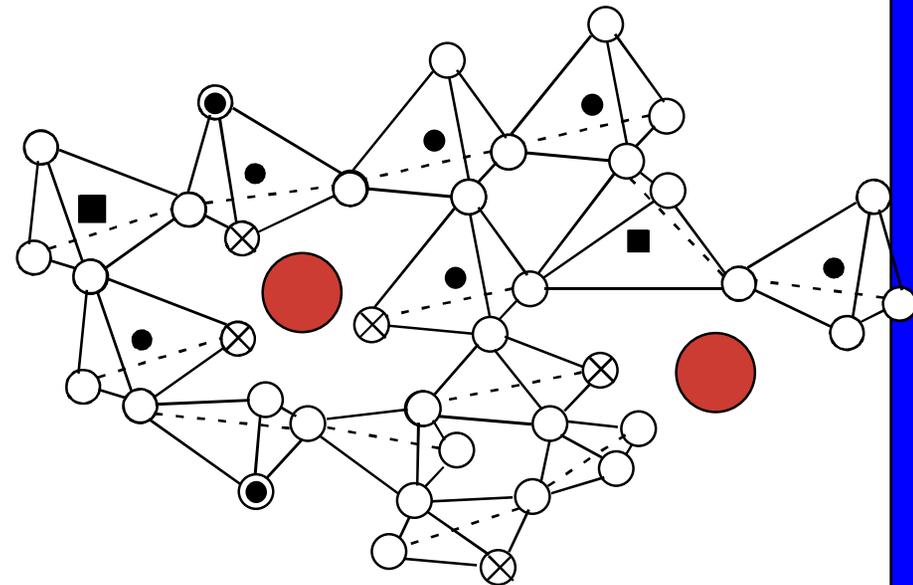


# Silicon Oxides: $\text{SiO}_2$

- **Uses:**
  - diffusion masks
  - surface passivation
  - gate insulator (MOSFET)
  - isolation, insulation
- **Formation:**
  - grown / “native”
    - thermal: “highest” quality
    - anodization
  - deposited:
    - C V D, evaporate, sputter
- **amorphous silica: material is a GLASS** under “normal” circumstances
  - can also find “crystal quartz” in nature
- **m.p. 1732° C; glass is “unstable” below 1710° C**
  - BUT devitrification rate (i.e. crystallization) below 1000° C negligible

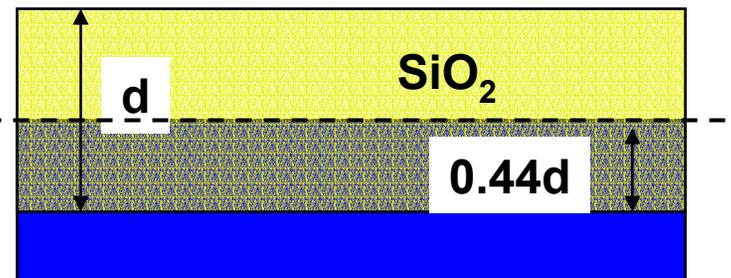


- bridging oxygen
- ⊗ non-bridging oxygen
- silicon
- network modifier
- network former
- ⊙ hydroxyl group

# Growth of SiO<sub>2</sub> from Si

- in dry ( $\ll 20$  ppm H<sub>2</sub>O) oxygen
  - $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$
  - once an oxide is formed, how does this chemical reaction continue?
    - does the oxygen go “in” or the silicon go “out”?
- density / formula differences
  - $\rho_{\text{SiO}_2} = 2.25 \text{ gm/cm}^3$ , GMW = 60
  - $\rho_{\text{Si}} = 2.3 \text{ gm/cm}^3$ , GMW = 28
  - oxide  $d$  thick consumes a layer  $0.44d$  thick of Si

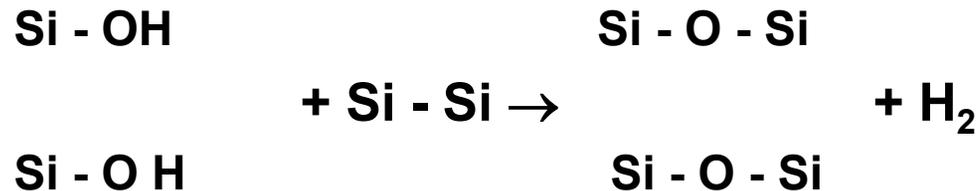
original silicon surface



- “bare” silicon in air is “always” covered with about 15-20 Å of oxide, upper limit of  $\sim 40$  Å
  - it is possible to prepare a hydrogen terminated Si surface to retard this “native” oxide formation

# “Wet” oxidation of Si

- overall reaction is
  - $\text{Si} + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + \text{H}_2$
- proposed process
  - $\text{H}_2\text{O} + \text{Si-O-Si} \rightarrow \text{Si-OH} + \text{Si-OH}$
  - diffusion of hydroxyl complex to  $\text{SiO}_2$  -Si interface

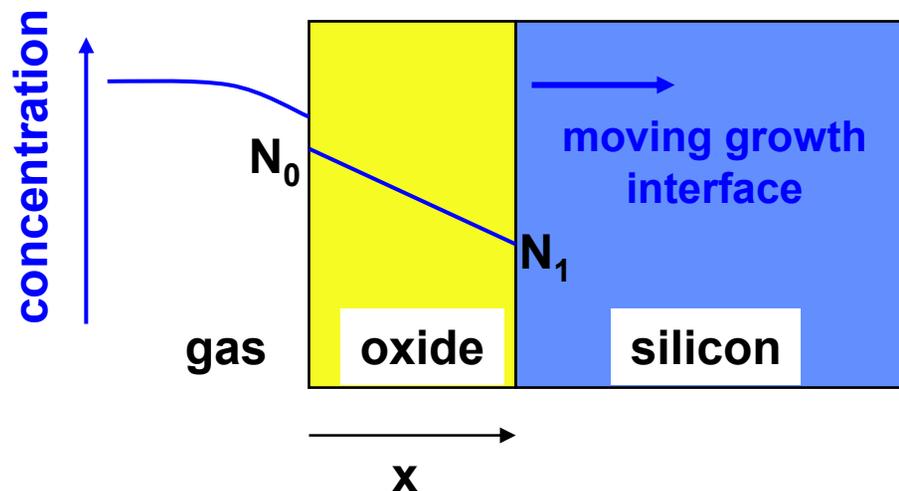


- this results in a more open oxide, with lower density, weaker structure, than dry oxide
  - $\rho_{\text{wet}} \approx 2.15 \text{ gm / cm}^3$

# Oxide growth kinetics

- basic model is the Grove and Deal Model
  - supply of oxidizer is limited by diffusion through oxide to growth interface

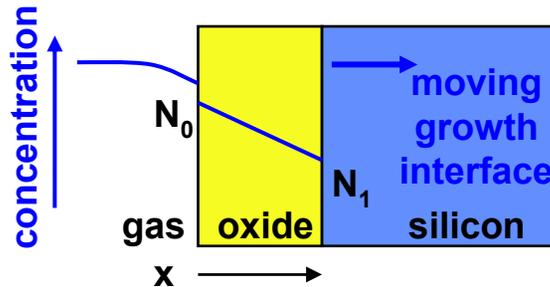
- Fick's First Law: flux  $j = -D \frac{\partial N_{\text{oxidizer}}}{\partial x}$



- simplest approximation:

$$\frac{\partial N}{\partial x} = - \frac{N_0 - N_1}{x}$$

# Oxidizer concentration gradient and flux



$$j = -D \cdot \frac{\partial N_{\text{oxidizer}}}{\partial x} \approx -D \cdot \left( -\frac{N_0 - N_1}{x} \right)$$

- $N_0$  is limited by the solid solubility limit of the oxidizer in the oxide!
  - $N_0^{\text{O}_2} \sim 5 \times 10^{16} \text{ cm}^{-3} @ 1000^\circ \text{ C}$
  - $N_0^{\text{H}_2\text{O}} \sim 3 \times 10^{19} \text{ cm}^{-3} @ 1000^\circ \text{ C}$
- flux of oxidizer  $j'$  at  $\text{SiO}_2 / \text{Si}$  interface consumed to form new oxide

$$j' = k \cdot N_1$$

- $k$  is the chemical reaction rate constant
- in steady state, flux in must equal flux consumed

$$j' \stackrel{\text{steady state}}{=} j \Rightarrow k \cdot N_1 = -D \cdot \left( -\frac{N_0 - N_1}{x} \right) \rightarrow$$

solve for  $N_1$ , sub  
back into flux eq

$$j = \frac{D \cdot N_0}{x + D/k}$$

# Relation between flux and interface position

- **flux: #oxidizer molecules crossing interface per unit area per unit time**
  - # cm<sup>-2</sup> sec<sup>-1</sup>
- **rate of change of interface position:**  
**dx / dt (interface velocity)**
  - cm sec<sup>-1</sup>
- **n: # of oxidizer molecules per unit volume of oxide:**

$$n = \frac{\rho_{\text{SiO}_2} \cdot N_A}{\text{GMW}_{\text{SiO}_2}} \cdot \begin{cases} 2 & \text{for H}_2\text{O} \\ 1 & \text{for O}_2 \end{cases} = 2.25 \times 10^{22} \text{ cm}^{-3} \cdot \begin{cases} 2 & \text{for H}_2\text{O} \\ 1 & \text{for O}_2 \end{cases}$$

– # cm<sup>-3</sup>

- **then relation is just**

$$\frac{d x}{d t} = \frac{j}{n} = \frac{DN_0/n}{x + D/k}$$

– now integrate with appropriate initial condition

# Grove and Deal relation

- **setting**
  - $2D/k = A$ 
    - function of what's diffusing, what it's diffusing in, and what it reacts with
  - $2DN_0/n = B$ 
    - function of what's diffusing and what it's diffusing in
  - initial condition  $x(t = 0) = x_i$
- **integration gives**

$$x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1 \right]$$



LiveMath

- where  $\tau$  represents an “offset” time to account for any oxide present at  $t = 0$

$$\tau = \frac{(x_i)^2 + A \cdot x_i}{B}$$

# Limiting behavior of Grove & Deal oxidation model

$$x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right]$$

- “short times”

$$t + \tau \ll A^2 / 4 B$$

$$x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right] \Rightarrow x(t) \approx \frac{A}{2} \cdot \left[ \left( 1 + \frac{1}{2} \cdot \frac{t+\tau}{A^2/4B} \right) - 1 \right] = \frac{B}{A} \cdot (t+\tau)$$

- thickness is linearly increasing with time
  - characteristic of a reaction rate limited process
- $B/A$  is the “linear rate constant”

$$\frac{B}{A} = \left( \frac{2 \cdot D \cdot N_0}{n} \right) / \left( \frac{2 \cdot D}{k} \right) = \frac{N_0 \cdot k}{n}$$

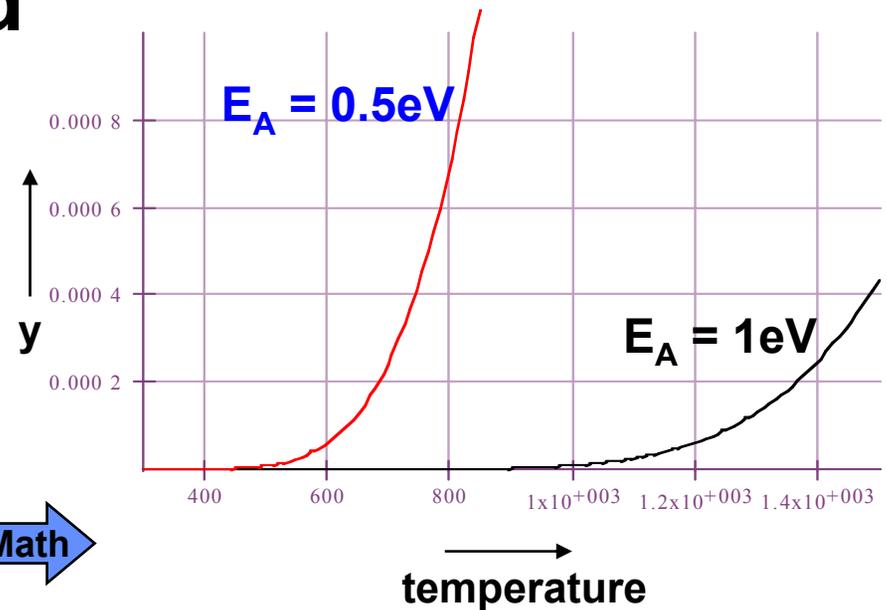
- linear rate constant depends on
  - reaction rate between oxidizer and silicon ( $k$ ) AND
  - solid solubility of oxidizer in oxide ( $N_0$ )
  - temperature dependence mainly from reaction rate

# Rate constants and Arrhenius plots

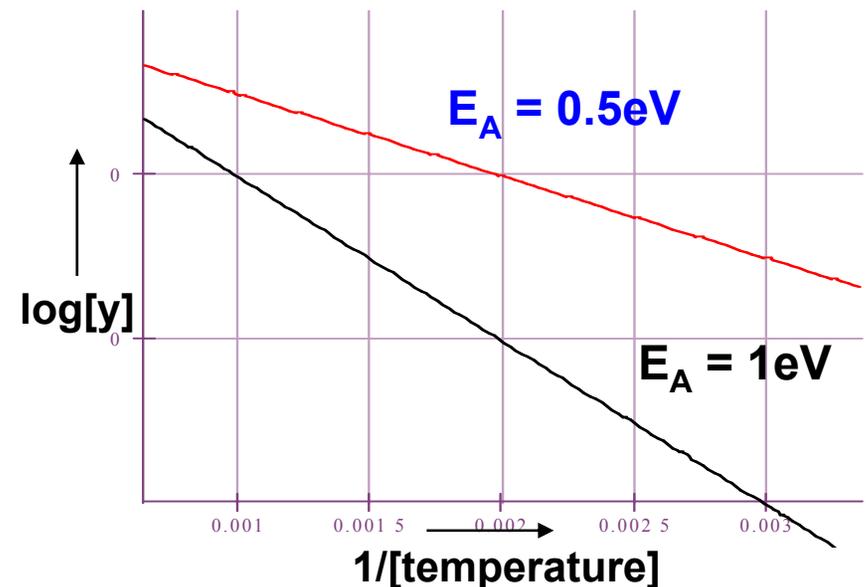
- thermally activated process
  - i.e., process must thermally overcome an energy barrier

$$y = y_0 \cdot e^{-E_A/kT}$$

LiveMath



- plot  $\log(y)$  vs  $1/T$ 
  - if process has the simple thermally-activated behavior you will get a straight line!



# Rate constant behavior: linear rate constant

$$x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right]$$

$t + \tau \ll A^2 / 4 B$

$$x(t) \approx \frac{B}{A} \cdot (t+\tau)$$

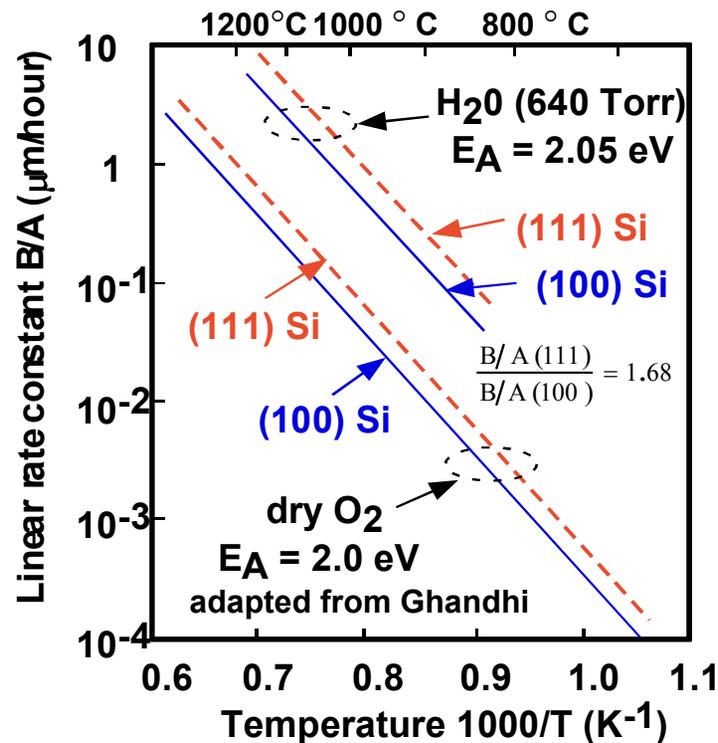
$$\frac{B}{A} = \left( \frac{2DN_0}{n} \right) / \left( \frac{2D}{k} \right) = \frac{N_0 \cdot k}{n}$$

– linear rate constant depends on

- reaction rate between oxidizer and silicon ( $k$ )
  - is orientation dependent
  - temperature dependence mainly from energy required to break Si-Si bond

– AND

- solid solubility of oxidizer in oxide ( $N_0$ )



plane	available bonds
(100)	$6.8 \times 10^{14} \text{cm}^{-2}$
(111)	$11.7 \times 10^{14} \text{cm}^{-2}$
ratio	1.7 (from Sze, 2nd ed., p. 110)

# Limiting behavior of Grove & Deal oxidation model

$$x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right]$$

- “long times”

$$t + \tau \gg A^2 / 4 B$$

$$x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right] \Rightarrow x(t) \approx \frac{A}{2} \cdot \left[ \sqrt{\frac{t+\tau}{A^2/4B}} \right] = \sqrt{B \cdot (t+\tau)}$$

- dependence is “parabolic”: (thickness)<sup>2</sup> ∝ time
  - characteristic of a diffusion limited process
- B is the “parabolic rate constant”

$$B = \frac{2 \cdot D \cdot N_0}{n}$$

- parabolic rate constant depends on
  - diffusivity of oxidizer in oxide (**D**) AND
  - solid solubility of oxidizer in oxide (**N<sub>0</sub>**)
  - temperature dependence mainly from diffusivity

# Rate constant behavior: parabolic rate constant

$$x(t) \approx \sqrt{B \cdot (t + \tau)}$$

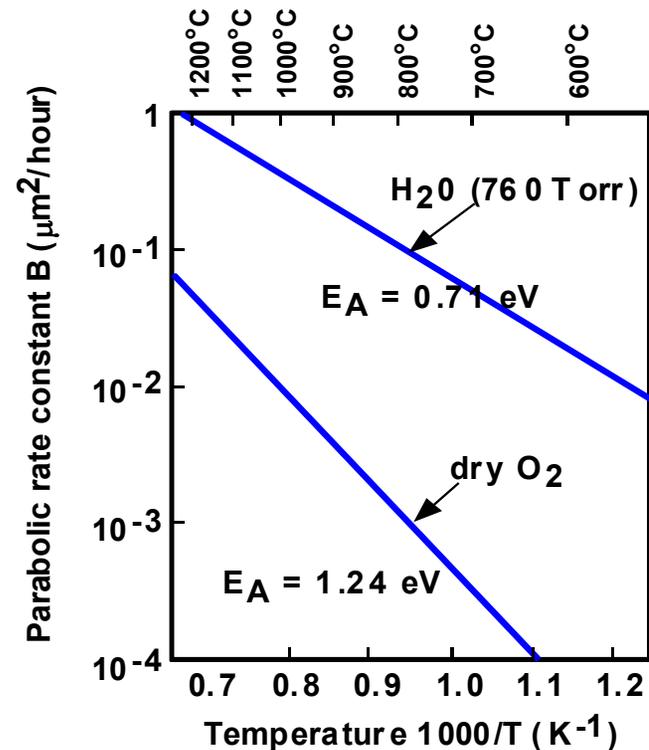
$$B = \frac{2 \cdot D \cdot N_0}{n}$$

- parabolic rate constant depends on
  - diffusivity of oxidizer in oxide (**D**) and solid solubility of oxidizer in oxide (**N<sub>0</sub>**)

Solid solubility  
@ 1000°C

H <sub>2</sub> O	3 x 10 <sup>19</sup> cm <sup>-3</sup>
O <sub>2</sub>	5 x 10 <sup>16</sup> cm <sup>-3</sup>

- is NOT orientation dependent
- IS oxidizer dependent
- temperature dependence mainly from diffusivity of oxidizer in oxide

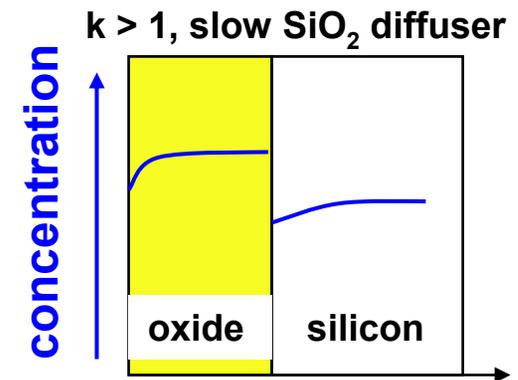


adapted from Gandhi

# Effect of Si doping on oxidation kinetics

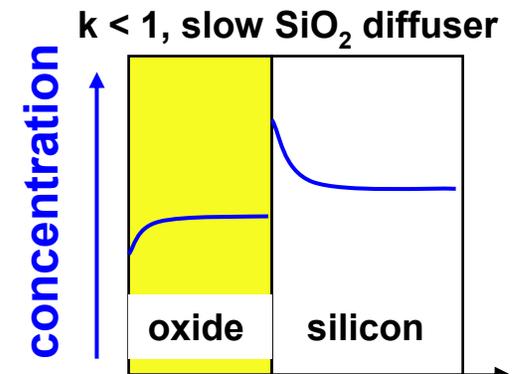
- boron

- $k = C_{\text{ox}} / C_{\text{Si}} \sim 3$
- dopants accumulate in oxide
  - little effect on linear rate constant  $B/A$  ( $= N_o k / n$ )
  - can increase parabolic rate constant  $B$  ( $= 2DN_o / n$ )
    - really only significant for  $N_{\text{boron}} > \sim 10^{20} \text{ cm}^{-3}$



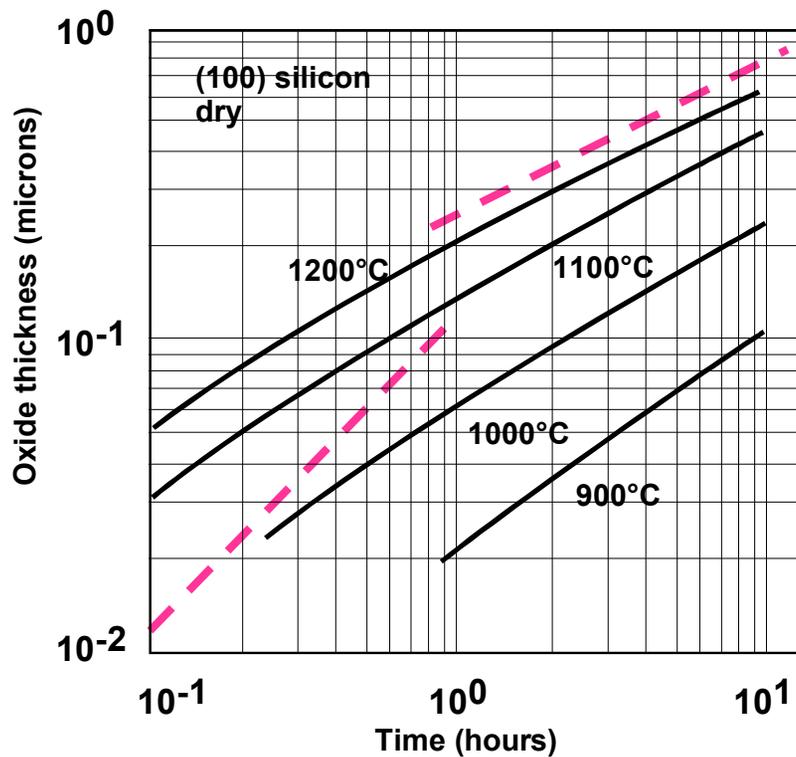
- phosphorus

- $k = C_{\text{ox}} / C_{\text{Si}} \sim 0.1$
- dopants “pile-up” at silicon surface
  - little effect on parabolic rate constant  $B$
  - increases linear rate constant  $B/A$ 
    - again, really only significant for  $N_{\text{phosphorus}} > \sim 10^{20} \text{ cm}^{-3}$



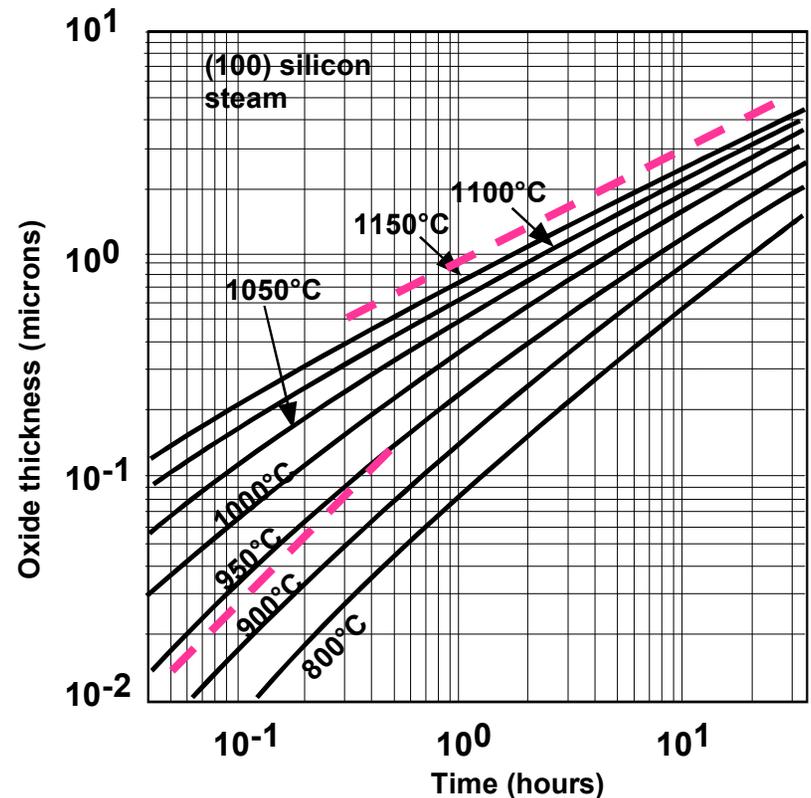
# Oxidation thicknesses

- dry oxidation



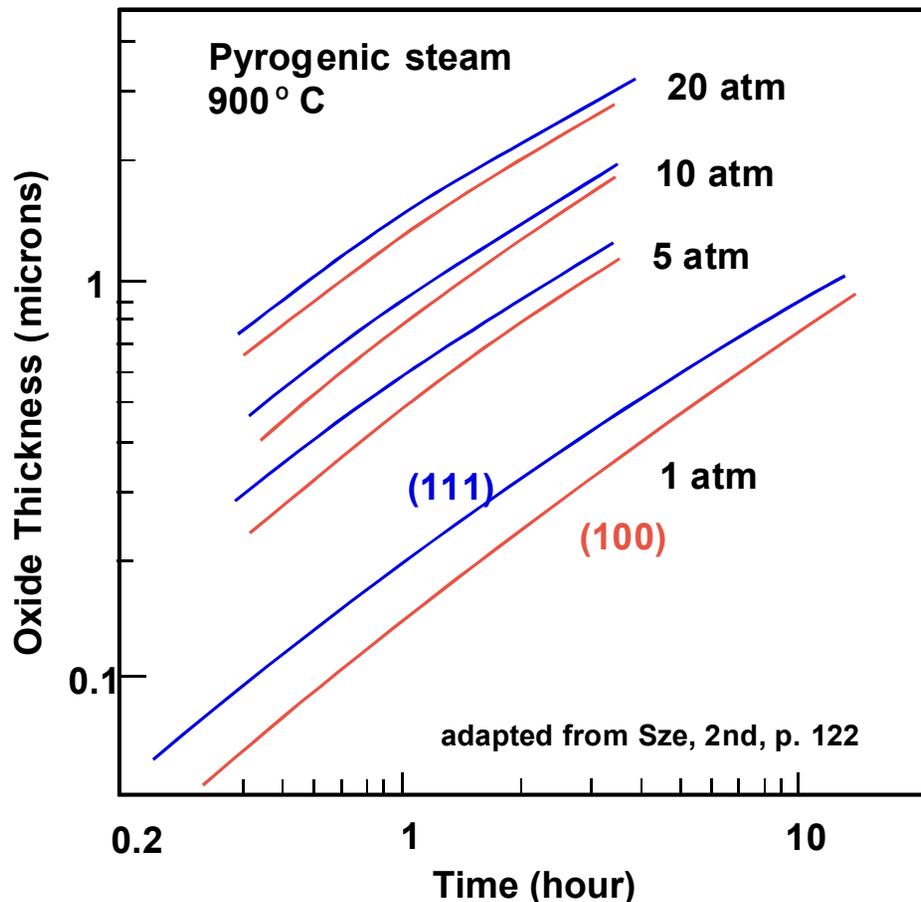
- wet oxidation

- 640 Torr partial pressure is typical (vapor pressure over liquid water @ 95°C)



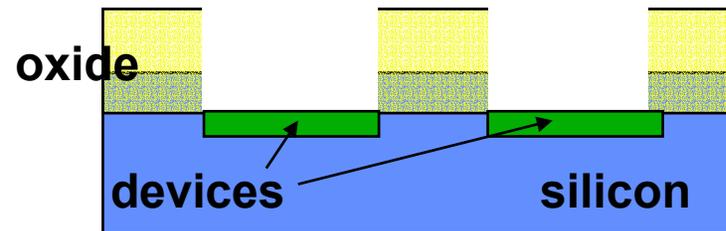
# Pressure Effects on Oxidation

- grow thick oxides at reduced time / temperature product
  - use elevated pressures to increase concentration of oxidizer in oxide
    - for steam, both B and B/A ~ linear with pressure
    - rule of thumb: constant growth rate, if for each increase of 1 atm pressure, temperature is reduced ~ 30° C.
  - pressures up to 25 atm have been used (commercial systems: HiPOx, FOX)



# Oxidation isolation

- how do you insulate (isolate) one device from another?
  - what about using an oxide?
    - try growing it first since it'll be long, high temp
    - now etch clear regions to build devices in

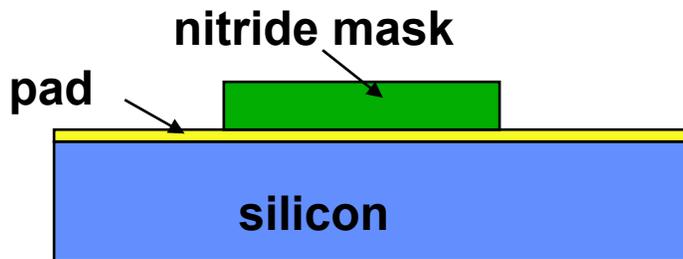


oxidation, etch

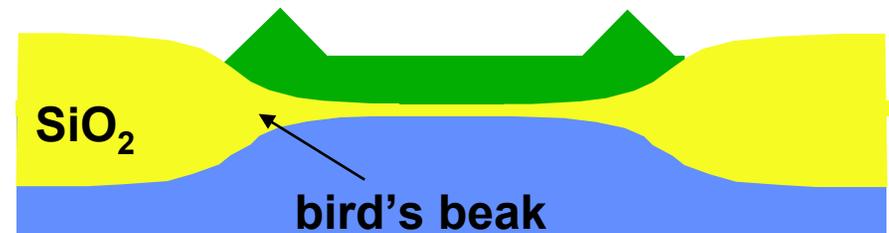
- it doesn't do any good!!

# Masking of oxidation and isolation techniques

- would like to form thick oxide between device regions with minimum step heights
  - mask oxidation using material with low water diffusivity / solubility: Local Oxidation of Silicon (LOCOS) process
    - $\text{Si}_3\text{N}_4$  (silicon nitride)
    - induces high stress, must place “pad layer” below to prevent dislocations
      - for oxide pad layer,  $t_{\text{pad}} \sim 0.25 t_{\text{nitride}}$
  - do have lateral diffusion at mask edge, produces “bird’s beak”
    - lateral encroachment  $\approx$  oxide thickness
    - can reduce using more complex “pads”
      - $\text{SiO}_2$  / poly / nitride ( $\sim 15\text{nm}/50\text{nm}/150\text{nm}$ ) helps



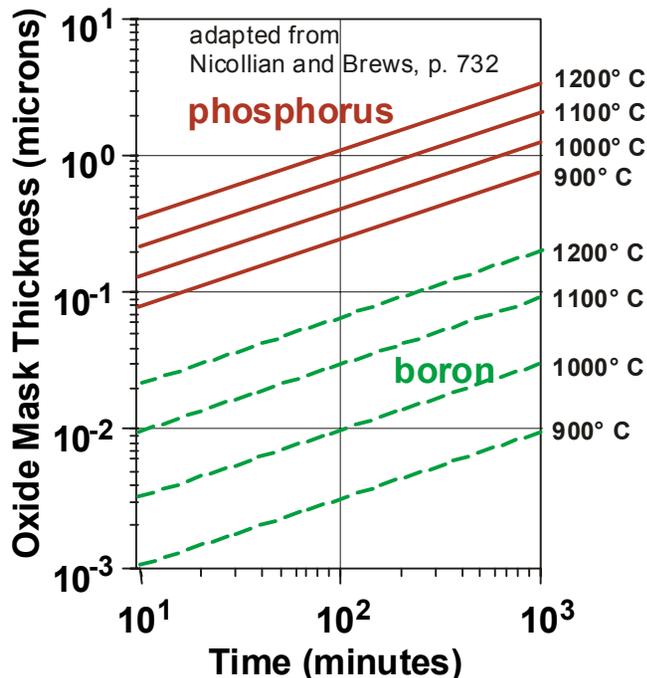
before oxidation



after oxidation

# Use of SiO<sub>2</sub> as a diffusion mask

- mask against boron, phosphorus, arsenic diffusion
  - most impurities transported to slice surface as an oxide
    - P<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub>
  - reacts with oxide to form mixed phosphosilicate (or borosilicate) glass
  - reaction continues until full thickness of masking oxide is converted
    - doping of underlying Si commences



simple parabolic relationship:

phosphorus:

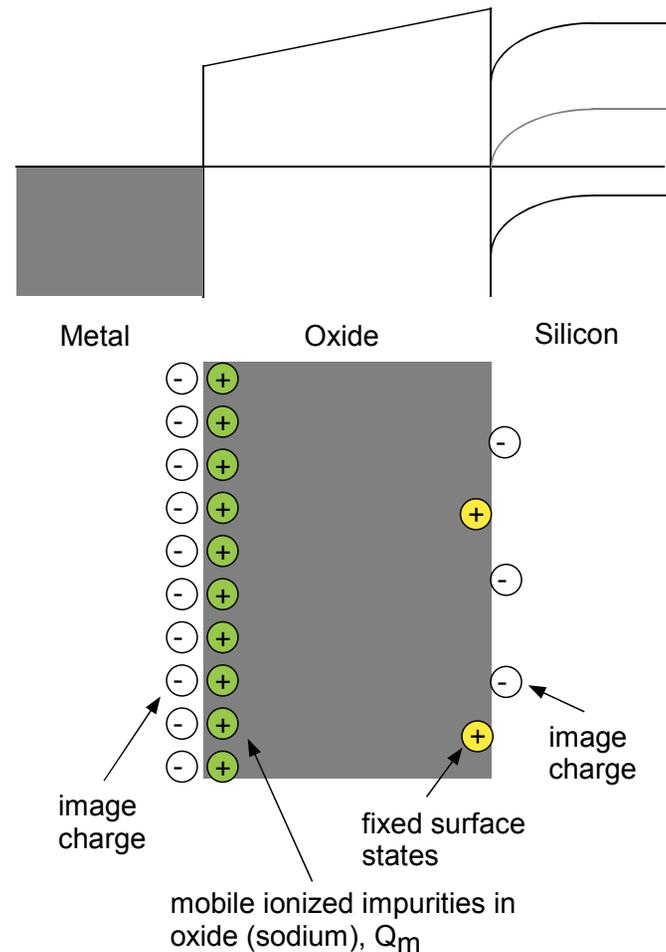
$$\frac{(x_m)^2}{t_m} = 1.7 \times 10^{-7} \cdot e^{-\frac{1.46\text{eV}}{kT}} \left( \frac{\text{cm}^2}{\text{sec}} \right)$$

boron:

$$\frac{(x_m)^2}{t_m} = 4.9 \times 10^{-5} \cdot e^{-\frac{2.80\text{eV}}{kT}} \left( \frac{\text{cm}^2}{\text{sec}} \right)$$

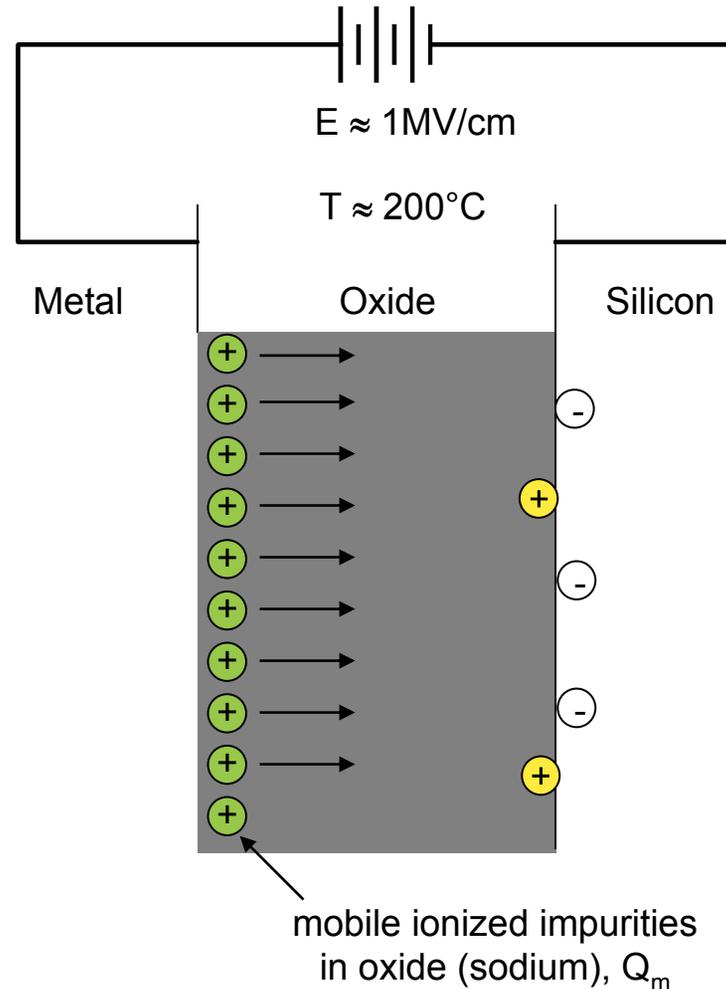
# Other problems in oxidation: MOS threshold stability

- for an MIS structure
  - if ionized impurities are in the insulator, what happens?
  - if the ionized impurities are close to the metal, they are screened, and the silicon surface remains “unchanged”
- threshold voltage of MOS device is critically dependent on the location and amount of mobile ionic contamination in  $\text{SiO}_2$  gate insulator
  - stability can be adversely affected



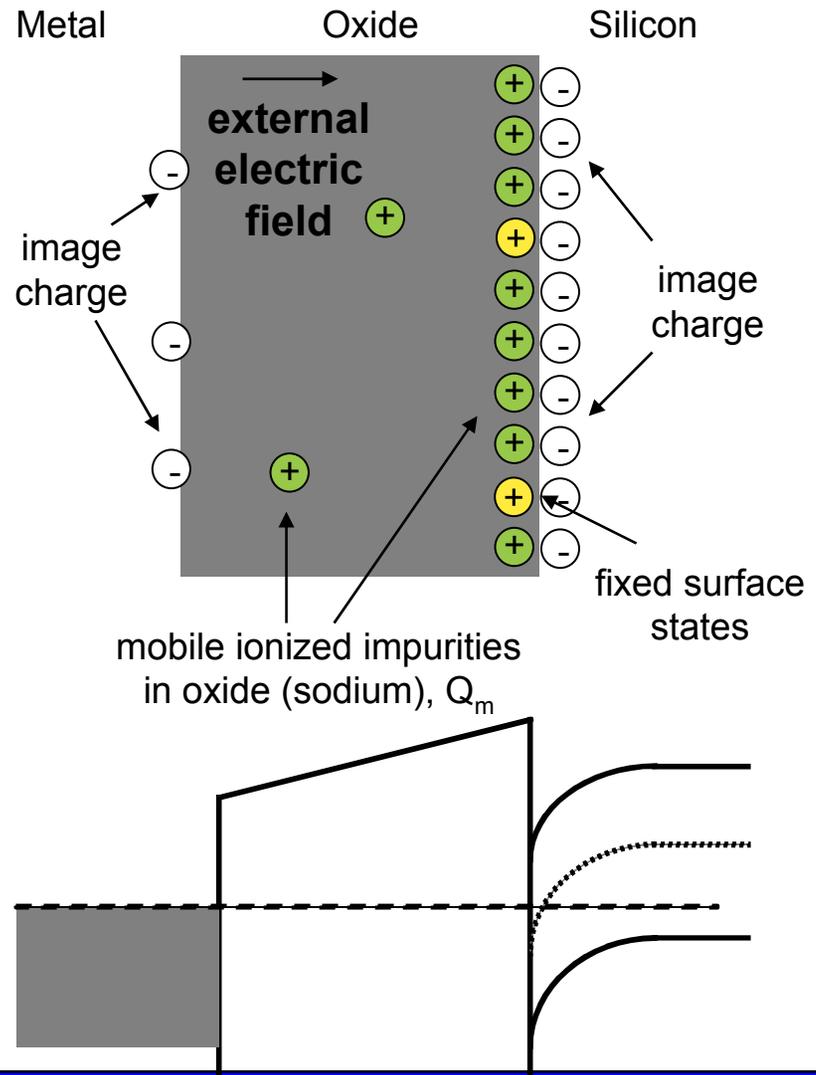
# Bias-Temperature-Stress (BTS) technique

- apply field of approximately 1MV/cm between capacitor metallization and substrate
- heat sample to  $\sim 200^{\circ}\text{C}$  to increase diffusion rate of  $\text{Na}^+$
- allows evaluation of contamination levels

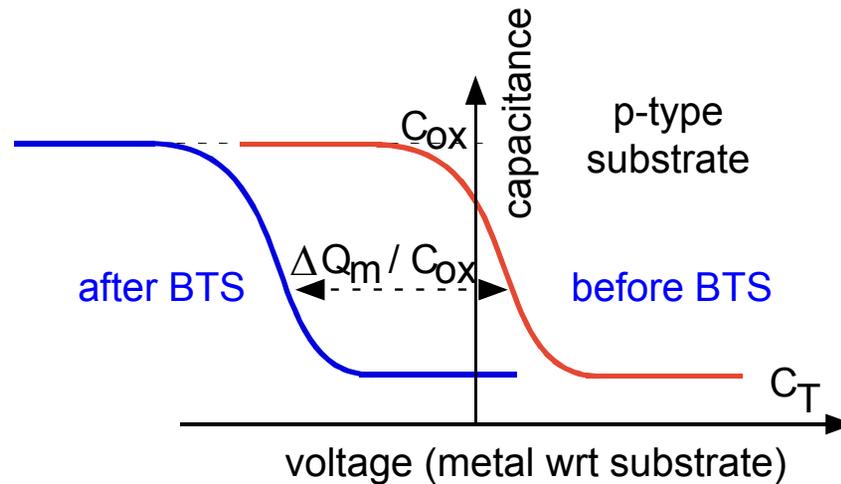


# BTS impurity drift

- apply field of approximately 1MV/cm across gate insulator
- heat sample to  $\sim 200^\circ\text{C}$  to increase diffusion rate of  $\text{Na}^+$
- most of the impurities have drifted to near the silicon surface
  - screening now due to electrons at silicon surface
  - can cause surface inversion!!
- process is reversible!



# C-V measurements



- **measure C-V curves before and after BTS**
  - $Q_m \approx C_{ox} \times \Delta V_t$
  - $\rho \approx Q_m / t_{ox} A_{cap} q$
- **this occurs even at room temperature!**
  - threshold voltage shift  $\Delta V_t$  can be **MANY** volts!

# Other problems in oxidation: oxidation induced stacking faults

- typically ~95% of all stacking faults are OSFs
- essentially an “extra” (111) plane
  - density can vary from ~0 to  $10^7$  / cm<sup>2</sup>
    - highly dependent on process (high temperature) history
  - “size” (length) at surface can be many microns
- growth is related to presence of excess “unoxidized” Si at Si-SiO<sub>2</sub> interface
- heterogeneous coalescence of excess Si on nucleation centers produce OSFs
  - any process that produces an excess of Si vacancies will inhibit OSF formation/growth

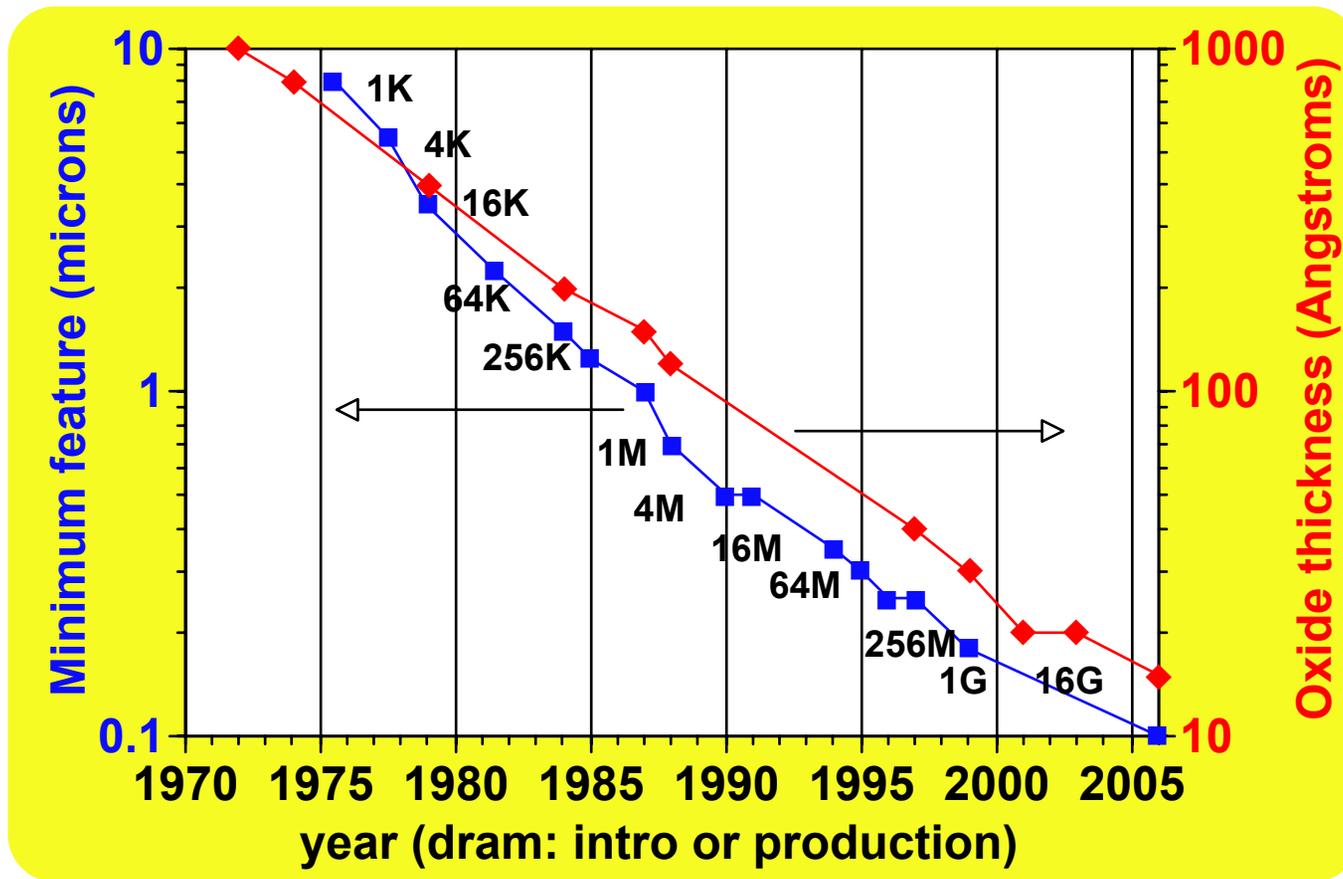
# Chlorine Gettering in SiO<sub>2</sub>

- **effects of chlorine during oxidation**
  - reduction of OSFs
  - increased dielectric breakdown strength
  - improved minority carrier lifetimes
  - improved MOS threshold stability
    - when oxide is grown in presence of chlorine the Cl<sup>-</sup> getters ionic contaminants such as Na<sup>+</sup>
    - Cl in gas stream reacts with Na diffusing from the furnace walls
    - Cl<sup>-</sup> is incorporated into the grown oxide near the silicon interface (~20nm from Si) and can capture mobile sodium preventing threshold instabilities
    - efficiency of chlorine gettinger can be evaluated by alternately drifting the Na<sup>+</sup> back and forth from metal to silicon side of the test capacitor
    - only effective for oxidation temperature above ~1100° C

# Restrictions on the use of Cl Gettering

- chlorine injection techniques
  - mix HCl in O<sub>2</sub> gas stream
    - must be VERY dry or severe corrosion problems can occur
    - produces large quantities of H<sub>2</sub>O in furnace:  $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$
  - mix trichloroethylene (TCE) / trichloroethane (TCA) in O<sub>2</sub> gas stream
    - produces less water:  
 $\text{C}_2\text{HCl}_3 + 2\text{O}_2 \rightleftharpoons \text{HCl} + \text{Cl}_2 + 2\text{CO}_2$
    - for TCE must have large excess of O<sub>2</sub> present to prevent carbon deposits
      - under low temperatures and low oxygen conditions can form phosgene COCl<sub>2</sub>
- only effective if oxidation temperature  $\geq 1100^\circ \text{C}$ 
  - large Cl concentrations, very high temperatures, or very long oxidation times can cause rough oxides
  - very high Cl can cause blisters and separation of SiO<sub>2</sub> from Si

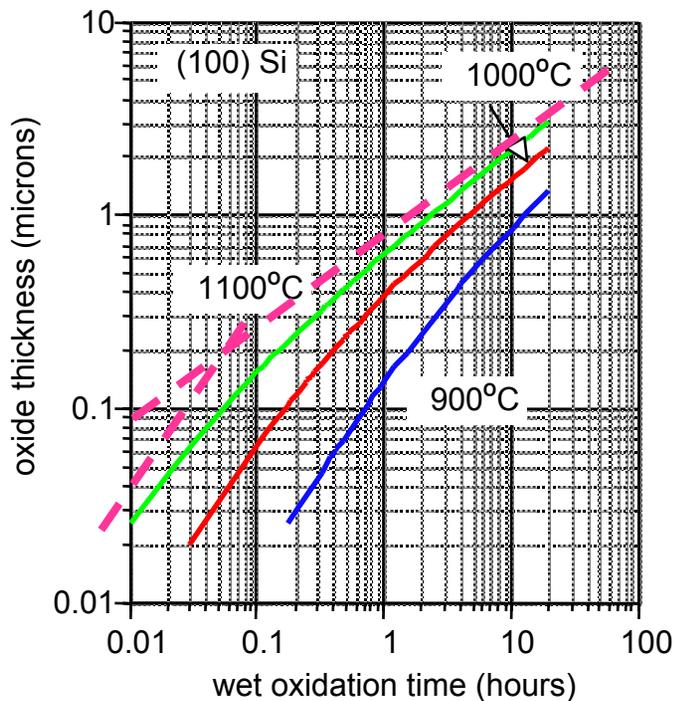
# Gate Oxide thickness trends



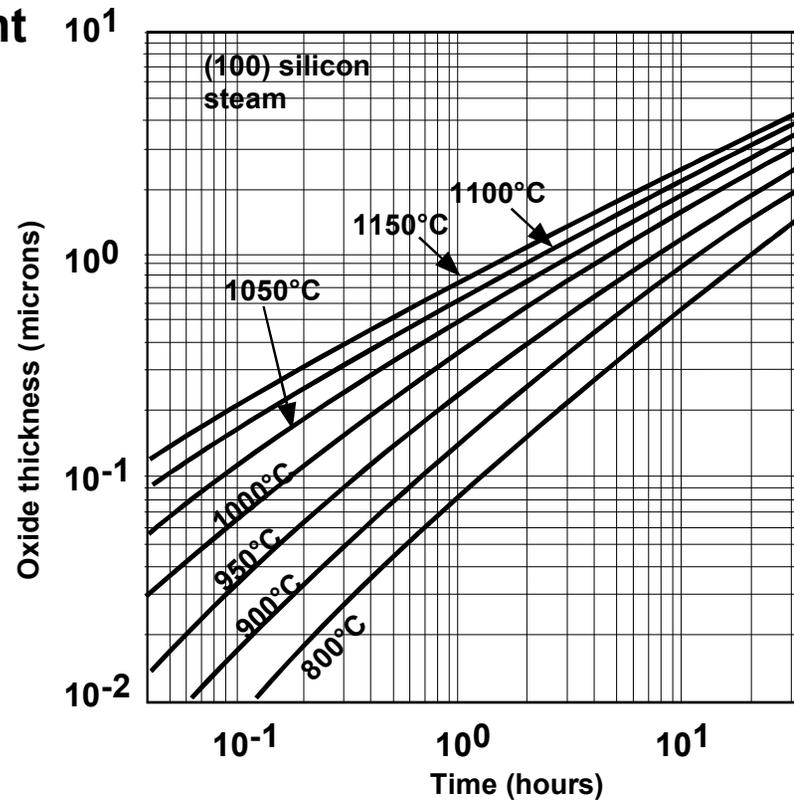
- MOS oxide thickness scales with gate length
  - circa 1998 thickness was ~ 4nm (64M and 256M DRAM technology)

# Oxidation thicknesses: Grove & Deal calculations

- wet oxidation
  - 640 Torr partial pressure
  - fits very well to measurement



calculation

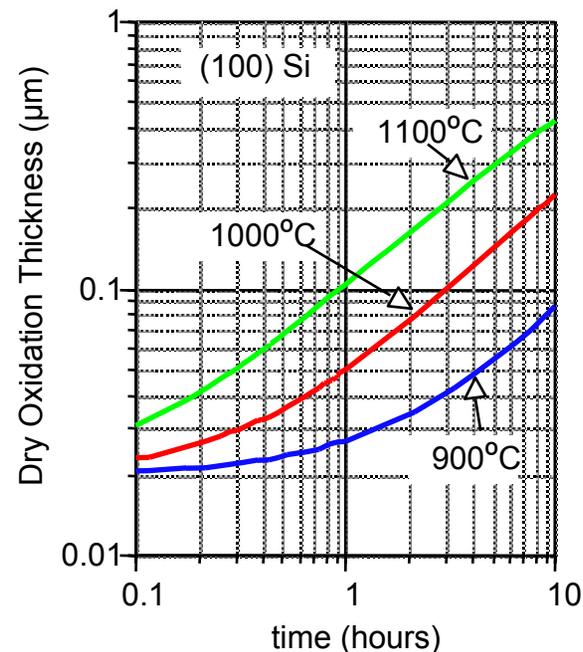


measurement

# Problems with the simple Grove/Deal model of oxidation

- Arrhenius plots of linear and parabolic rate constants are not straight at low temperatures ( $T < 900^\circ \text{C}$ ).
- dry oxidation growth curves do not extrapolate back to zero oxide thickness at zero time

	T ( $^\circ\text{C}$ )	A ( $\mu\text{m}$ )	B ( $\mu\text{m}^2/\text{hr}$ )	B/A ( $\mu\text{m}/\text{hr}$ )	$\tau$ (hr)	$x_i$ (nm)
Wet (640 Torr $\text{H}_2\text{O}$ )	1200	0.05	0.720	14.4	0	0
	1100	0.11	0.51	4.64	0	0
	1000	0.226	0.287	1.27	0	0
	920	0.5	0.203	0.406	0	0
Dry (760 Torr $\text{O}_2$ )	1200	0.04	0.045	1.12	0.027	20
	1100	0.09	0.027	0.30	0.076	19
	1000	0.165	0.0117	0.071	0.37	23
	920	0.235	0.0049	0.02	1.4	26
	700	?	?	$\sim 2.6 \times 10^{-3}$	81	



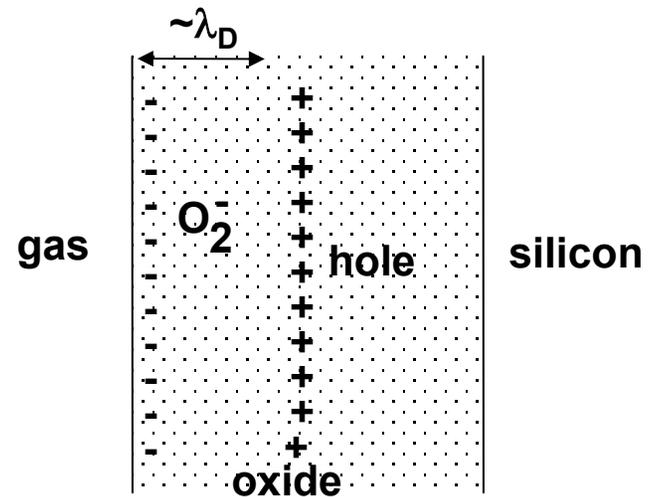
- must use non-physical boundary condition of either an offset time  $\tau$  or  $x_i \approx 200 \text{ \AA}$  in order to fit data

# Possible models to explain “rapid” initial growth

- micropores and intrinsic stress in low temperature thin oxides
  - micropores:
    - ~10 Å about 100 Å apart
    - can visualize as small irregularities that mask oxidation, adjacent regions grow up around "holes"
    - diffusion of O<sub>2</sub> down pores can fit rapid initial growth stage and curvature of Arrhenius plots

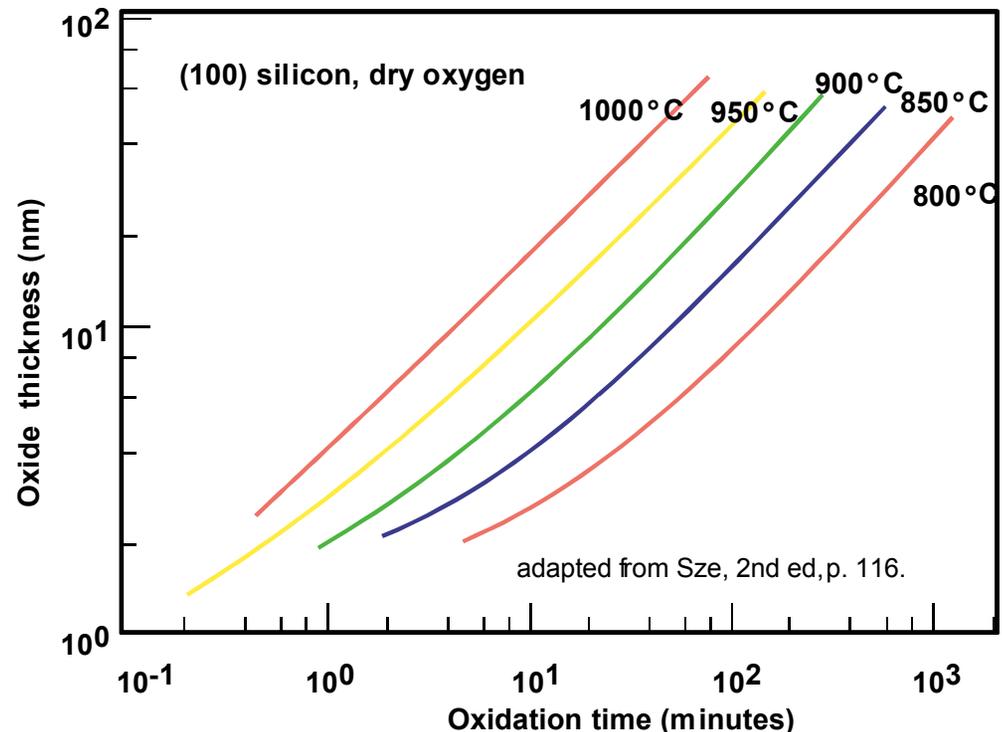
# Field-Enhanced Diffusion

- experiments with external applied fields imply  $O_2$  is charged during oxidation:
  - $O_2 \rightarrow O_2^- + h^+$
- because of mobility differences have ambipolar diffusion effects:
- range of effect is approximately the Debye length  $\lambda_D$ 
  - $\lambda_D \propto 1/\sqrt{N}$ 
    - $\sim 150\text{-}200 \text{ \AA}$  for  $O_2$  in  $SiO_2$
    - $\sim 5 \text{ \AA}$  for  $H_2O$  in  $SiO_2$



# Thin oxide growth

- thin oxides can be grown controllably
  - use reduced pressure
    - usually dry O<sub>2</sub> oxidation
    - need “pressure” (1 atm = 3x10<sup>19</sup>) near solid solubility limit (5x10<sup>16</sup> @ 1000°C)
      - ~ 10<sup>-3</sup> atm (0.25 - 2 Torr used)
  - use low temperature!!!
  - intrinsic stress in low temperature-grown oxides:
    - low temp oxides tend to have higher density
    - not thermal expansion stress
      - at high temp viscosity of SiO<sub>2</sub> low enough to allow plastic flow
      - at low temp viscosity is too high



# ITRS roadmap (2000) requirements

(<http://public.itrs.net/Files/2001ITRS/Home.htm> )

“technology node” (nm)	year	min gate length (nm)	equivalent gate oxide thickness (nm)
130	2002	85-90	1.5-1.9
90	2005	65	1.0-1.5
60	2008	45	0.8-1.2
40	2011	32	0.6-0.8

- 2005 projections require  $l_{\text{gate}} \sim 65\text{nm}$ , “effective oxide thickness”  $\sim 1\text{-}1.5\text{nm}$

- “EOT” : 
$$EOT = t_{\text{physical}} \cdot \frac{\epsilon_r}{\epsilon_{r\text{SiO}_2}}$$

- problem: excessive leakage current and boron penetration for oxide thicknesses  $< 1.5\text{nm}$
- alternative “high k” dielectrics

# Diffusion Mechanisms

- probability of movement

- $\nu \cong 4 \nu_0 e^{-E/kT}$ ,  $\nu_0 \sim 10^{13} - 10^{14} \text{ sec}^{-1}$

- interstitial diffusers

- $E_{\text{move}} \sim 0.6 - 1.2 \text{ eV}$

- $T = 300\text{K}$ :  $\nu \sim 1 \text{ jump per minute}$

- $T = 1300\text{K}$ :  $\nu \sim 10^9 \text{ jumps per sec}$

- substitutional diffusers

- $E_{\text{move}} \sim 3 - 4 \text{ eV}$

- $T = 300\text{K}$ :  $\nu \sim 1 \text{ jump per } 10^{30} - 10^{40} \text{ years!}$

- $T = 1300\text{K}$ :  $\nu \sim \text{few jumps per sec}$

