was first proposed - it does not correctly model thin O_2 growth kinetics.
- Experimentally O_2 oxides grow much faster for ≈ 20 nm than Deal Grove predicts
- MANY models have been suggested in the literature.

1. Reisman et. al. Model

$$x_O = a(t+t_i)^b \quad \text{or} \quad x_O = a\left(t+\left(\frac{x_i}{a}\right)^{\frac{1}{b}}\right)^b \qquad (17)$$

- Power law "fits the data" for all oxide thicknesses.
- a and b are experimentally extracted parameters.
- Physically - interface reaction controlled, volume expansion and viscous flow of SiO_2 control growth.

2. Han and Helms Model

$$\frac{dx_O}{dt} = \frac{B_1}{2x_O + A_1} + \frac{B_2}{2x_O + A_2} \qquad (18)$$

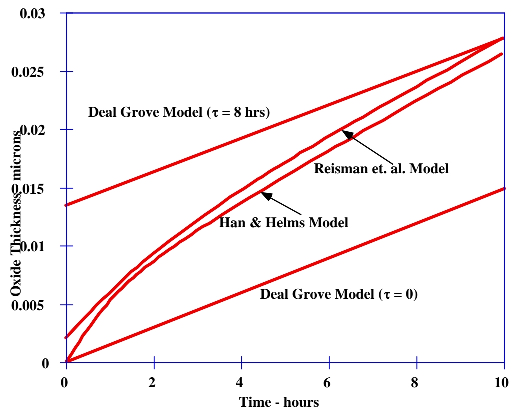
- Second parallel reaction added - "fits the data" " for all oxide thicknesses.
- Three parameters (one of the A values is 0).
- Second process may be outdiffusion of O_V and reaction at the gas/SiO_2 interface

3. Massoud et. al. Model

$$\frac{dx_O}{dt} = \frac{B}{2x_O + A} + C\exp\left(-\frac{x_O}{L}\right) \qquad (19)$$

- Second term added to Deal Grove model - higher dx/dt during initial growth.
- L ≈ 7 nm, second term disappears for thicker oxides.
- Easy to implement along with the DG model, ∴ used in process simulators.
- Data agrees with the Reisman, Han and Massoud models. (800˚C dry O_2 model comparison below.)

See Campbell : equations 4.16 & 4.17/18 for other models



Structure

Oxygen
Silicon

Figure 4.7 The physical structure of SiO_2 consists of silicon atoms sitting at the center of oxygen polyhedra.

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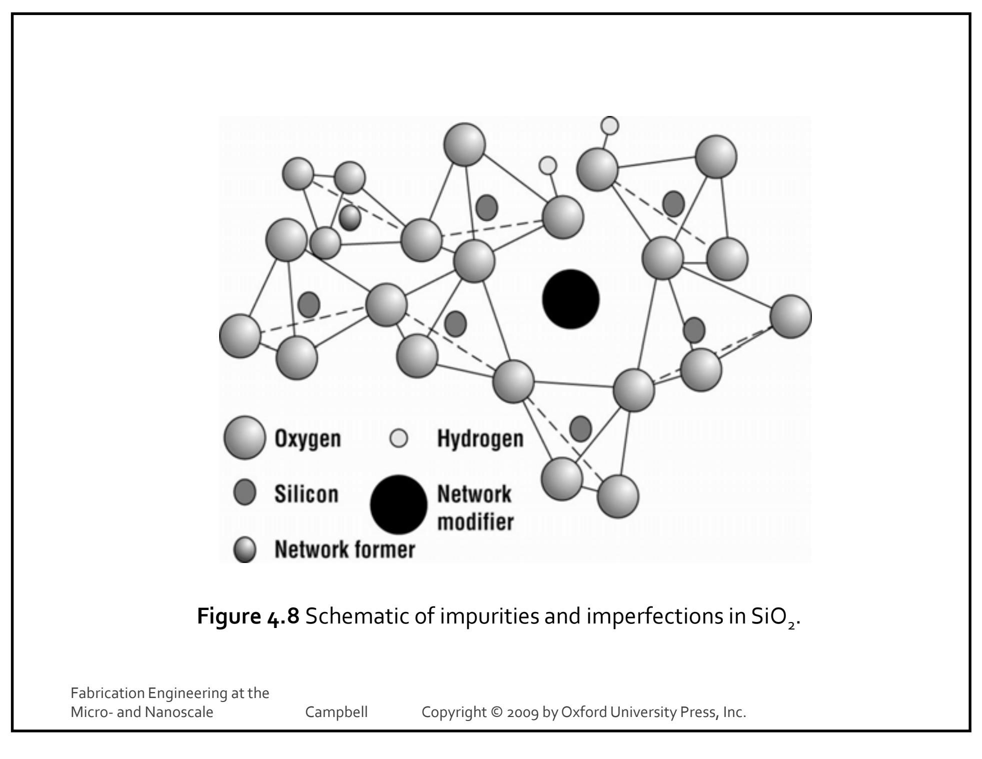

Figure 4.8 Schematic of impurities and imperfections in SiO_2.

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Thickness measurement by color

Ellipsometry; Interference $t_{ox} = \frac{\Delta\lambda}{2n_{ox}}$ → variable λ constructive interference

Color	SiO_2 thickness (nm)	Si_3N_4 thickness (nm)
Silver	<27	<20
Brown	<53	<40
Yellow-brown	<73	<55
Red	<97	<73
Deep blue	<100	<77
Blue	<120	<93
Pale blue	<130	<100
Very pale blue	<150	<110
Silver	<160	<120
Light yellow	<170	<130
Yellow	<200	<150
Orange-red	<240	<180
Red	<250	<190
Dark red	<280	<210
Blue	<310	<230
Blue-green	<330	<250
Light green	<370	<280
Orange-yellow	<400	<300
Red	<440	<330

Figure 4.9 Typical breakdown histogram for an oxide.

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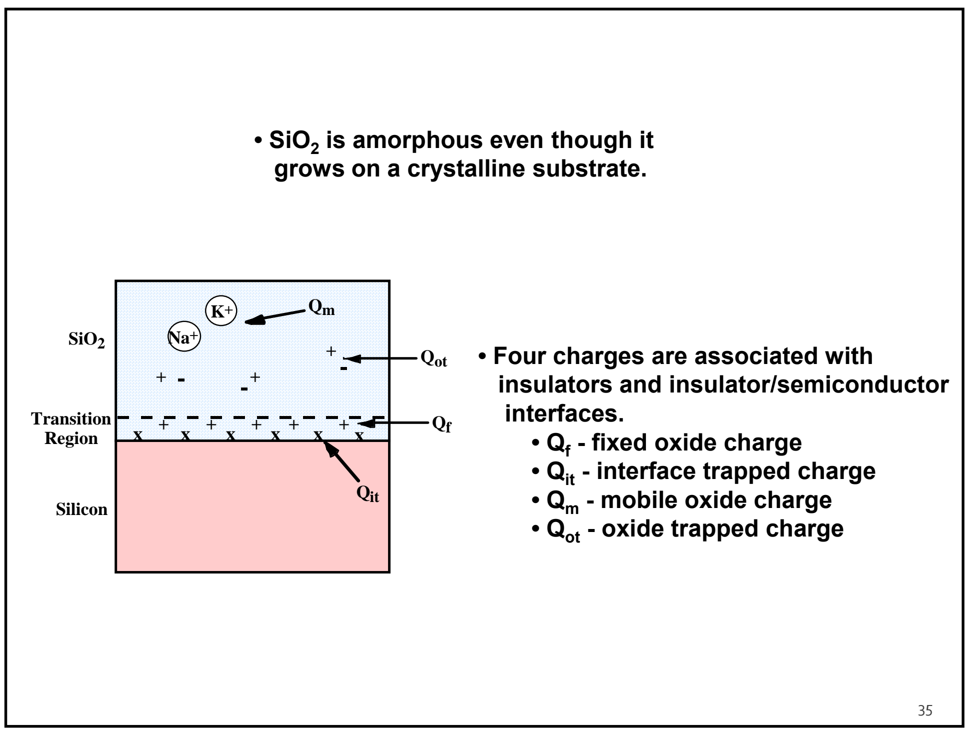

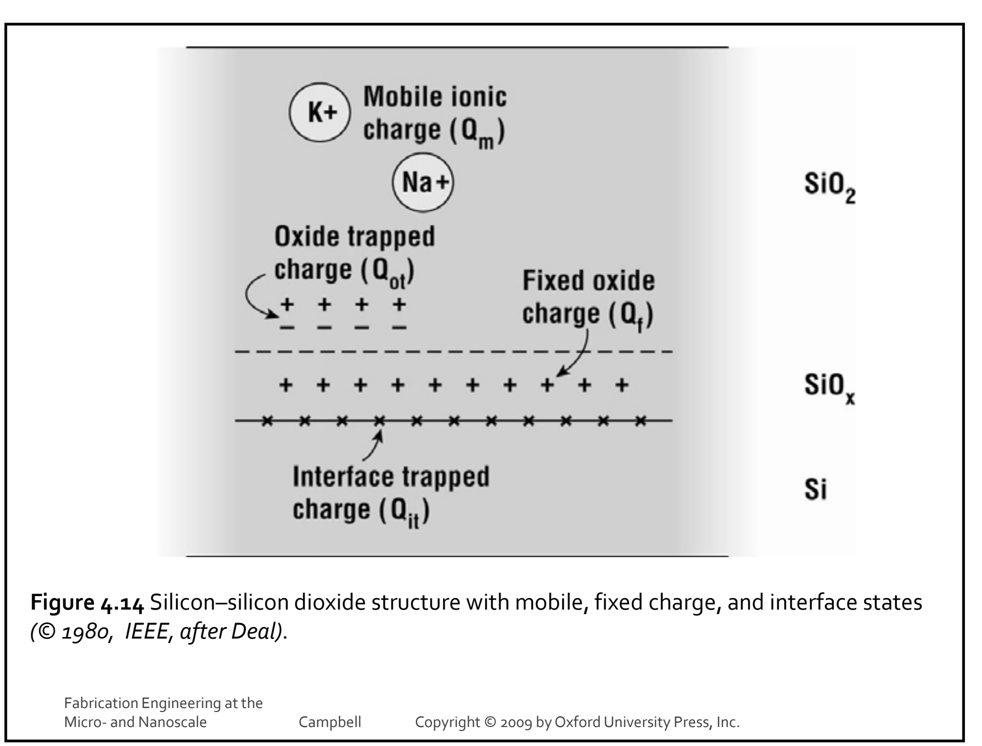

Figure 4.14 Silicon–silicon dioxide structure with mobile, fixed charge, and interface states *(© 1980, IEEE, after Deal).*

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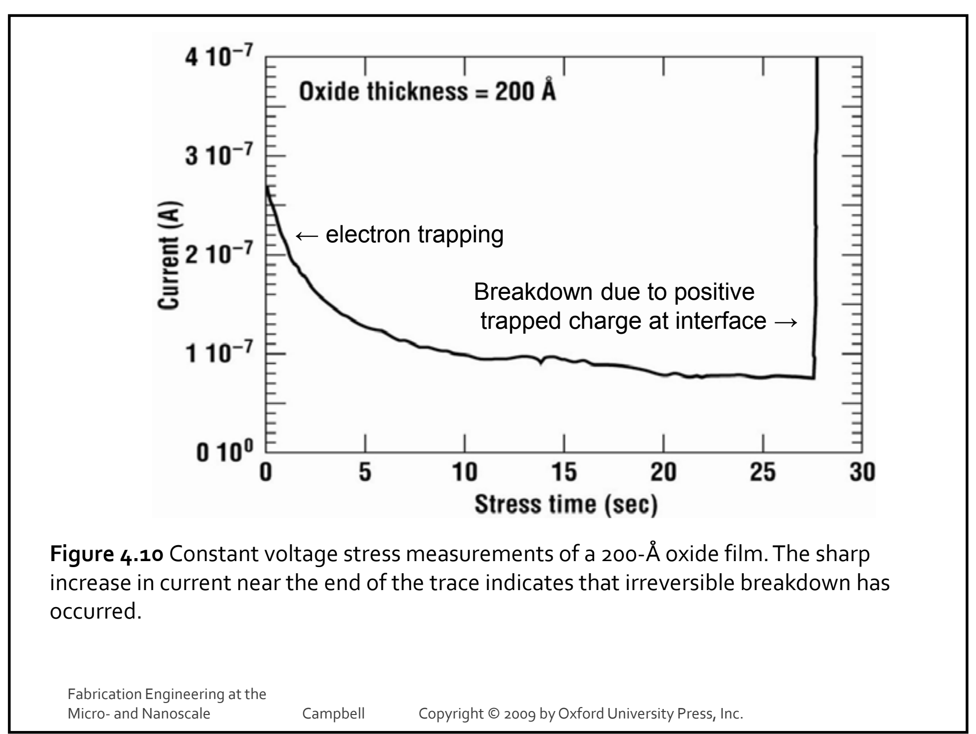

Figure 4.10 Constant voltage stress measurements of a 200-Å oxide film. The sharp increase in current near the end of the trace indicates that irreversible breakdown has occurred.

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Thin oxide: no trapping

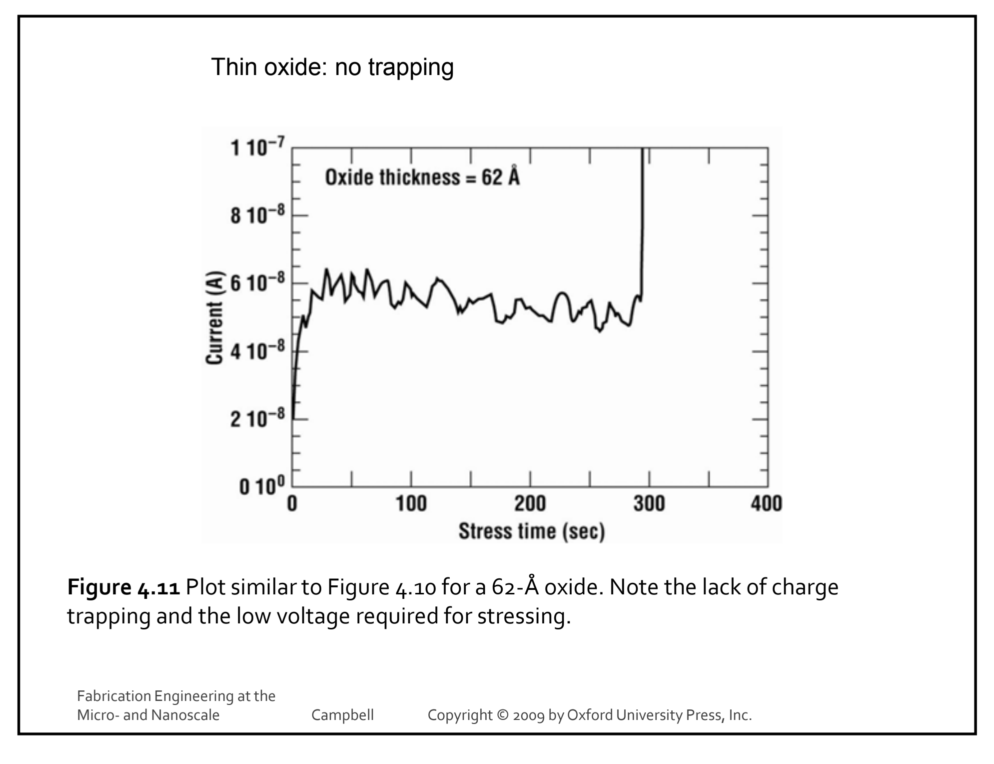

Figure 4.11 Plot similar to Figure 4.10 for a 62-Å oxide. Note the lack of charge trapping and the low voltage required for stressing.

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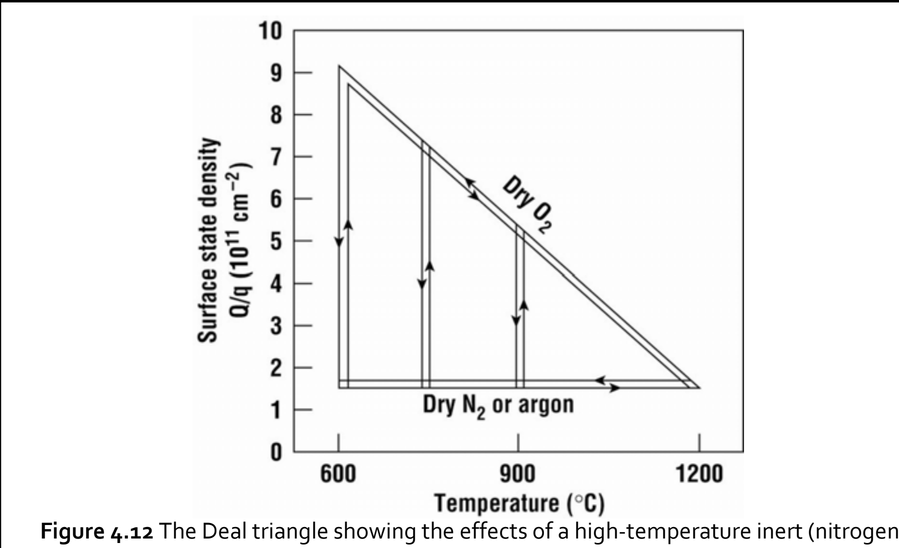

Figure 4.12 The Deal triangle showing the effects of a high-temperature inert (nitrogen or argon) postoxidation anneal on interface states and fixed charge density *(after Deal et al., reprinted by permission, The Electrochemical Society).*

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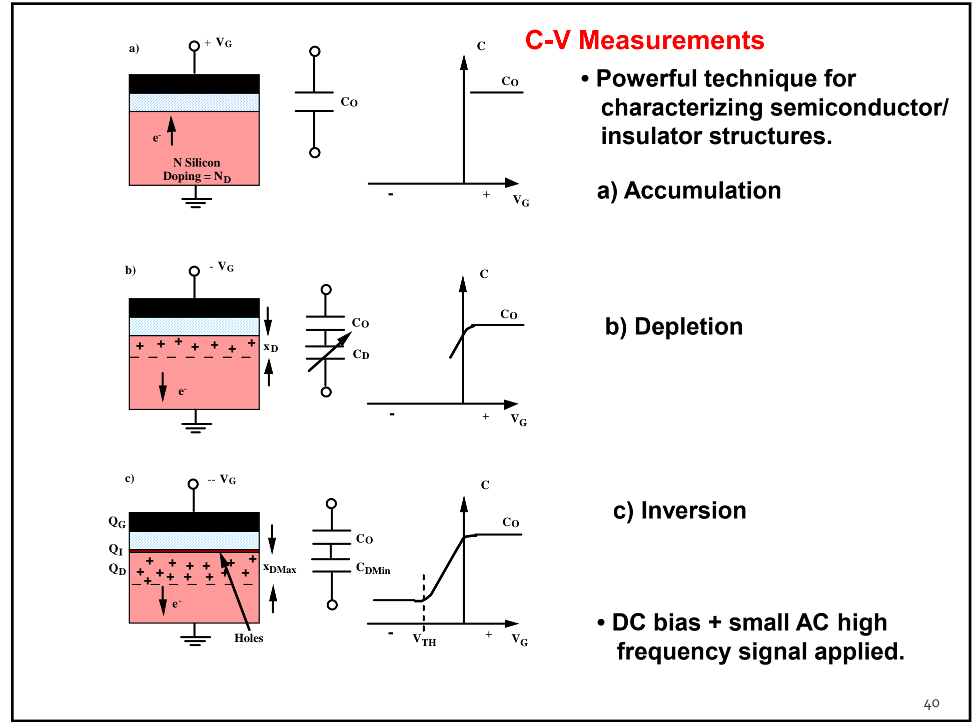

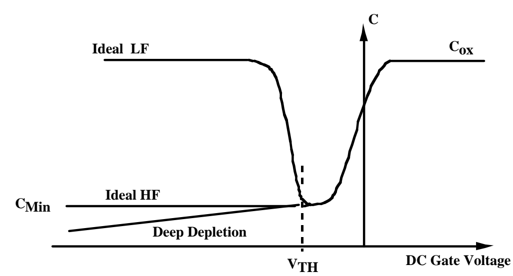

- **Electric field lines pass through the "perfect" insulator and Si/SiO_2 interface, into the substrate where they control charge carriers.**
- **Accumulation, depletion and inversion result.**
- **HF curve - inversion layer carriers cannot be generated fast enough to follow the AC signal so C_{inv} is $C_{ox} + C_D$.**
- **LF curve - inversion layer carriers can be created and recombine at AC signal frequency so C_{inv} is just C_{ox}.**
- **Deep depletion - "DC" voltage is applied fast enough that inversion layer carriers cannot follow it, so C_D must expand to balance the charge on the gate.**
- **C-V measurements can be used to extract quantitative values for:**
  - **t_{ox} - oxide thickness**
  - **N_A - the substrate doping profile**
  - **Q_f, Q_{it}, Q_m, Q_{ot} - oxide, interface charges**

41

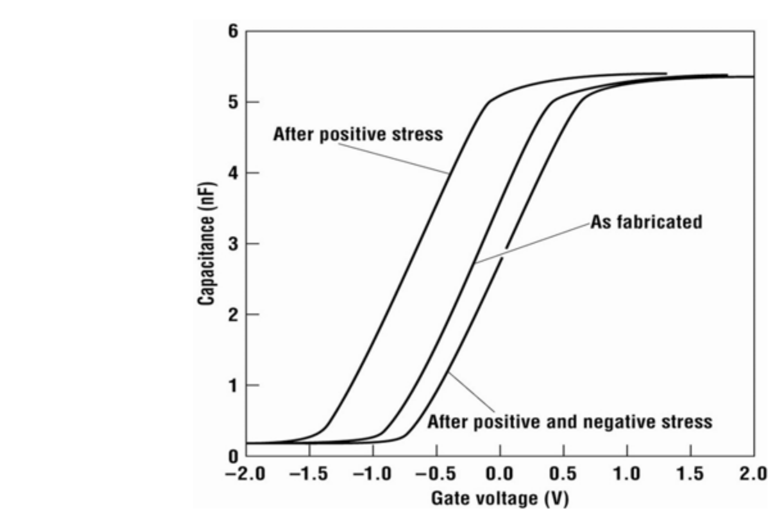

Figure 4.13 Typical C-V traces from temperature bias stress measurements of an oxide contaminated with a positive ion impurity.

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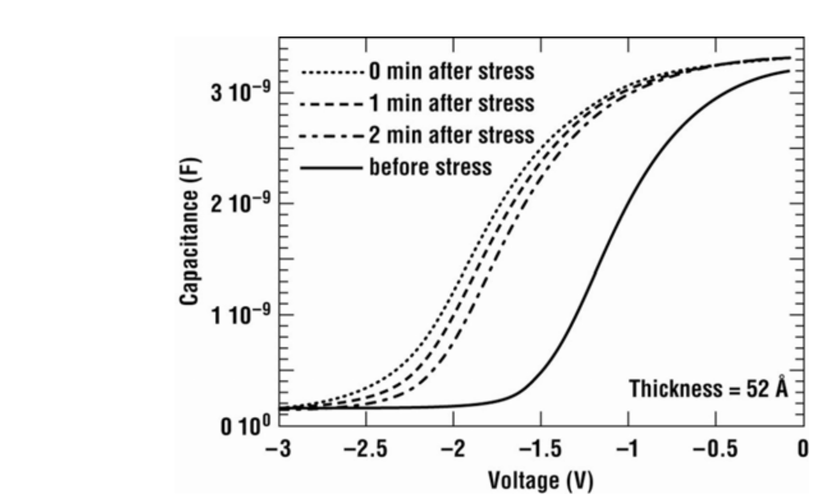

Figure 4.15 High frequency C–V traces showing the effects of interface states and fixed charge.

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Dopant Redistribution #1

Oxidation consumes (doped) Si

Redistribution due to:

- Segregation Coefficient

(abrupt discontinuity at interface)

- Diffusion

(depends on relative diffusion rates & rate of interface movement)

Segregation coefficient m=1

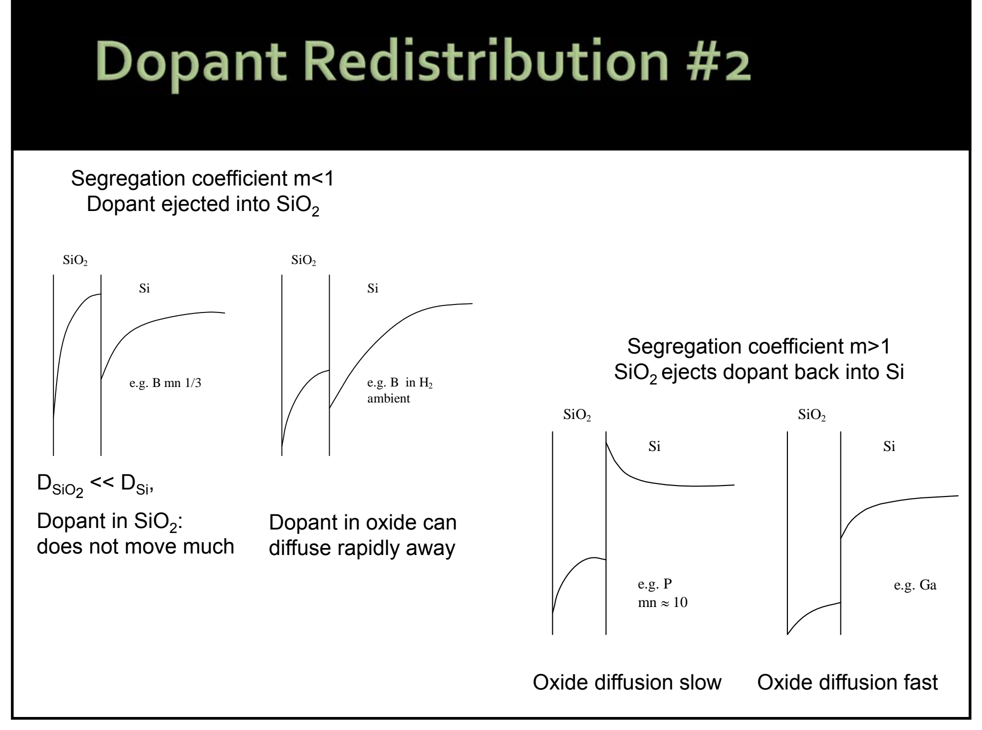
- i.e. diffusion only

-- impurity depletion from Si at interface

- Si approx. doubles in volume

-- ∴Dopant density approx halved in SiO_2

- diffusion from Si --> SiO_2 due to concentration gradient



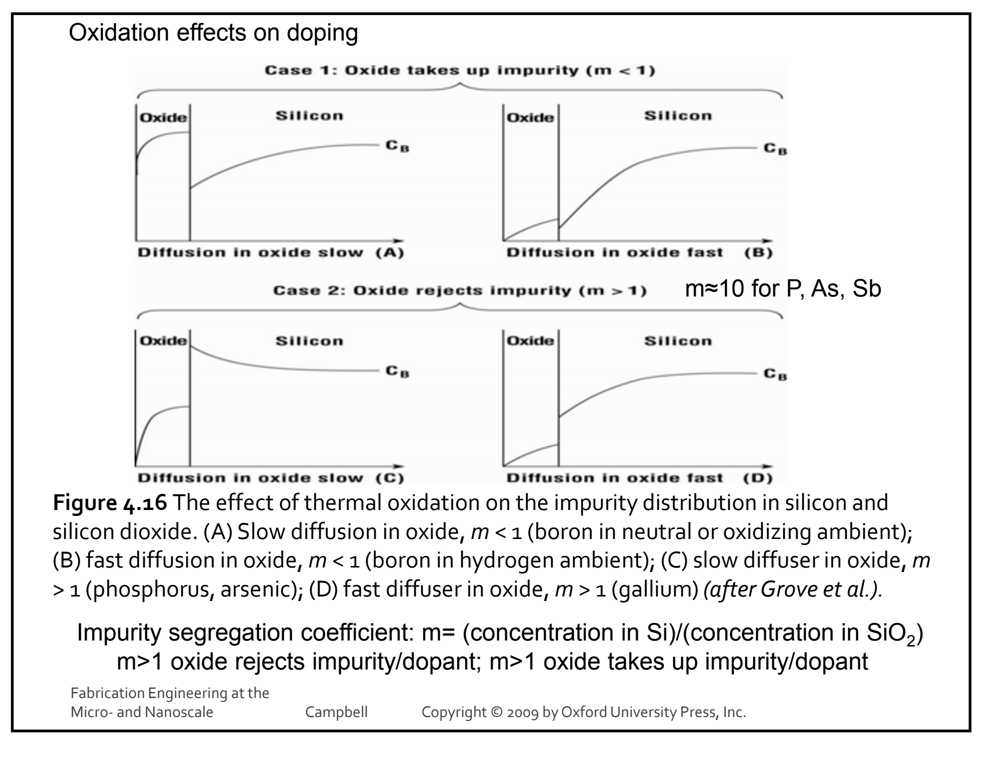


Figure 4.16 The effect of thermal oxidation on the impurity distribution in silicon and silicon dioxide. (A) Slow diffusion in oxide, $m < 1$ (boron in neutral or oxidizing ambient); (B) fast diffusion in oxide, $m < 1$ (boron in hydrogen ambient); (C) slow diffuser in oxide, $m > 1$ (phosphorus, arsenic); (D) fast diffuser in oxide, $m > 1$ (gallium) *(after Grove et al.)*.

Impurity segregation coefficient: m= (concentration in Si)/(concentration in SiO_2)
m>1 oxide rejects impurity/dopant; m>1 oxide takes up impurity/dopant

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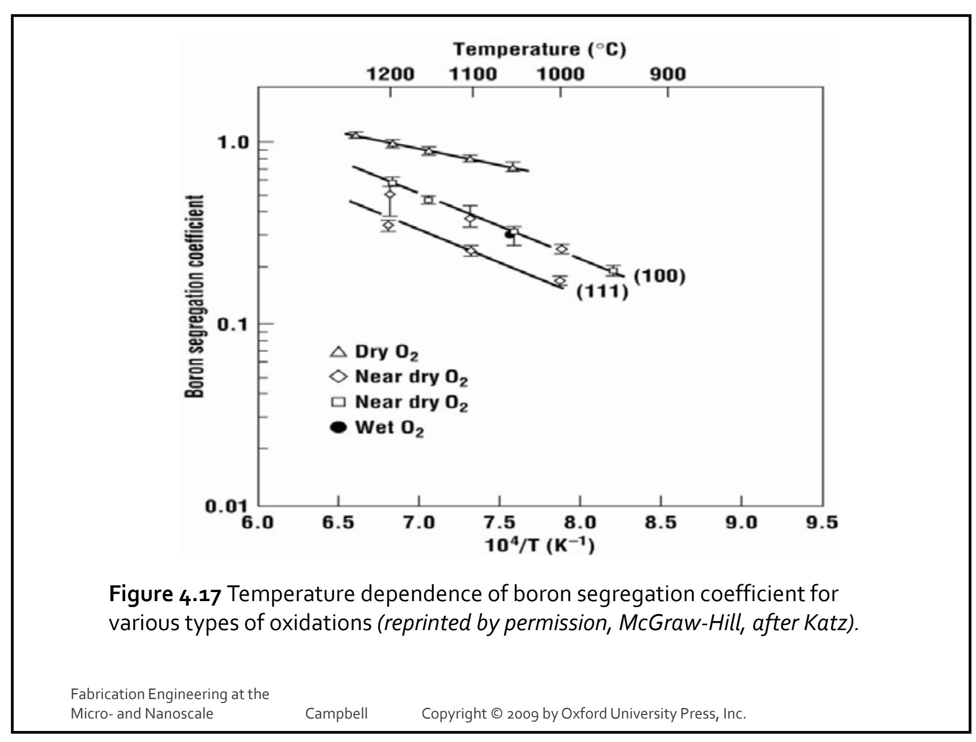

Figure 4.17 Temperature dependence of boron segregation coefficient for various types of oxidations *(reprinted by permission, McGraw-Hill, after Katz).*

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SiO_2 growth rates increased by doping of Si

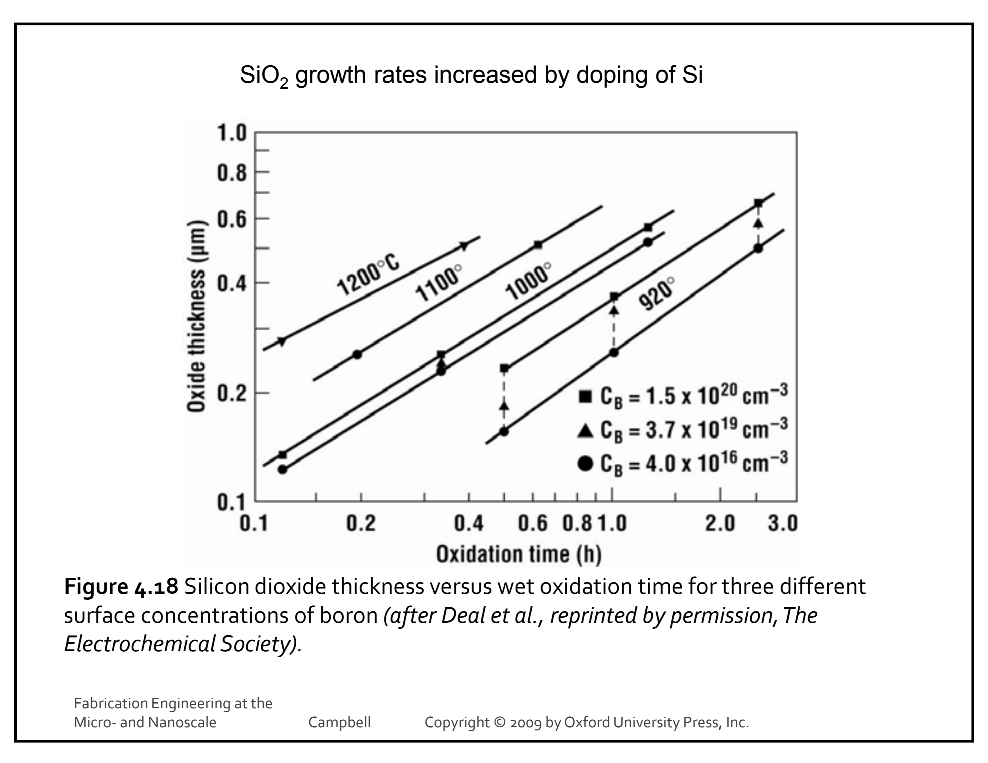

Figure 4.18 Silicon dioxide thickness versus wet oxidation time for three different surface concentrations of boron *(after Deal et al., reprinted by permission, The Electrochemical Society).*

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Dopants affect rate constants

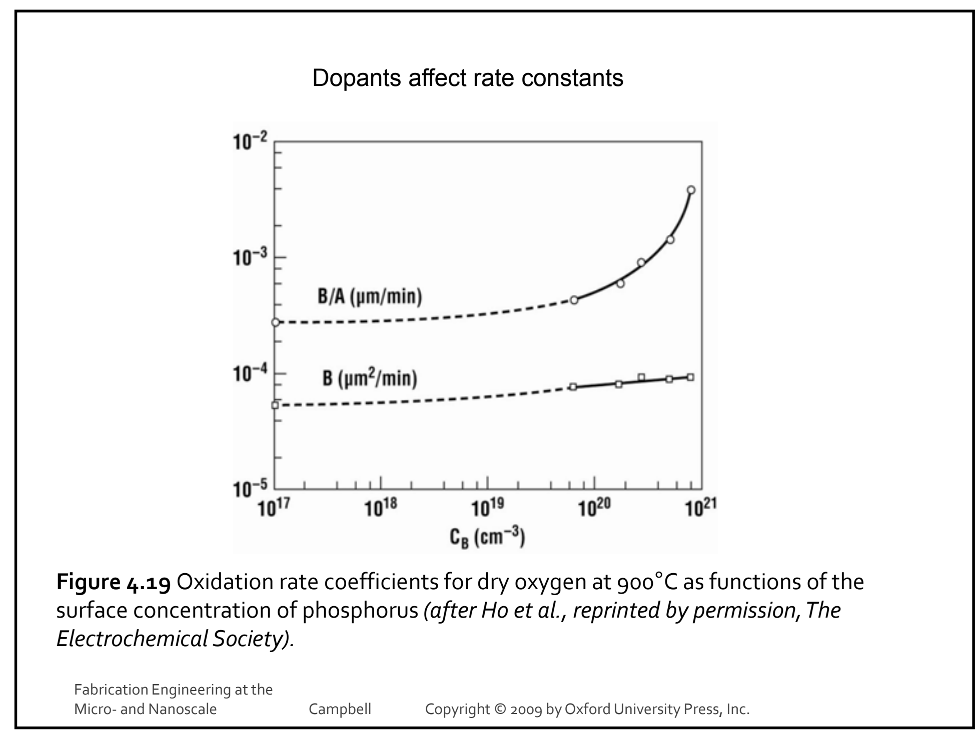

Figure 4.19 Oxidation rate coefficients for dry oxygen at 900°C as functions of the surface concentration of phosphorus *(after Ho et al., reprinted by permission, The Electrochemical Society).*

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Oxynitride: NH_3 anneal SiO_2

SiO_xN_y growth in NO

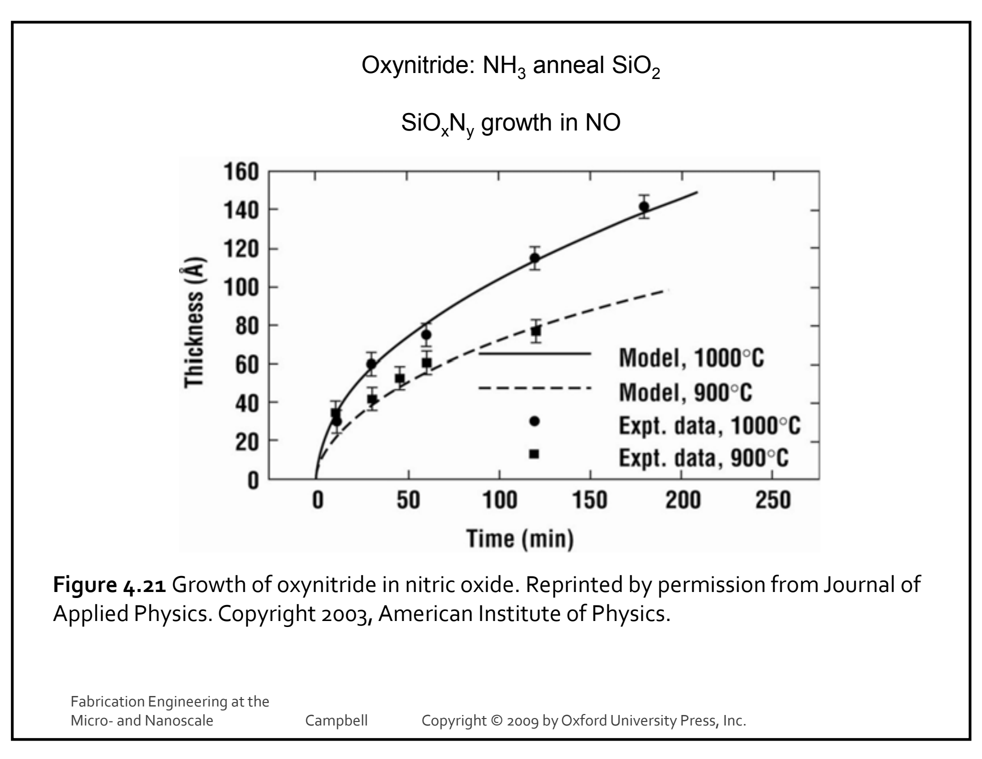

Figure 4.21 Growth of oxynitride in nitric oxide. Reprinted by permission from Journal of Applied Physics. Copyright 2003, American Institute of Physics.

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SiO_2 Properties: Structure

•Silicia glass: unstable at < 1710ºC

•returns to crystalline, but very slowly < 1000ºC

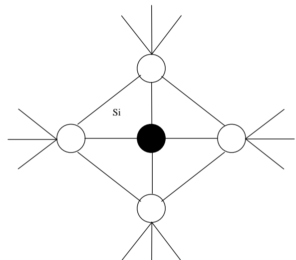
•Basic Unit: tetrahedron

•O links to next (bridging O)

•All O's bridging

--> cryst SiO_2

•(Campbell Fig 4.7)



•Can replace bridging O by:

•non bridging O (no link)

•OH^- (H_2O + Si-O-Si = 2 Si-OH) makes porous

•Substitutional impurities:

•B^{3+}/P^{5+} replace Si^{2+} (network formers)

•charge defects

•Interstitial impurities:

•Na^+, K^+, Pb^{2+}, Ba^{2+} (network modifiers)

•Na_2O + Si-O-Si = 2Si-O + 2Na

•makes structure more porous

•See Campbell Fig. 4.8

SiO_2 Properties: Diffusion

•For Si to move

•break 4 Si-O bonds

•For O to move

•break 2 Si-O bonds

•∴O moves more easily,

•Si relatively fixed

•(for ideal crystal)

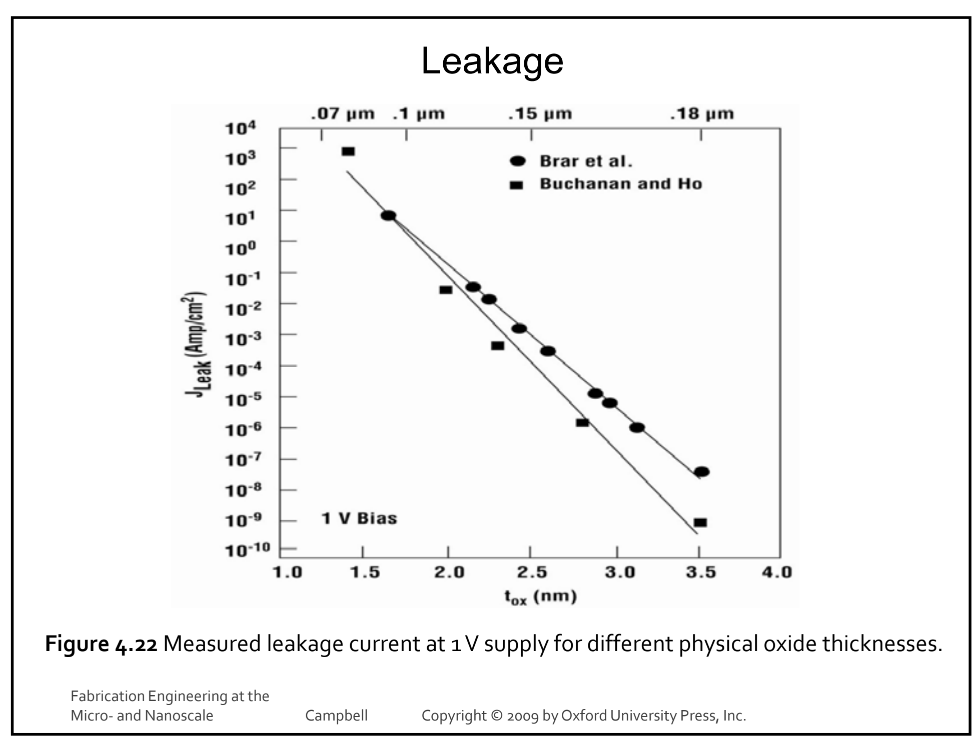


Figure 4.22 Measured leakage current at 1 V supply for different physical oxide thicknesses.

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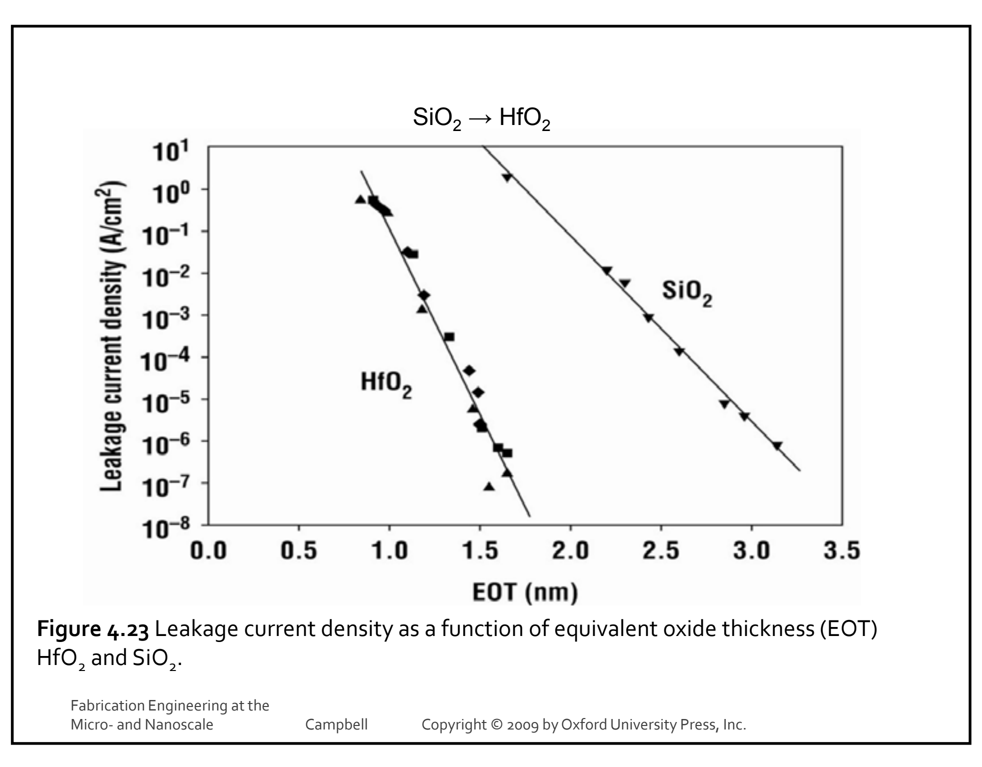

Figure 4.23 Leakage current density as a function of equivalent oxide thickness (EOT) HfO_2 and SiO_2.

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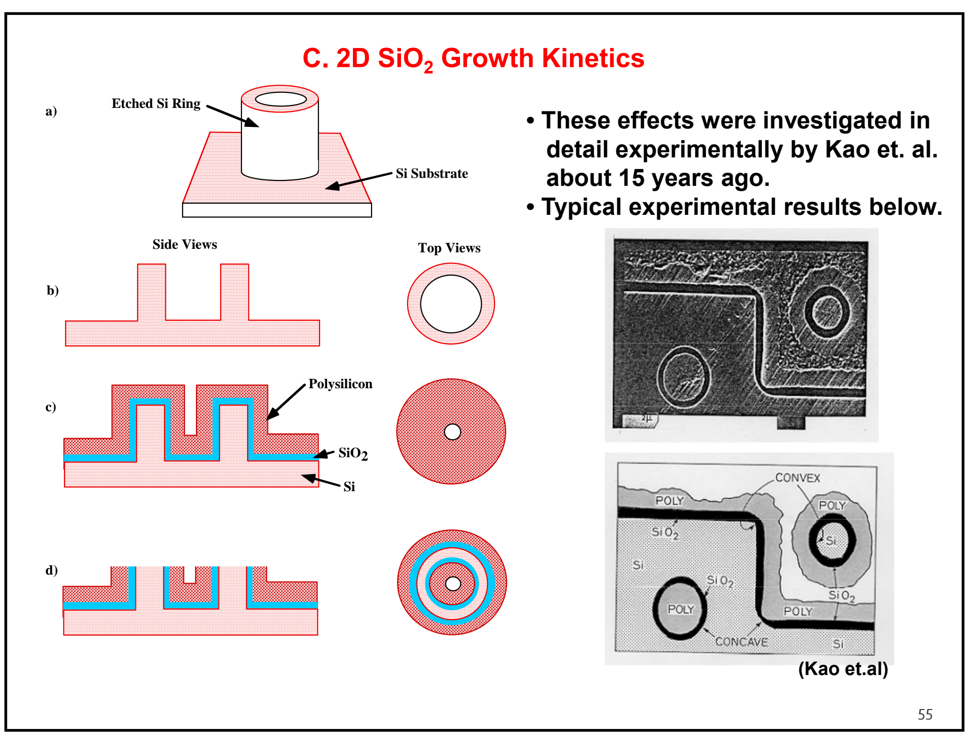
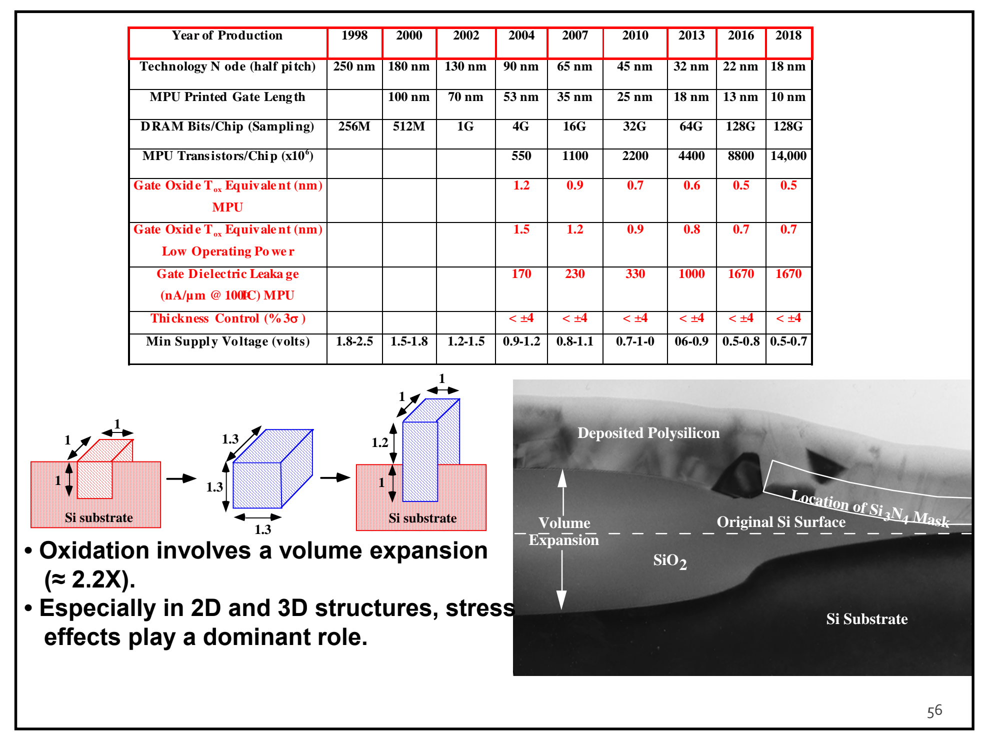
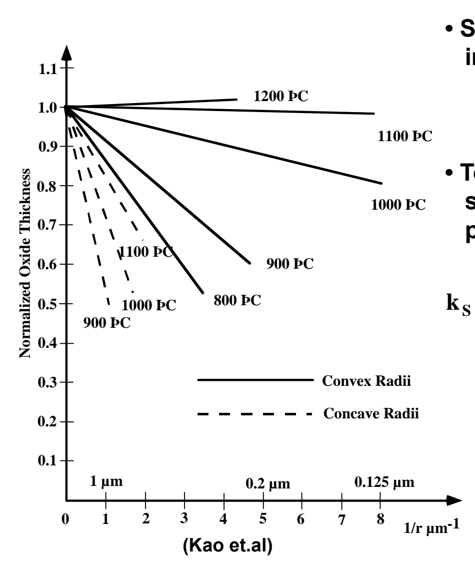




Year of Production	1998	2000	2002	2004	2007	2010	2013	2016	2018
Technology N ode (half pitch)	250 nm	180 nm	130 nm	90 nm	65 nm	45 nm	32 nm	22 nm	18 nm
MPU Printed Gate Length		100 nm	70 nm	53 nm	35 nm	25 nm	18 nm	13 nm	10 nm
DRAM Bits/Chip (Sampling)	256M	512M	1G	4G	16G	32G	64G	128G	128G
MPU Transistors/Chip ($x10^6$)				550	1100	2200	4400	8800	14,000
Gate Oxide T_{ox} Equivalent (nm) MPU				1.2	0.9	0.7	0.6	0.5	0.5
Gate Oxide T_{ox} Equivalent (nm) Low Operating Power				1.5	1.2	0.9	0.8	0.7	0.7
Gate Dielectric Leakage (nA/µm @ 100ºC) MPU				170	230	330	1000	1670	1670
Thickness Control (% 3σ)				< ±4	< ±4	< ±4	< ±4	< ±4	< ±4
Min Supply Voltage (volts)	1.8-2.5	1.5-1.8	1.2-1.5	0.9-1.2	0.8-1.1	0.7-1-0	06-0.9	0.5-0.8	0.5-0.7



- Several physical mechanisms seem to be important:
  - Crystal orientation
  - 2D oxidant diffusion
  - Stress due to volume expansion
- To model the stress effects, Kao et. al. suggested modifying the Deal Grove parameters.

$$k_S(\text{stress}) = k_S \exp\left(-\frac{\sigma_n V_R}{kT}\right)\exp\left(-\frac{\sigma_t V_T}{kT}\right) \quad (20)$$

$$D(\text{stress}) = D \exp\left(-\frac{(P)(V_D)}{kT}\right) \quad (21)$$

$$C^*(\text{stress}) = C^* \exp\left(-\frac{(P)(V_S)}{kT}\right) \quad (22)$$

where σ_n and σ_t are the normal and tangential stresses at the interface. V_R, V_T and V_S are reaction volumes and are fitting parameters.

57

- In addition, the flow properties of the SiO_2 need to be described by a stress dependent viscosity

$$\eta(\text{stress}) = \eta(T)\frac{\sigma_S V_C / 2kT}{\sinh(\sigma_S V_C / 2kT)} \quad (23)$$

Where σ_S is the shear stress in the oxide and V_C is again a fitting parameter.

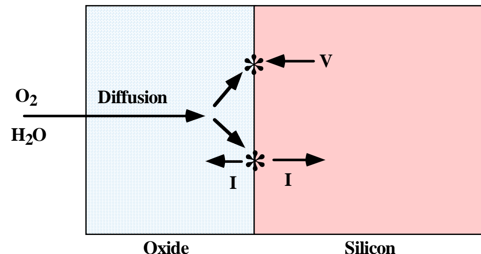
Parameter	Value
V_R	0.0125 nm^3
V_D	0.0065 nm^3
V_S, V_T	0
V_C	0.3 nm^3 @ 850ÞC 0.72 nm^3 @ 1050ÞC
η(T)	
η(T)	

- These models have been implemented in modern process simulators and allow them to predict shapes and stress levels for VLSI structures (above right).
- ATHENA simulation: Left - no stress dependent parameters, Right - including stress dependence.

58

D. Point Defect Based Models

• The oxidation models we have considered to this point are macroscopic models (diffusion coefficients, chemical reactions etc.).

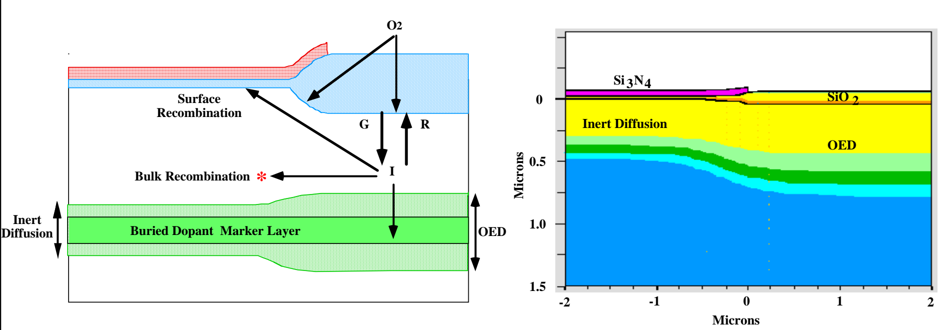


• There is also an atomistic picture of oxidation that has emerged in recent years.
• Most of these ideas are driven by the volume expansion occurring during oxidation and the need for "free volume".

• Surface oxidation can be thought of as

$$(1+2\gamma)Si_{Si} + 2O_I + 2\beta V \leftrightarrow SiO_2 + 2\gamma I + stress \qquad (24)$$

• The connection between oxidation and other processes can then be modeled as shown below.

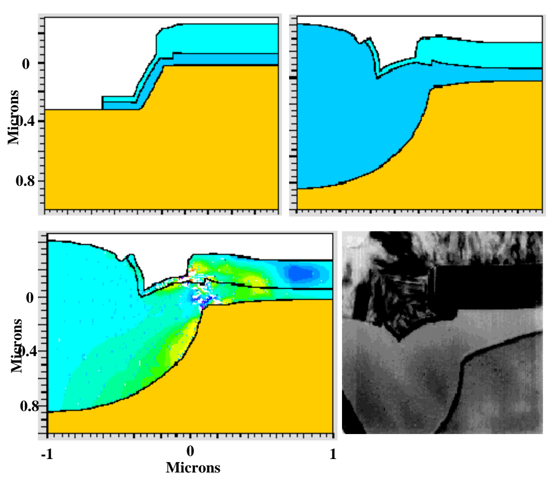


Example - ATHENA simulation of OED.

• Oxidation injects interstitials to create "free volume" for the oxidation process.
• Oxidation can also consume vacancies for the same reason.
• These processes increase I concentrations and decrease V concentrations in nearby silicon regions.
• Any process (diffusion etc) which occurs via I and V will be affected.

E. Complete Process Simulation of Oxidation

- Many of these models (and others), have been implemented in programs like SUPREM.



- Simulation of an advanced isolation structure (the SWAMI process originally developed by Hewlett-Packard), using SSUPREM IV. The structure prior to oxidation is on the top left. A 450 min H_2O oxidation at 1000 ˚C is then performed which results in the structure on the top right. An experimental structure fabricated with a similar process flow is shown on the bottom right. The stress levels in the growing SiO_2 are shown at the end of the oxidation on the bottom left.

61

Anodization

Normally used for GaAs
- Low T, avoids dissociation due to As
- No impurity redistribution
- Not good for Si --> porous films

Use to remove accurate amounts of Si
- semiconductor analysis
- anodize <---> dissolve

Electrolyte must contain OH^- ions

H_2O: $H_2O \leftrightarrow H^+ + OH^-$

- equilibrium constant K
- $K=[H^+][OH^-]=10^{-14}$ at 24° C
- ∴ $[H^+] = [OH^-] = 10^{-7}$, pH=7
- Use acid/base pH modifiers:

H_2PO_4 acid / NH_4OH base / $(NH_4)_2HPO_4$ neutral

Non-aqueous: ethylene/propylene glycol

At Pt cathode: $2H^+ + 2e^- \rightarrow H_2$

At Si anode: $Si + 2h^+ \rightarrow Si^{2+}$

Holes from Si bulk continually supplied by battery --> positive surface charge

- $Si^{2+} + 2(OH^-) \rightarrow Si(OH)_2$
- $Si(OH)_2 \rightarrow SiO_2 + H_2$

Overall: $Si^{2+} + 2(OH^-) + 2H^+ \rightarrow SiO_2 + 2H_2$

Anodization: Growth Kinetics

Assume field in oxide approx. constant
$E_{OX} \sim 1 - 2 \times 10^7$ v/cm for Si
Then $V_{OX} \approx x_{OX} E_{OX}$ & $x_{OX} = \alpha \int_0^t i dt = \alpha Q_{delivered}$
where α = formation rate = f_d/I_d
= thickness / A.sec.unit area
f_d = dissolution rate in electrolyte V=0
I_d = equivalent current to stop dissolution

Formation: $V_a - V_r = i (R_s + R_a) + V_{OX}$
$= i (R_S + R_a + \alpha E_{OX} \int_0^t i\, dt)$
Vr = "rest potential" of cell
i.e. reverse emf of cell used by battery

Try solution: $i = I_0 \exp - t / \tau$
So $\int_0^t i\, dt = - \tau I_0 [\exp - t / \tau - 1]$
& $V_A - V_R = (I_0 \exp - t/\tau)(R_S + R_a) + \alpha E_{OX}(1 - \exp - t / \tau] \tau I_0$
At t=0, $I_0 = (V_A - V_r)/(R_S + R_a)$
& at t-->∞, $V_A - V_r = \alpha E_{OX} \tau I_0$
$\therefore \tau = (V_A - V_r) / I_0 \alpha E_{OX} = (R_S + R_a) / \alpha E_{OX}$

Growth Rate α i

Compare capacitor:

$dv_c/dt \; \alpha \; i_c$, $i_c = I_0 e^{-t/\tau}$,
$v_c(t) = V(1 - e^{-t/\tau})$
$\therefore x = x_\infty(1 - \exp - t / \tau)$

Final film thickness x_∞ when no net growth

i.e. growth rate = dissolution rate, i=0
$x_\infty = (1 - I_d/I_0)(V_A - V_r) / E_{OX} \sim 0.3$nm/volt for Si

i.e. control final thickness with voltage

Note: if I_d=0, no dissolution --> $x_\infty E_{OX} = V_A - V_r$
if $I_d = I_0$, no growth --> $x_\infty = 0$

Anodization: Notes

W (gms Si consumed/C) = W_e / qN
- W_e = electrochemical equivalent weight
= gm molec wt / valence charge in reaction

-qN = $1.6 \times 10^{-19} \times 6.023 \times 10^{23}$ C/mole

Current efficiency = experimental W / theoretical W
≈ 95% for GaAs, ≈ 1-3% for Si

Can oxidize with constant current --> dx/dt constant
- for E_{OX} const, V_{OX} α x and increases linearly
- monitor V_{OX} and stop at desired thickness

Anodized SiO_2
- porous, etches 5x faster than thermal oxide
- trapped H_2O can be reduced by heating
- interface charge states 10x thermal oxide
(no good for MOS)

Anodization: Plasma

See later for plasmas

High energy in plasma

(electron temperature ≈ 10^4 K)

But low temperature in Si

∴ minimal dopant redistribution

SiO_2 not as good as thermal

Summary of Key Ideas

- **Thermal oxidation has been a key element of silicon technology since its inception.**
- **Thermally, chemically, mechanically and electrically stable SiO_2 layers on silicon distinguish silicon from other possible semiconductors.**
- **The basic growth kinetics of SiO_2 on silicon are controlled by oxidant diffusion and Si/SiO_2 interface chemical reaction.**
- **This simple Deal-Grove model has been extended to include 2D effects, high dopant concentrations, mixed ambients and thin oxides.**
- **Oxidation can also have long range effects on dopant diffusion (OED or ORD) which are modeled through point defect interactions.**
- **Process simulators today include all these physical effects (and more) and are quite powerful in predicting oxidation geometry and properties.**
- **Anodization is also possible.**

66