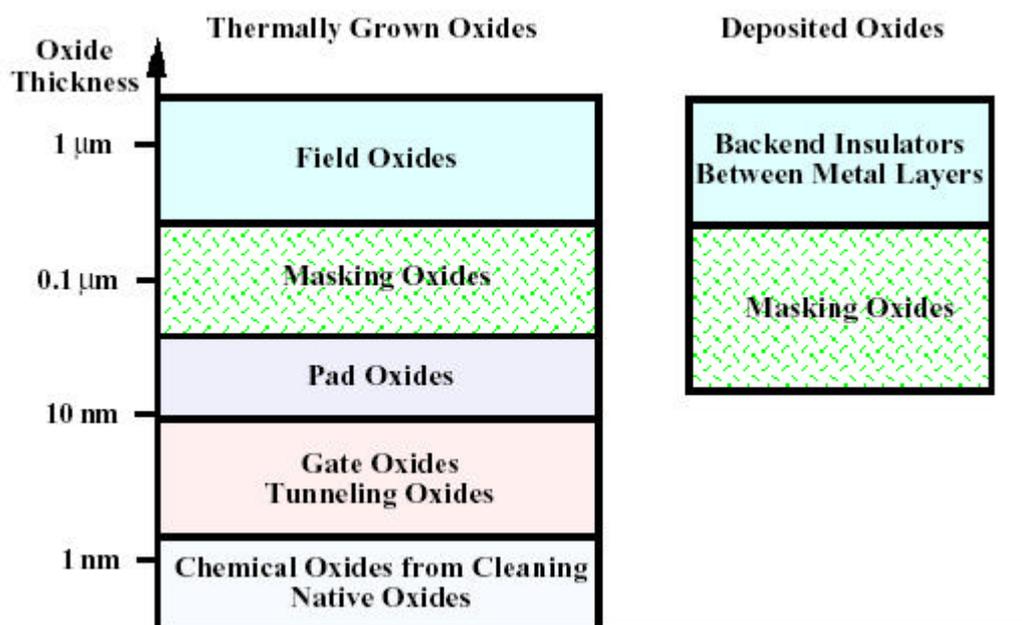


Chap 6. Thermal Oxidation and the Si/SiO₂ Interface

6.1 Introduction

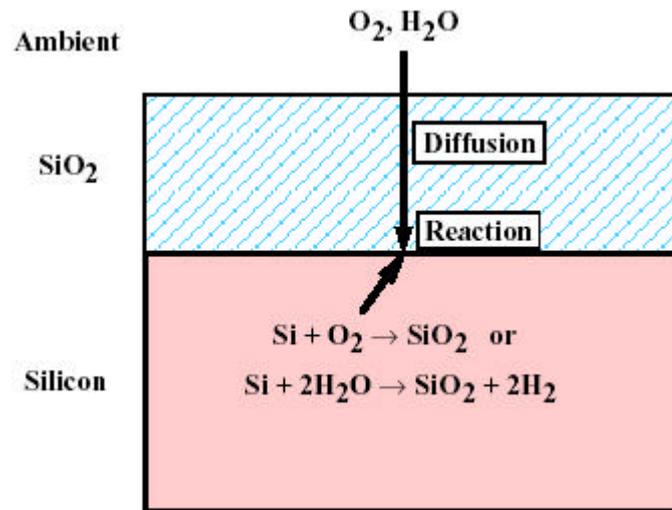
- SiO₂ and the Si / SiO₂ interface are the principal reasons for silicon's dominance in the IC industry
- SiO₂:
 - Easily selectively etched using lithography
 - Masks most common impurities (B, P, As, Sb)
 - Excellent insulator ($\rho > 10^{16}$ Ocm, $E_g > 9\text{eV}$)
 - High breakdown field (10^7 Vcm⁻¹)
 - Excellent junction passivation
 - Stable bulk electrical properties
 - Stable and reproducible interface with Si
- Even at room T, native oxide will be grown
 - ┌ rapid growth : 0.5 – 1nm
 - └ slow growth : 1 – 2nm



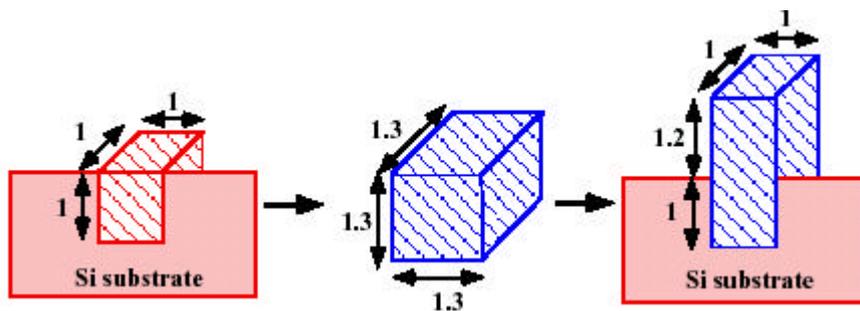
Year of 1st DRAM Shipment	1997	1999	2003	2006	2009	2012
Minimum Feature Size (nm)	250	180	130	100	70	50
DRAM Bits/Chip	256M	1G	4G	16G	64G	256G
Minimum Supply Voltage (volts)	1.8-2.5	1.5-1.8	1.2-1.5	0.9-1.2	0.6-0.9	0.5-0.6
Gate Oxide T_{ox} Equivalent (nm)	4-5	3-4	2-3	1.5-2	<1.5	<1.0
Thickness Control (% 3σ)	± 4	± 4	$\pm 4-6$	$\pm 4-8$	$\pm 4-8$	$\pm 4-8$
Equivalent Maximum E-field ($MV\ cm^{-1}$)	4-5	5	5	>5	>5	>5
Gate Oxide Leakage (DRAM) ($pA\ \mu m^{-2}$)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tunnel Oxide (nm)	8.5	8	7.5	7	6.5	6
Maximum Wiring Levels	6	6-7	7	7-8	8-9	9
Dielectric Constant, K for Intermetal Insulator	3.0-4.1	2.5-3.0	1.5-2.0	1.5-2.0	<1.5	<1.5

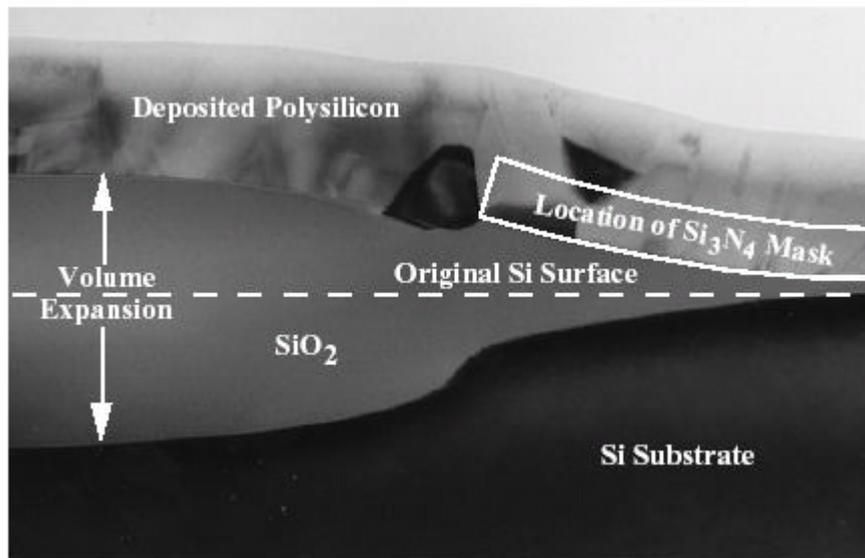
- Deposited oxides are usually not used for layers thinner than $\sim 10nm$
- The simplest way to “anneal” a deposited oxide / Si interface is simply to grow a thin thermal oxide underneath the deposited oxide

6.2 Historical Development and Basic Concept

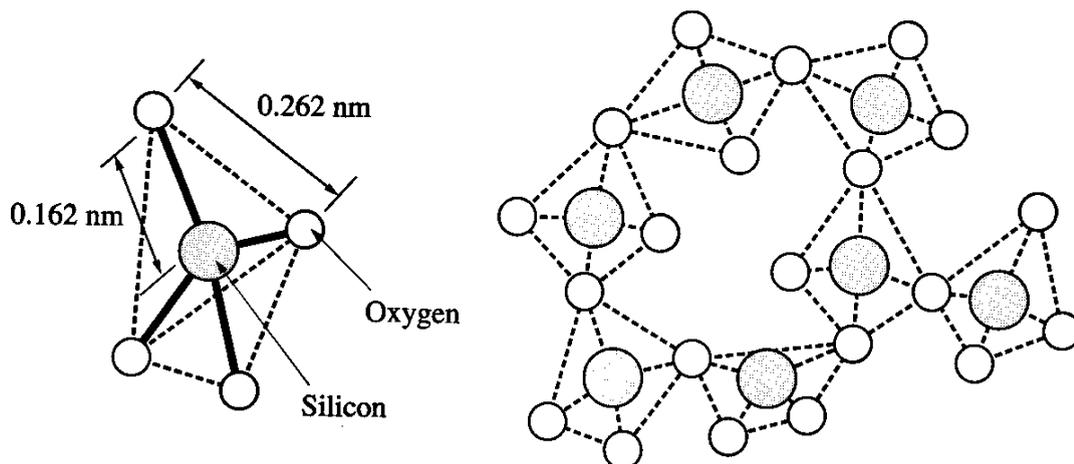


- The Si atoms in the substrate are bonded to other Si atoms. These bonds must be broken, oxygen atoms inserted between the silicon atoms, and finally Si-O bonds formed
 ? volume expansion ? by 30% in all three dimensions

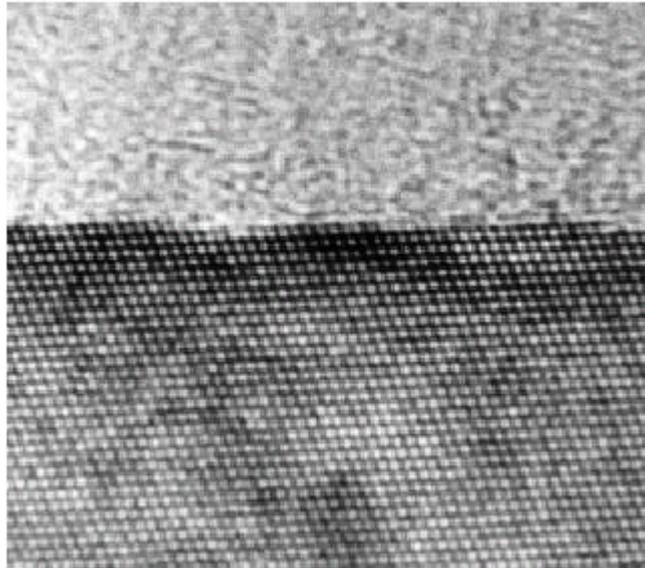


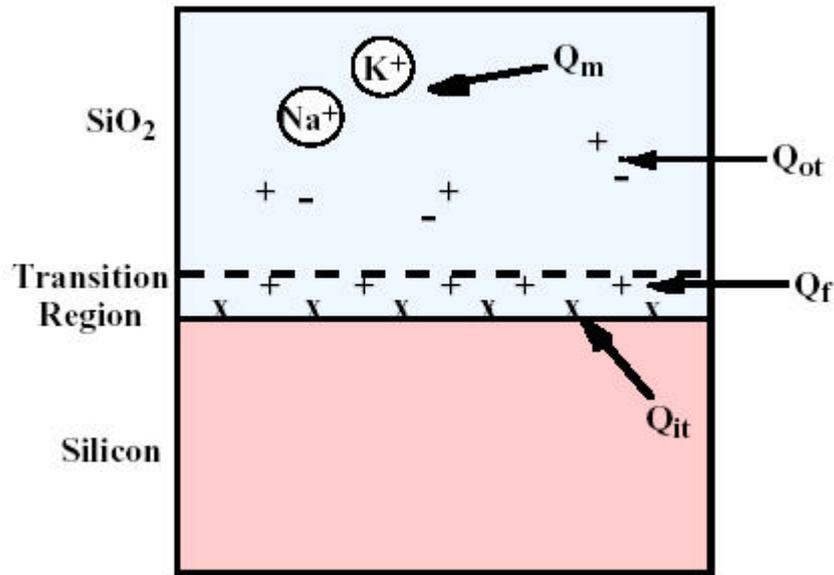


- “Bird’s beak”
- Oxide layers grown on silicon are amorphous. There are no crystalline forms of SiO₂ whose lattice size closely matches the silicon substrate
- The oxide has short-range order (SiO₄ tetrahedra)



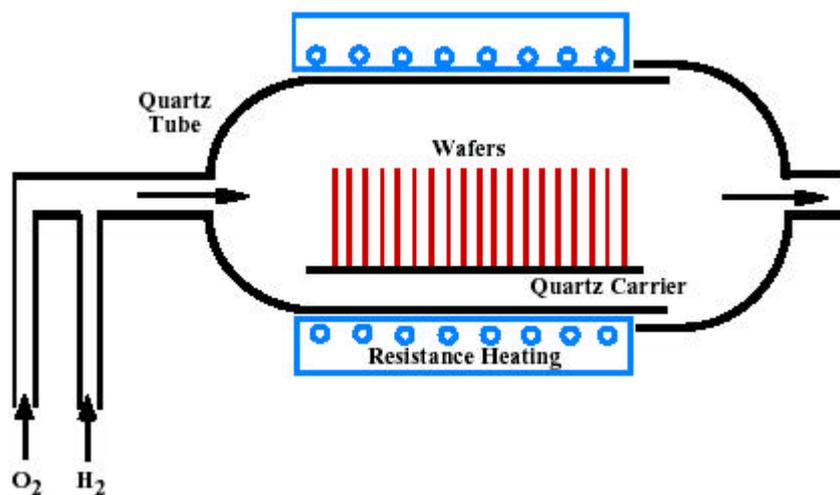
- **Fused silica : in the amorphous forms of SiO_2 there may be some non-bridging oxygen atoms**
- **At normal processing T, the thermodynamically stable form is one of the crystalline forms. These forms are rarely observed in IC structures because the time required to rearrange itself into a crystalline form is very long**
- **The oxide layers that grow on Si are normally in compressive stress (the oxide can expand only upward)**
- **The stress can be as large as 5×10^9 dynes cm^{-2}**
- **Large difference in the thermal expansion coefficients**





- A process that results in a high value of Q_f will also result in a high density of Q_{it}
- Q_{ot} : broken Si-O bonds in the bulk of the oxide
- To minimize charges : high-T inert anneals in Ar or N₂ toward the end of the process flow, and by a final moderate T anneal in H₂ or forming gas at the end of the process

6.3 Manufacturing Methods and Equipment



- **Uniformity, reproducibility, and cleanliness**
- **T uniformity = $\pm 0.5^\circ\text{C}$**
- **The oxidant species introduced at the back end and the wafers at the front**
- **Vertical furnace : less floor space**
- **Liquid sources of O_2 and H_2 are commonly used**
- **Gases are carried through high-purity stainless steel lines**
- **For H_2O oxidation, O_2 and H_2 are burned in the back end of the furnace**
- **Gaseous HCl or TCA provide a Cl source**


 clean the tube prior to oxidation
 small percentage additive

React with many metal ions and
 produce gas phase byproducts
 Cl incorporated in the growing layer
 provides some degree of protection
 from Na^+ and also changes the growth
 kinetics

- **Cantilever systems carry the wafers into the furnace without actually touching the furnace walls**
- **In the case of vertical furnaces, elevators are used**
- **Furnace is normally divided in three to five zones for temperature control. The outer zones are designed to help compensate for heat losses so that a long central section with uniform T can be maintained**

- To avoid large thermal gradients across the wafers, which can induce crystallographic defects, the wafers are normally loaded at a moderate T (~ 800°C) and the furnace is then ramped up to the oxidation T after the wafers are in the central hot zone
- Ramp rates ~ 1°C sec⁻¹
- At 1000°C, oxidation rates in H₂O are on the order of 0.1nmsec⁻¹ and approximately double for a 100°C temperature rise
- High pressure oxidation : thick thermal oxide growth with minimum Dt
- Low pressure oxidation is done by diluting the oxidant gas with an inert gas such as Ar or N₂
- Rapid Thermal Oxidation (RTO) : lamp heated chamber at a rate of 100°C/sec
- Usually single-wafer machines
- Difficulty : measuring the exact T of the wafer

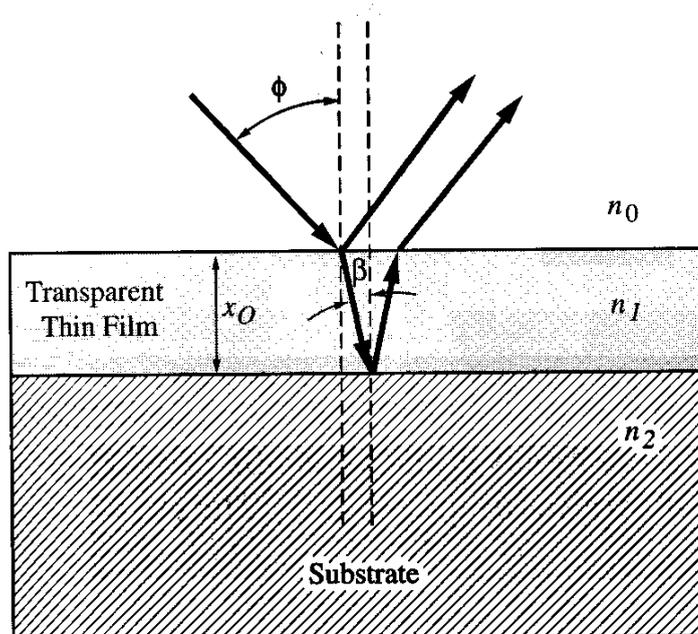
6.4 Measurement Methods

- Thickness, K, index of refraction, dielectric strength, defect density, and uniformity of all these parameters
 - Physical measurements (often destructive)
 - Optical techniques
 - Electrical measurements (usually nondestructive and are potentially most powerful)

6.4.1 Physical Measurements

- The dielectric is etched away in some regions
- A small needle stylus is moved across the step
- Mechanically or electrically amplifying the small signal produces a measurement of the step height
- Resolution below 10nm
- Scanning tunneling microscope, the Atomic Force Microscope (AFM) have pushed the resolution to atomic dimensions
- Cross sectional SEM images
- High resolution TEM cross-sectional images
- Require sample preparation and are not well suited to in-process measurements
- Only provide information on film thickness

6.4.2 Optical Measurement



- The maxima and minima occur at

$$l_{\text{min, max}} = \frac{2n_1x_0 \cos b}{m}$$

$$\text{where } b = \sin^{-1} \left(\frac{n_0 \sin \theta}{n_1} \right)$$

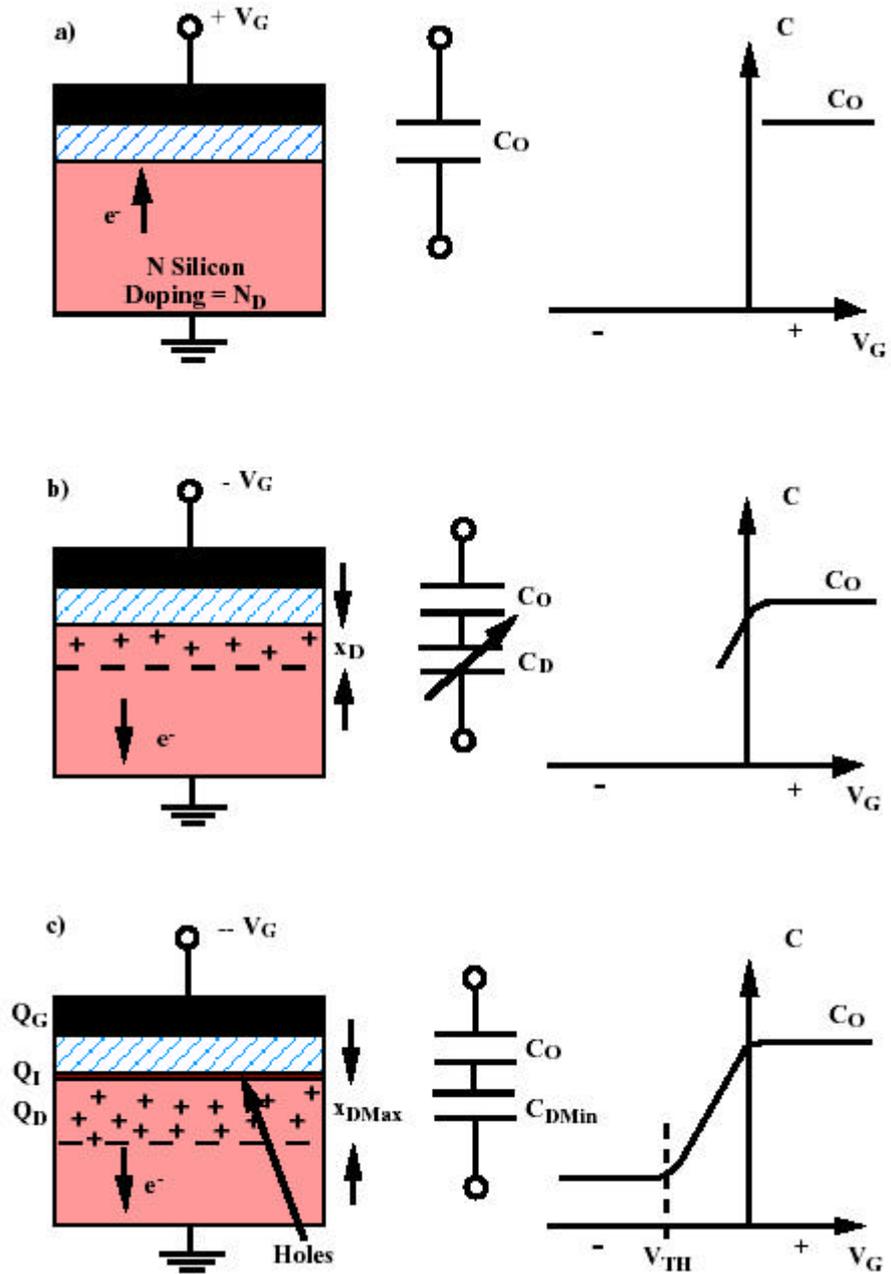
$$m = 1, 2, 3, \dots \text{ for maxima}$$

$$m = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \text{ for minima}$$

- Spectrophotometers to sweep ? with F constant
- Works reliably for $x_0 >$ a few tens of nm
- For thinner films, it is difficult to detect the first minimum unless very short λ is used
- n_1 , must be known
- $x_0 <$ a few tens of nm or n_1 , is not known
? use ellipsometry
- Polarized light is used and the change in the polarization is measured
- When the optical properties of the substrate are known and the film is transparent at the wavelengths, the change in polarization depends only on x_0 and n_1
- Can measure films down to 1nm
- Color cards : the simplest technique for x_0
- The colors repeat about every 300nm for SiO_2 and about every 200nm for Si_3N_4 ? standards are often used
- Oxides thinner than $\sim 50\text{nm}$ do not have any characteristic color

6.4.3 Electrical Measurements – The MOS Capacitor

- CV method
- MOS capacitor



skip

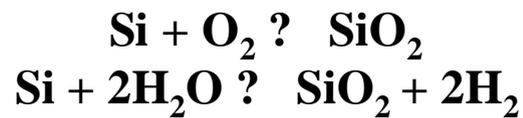
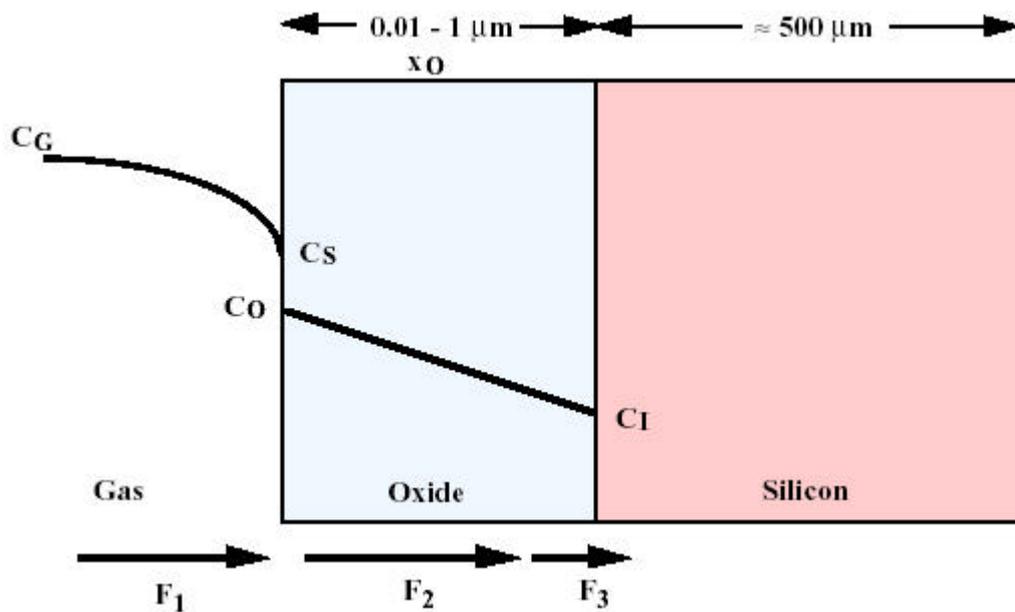
6.5 Models and Simulation

- Deal and Grove model

: can not explain

[shaped surfaces
 [mixed ambients
 [very thin oxides

6.5.1 First-Order Planar Growth Kinetics – The Linear Parabolic Model



- $F_1 = h_G(C_G - C_S) =$ transport of the oxidant in the gas phase to the oxide surface
- Gas phase diffusion through the boundary or stagnant layer that always forms adjacent to a solid object placed in a gas which is flowing over its surface
- F_1 is unimportant because F_1 is very fast process
 pressure in the gas phase adjacent to the oxide surface
 $C_0 = HP_S$: Henry's law, C_0 is the concentration of the oxidant
 $C^* = HP_G$
 $C^* =$ oxidant concentration in the oxide that would be in equilibrium with P_G
- Since F_1 is not the rate limiting step, $C^* \sim C_0$ and $P_G \sim P_S$
 C^* really represents the solubility of the oxidant in the SiO_2

$$C_G = \frac{P_G}{kT} \quad \& \quad C_S = \frac{P_S}{kT}$$

$$F_1 = h(C^* - C_0)$$

$$\text{where } h = \frac{h_G}{HkT}$$

- Fick's law

$$F_2 = -D \frac{\partial C}{\partial X} = D \frac{\partial C_0 - C_1}{\partial X_0 - X_1}$$

- **Assumption : process is in steady state & there is no loss of oxidant**
 - ? F_2 must be constant through the oxide
 - ? Oxide concentration falls off linearly through the oxide

- $\left[\begin{array}{l} \text{O}_2 \text{ diffuses in molecular form, likely interstitially} \\ \text{between the atoms} \\ \text{H}_2\text{O seems to diffuse in a more complex manner,} \\ \text{interacting with the SiO}_2 \text{ matrix} \end{array} \right.$

- The effective diffusivities of both O_2 and H_2O are on the same order ($\sim 5 \times 10^3 \mu\text{m}^2/\text{hr}$ at 1100°C)

- The reaction at the Si/SiO_2 interface

$$F_3 = k_s C_I$$

- C_I , Si-Si bond breaking, Si-O bond formation, and possibly O_2 or H_2O dissociation

- k_s = interface reaction rate constant (cm/sec)

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

$$C_I = \frac{C^*}{1 + \frac{k_s}{h} + \frac{k_s X_0}{D}} @ \frac{C^*}{1 + \frac{k_s X_0}{D}}$$

h is very large (experimentally)

$$C_0 = \frac{C_G^* \left(1 + \frac{k_s X_0}{D} \right)}{1 + \frac{k_s}{h} + \frac{k_s X_0}{D}} @ C^*$$

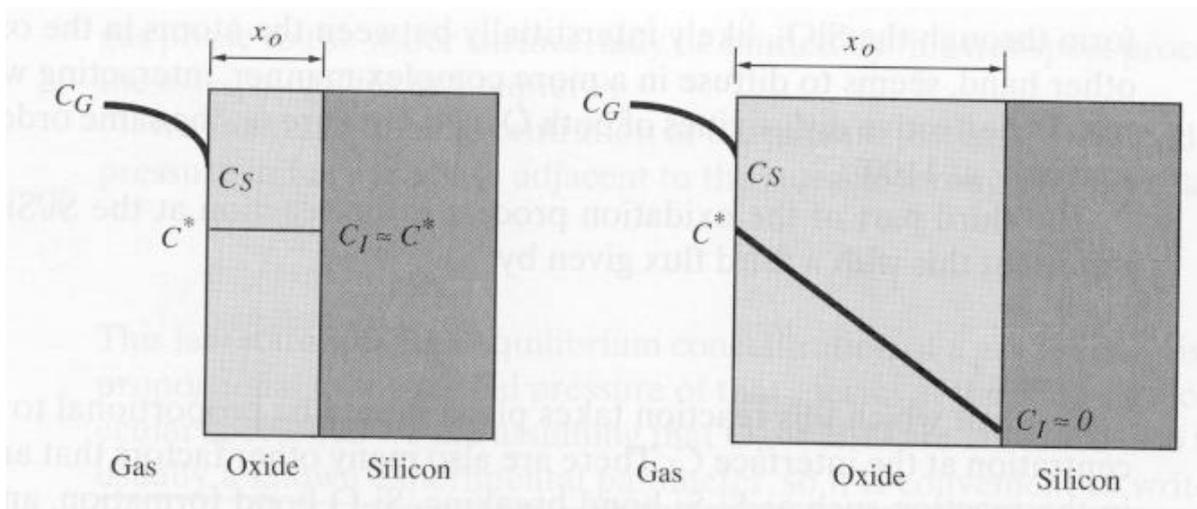
h is very large (experimentally)

- Interface reaction process at the oxide surface (gas absorption)

↑ + diffusion + process at the Si/SiO₂

fast slow

k_s/h can be neglected compared to $\frac{k_s X_0}{D}$



$$\frac{k_s x_0}{D} \ll 1 \quad \text{②} \quad C_i \gg C^*$$

- Reaction rate controlled
- $\frac{k_s x_0}{D} \gg 1$ for $x_0 \gg 50 - 200 \text{ nm}$

$\frac{k_s x_0}{D} \gg 1 \quad \text{②} \quad$ the oxidant profile becomes linear, with $C_i \gg 0$

- Diffusion controlled region

$$\frac{dx_0}{dt} = \frac{F}{N_1} = \frac{k_s C^*}{N_1 \left(1 + \frac{k_s}{h} + \frac{k_s x_0}{D} \right)}$$

N_1 = No. of oxidant molecules incorporated per unit volume of oxide grown

$$= \begin{cases} 2.2 \times 10^{22} / \text{cm}^3 \text{ for } \text{O}_2 \\ 2 \times (2.2 \times 10^{22}) / \text{cm}^3 \text{ for } \text{H}_2\text{O} \end{cases}$$

$$N_1 \left(1 + \frac{k_s}{h} + \frac{k_s x_0}{D} \right) dx_0 = k_s C^* dt$$

$$\int \frac{x_0^2 - x_i^2}{B} + \frac{x_0 - x_i}{A} = t$$

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

$$\frac{B}{A} = \frac{C^*}{N_1 \left(1 + \frac{k_s}{h} \right)} \gg \frac{C^* k_s}{N_1} \text{ : linear rate constant}$$

contribution of F_3

contribution of F_2

$$\frac{x_0^2}{B} + \frac{x_0}{\frac{B}{A}} = t + \tau$$

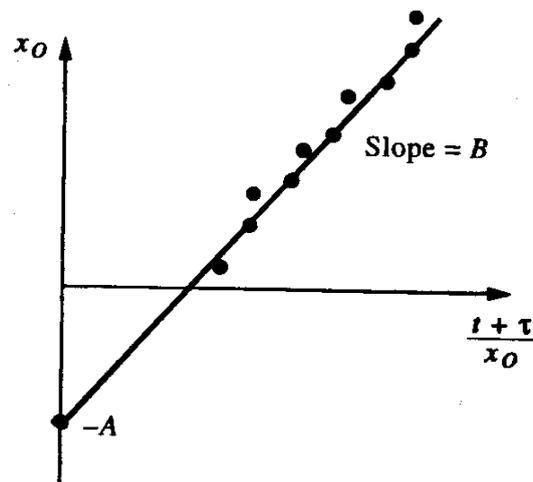
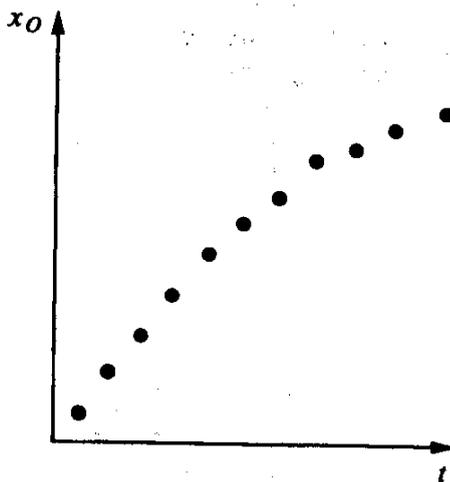
$$\text{where } t = \frac{x_i^2 + Ax_i}{B}$$

x_i or τ account for any oxide present at the start of oxidation

$$x_0 = \frac{A}{2} \sqrt{1 + \frac{t + \tau}{A^2/4B}} - \frac{A}{2}$$

$$x_0 @ \frac{B}{A}(t + \tau) \text{ or } x_0^2 @ B(t + \tau)$$

- B and B/A are normally determined experimentally by extracting them from growth data

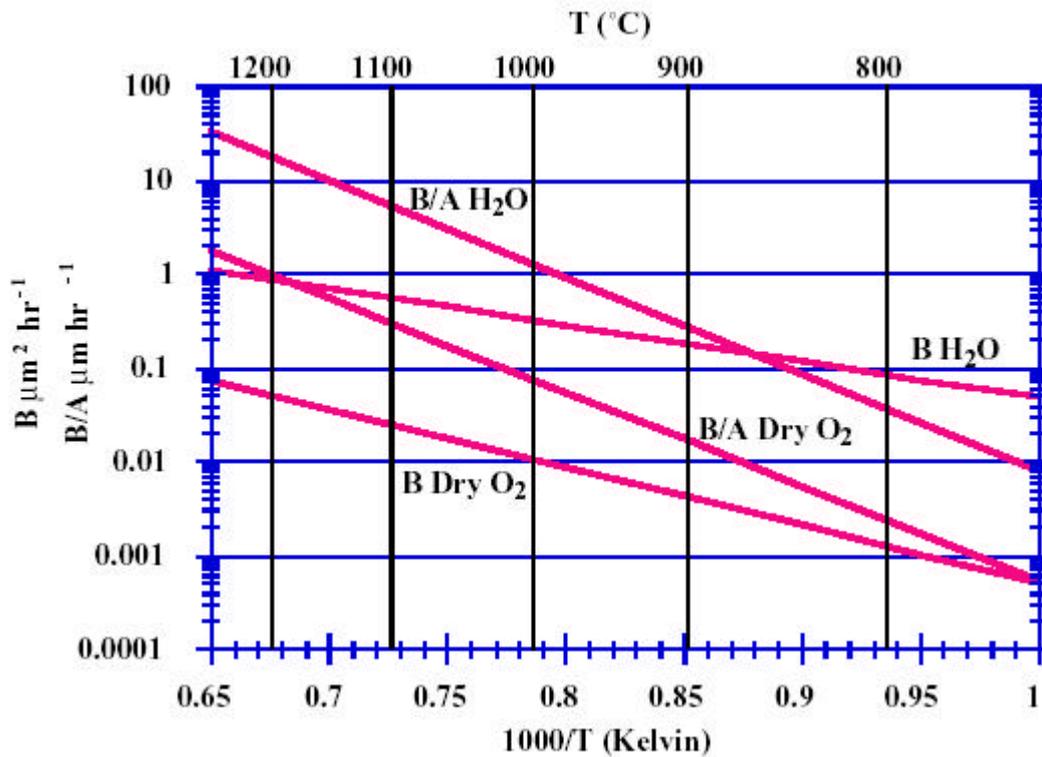


- flat unpatterned surfaces
 - lightly doped substrates
 - simple O₂ or H₂O ambients
 - x₀ > ~ 20nm
- ü
i
y
i
b
- linear parabolic law

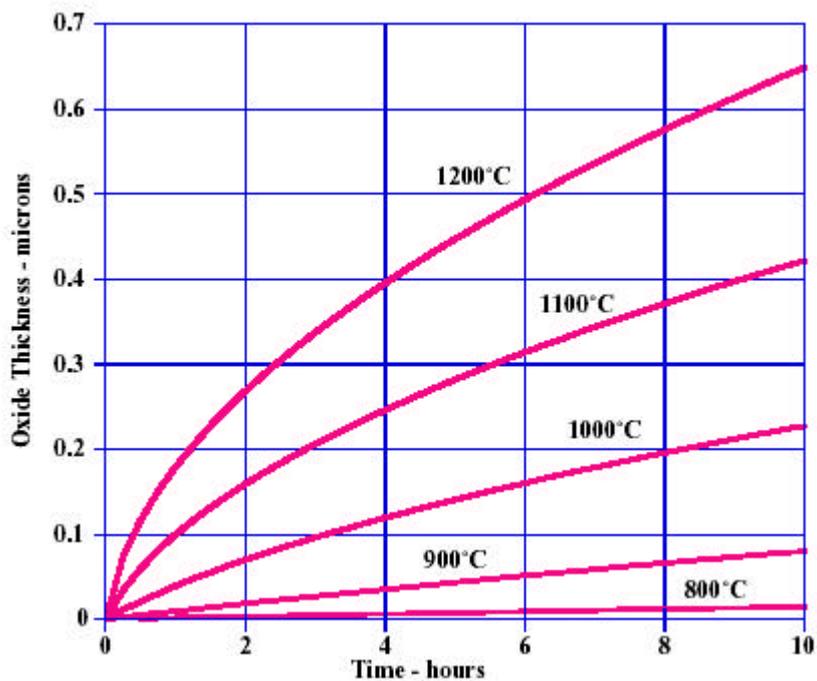
$$B = C_1 \exp(-E_1/kT)$$

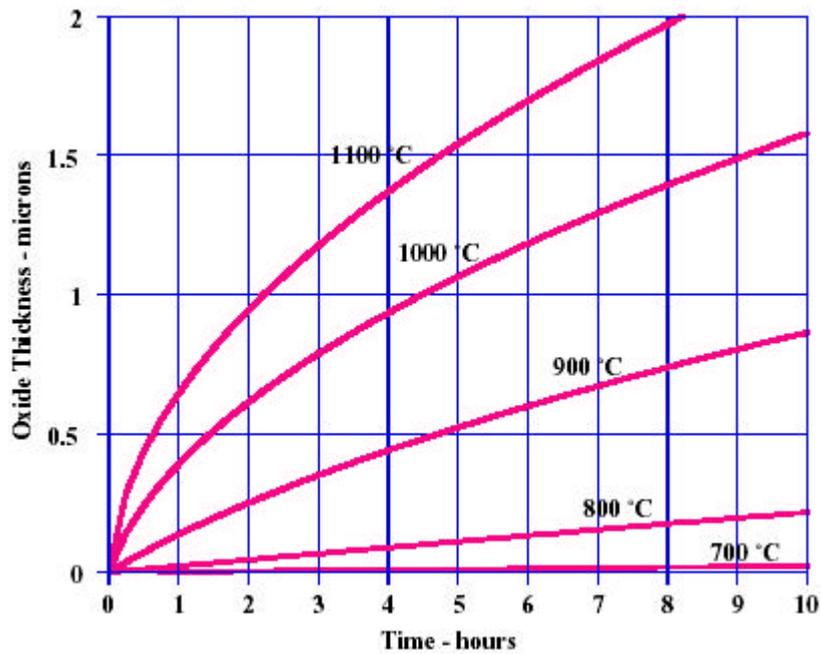
$$\frac{B}{A} = C_2 \exp(-E_2/kT)$$

Ambient	B	B/A
Dry O ₂	C ₁ = 7.72 x 10 ² μ ² hr ⁻¹ E ₁ = 1.23 eV	C ₂ = 6.23 x 10 ⁶ μ hr ⁻¹ E ₂ = 2.0 eV
Wet O ₂	C ₁ = 2.14 x 10 ² μ ² hr ⁻¹ E ₁ = 0.71 eV	C ₂ = 8.95 x 10 ⁷ μ hr ⁻¹ E ₂ = 2.05 eV
H ₂ O	C ₁ = 3.86 x 10 ² μ ² hr ⁻¹ E ₁ = 0.78 eV	C ₂ = 1.63 x 10 ⁸ μ hr ⁻¹ E ₂ = 2.05 eV



- “Wet O₂” : O₂ is bubbled through H₂O at 95°C
- E₁ for O₂ and H₂O are different due to the difference in diffusion constants
- E₂ values are all quite close to 2eV. The physical origin of E₂ is likely connected with k_S. E₂ is essentially independent of substrate crystal orientation





- **SiO₂ grows much faster in an H₂O ambient than it does in dry O₂ (C* is much higher)**
 - At 1100°C, C* ~ 5×10¹⁶/cm³ for dry O₂
 - ~ 3×10¹⁹/cm³ for H₂O
 - ? both B and B/A are much larger for H₂O

6.5.2 Other Models for Planar Oxidation Kinetics

- Measurements of oxide growth rates in dry O₂ are not accurately predicted by Deal-Grove model for $x_0 < \sim 20\text{nm}$
- Reisman

$$x_0 = a(t + t_i)^b \quad \text{or} \quad x_0 = a \left(\frac{C}{e} t + \frac{a x_i}{e a \theta} \right)^{\frac{1}{b}}$$

- The interface reaction controlled the process at all times and the volume expansion was provided by viscous flow of the oxide layer
- Han and Helms

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

All of the rate constants were found to fit Arrhenius expressions

Table 6-3 Experimental rate constants for the parallel oxidation model of Han and Helms [6.15]

	B_1	B_1/A_1	B_2	B_2/A_2
C	$3.9 \times 10^5 \mu\text{m}^2 \text{hr}^{-1}$	∞	$1.56 \times 10^4 \mu\text{m}^2 \text{hr}^{-1}$	$4.98 \times 10^6 \mu\text{m} \text{hr}^{-1}$ (111)
				$1.56 \times 10^6 \mu\text{m} \text{hr}^{-1}$ (100)
E_A	2.2 eV		1.6 eV	1.9 eV

$$(x_0^2 - x_i^2) + C(x_0 - x_i) - G \ln \frac{2Ex_0 - F}{2Ex_i + F} = Et$$

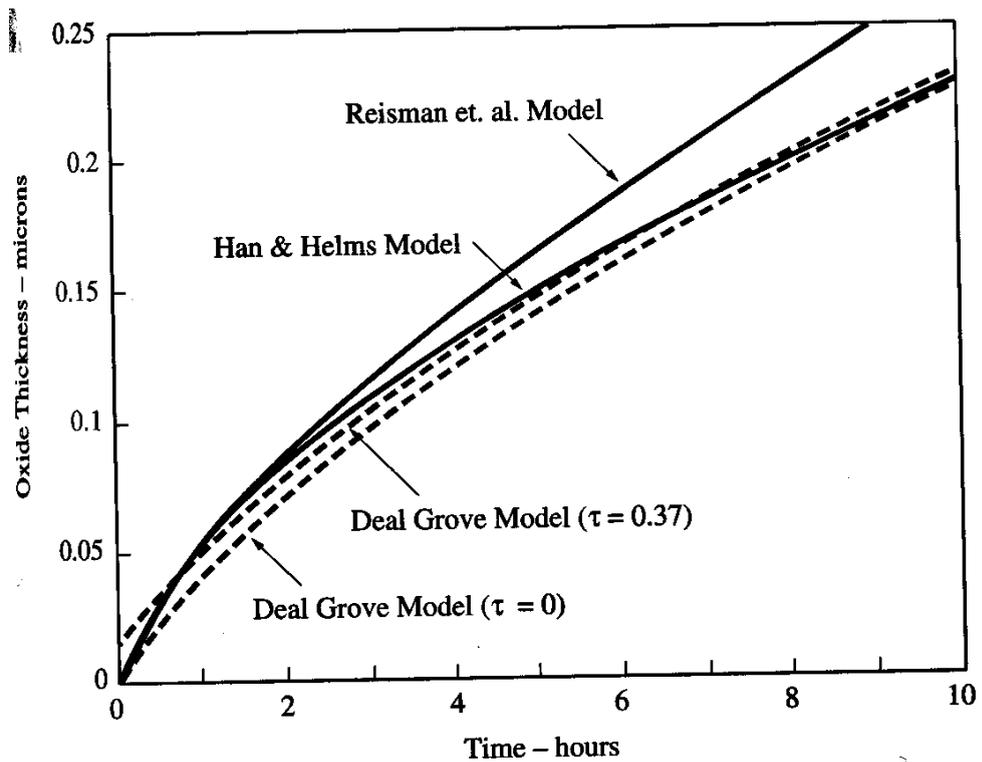
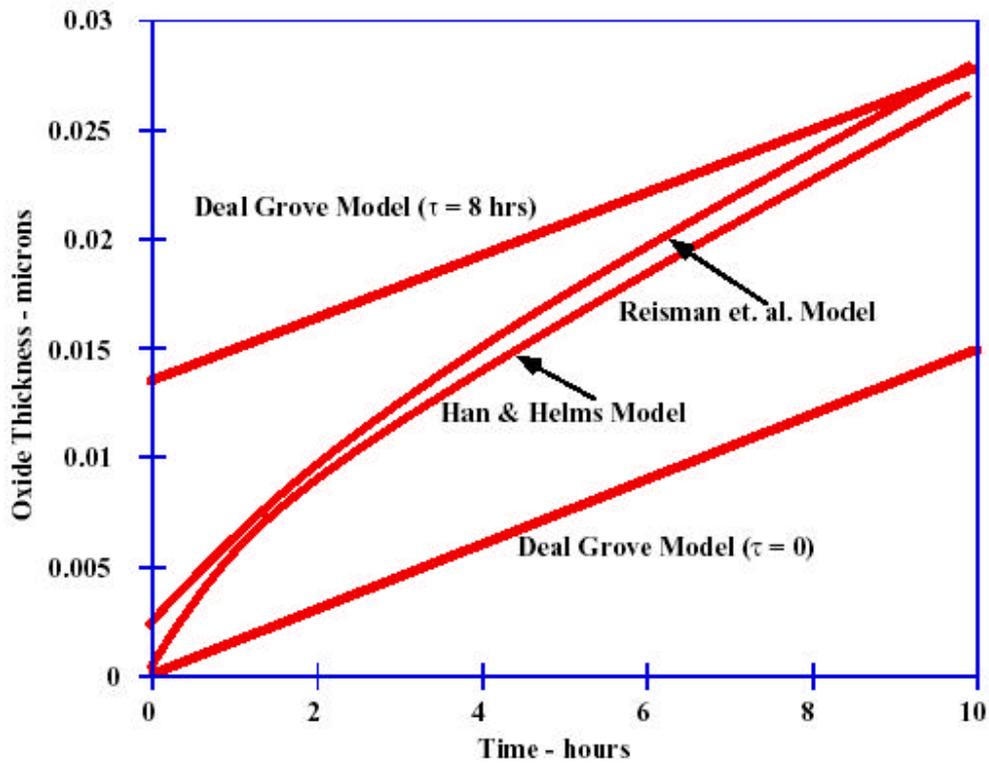
where $C = \frac{A_1 B_1 + A_2 B_2}{B_1 + B_2}$, $E = B_1 + B_2$, $F = A_1 B_2 + A_2 B_1$

$$G = \frac{B_1 B_2 (A_1 - A_2)^2}{2(B_1 + B_2)^2}$$

• Ghez and Van der Meulen

$$\frac{B}{A} \propto P^n$$

- ┌ n ? 0.5 at low T : O reaction
- └ n ? 1 at high T : O₂ reaction



- For $x_0 > \sim 20\text{nm}$, all three models converge to approximately the same result

6.5.3 Thin Oxide SiO_2 Growth Kinetics

- Chemical cleaning procedures prior to oxidation have been shown to significantly affect the kinetics
- Massoud

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

$$\text{where } C = C_0 \exp\left(-\frac{E_A}{kT}\right)$$

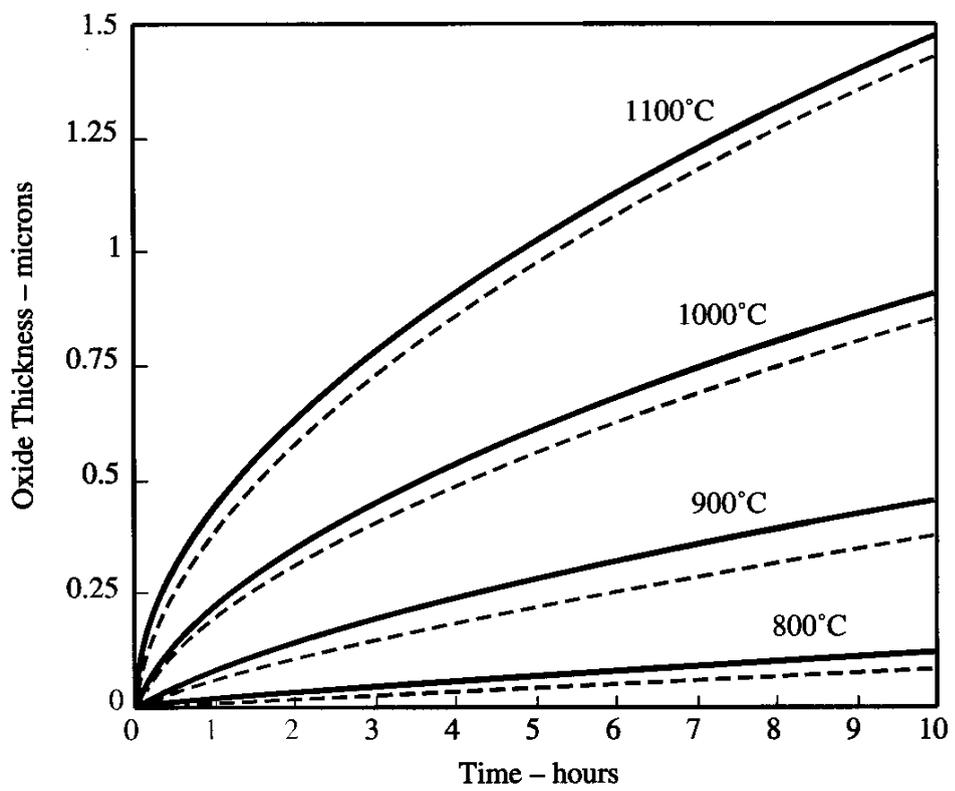
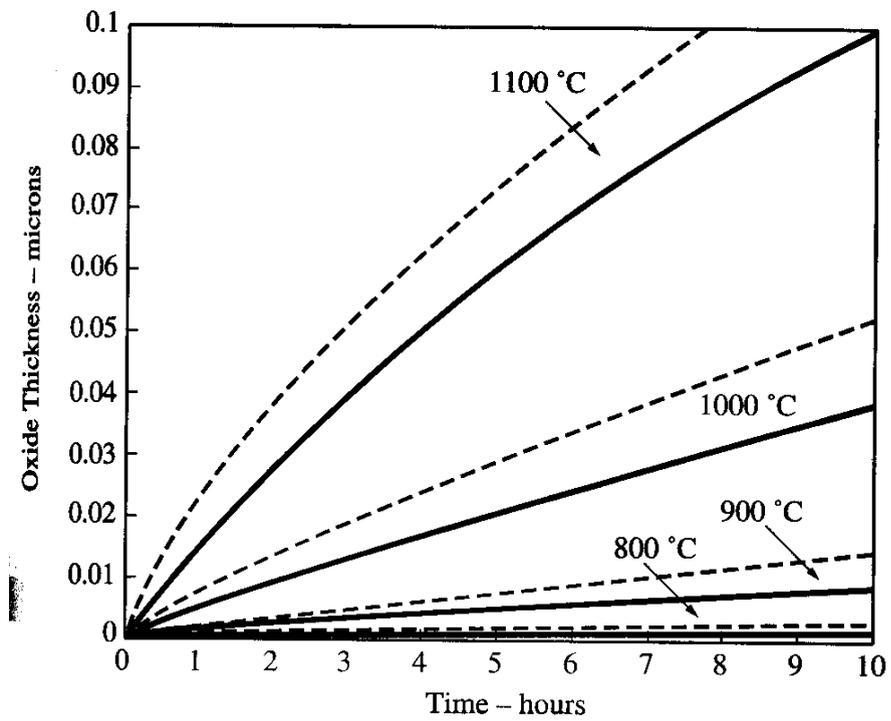
$$C_0 \sim 3.6 \times 10^8 \mu\text{m/hr}$$

$$E_A \sim 2.35 \text{ eV}$$

$$L \sim 7 \text{ nm}$$

6.5.4 Dependence of Growth Kinetics on Pressure

- $\frac{dx_0}{dt} \propto C^* \propto P^0$ for H_2O Oxidation
- $B \propto P$ and $\frac{B}{A} \propto P^n$ where $0.5 < n < 1$ for dry O_2 oxidation
- $\frac{B}{A} = \frac{B_0}{A_0} P^n$ $B = (B_0)^i P$ for H_2O
- $\frac{B}{A} = \frac{B_0}{A_0} P^n$ $B = (B_0)^i P$ for O_2 where $n \approx 0.7 - 0.8$



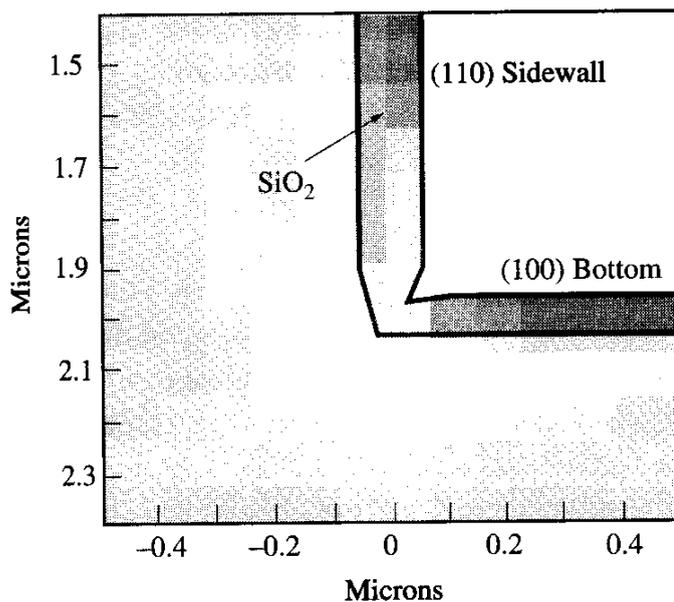
- For $P < 1 \text{ Atm}$, x_0 is increased
- For $P > 1 \text{ Atm}$, x_0 is decreased

6.5.5 Dependence of Growth Kinetics on Crystal Orientation

- Growth rates are faster on (111) surfaces than they are on (100) surfaces
- The no. of “available” bonds/cm² are larger for (111)
- B should not be orientation dependent since B represents oxidant diffusion through the SiO₂
- $\frac{B}{A}$ should be orientation dependent

$$\frac{\partial B}{\partial A} \Big|_{(111)} = 1.68 \frac{\partial B}{\partial A} \Big|_{(100)}$$

$$\frac{\partial B}{\partial A} \Big|_{(110)} = 1.45 \frac{\partial B}{\partial A} \Big|_{(100)}$$



- The orientation effect apparently changes for very thin oxides grown at low O₂ partial pressures and also for high P steam oxides grown at low T

- slow : the mechanism is apparently different
 - fast : high P steam oxides : Ligenza observed the (100) surface to oxidize faster than the (111) surface at 800°C and below

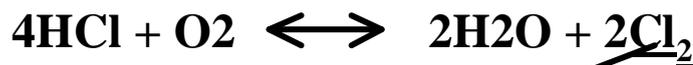
At low T, the relaxation due to glass flow is more difficult because the oxide cannot flow as easily. Also more difficult if the oxide is growing very rapidly

- ? high stresses built up
- ? unusual orientation effects

6.5.6 Mixed Ambient Growth Kinetics

- H₂O (about 95% typically) and O₂ (about 5%)
- HCl + O₂

→ reduce oxide defect densities and to reduce contamination levels



← reacts with trace metals and other contaminants to produce volatile chlorides as byproducts

- If it is assumed each of the oxidants acts independently, Han and Helms model

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

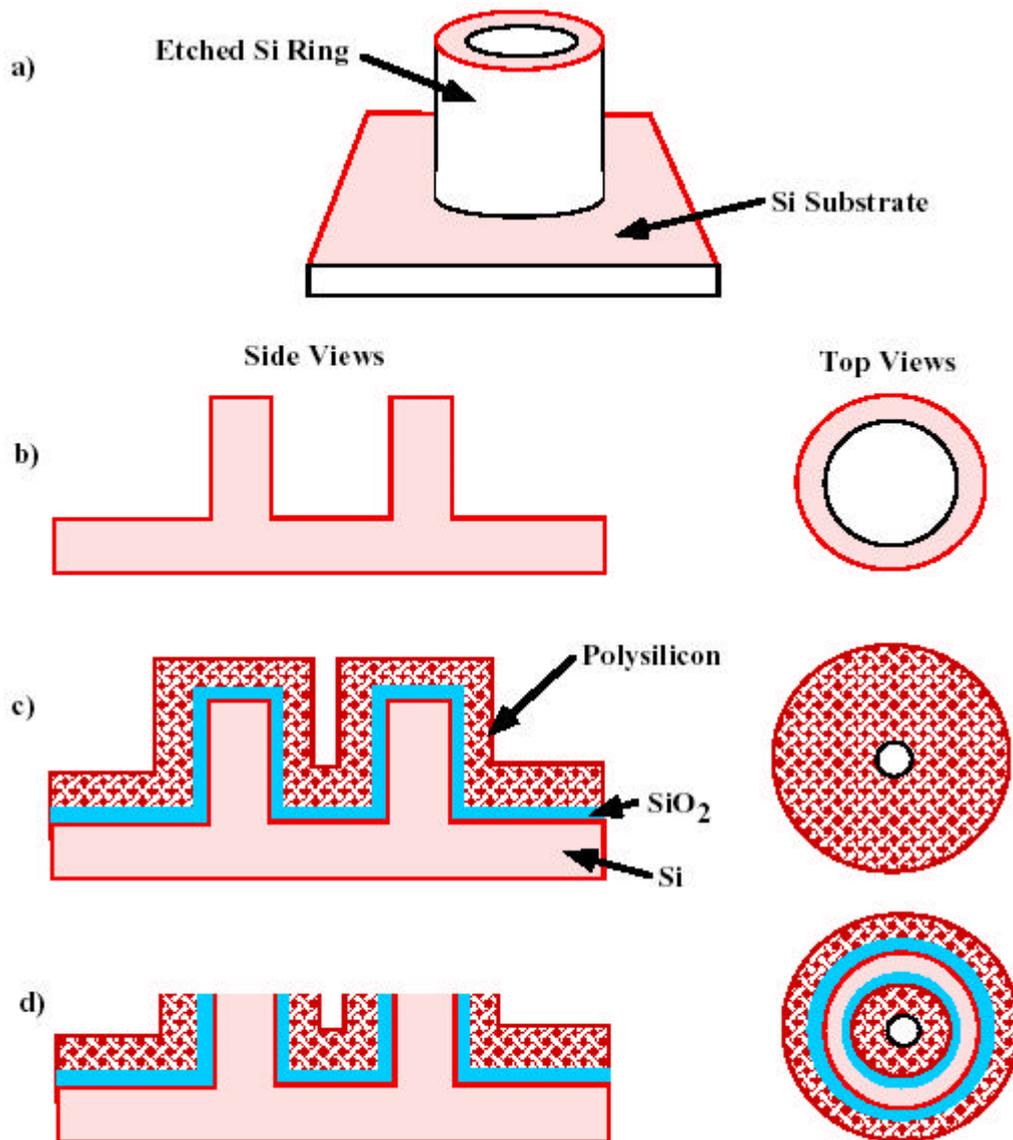
- Cl is known to be incorporated into the growing SiO₂ film

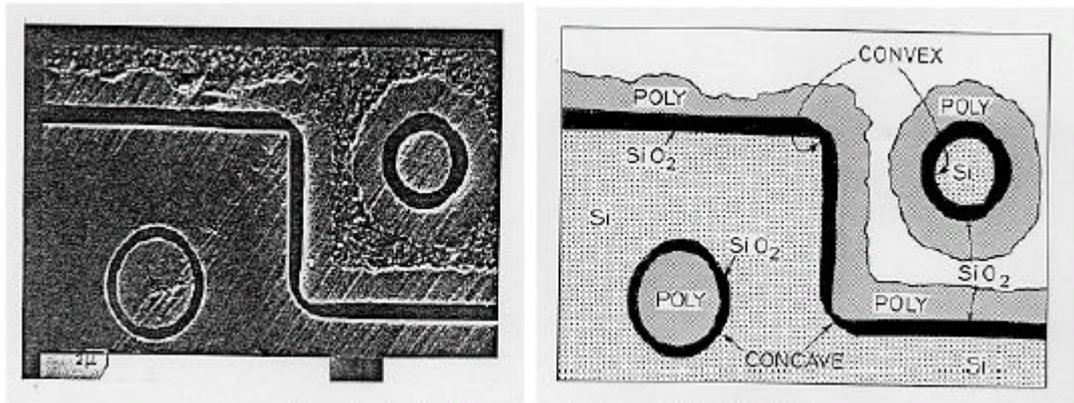
- $\frac{B}{A}$ & $\frac{B}{A}$ increase with HCl percentage

- $\frac{B}{A} = \frac{\alpha B_0}{\zeta \epsilon A_0} d$ and $B = (B)^i c$

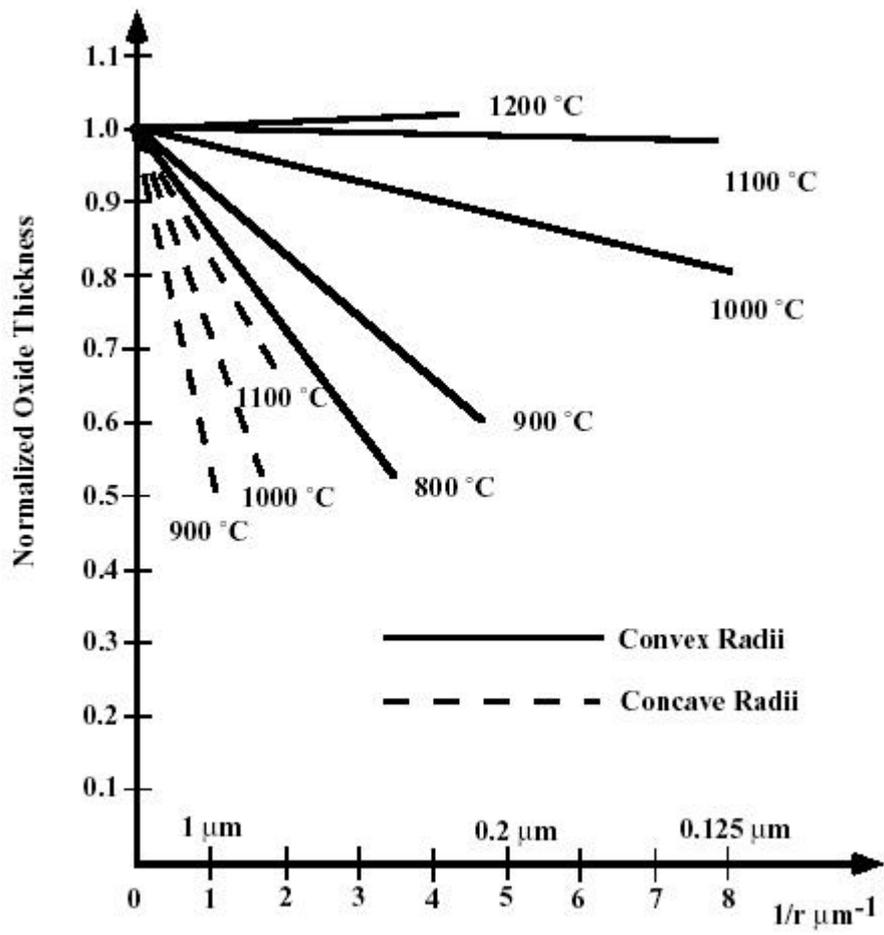
d and c are functions of the HCl concentration

6.5.7 2D SiO₂ Growth Kinetics





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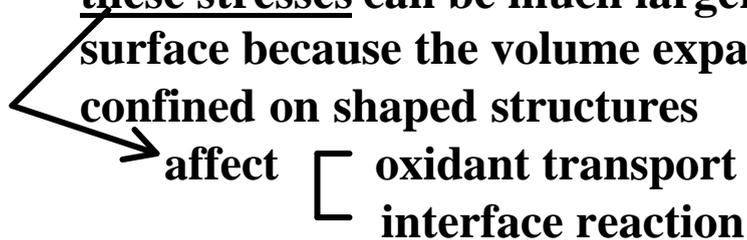


- The retardation (a factor of two) is very significant
- The retardation is much more pronounced for low T
- Virtually no corner effect at 1200°C
- Interior (concave) corners > exterior (convex) corners

1. Crystal orientation

2. 2D Oxidant Diffusion

3. Stress due to volume expansion : on shaped surfaces, these stresses can be much larger than those on a flat surface because the volume expansion is dimensionally confined on shaped structures



$$k_s(\text{stress}) = k_s \exp\left\{-\frac{s_n V_R}{kT}\right\} \exp\left\{-\frac{s_t V_T}{kT}\right\}$$

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

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

s_n = stress normal to the growing interface

s_t = stress tangential to the growing interface

V_R, V_T, V_D, V_S = stress-dependent activation volumes
and should be regarded as fitting
parameters

- **SiO₂ can relax some of the stresses that build up during oxidation by viscoelastic flow**

$$h(\text{stress}) = h(T) \frac{\frac{s_s V_c}{2kT}}{\sinh \left(\frac{s_s V_c}{2kT} \right)}$$

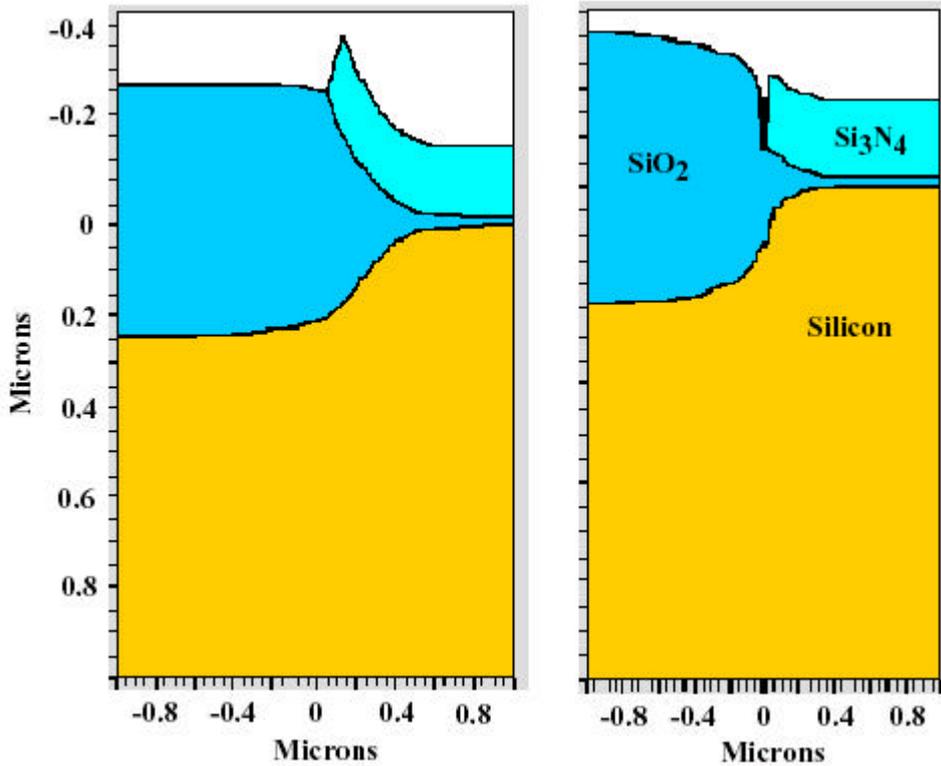
s_s = shear stress in the oxide

V_c = fitting parameter

- **Since the shape of the growing oxide changes with time, k_s(stress), D(stress), and ?(stress) all change with time**

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 @ 850°C 0.72 nm ³ @ 1050°C
η(T) - SiO ₂	3.13 x 10 ¹⁰ exp(2.19 eV/kT) poise
η(T) - Si ₃ N ₄	4.77 x 10 ¹⁰ exp(1.12 eV/kT) poise

- $V_s \sim 0$ implies that C^* is not highly stress dependent



Viscosity and stress dependence

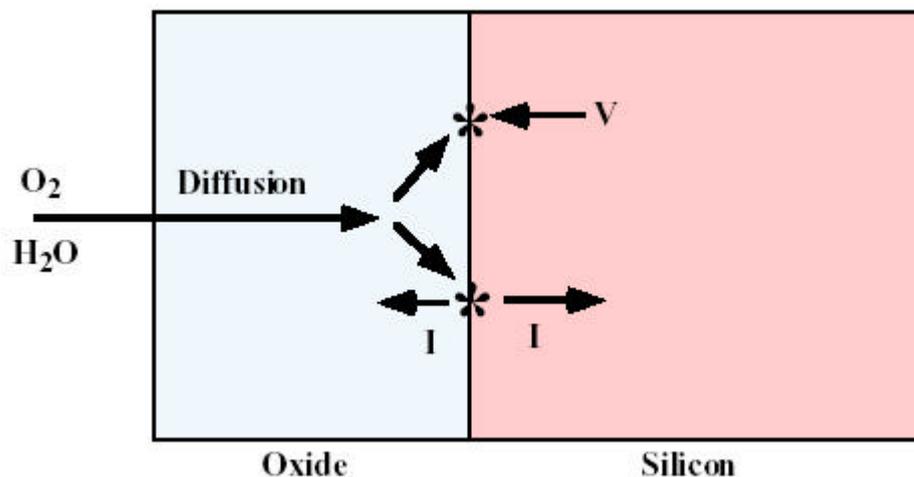
- Multiple oxidations

First	Second	The initial growth rate of the second oxidation
High T	Low T	Faster the stress levels are lower than expected
Low T	High T	Slower the stress levels are higher than expected

- If rapid thermal processing is combined with oxidation, the oxidation rates may be quite different than expected and will certainly depend on history
- Uniform oxide growth on shaped structures
 - 1200°C
 - O₂/NF₃
 - Corona discharge above the wafer during the oxidation

6.5.8 Advanced Point Defect Based Models for Oxidation

- OED (Oxidation Enhanced Diffusion) : dopant diffusion are increased by surface oxidation
- ORD (Oxidation Retarded Diffusion) : slowed down

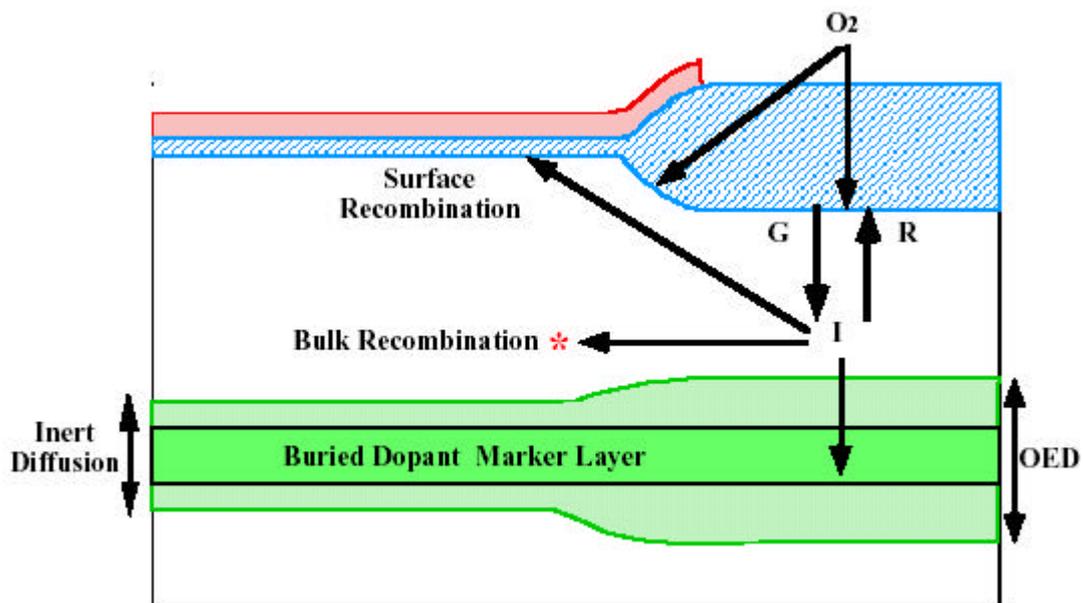


- Two types of point defects
 - Vacancies(V) or missing Si atoms
 - Interstitials(I) or excess Si atoms
- Volume for the oxidation reaction can be provided either by consuming vacancies or by generating interstitials

$$(1+2?)\text{Si} + 2\text{O}_I + 2\beta\text{V} \longleftrightarrow \text{SiO}_2 + 2?I + \text{stress}$$

? = no. of I that contribute to the process per O atom joining the SiO₂

β = similar fraction for V
- I can diffuse for away from the Si/SiO₂ interface and change the diffusivity of dopants which interact with I



- The net result is a flux of interstitials away from the surface

- $G = q \frac{dx_0}{dt} N$

$$R = K_{\text{inert}} K_{\text{rat}} \frac{\alpha \frac{dx_0}{dt} \frac{1}{B/A} \frac{1}{\theta} K_{\text{POW}}}{\epsilon} + K_{\text{inert}}$$

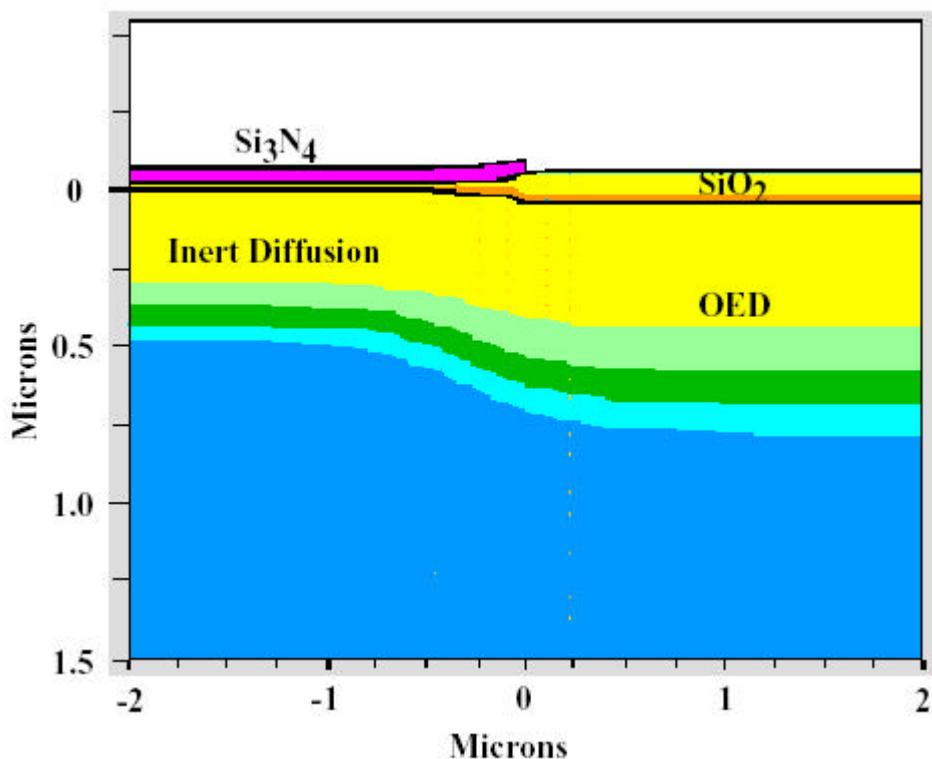
? = fraction of oxidized silicon atoms that are injected into the substrate as interstitials

$\frac{dx}{dt}$ = oxidation velocity

N = no. of Si atoms per unit volume

K_{inert} = recombination velocity at an inert Si/SiO₂ interface

Krat = increased recombination rate at an oxidizing interface



6.5.9 Substrate Doping Effects

- Highly doped substrates oxidize more rapidly than do lightly doped wafers (N^+ regions $>$ P^+ regions, low T $>$ high T)

- $\frac{B}{A}$ is affected, B is not affected

N-type dopants tend to segregate into the silicon
 ? the dopant concentrations in the SiO₂ layer are fairly small
 ? the properties of the SiO₂ layer are independent of the substrate doping

- Oxidation requires volume expansion

↑
 provided by consuming V

- The total number of V is much higher in extrinsic, highly doped regions than in intrinsic, lightly doped material

$$\frac{B}{A} = R_1 + K C_{V,T}$$

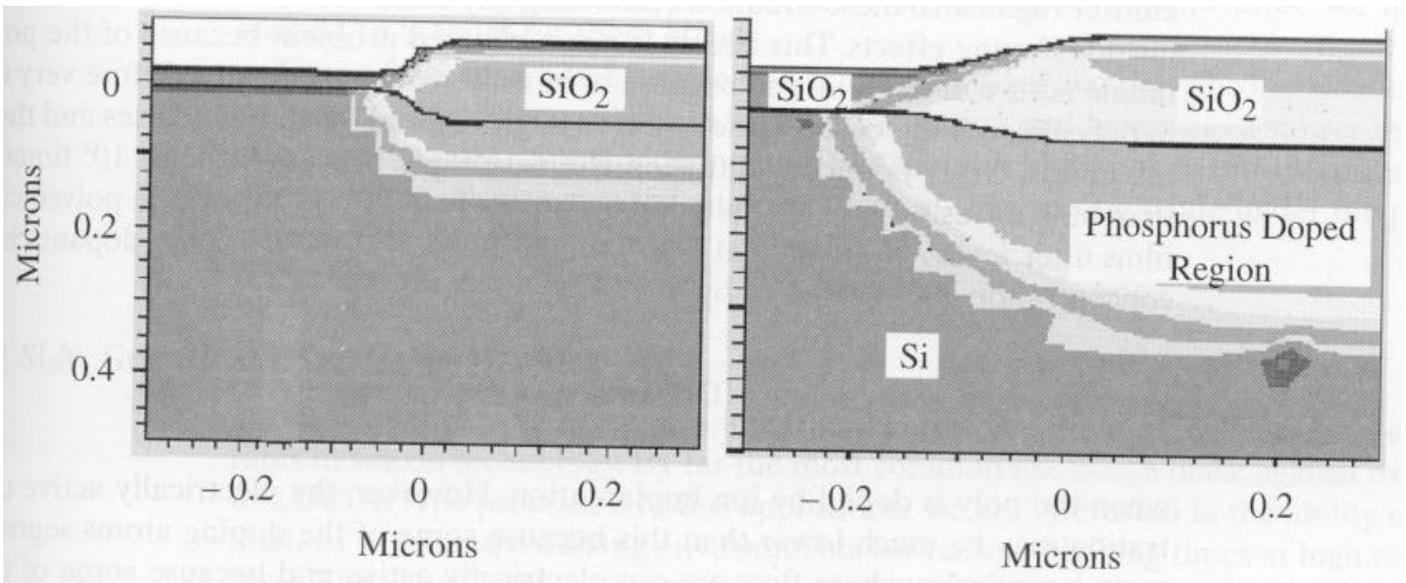
↓ ↓
 total vacancy population

all mechanisms other than the vacancy driven process

$$\frac{B}{A} = \frac{B}{A} + 2.62 \cdot 10^3 \exp\left(-\frac{1.1eV}{kT}\right) \frac{C_{V,T}}{C_{V_i,T}}$$

$C_{V_i,T}$ = total vacancy concentration in intrinsic material

- Fewer total vacancies in P⁺ regions than in N⁺ regions



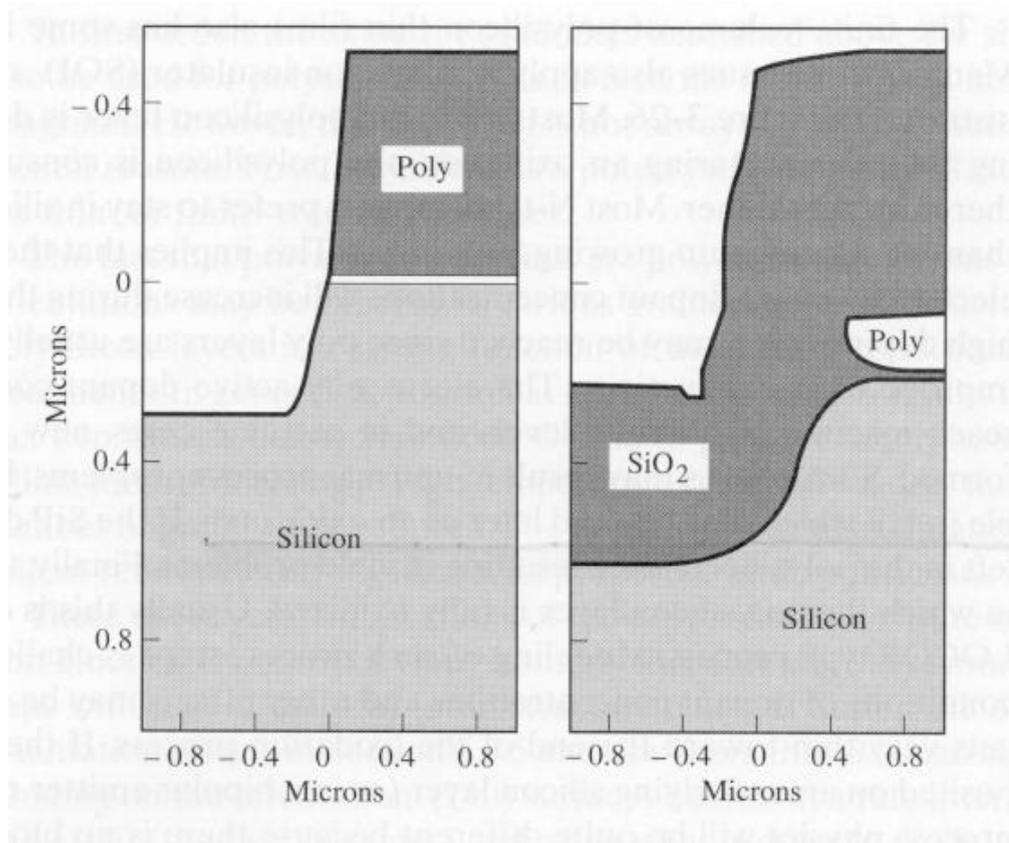
6.5.10 Polysilicon Oxidation

- To first order, the same set of models for single-crystal silicon can also be used for polysilicon
- Polysilicon $\left[\begin{array}{l} \text{polycrystalline material} \\ \text{thin- or finite-volume structures} \end{array} \right.$
- Polycrystalline : a variety of crystal orientations may be present in various grains
- In general, deposition at lower T results in smaller sizes
- Below 600°C, amorphous
- Annealing at high T generally causes the grains to grow
- B/A will vary from grain to grain and perhaps with time if the poly grain structure change during the oxidation

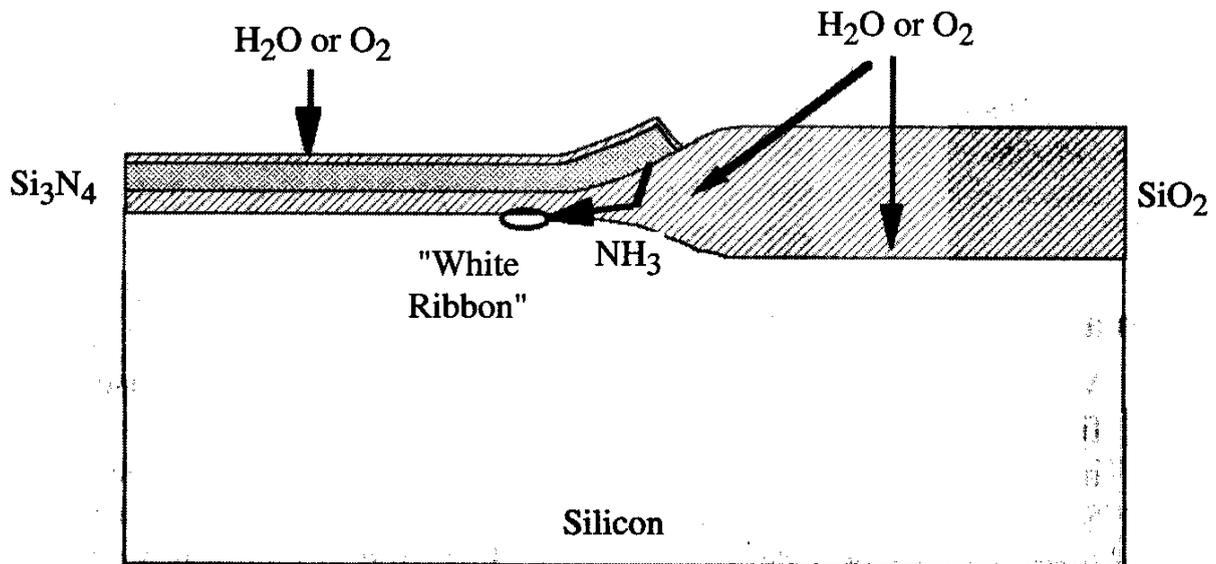
- Often use an average B/A value characteristic of the (110)
- For thin oxide, variations in oxide thickness across a polysilicon surface
- Dopants diffuse very rapidly in polysilicon films, because they tend to migrate along grain boundaries and then into the grains ? dopant profiles tend to be uniform

$$[\text{Dopant}]_{\text{chem}} = \frac{\text{Im plantDose}}{\text{PolyThickn ess}}$$

- Electrically active concentration may be much lower than this because some of the dopants segregate to boundaries where they are not electrically active and because some of the free carriers are also trapped at boundaries



6.5.11 Si₃N₄ Growth and Oxidation Kinetics



$$D_{\text{XN}} = 1.1 \cdot 10^7 \exp\left\{-\frac{1.9\text{eV}}{kT}\right\} t^{0.7} P$$

D_{XN} = the thickness of the nitride consumed in nm

t = oxidation time in min

P = H₂O oxidant pressure in Atm

the oxide thickness = $1.6D_{\text{XN}}$

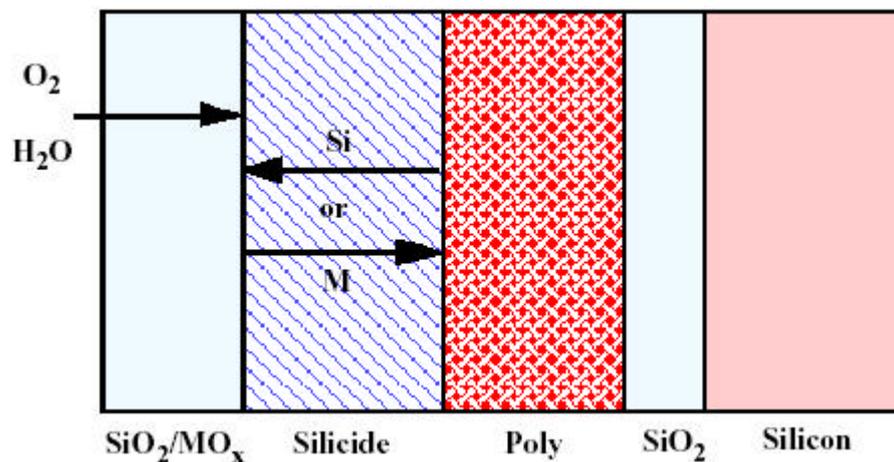
- The oxidation rate in O₂ ambient is much slower than in an H₂O ambient

- “White ribbon” : H_2O diffuses through the growing SiO_2 layer
 NH_3
 NH_3 diffuses to the Si/SiO_2 interface
 thermally grown Si_3N_4 layer
- White ribbon effect = Kooi effect
- Thermal nitridation

$$3\text{Si} + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{H}_2$$
- The growth rate of thermal nitride can be enhanced by growing the layers in an N_2 or NH_3 plasma

6.5.12 Silicide Oxidation

- Polysilicon resistivities cannot be made much lower than about $400\mu\text{Ocm}$



- Either SiO₂ or the metal oxide MO_x could grow
- MO_x is favored on Hf, Zr, and perhaps Ti silicides
- SiO₂ appears to grow in all other cases
- The Si atoms can be provided either by diffusion upward from the poly, or by M-Si bonds being broken



the metal atoms diffuse downward to form a new layer of silicide at the silicide/poly interface

- CrSi₂, CoSi₂, NiSi₂, PdSi, and PtSi : dissociation of the silicide
- TiSi₂, WSi₂, TaSi₂ : diffusion of Si atoms

$$\frac{x_0^2 - x_i^2}{B} + \frac{x_0 - x_i}{B/A} = t$$

$$B(\text{silicide}) = B(\text{Si})$$

$$\frac{B}{A}(\text{silicide}) = (10 - 20) \cdot \frac{B}{A}(\text{Si})$$

- In practice, the oxide growth is often simply parabolic
- If a barrier layer such as a thin native oxide exists between the poly and silicide layers, the reaction at that interface may be slowed down significantly