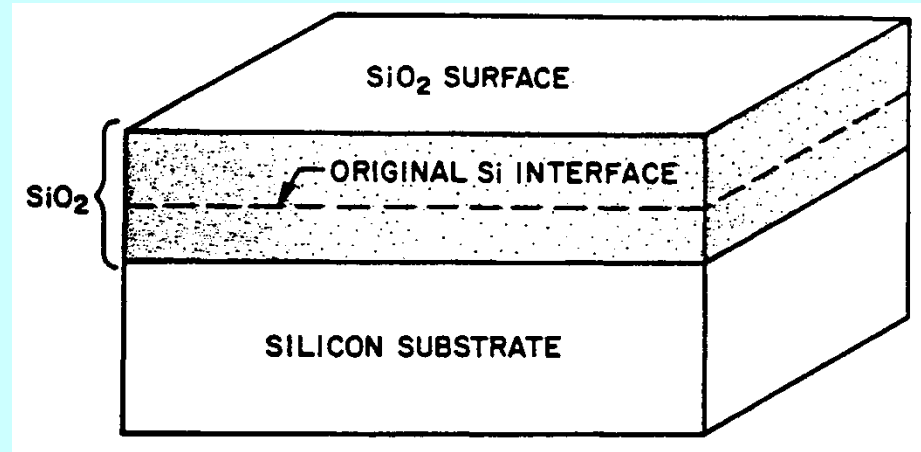# Chapter 4

Oxidation

Professor Paul K. Chu

Roles of SiO$_2$

- Mask against implant or diffusion of dopant into silicon

- Surface passivation

- Device isolation

- Component in MOS structures (gate oxide)

- Electrical isolation of multi-level metallization systems

Oxide Growth

Si (solid) + O$_2$ (gas) $\rightarrow$ SiO$_2$ (solid)
Si (solid) + 2H$_2$O (gas) $\rightarrow$ SiO$_2$ (solid) + 2H$_2$ (gas)

During the oxidation process, oxygen or water molecules diffuse through the surface oxide into the silicon substrate, and the Si-SiO$_2$ interface migrates into the silicon. Thermal oxidation of silicon results in a random three-dimensional network of silicon dioxide constructed from tetrahedral cells. Since the volume expands, the external SiO$_2$ surface is not coplanar with the original silicon surface. For the growth of an oxide of thickness *d*, a layer of silicon equal to a thickness of **0.44*d*** is consumed.

Deal - Grove Model
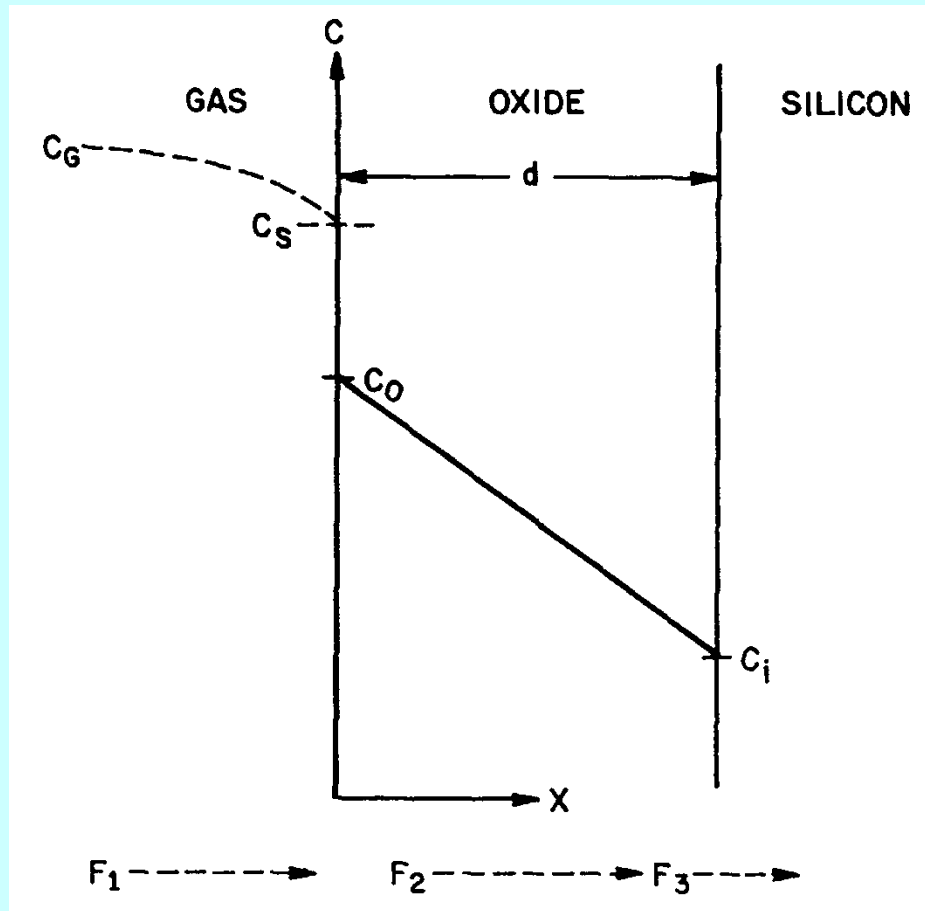
F_1 - flux of oxidizing species transported from the gas phase to the gas-oxide interface)

F_2 - flux across the existing oxide toward the silicon substrate)

F_3 - flux reacting at the Si-SiO$_2$ interface)

In steady state, the three fluxes F_1, F_2, and F_3 are equal

F_1 can be approximated to be proportional to the difference in concentration of the oxidizing species in the gas phase and on the oxide surface: $F_1 = h_G(C_G - C_S)$

where h_G is the gas-phase mass-transfer coefficient, C_G is the oxidant concentration in the gas phase, and C_S is the oxidant concentration adjacent to the oxide surface. Substituting $C = P/kT$,

$F_1 = (h_G/kT)(P_G - P_S)$.

Henry's Law states that, in equilibrium, the concentration of a species within a solid is proportional to the partial pressure of that species in the surrounding gas. Thus, $C_o = HP_S$, where C_o is the equilibrium concentration of the oxidant in the oxide on the outer surface, H is the Henry's Law constant, and P_S is the partial pressure of oxidant in the gas phase adjacent to the oxide surface.

We denote the equilibrium concentration in the oxide, that is, the concentration which would be in equilibrium with the partial pressure in the bulk of the gas P_G by the symbol C^*, and

$$C^* = HP_G$$

$$C^* - C_o = H (P_G - P_S)$$

$$F_1 = (h_G/HkT)(C^* - C_o) = h (C^* - C_o)$$

where $h = h_G/HkT$ is the gas-phase mass-transfer coefficient in terms of concentration in the solid.

Oxidation is thus a non-equilibrium process with the driving force being the deviation of concentration from equilibrium. Henry's Law is valid only in the absence of dissociation effects at the gas-oxide interface, thereby implying that the species diffusing through the oxide is molecular.

The flux of the oxidizing species across the oxide is taken to follow Fick's Law at any point d in the oxide layer. Hence,

$$F_2 = D(C_o - C_i)/d_o$$

where D is the diffusion coefficient, C_i is the oxidizer concentration in the oxide adjacent to the SiO_2 / Si interface, and d_o is the oxide thickness.

The chemical reaction rate at the SiO_2 / Si interface is assumed to be proportional to the reactant concentration. Therefore,

$$F_3 = k_S C_i$$

where k_S is the rate constant.

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

$h(C^* - C_o) = D(C_o - C_i)/d_o = k_S C_i$
$C_i = DC_o/(k_S d_o + D)$
$C_i = C^*/[1 + k_S/h + k_S d_o/D]$
$C_o = [(1 + k_S d_o/D)C^*]/[1 + k_S/h + k_S d_o/D]$

When D is large, the second equation becomes $C_i = C_o$, implying that the oxidation rate is controlled by the reaction rate constant k_S and by C_i ($= C_o$), that is, a **reaction-controlled case**.

When D is very small, $h(C^* - C_o) = 0 = k_S C_i$. Therefore, $C^* = C_o$ and $C_i = 0$. The latter case is called **diffusion-controlled case**, as the oxidation rate depends on the supply of oxidant to the interface.

In order to calculate the oxide growth rate, we define N_1 as the number of oxidant molecules incorporated into a unit volume of the oxide layer. If oxygen is the reactant, N_1 = 2.2 x 10^{22} atoms/cm^3 because the density of SiO$_2$ is 2.2 x 10^{22} cm^{-3}. If water is used, N_1 becomes 4.4 x 10^{22} cm^{-3} as two H$_2$O molecules are incorporated into each SiO$_2$ molecule. The differential equation for oxide growth is given by

$$N_1 \left[\frac{d(d_o)}{dt} \right] = k_s C_i = \frac{k_s C^*}{1 + \dfrac{k_s}{h} + \dfrac{k_s d_o}{D}}$$

With an initial condition of $d_o(t = 0) = d_i$, the solution is

$$d_o^2 + Ad_o = B\,(t + \tau)$$

where $A \equiv 2D\,[1/k_S + 1/h]$, $B \equiv 2DC^*/N_1$, and $\tau \equiv (d_i^2 + Ad_i)/B$.

The quantity τ represents a shift in the time coordinate to account for the presence of the initial oxide layer d_i. Solving for d_o as a function of time gives

$$\frac{d_o}{A/2} = \left[1 + \frac{t + \tau}{A^2/4B}\right]^{1/2} - 1$$

For long oxidation times, i.e., $t \gg \tau$ and $t \gg A^2/4B$, $d_o^2 \cong Bt$. B is therefore called the parabolic rate constant. For short times, i.e., $(t + \tau) \ll A^2/4B$, $d_o \cong [B/A](t + \tau)$, and B/A is referred to as the linear rate constant.

Rate constants for wet oxidation of silicon

Oxidation temperature (^{o}C)	A (µm)	Parabolic rate constant B (µm^2/h)	Linear rate constant B/A (µm/h)	τ (h)
1200	0.05	0.720	14.40	0
1100	0.11	0.510	4.64	0
1000	0.226	0.287	1.27	0
920	0.50	0.203	0.406	0

Rate constants for dry oxidation of silicon

Oxidation temperature (^{o}C)	A (μm)	Parabolic rate constant (μm^2/h)	Linear rate constant B/A (μm/h)	τ (h)
1200	0.040	0.045	1.12	0.027
1100	0.090	0.027	0.30	0.076
1000	0.165	0.0117	0.071	0.37
920	0.235	0.0049	0.0208	1.40
800	0.370	0.0011	0.0030	9.0

Oriental Dependence

The rate of oxidation depends on the availability of reaction sites on the silicon substrates. Hence, as the surface areal density of atoms is dependent on crystal orientation, oxidation rates are expected to be orientation dependent. Oxidation on the <111> crystal plane occurs at a higher rate because there are a higher number of surface atoms, i.e. reaction sites or chemical bonds, when compared to a <100> plane.

Orient-ation	Area of unit cell (cm^2)	Si atoms in area	Si bonds in area	Bonds available	Available bonds, N (10^{14} cm^{-2})	N relative to <110>
<110>	$\sqrt{2}a^2$	4	8	4	9.59	**1.000**
<111>	$\frac{1}{2}\sqrt{3}a^2$	2	4	3	11.76	**1.227**
<100>	a^2	2	4	2	6.77	**0.707**

Rate constants for silicon oxidation in H₂O (640 Torr)

Oxidation Temp (°C)	Orientation	A (μm)	Parabolic rate constant B (μm²/h)	Linear rate constant B/A (μm/h)	B/A ratio <111>/<100>
900	<100>	0.95	0.143	0.150	1.68
	<111>	0.60	0.151	0.252	
950	<100>	0.74	0.231	0.311	1.68
	<111>	0.44	0.231	0.524	
1000	<100>	0.48	0.314	0.664	1.75
	<111>	0.27	0.314	1.163	
1050	<100>	0.295	0.413	1.400	1.65
	<111>	0.18	0.413	2.307	
1100	<100>	0.175	0.521	2.977	1.65
	<111>	0.105	0.517	4.926	

Average 1.68

# Oxide thickness versus oxidation time for silicon in H_2O at 640 Torr
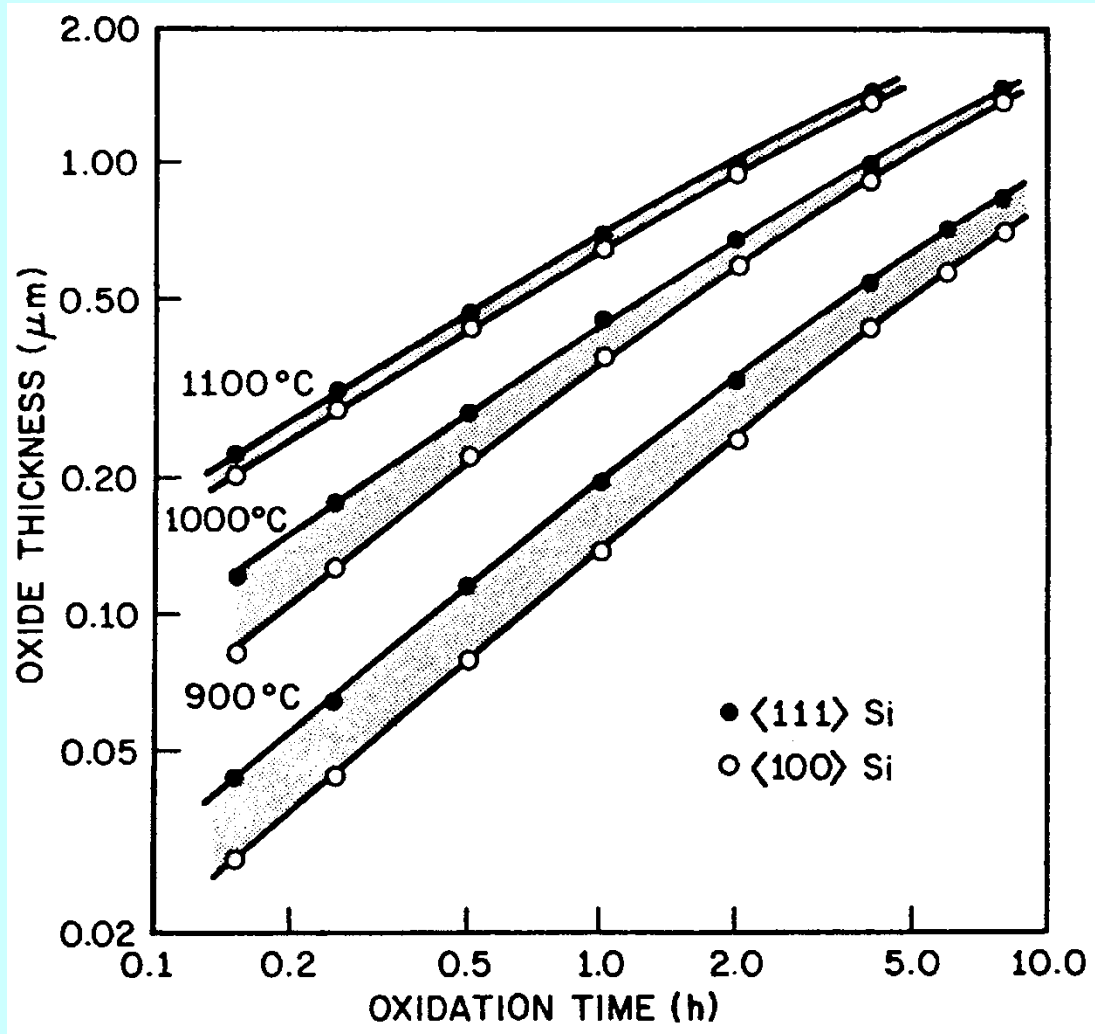
Effects of Impurities

- Moisture – much higher oxidation rate with traces of water in the ambient

- Boron (segregation into oxide) – enhanced diffusion through the weakened bonds

- Phosphorus (segregation into silicon) - concentration dependence observed only at lower temperature, where the surface reaction becomes important. This dependence may be the result of phosphorus being segregated into the silicon
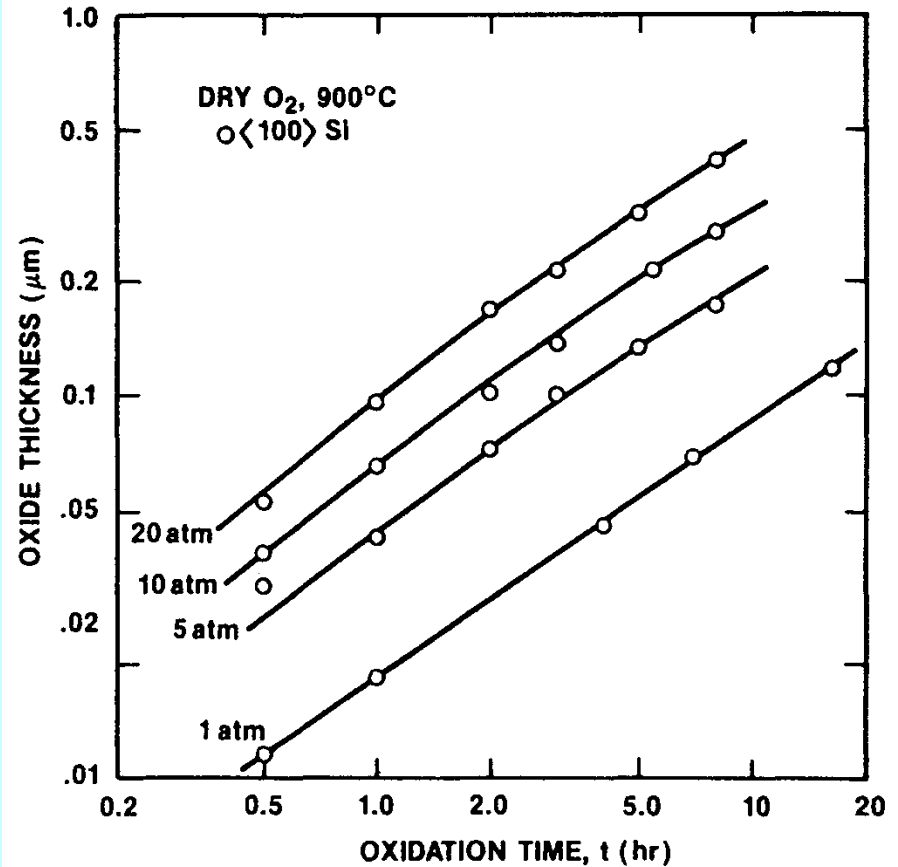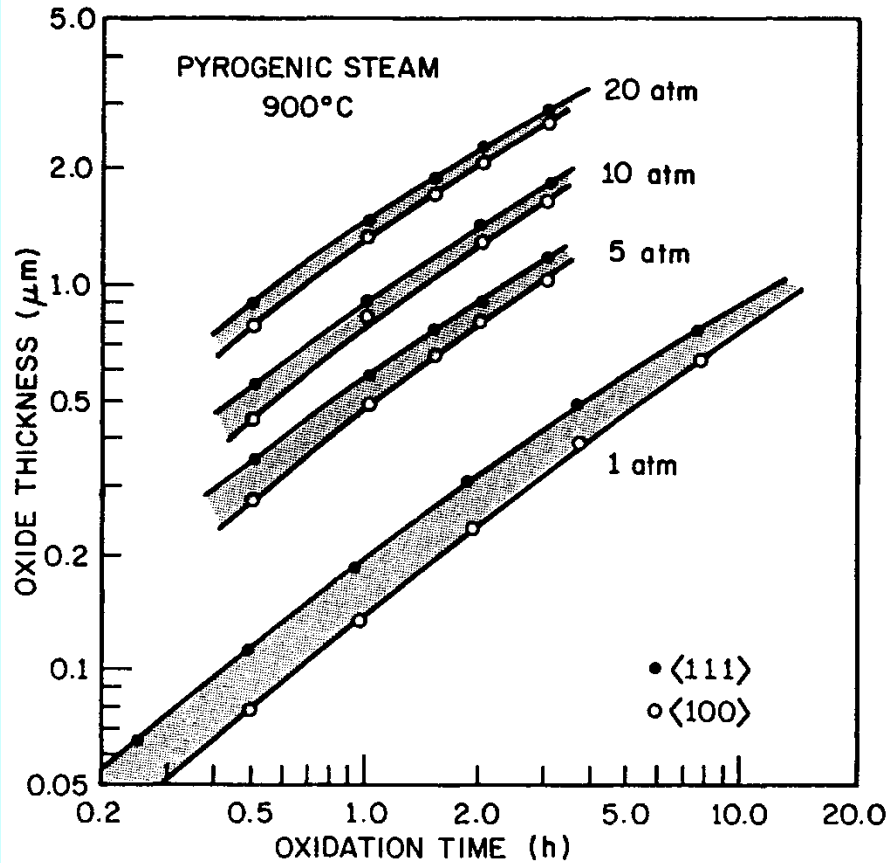
Oxidation of boron-doped silicon in wet oxygen as a function of temperature and boron concentration
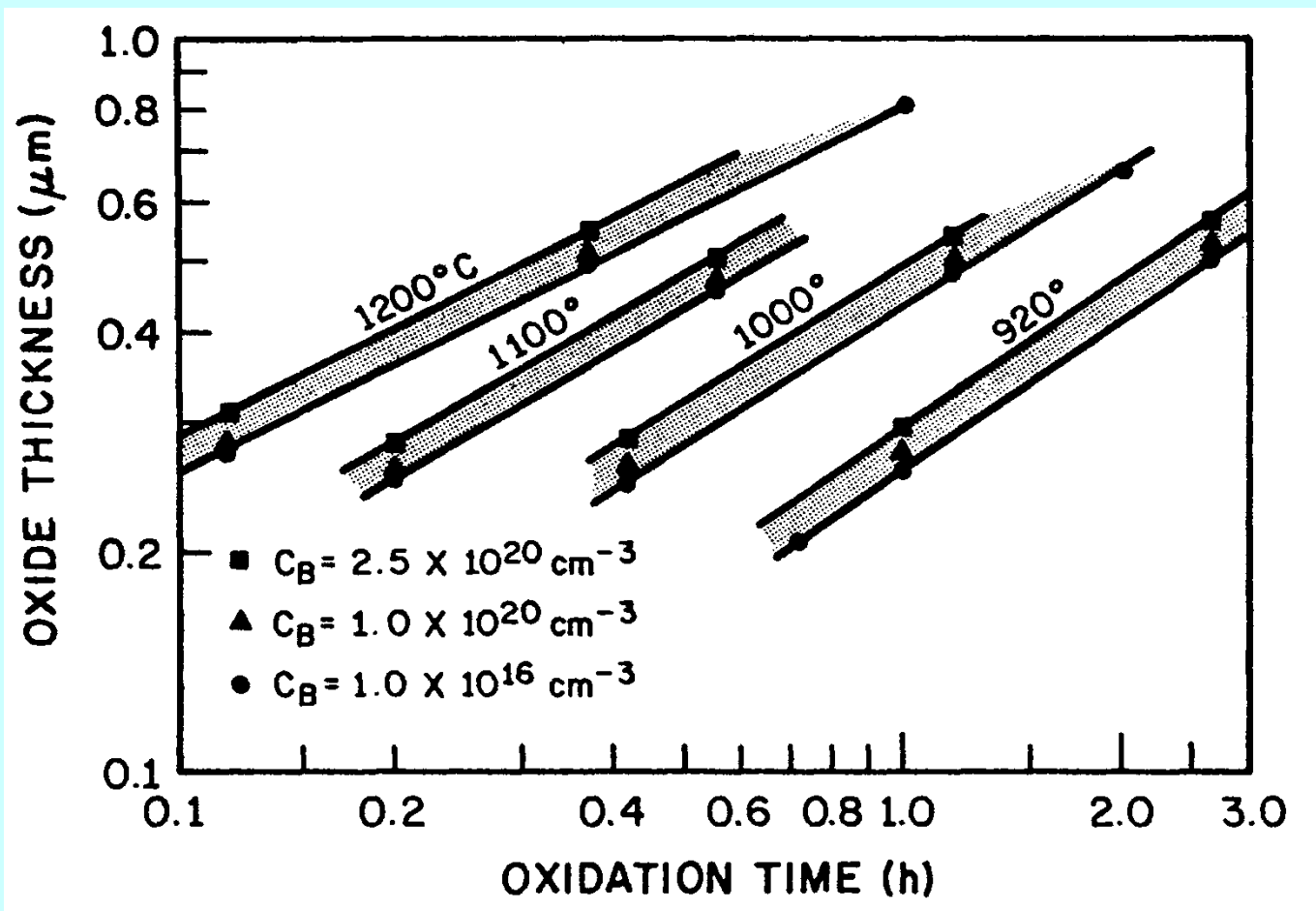
Oxidation of phosphorus-doped silicon in wet oxygen as a function of temperature and phosphorus concentration
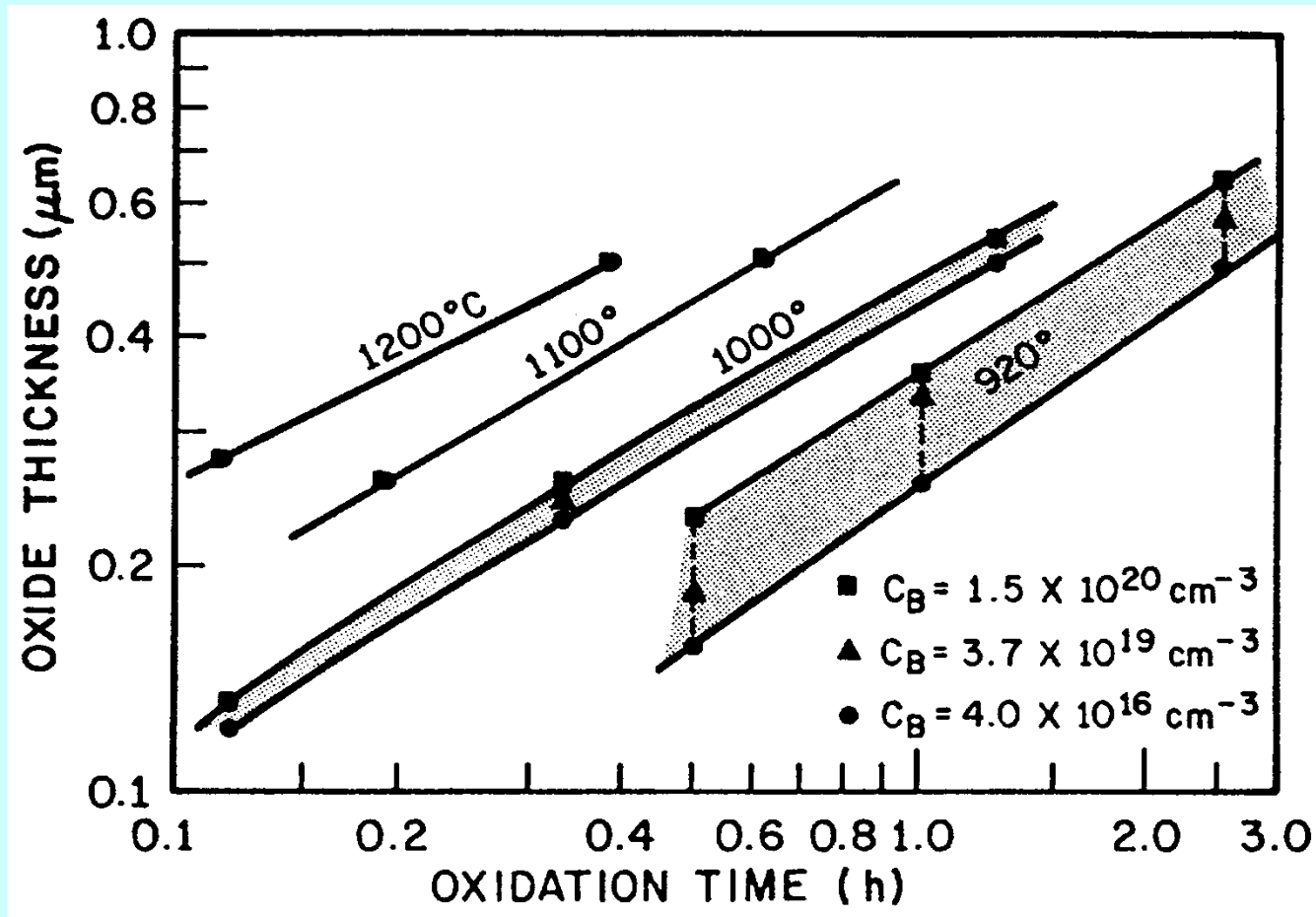
High Pressure Oxidation

Plasma Oxidation

Anodic plasma oxidation has all the advantages associated with the high-pressure technique and also offers the possibility of growing high-quality oxides at even lower temperatures. Plasma oxidation is a low-pressure process usually carried out in a pure oxygen discharge. The plasma is sustained either by a high-frequency or DC discharge. Placing the wafer in the uniform density region of the plasma and biasing it slightly negatively against the plasma potential allows it to collect active charged oxygen species. The oxidation rate typically increases with higher substrate temperature, plasma density, and substrate dopant concentration.

Rapid Thermal Oxidation

Rapid thermal oxidation (RTO) is increasingly used in the growth of thin, high-quality dielectric layers. The primary issues that differentiate RTO from conventional thermal oxidation are the more complex chamber design, radiation source, as well as temperature monitoring. From the point of view of oxide-growth kinetics, RTO may be influenced by both thermally activated processes and a non-thermal, photon-induced process involving monatomic O atoms generated by UV and creating a parallel oxidation reaction that dominates at lower temperature.

RTO growth kinetics exhibit activation energies differing from those measured in conventionally grown oxides. In the initial stage (on the order of 20 seconds), the RTO growth rate is linear followed by nonlinear growth. The duration of the linear region is hardware dependent, particular the heating source.

Oxide Properties

A silicon dioxide layer can provide a selective mask against the diffusion of dopant atoms at elevated temperature, a very useful property in IC processing. For it to work, the dopant diffusion rate in the oxide must be slow with respect to that in silicon, so that the dopant does not diffuse through the oxide in the masked region into the silicon. The masking oxide thickness must also be large enough to prevent it from reaching the silicon substrate.

The often used n-type impurities as well as boron have very small diffusion coefficients in oxide and are compatible with oxide masking. However, this is not true for gallium, indium, and aluminum.

Diffusion constants in SiO$_2$

Dopants	Diffusion constants at 1100°C (cm^2/s)
B	3.4×10^{-17} to 2.0×10^{-14}
Ga	5.3×10^{-11}
P	2.9×10^{-16} to 2.0×10^{-13}
As	1.2×10^{-16} to 3.5×10^{-15}
Sb	9.9×10^{-17}

Oxide Charges

Various charges and traps exist in thermally grown oxide films. If a charge is present close to the Si/SiO$_2$ interface, it can induce a charge of the opposite polarity in the underlying silicon, thereby affecting the ideal characteristics of the device, such as the threshold voltage of a MOS capacitor.

Oxide-trapped charges (Q_{ot}) may be positive or negative, due to holes or electrons being trapped in the bulk of the oxide. They can be annealed out by low-temperature treatment.
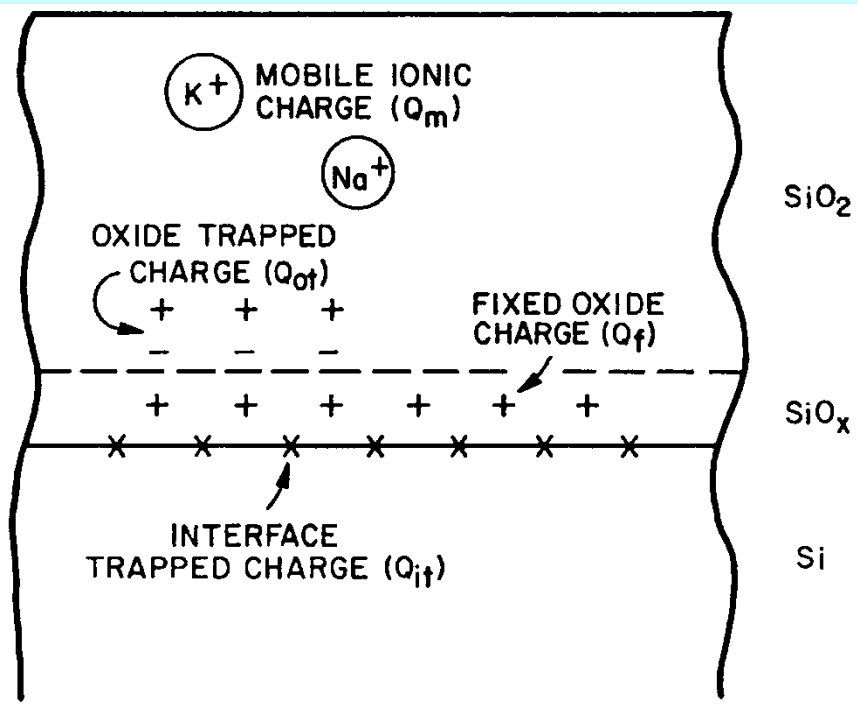
Mobile ion charges (Q_m) are attributed to alkali ions such as Na, K, and Li, as well as negative ions and heavy metals. They originate from processing materials, chemicals, ambient, or handling. Common techniques employed to minimize Q_m include cleaning the furnace tube in a chlorine ambient, gettering with phosphosilicate glass (PSG), and using masking layers such as silicon nitride.

Fixed oxide charges (Q_f) are located in the oxide within approximately 3 nm of the SiO_2 / Si interface. Q_f cannot be charged or discharged easily.

Interface-trapped charges (Q_{it}) can interact with the underlying silicon. They originate from structural defects related to the oxidation process, metallic impurities, and bond-breaking processes. A low temperature hydrogen anneal at 450°C effectively neutralizes most interface-trapped charges.

Dopant Redistribution

During thermal oxidation, the interface advances into the silicon substrate, and doping impurities will redistribute at the interface until its chemical potential is the same on each side of the interface. The ratio of the equilibrium concentration of the impurity in silicon to that in SiO_2 at the interface is called the equilibrium segregation coefficient. Two additional factors that influence the redistribution process are the diffusivity of the impurity in the oxide (if large, the dopant can diffuse through the oxide rapidly, thereby affecting the profile near the Si - SiO_2 interface) and the rate at which the interface moves with respect to the diffusion rate.