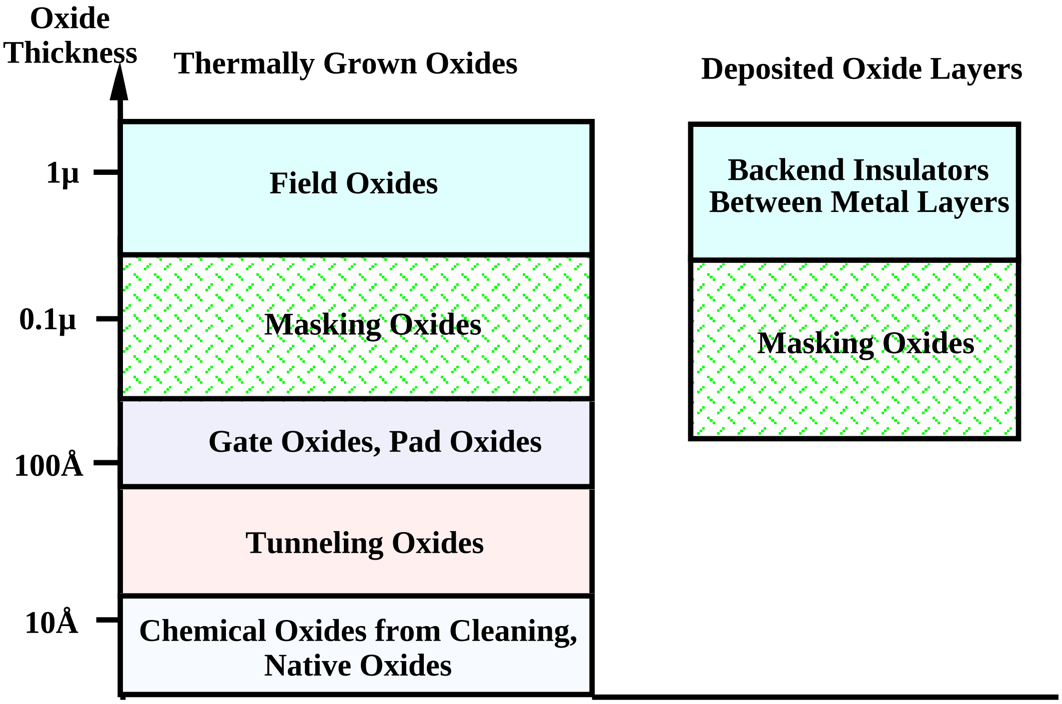
EE 212 FALL 1999-00

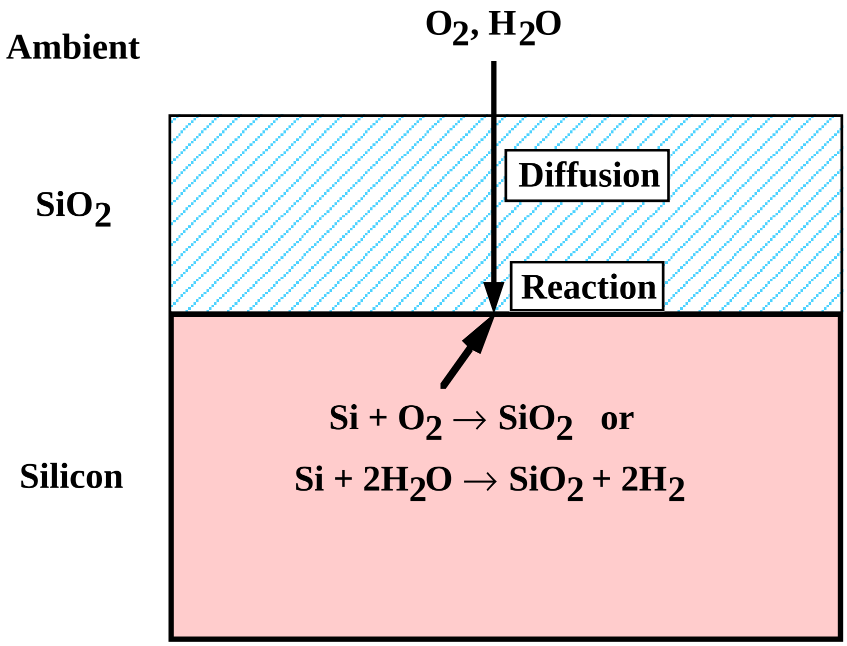
THERMAL OXIDATION - Chapter 6

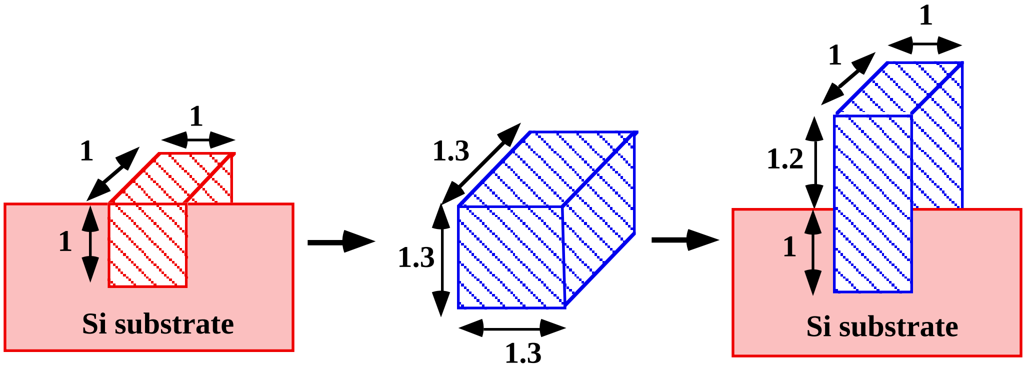
Basic Concepts

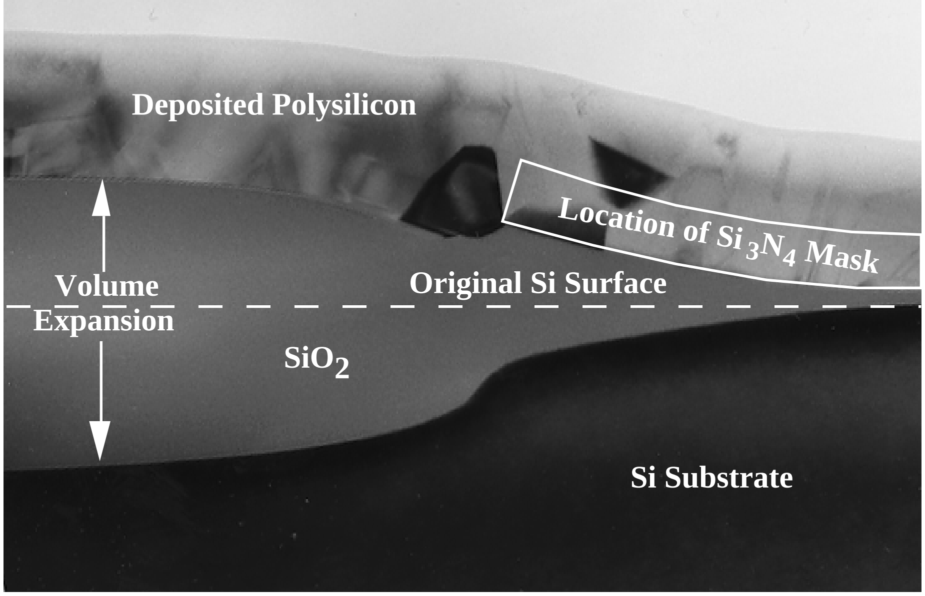
- **SiO_2 and the Si/SiO_2 interface are the principal reasons for silicon's dominance in the IC industry.**
- **SiO_2:**
  - **Easily selectively etched using lithography.**
  - **Masks most common impurities (B, P, As, Sb).**
  - **Excellent insulator ($\rho > 10^{16}\ \Omega cm$, $E_g > 9$ eV).**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



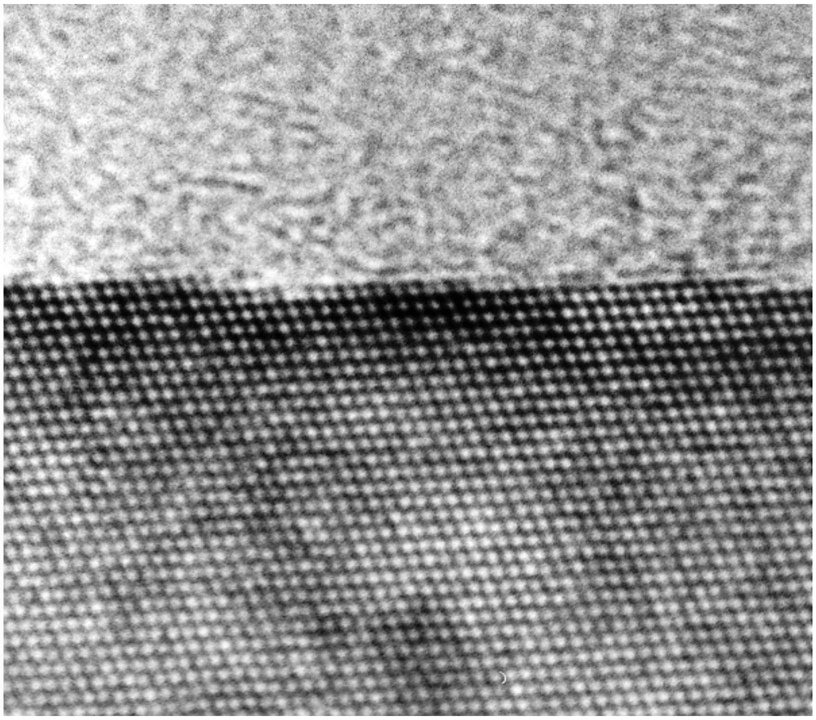
Year of 1st DRAM Shipment	1997	1999	2003	2006	2009	2012
Minimum Feature Size	0.25μ	0.18μ	0.13μ	0.10μ	0.07μ	0.05μ
DRAM Bits/Chip	256M	1G	4G	16G	64G	256G
Minimum Supply Voltage (volts)	1.8-2.5	1.5-1.8	1.2-1.5	0.9-1.2	0.6-0.9	0.5-0.6
Gate Oxide T_{ox} Equivalent (nm)	4-5	3-4	2-3	1.5-2	<1.5	<1.0
Thickness Control (% 3σ)	± 4	± 4	± 4-6	± 4-8	± 4-8	± 4-8
Equivalent Maximum E-field (MV cm^{-1})	4-5	5	5	>5	>5	>5
Gate Oxide Leakage (DRAM) (pA μm^{-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, κ for Intermetal Insulator	3.0-4.1	2.5-3.0	1.5-2.0	1.5-2.0	<1.5	<1.5



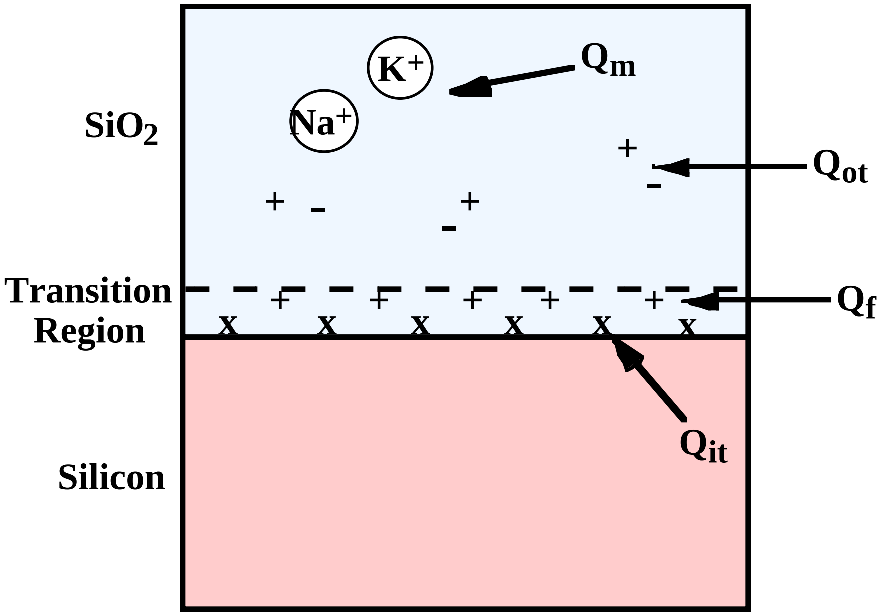




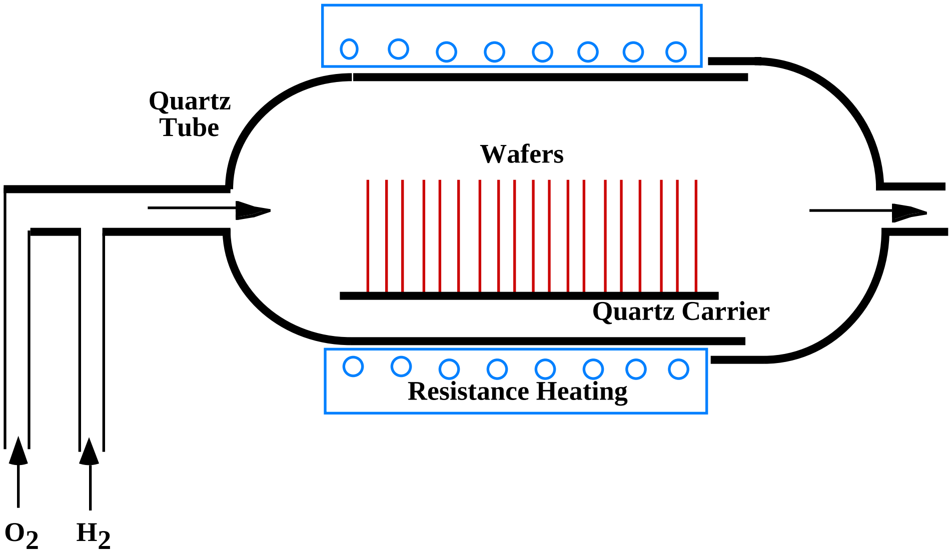
- **Oxidation involves a volume expansion (≈ 2.2X).**
- **Especially in 2D and 3D structures, stress effects play a dominant role.**



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



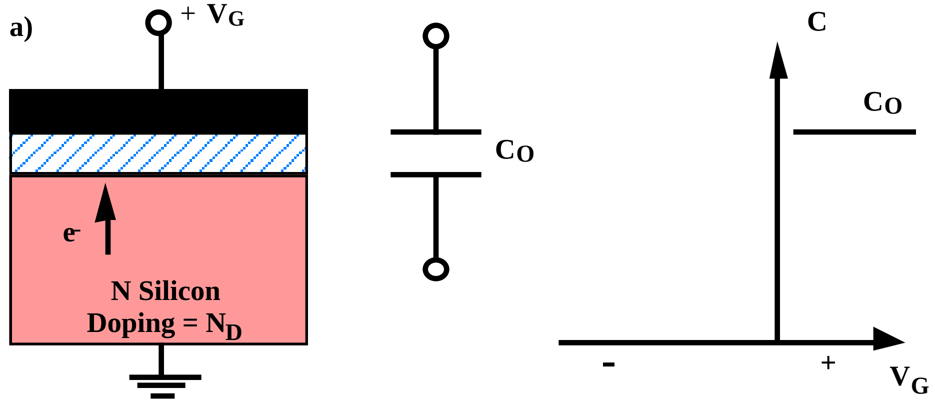
- Four charges are associated with insulators and insulator/semiconductor interfaces.
  - Q_f - fixed oxide charge
  - Q_{it} - interface trapped charge
  - Q_m - mobile oxide charge
  - Q_{ot} - oxide trapped charge

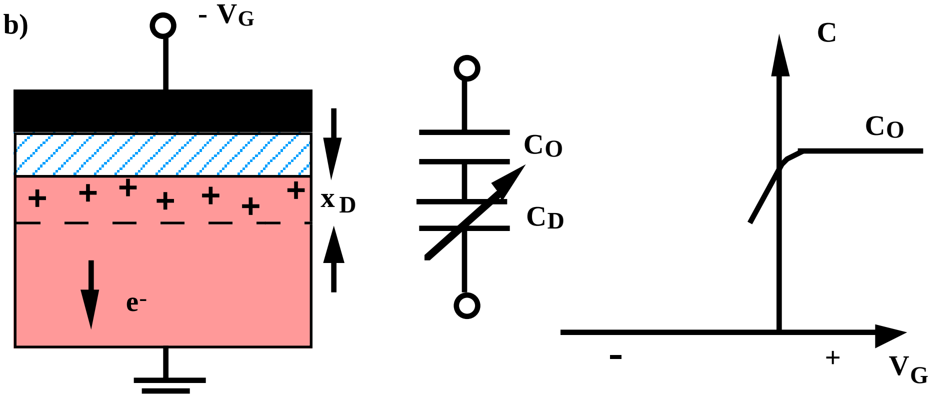


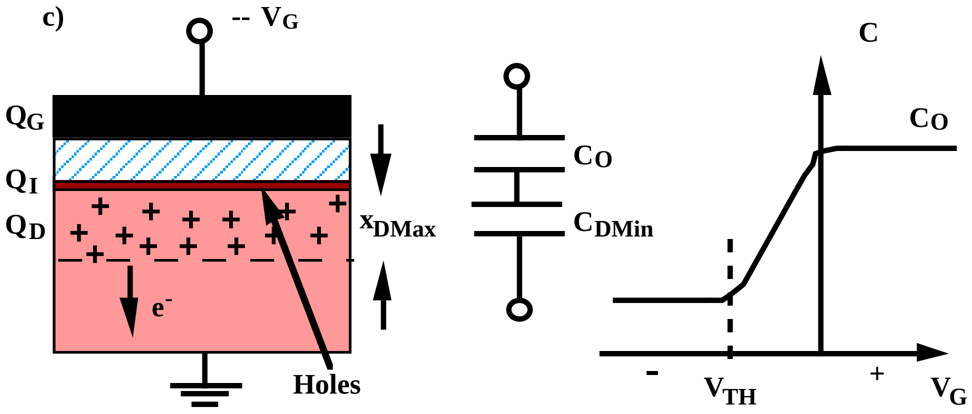
- Oxidation systems are conceptually very simple.
- In practice today, vertical furnaces, RTO systems and fast ramp furnaces all find use.

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.

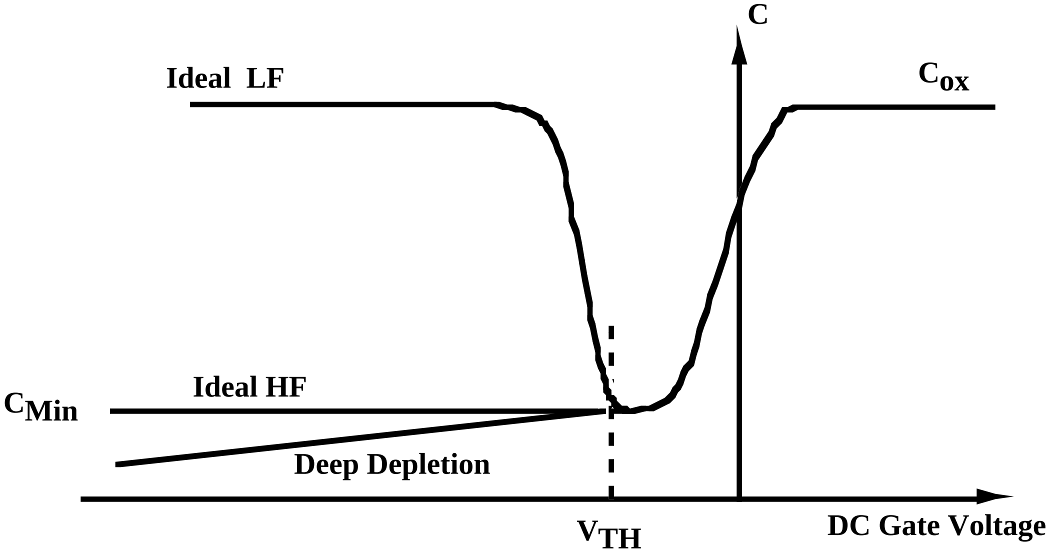






- **Electric field lines pass through the "perfect" insulator and Si/SiO$_2$ interface, into the substrate where they control charge carriers.**
- **Accumulation, depletion and inversion result.**

$$Q_G = qN_D x_D + Q_I \qquad (1)$$

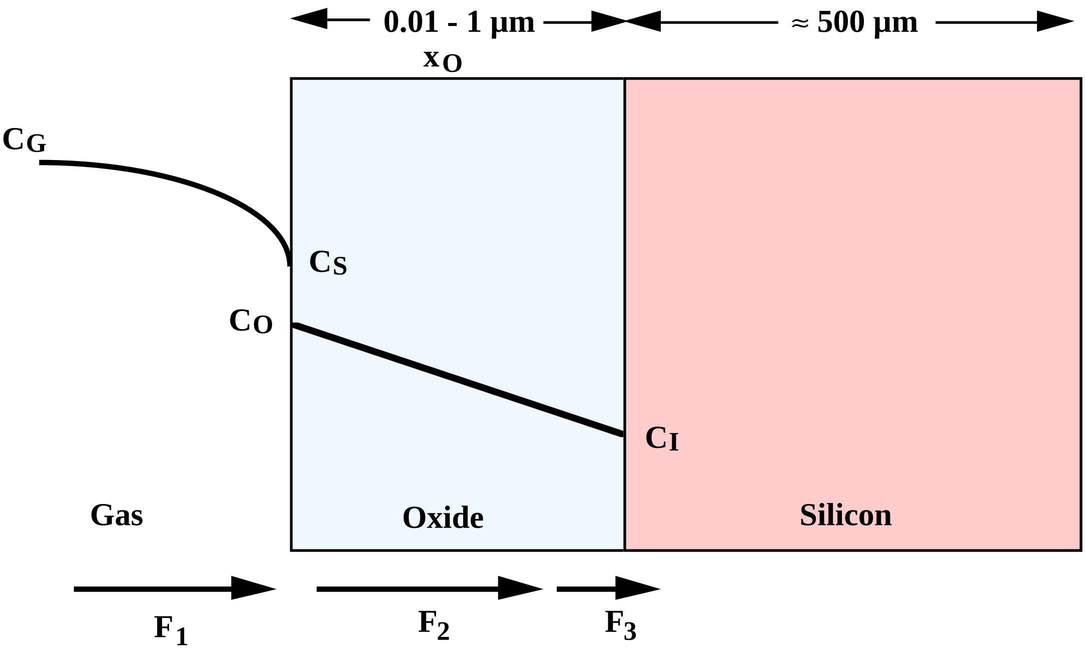


- **HF curve - inversion layer carriers cannot be generated fast enough to follow the AC signal so C$_{inv}$ is C$_{ox}$ + C$_D$.**
- **LF curve - inversion layer carriers follow the AC signal so C$_{inv}$ is just C$_{ox}$.**
- **Deep depletion - "DC" voltage is applied fast enough that inversion layer 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$_m$, and Q$_{ot}$ - oxide & interface charges.**

- **See text for more details on these measurements.**

SiO_2 Growth Kinetics Models
A. Deal Grove Model



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

$$\mathrm{Si} + \mathrm{O_2} \rightarrow \mathrm{SiO_2} \qquad (2)$$

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

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

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

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

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

- 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.

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

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

- 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)

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

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

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

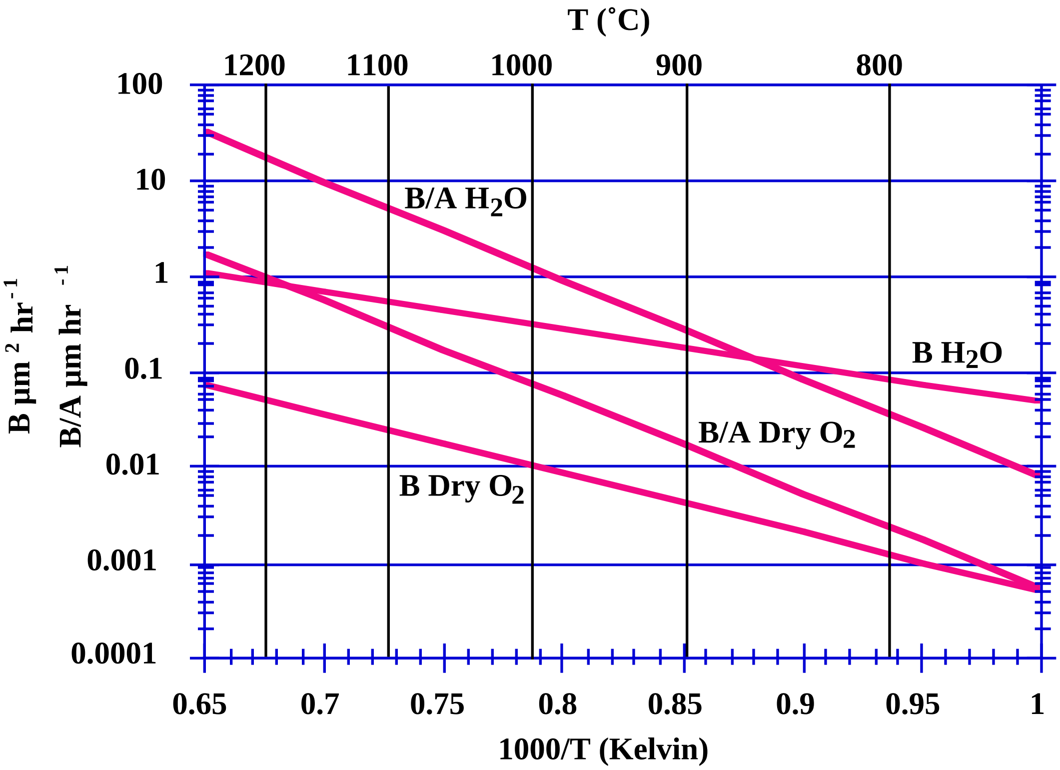
where $$\tau=\frac{x_i^2+Ax_i}{B}\qquad (14)$$

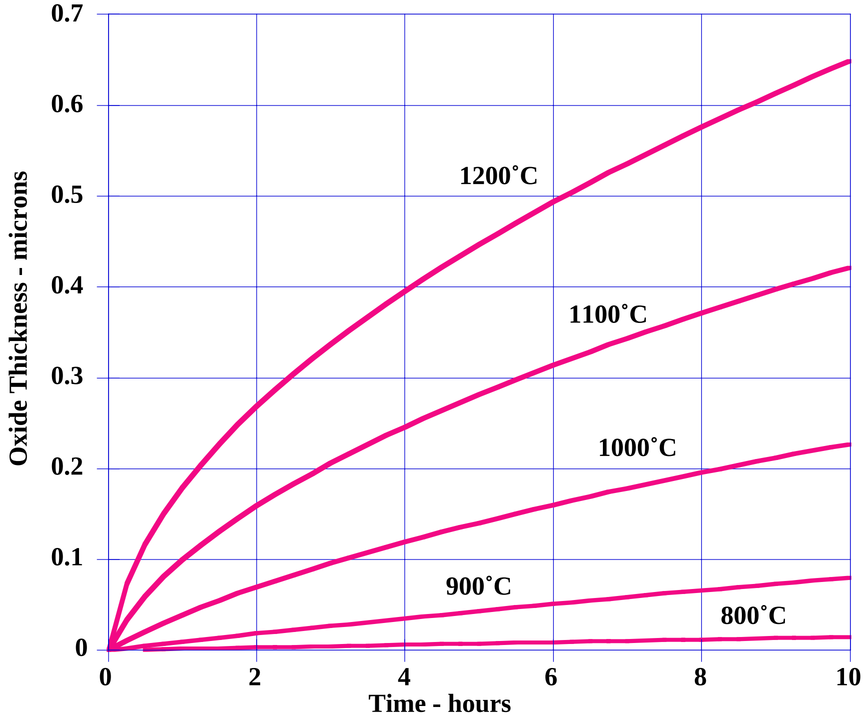
- **The rate constants B and B/A have physical meaning (oxidant diffusion and interface reaction rate respectively).**

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

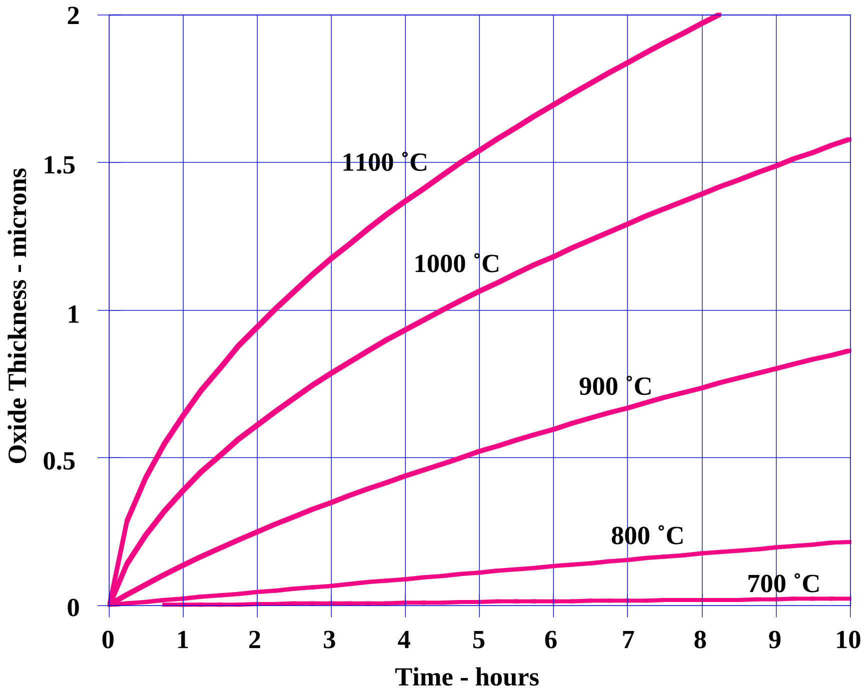
$$\frac{B}{A}=C_2\exp(-E_2/kT)\qquad (16)$$

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





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



- Calculated H_2O oxidation rates using Deal Grove.

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 ≈ 200 Å than Deal Grove predicts.
- MANY suggestions have been made in the literature about why. None have been widely accepted.

1. Reisman et. al. Model

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

- **Simple power law "fits the data" over the whole range of 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

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

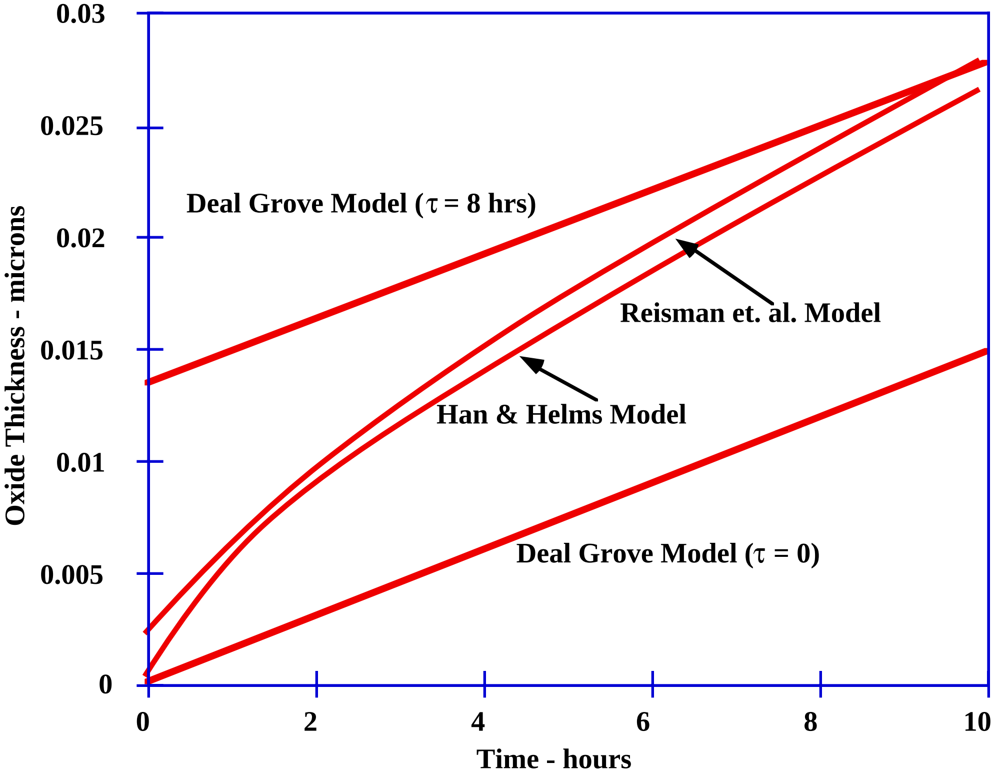
- **Second parallel reaction added - "fits the data" " over the whole range of oxide thicknesses.**
- **Three parameters (one of the A values is 0).**
- **Physically - second process may be outdiffusion of O_V and reaction at the gas/SiO_2 interface.**

3. Massoud et. al. Model

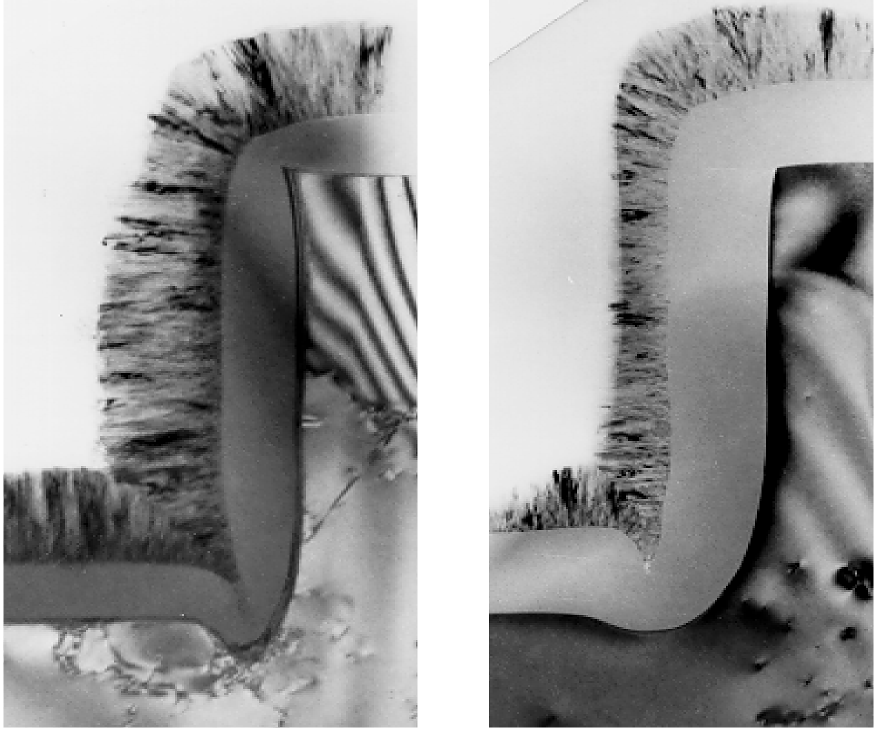
$$\frac{dx_O}{dt} = \frac{B}{2x_O + A} + C\exp\left(-\frac{x_O}{L}\right) \qquad (19)$$

- **Second term added to Deal Grove model which gives a higher dx/dt during initial growth.**
- **$L \approx 70$ Å so the second term disappears for thicker oxides.**
- **Because it is simply implemented along with the Deal Grove model, this model has been used in process simulators.**

- **Experimental data agrees with the Reisman, Han and Massoud models. (800˚C dry O_2 model comparison below.)**

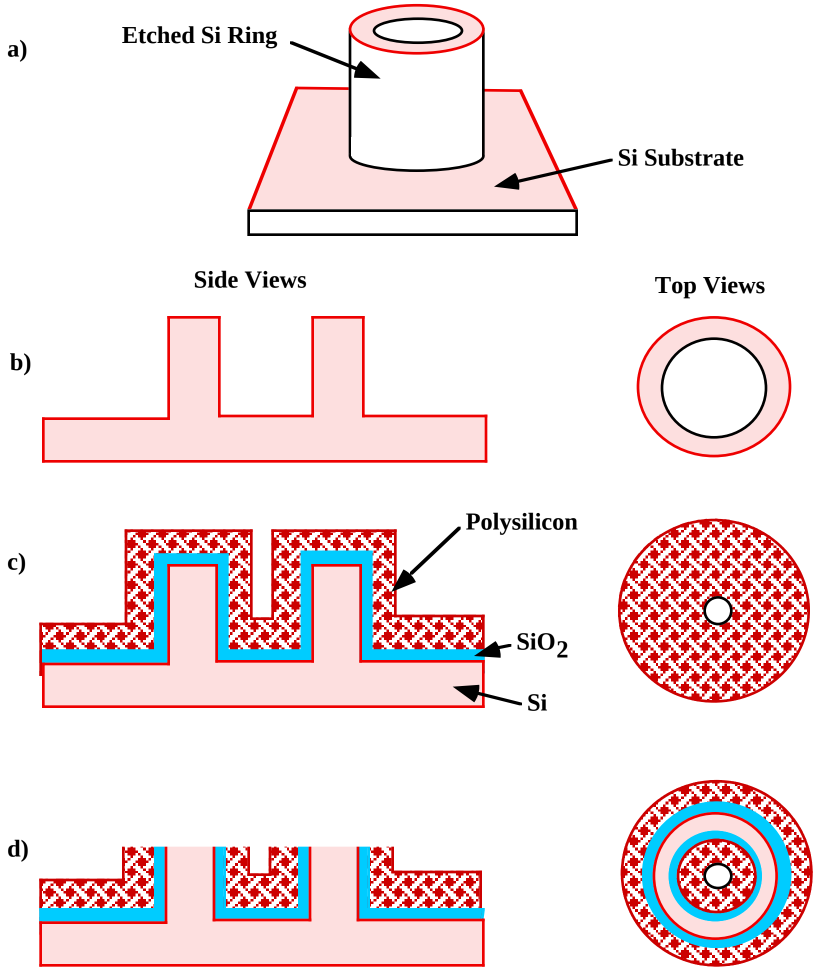


C. 2D SiO_2 Growth Kinetics

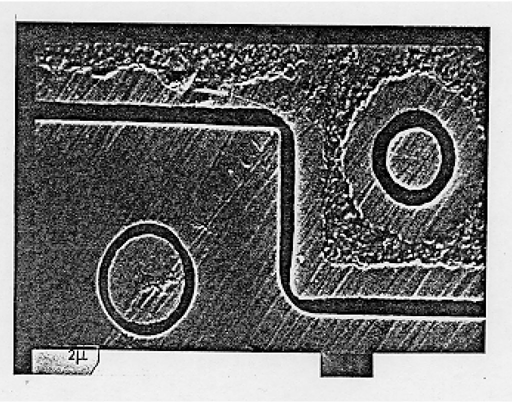


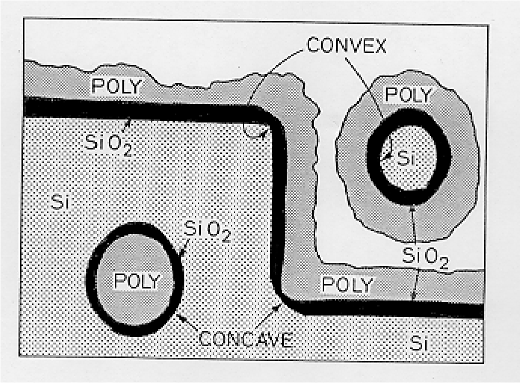
- 950 ˚C oxidation (left), 1100 ˚C oxidation right (Marcus and Sheng).

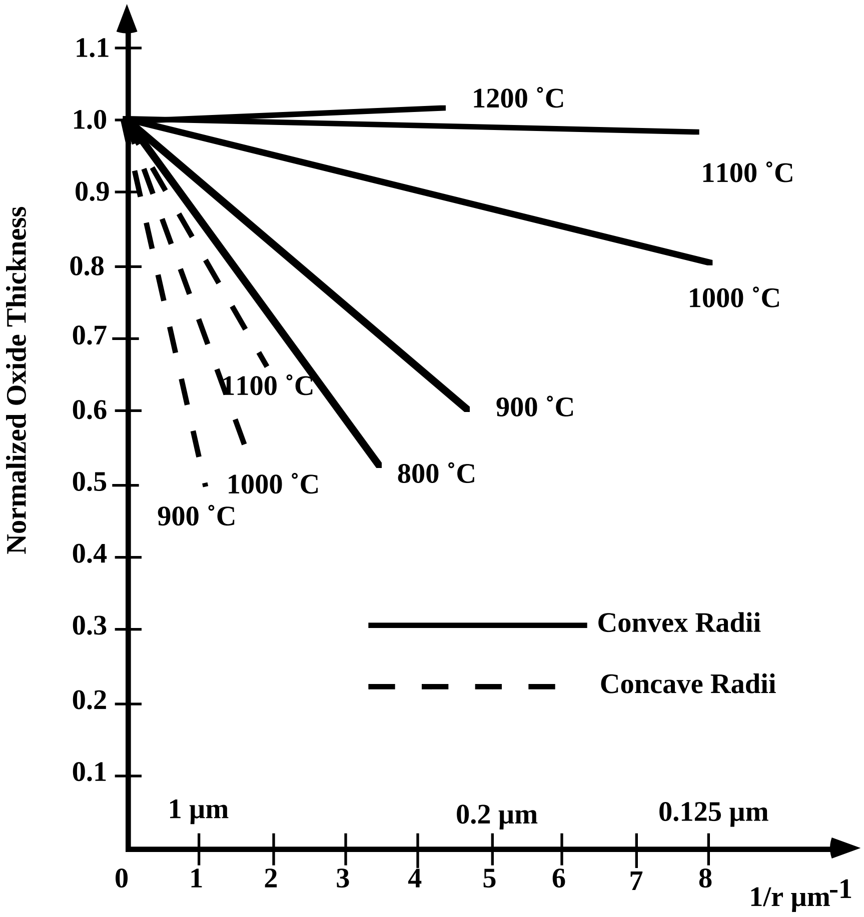
- **These effects were investigated in detail experimentally by Kao et. al. about 10 years ago.**



- **Typical experimental results (from Kao et.al.)**







- **Several physical mechanisms are important in explaining these results:**
  - **Crystal orientation**
  - **2D oxidant diffusion - simple to implement in a 2D numerical simulator**
  - **Stress due to volume expansion**

- **To model the stress effects, Kao et. al. suggested modifying the Deal Grove parameters.**

$$\mathbf{k_S(stress) = k_S \exp\left(-\frac{\sigma_n VR}{kT}\right)\exp\left(-\frac{\sigma_t VT}{kT}\right)} \quad \mathbf{(20)}$$

$$\mathbf{D(stress) = D\exp\left(-\frac{(P)(VD)}{kT}\right)} \qquad \mathbf{(21)}$$

$$\mathbf{C^*(stress) = C^*\exp\left(-\frac{(P)(VS)}{kT}\right)} \qquad \mathbf{(22)}$$

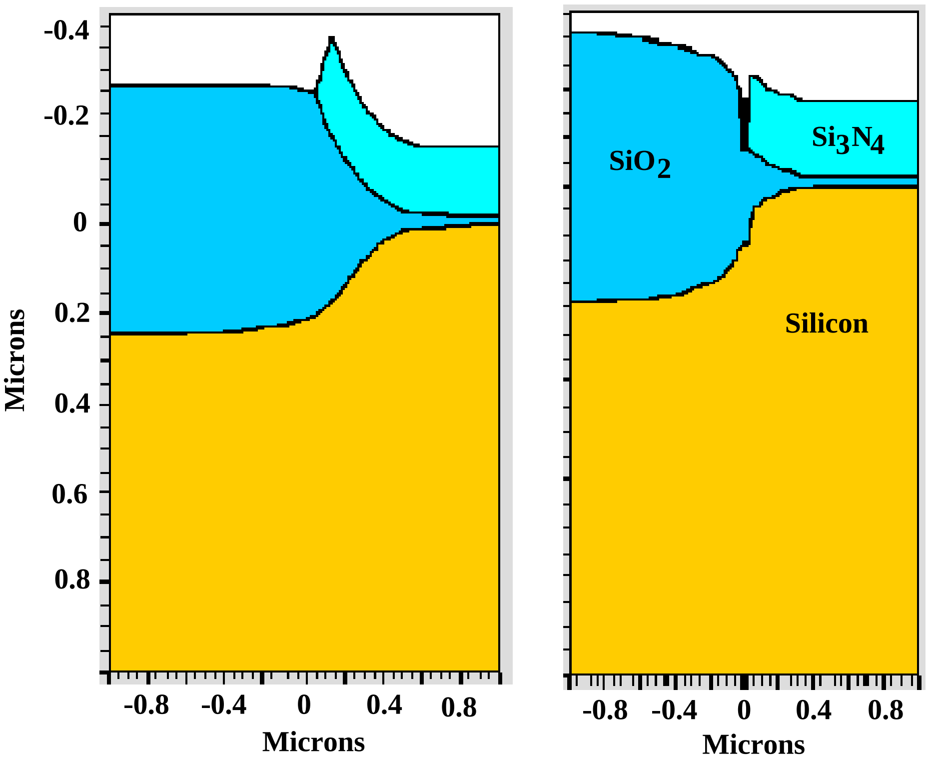
where σ_n and σ_t are the normal and tangential stresses at the interface. VR, VT and VS are reaction volumes and are fitting parameters.

- **Finally, the flow properties of the SiO_2 are described by a stress dependent viscosity**

$$\mathbf{\eta(stress) = \eta(T)\frac{\sigma_S VC/2kT}{\sinh(\sigma_S VC/2kT)}} \qquad \mathbf{(23)}$$

where σ_S is the shear stress in the oxide and VC is again a fitting parameter.

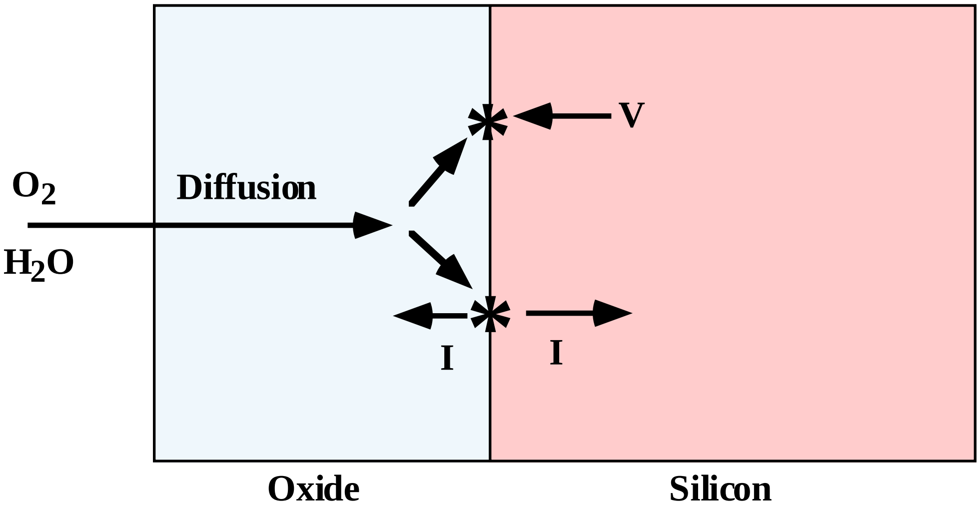
- **These models have been implemented in modern process simulators and allow them to predict shapes and stress levels for VLSI structures.**



- **Left - no stress dependent parameters. Right - including stress dependence. (ATHENA.)**

D. Point Defect Based Models

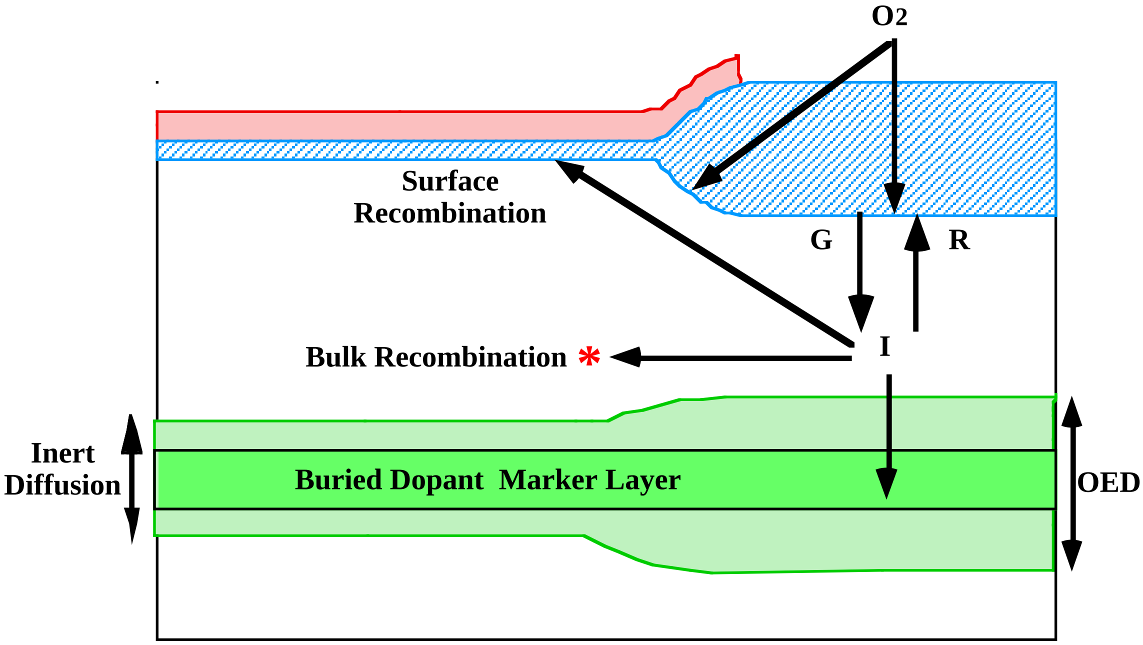
- **The oxidation models we have considered to this point are macroscopic models (diffusion coefficients, chemical reactions etc.).**
- **There is also an atomistic picture of oxidation that has emerged in recent years.**
- **Most of these ideas are driven by the volume expansion occurring during oxidation and the need for “free volume”.**

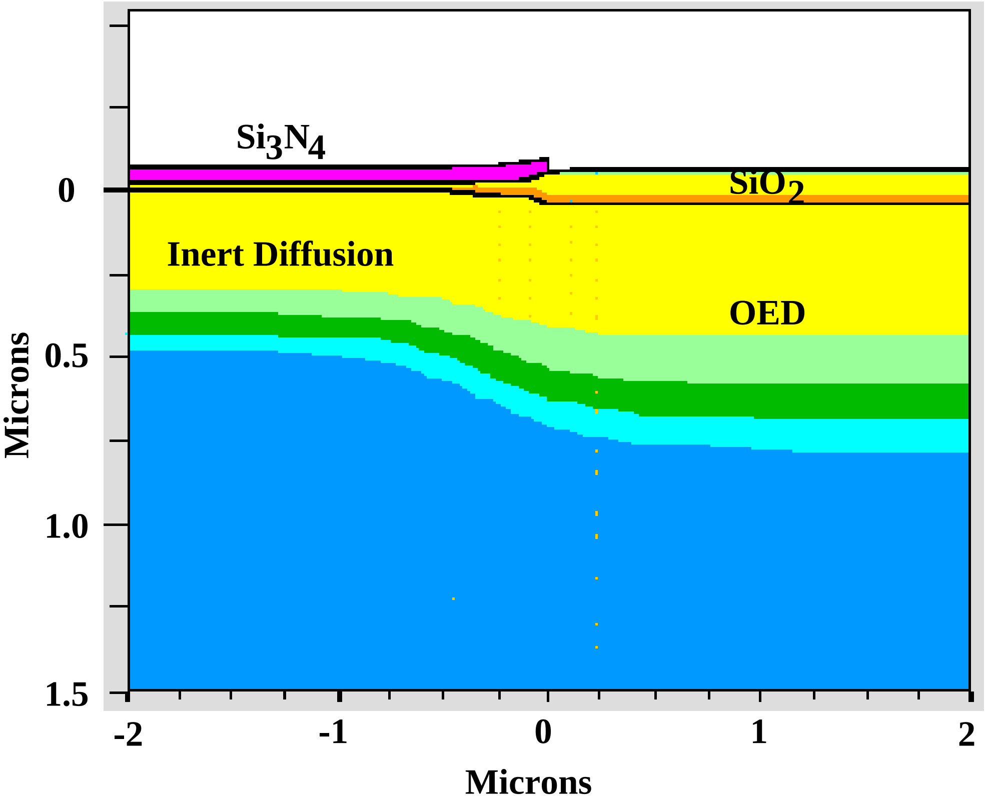


- **In Chapter 3 we described internal oxidation in the following way:**

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

- **Surface oxidation can be thought of in the same way.**
- **The connection between oxidation and other processes can then be modeled as shown below.**

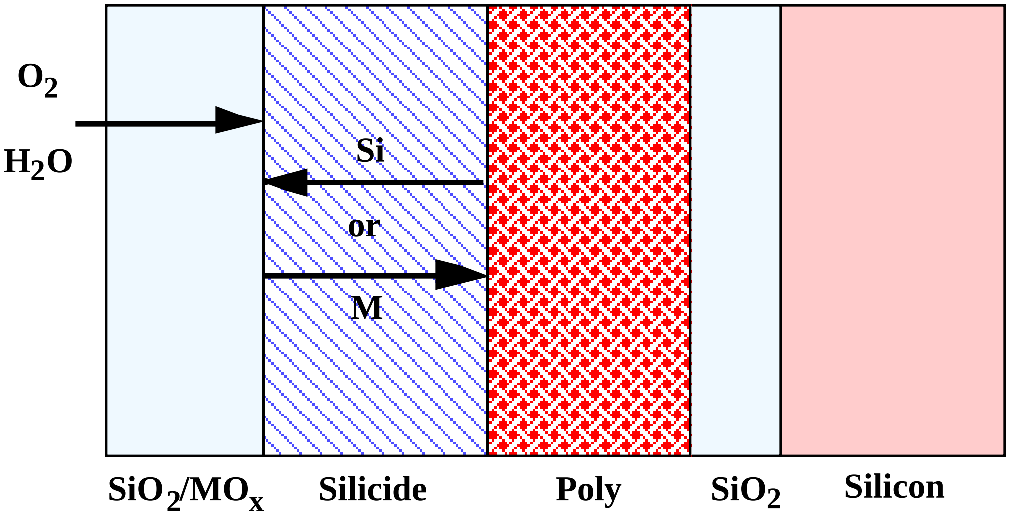




- **Example - ATHENA simulation of OED.**

E. Silicide Oxidation Models

- **Other materials are often oxidized in silicon structures (poly, silicides). Models have been developed, based on the Deal Grove model for Si oxidation.**



- **In silicides, the physical processes include oxidant diffusion through the oxide and reaction at the oxide/silicide interface.**
- **Thus the basic linear parabolic model usually works.**

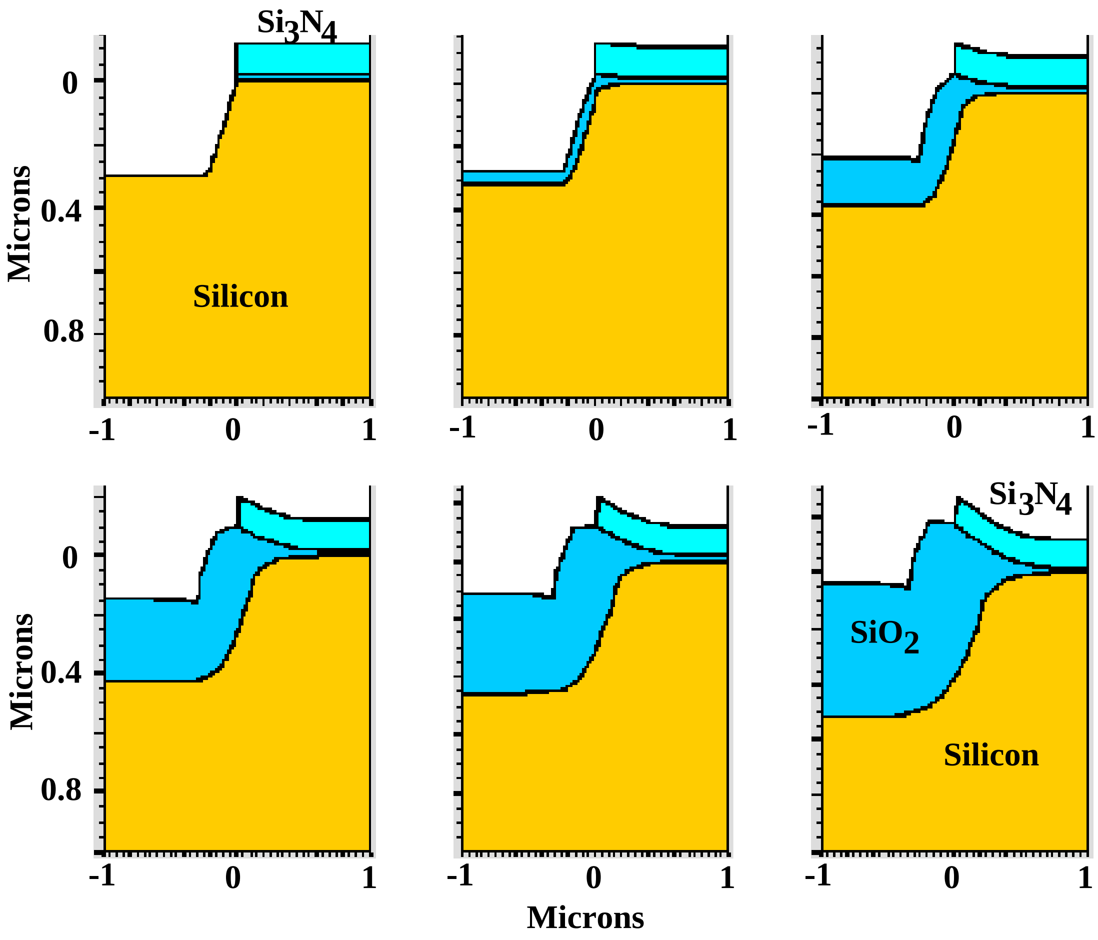
$$\frac{x_O^2 - x_i^2}{B} + \frac{x_O - x_i}{B/A} = t \qquad (10)$$

- **In most cases, SiO_2 forms rather than Mo_x (see text).**
- **If SiO_2 forms, then B is the same as for Si oxidation.**

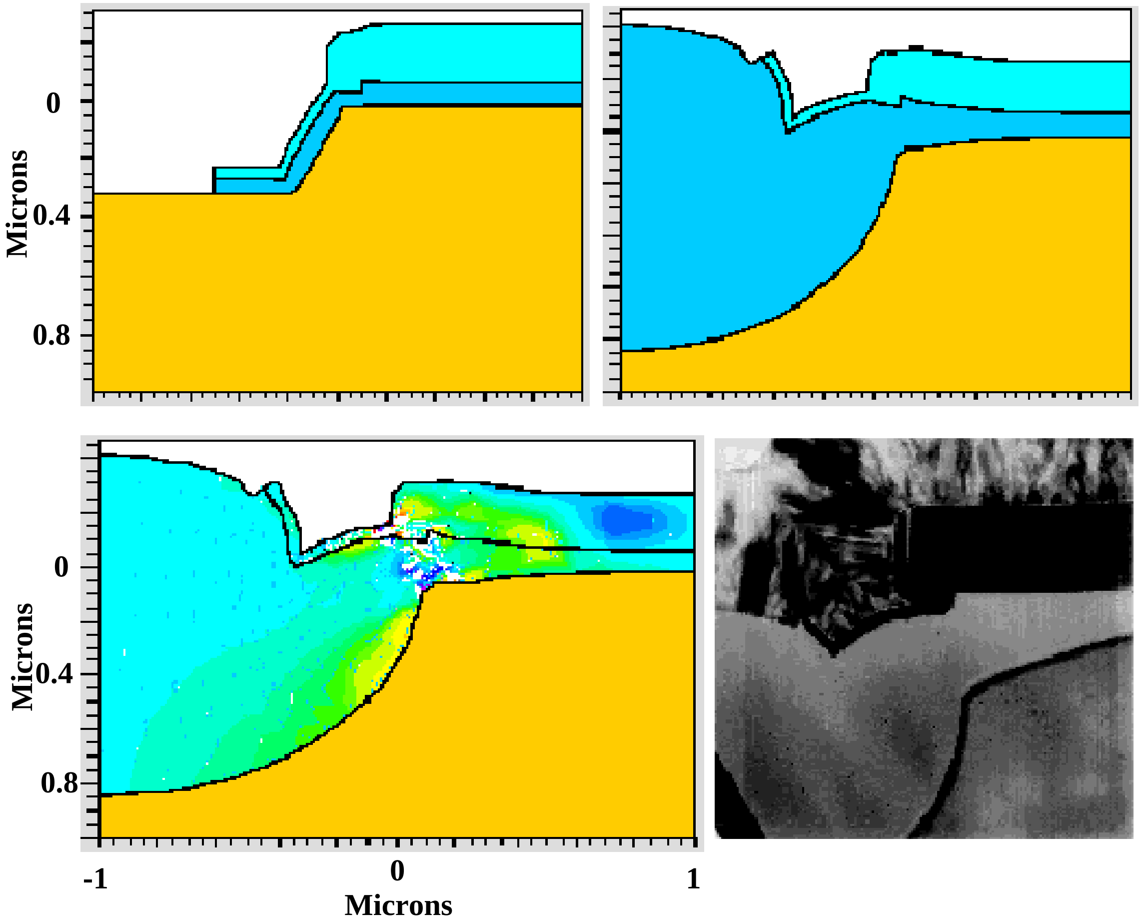
- **B/A values for silicide oxidation are generally much larger than the Si values (10 - 20X).**
- **Apparently the bond breaking process at the SiO_2/silicide interface is much easier than at the SiO_2/Si interface.**
- **Therefore the overall kinetics may be just parabolic.**

F. Complete Process Simulation of Oxidation

- **Many of the models described above (and others that are in Chapter 5), have been implemented in programs like SUPREM.**
- **In an integrated simulator, these models must work in harmony with each other.**



- **Simulation of a recessed LOCOS isolation structure using SSUPREM IV. The initial structure (top left) is formed by depositing an SiO_2/Si_3N_4 structure followed by etching of this stack on the left side. The silicon is then etched to form a recessed oxide and the structure is oxidized for 90 min at 1000 ˚C in H_2O. The time evolution of the bird's head shape during the oxidation is shown in the simulations.**



- 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. This structure is formed by depositing an oxide followed by a thick Si_3N_4 layer, both of which are etched away on the right side. A silicon etch on the right side is then followed by a second oxide and nitride deposition. These layers are then etched away on the far right side, leaving the thin SiO_2/Si_3N_4 stack covering the sidewall of the silicon. 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 100 min into the oxidation on the bottom left.