

# Oxide growth model

Known as the Deal-Grove or linear-parabolic model

Important elements of the model:

- Gas molecules (oxygen or water) are incident on the surface of the wafer.
- Molecules diffuse through any already-formed oxide.
- Chemical reaction occurs at the Si-SiO<sub>2</sub> interface. (The SiO<sub>2</sub> layer grows “from the bottom up”).

There are three rates to consider:

- rate at which gas molecules arrive at the surface,
- rate at which molecules diffuse through already-formed oxide,
- rate at which the reaction occurs at the interface.

At steady-state, the three rates must all be the same. Then the slowest of the three becomes the limiting factor and will determine the overall growth rate.

# Key concepts

- Concentration - number of oxygen or water molecules per unit volume, in  $\text{m}^{-3}$  (or  $\text{cm}^{-3}$ )
- Flux - number of molecules passing per unit area per unit time, in  $\text{m}^{-2}\text{s}^{-1}$  (or  $\text{cm}^{-2}\text{s}^{-1}$ )
- We'll look for relationships between fluxes and concentrations. Then eliminate the concentration and relate flux to oxide film growth rate.
- Start by assuming that the arrival rate of the gas will never be the limiting factor, and so ignore it at the outset. (Deal & Grove initially included this in their analysis, but soon dropped it as a possible rate limiter.)

Analogy – people entering/leaving a room

surface  
concentration

$N_s$

interface  
concentration

$N_i$

oxide

silicon



incident  
flux



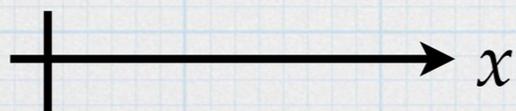
diffusion  
flux  
 $\mathcal{F}_d$



reaction  
flux  
 $\mathcal{F}_r$



$t_{ox}$



$x = 0$

$x$

## Fick's law for diffusion

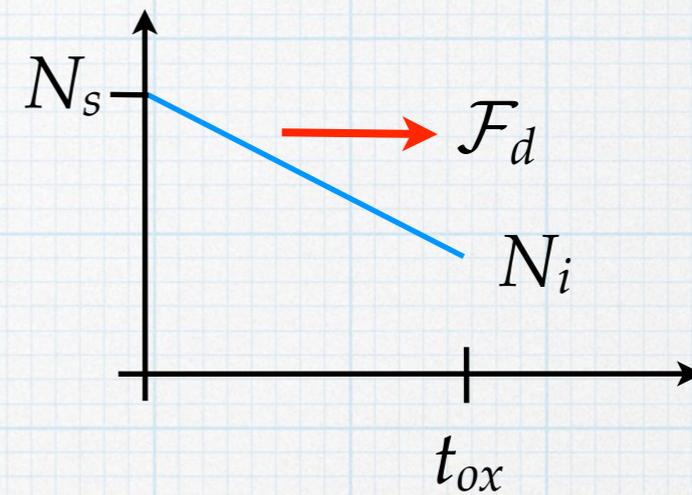
$$\mathcal{F} = -\frac{\partial N}{\partial x}$$

Applying this to the oxide

$$\frac{\partial N}{\partial x} \approx -\frac{N_s - N_i}{t_{ox}} \quad (\text{Assuming } N_s > N_i.)$$

where  $N_s$  is the concentration of the molecules at the surface and  $N_i$  is the concentration at the interface.

$$\mathcal{F}_d = \frac{D}{t_{ox}} (N_s - N_i)$$



Reaction flux at the interface

$$\mathcal{F}_r = k_s N_i$$

where  $k_s$  is a reaction-rate coefficient.

Equating the two fluxes,

$$\mathcal{F}_r = \mathcal{F}_d$$

$$k_s N_i = \frac{D}{t_{ox}} (N_s - N_i)$$

Solving for  $N_i$ :

$$N_i = \frac{N_s}{1 + \frac{k_s}{D} t_{ox}}$$

Each incoming molecule will add a bit of volume to the growing oxide layer. The oxide growth rate is directly related to the flux of molecules reacting at the interface.

$$\text{GR} = \frac{dt_{ox}}{dt} = \frac{\mathcal{F}_i}{M}$$

where  $M$  is number of oxidant molecules incorporated per unit volume of oxide grown.  $M \approx 2.2 \times 10^{22} \text{ cm}^{-3}$  for dry growth and  $4.4 \times 10^{22} \text{ cm}^{-3}$  for wet.

$$\frac{dt_{ox}}{dt} = \frac{k_s N_i}{M} = \frac{k_s N_s}{M \left(1 + \frac{k_s}{D} t_{ox}\right)}$$

Note that the *rate* goes inversely with thickness. As the oxide grows thicker, the rate slows.

$$\frac{dt_{ox}}{dt} = \frac{k_s N_s}{M \left(1 + \frac{k_s}{D} t_{ox}\right)}$$

In principle, we could measure all these different quantities,  $D$ ,  $k_s$ ,  $M$ , and  $N_s$ , and then plug those values in the above equation. However, Deal and Grove chose to simplify things and combined the four parameters above into two reduced parameters.

$$\frac{dt_{ox}}{dt} = \frac{k_s N_s}{M \left(1 + \frac{k_s}{D} t_{ox}\right)} = \frac{\frac{B}{2}}{\frac{A}{2} + t_{ox}} \quad \frac{A}{2} = \frac{D}{k_s} \quad \frac{B}{2} = \frac{DN_s}{M}$$

In their experiments, Deal and Grove measured  $A$  and  $B$  – actually  $B$  and  $B/A$ , as we will see those values shortly.

# The rate equation

$$\frac{dt_{ox}}{dt} = \frac{\frac{B}{2}}{\frac{A}{2} + t_{ox}}$$

First, examine some limits.

If  $t_{ox} \ll A/2$  (thin oxide limit):  $\frac{dt_{ox}}{dt} \approx \frac{B}{A} \longrightarrow t_{ox} = \frac{B}{A}t$

At a given temperature, the growth rate is a constant, meaning that the oxide thickness increases linearly with time. When the oxide is thin, the molecules diffuse through easily, and so the oxidation is limited by the reaction rate. The quantity  $B/A$  is known as the linear rate coefficient and determines the growth during the early stages when the oxide is very thin.

If  $t_{ox} \gg A/2$  (thick oxide limit):  $\frac{dt_{ox}}{dt} \approx \frac{B}{t_{ox}} \longrightarrow t_{ox} = \sqrt{2Bt}$

As the thickness increases, it takes a longer for the molecules to diffuse through, and so the oxidation is limited by the diffusion rate. The oxide thickness will increase with the square-root of time. The quantity  $B$  is known as the parabolic rate coefficient.

Now solve the general case. We should use the general result rather than limiting-case expressions, because it always applies – we don't need to worry about checking limits.

$$\frac{dt_{ox}}{dt} = \frac{\frac{B}{2}}{\frac{A}{2} + t_{ox}}$$

$$\left(\frac{A}{2} + t_{ox}\right) dt_{ox} = \frac{B}{2} dt$$

$$\int_{t_{oxi}}^{t_{ox}} \left(\frac{A}{2} + t'_{ox}\right) dt'_{ox} = \int_0^t \frac{B}{2} dt'$$

where  $t_{ox,i}$  is the initial oxide thickness – we must include the possibility that the wafer already had some oxide on the surface.

$$\frac{At_{ox}}{2} + \frac{t_{ox}^2}{2} - \frac{At_{oxi}}{2} - \frac{t_{oxi}^2}{2} = \frac{Bt}{2}$$

$$\frac{A}{B}t_{ox} + \frac{t_{ox}^2}{B} - \left[ \frac{A}{B}t_{oxi} + \frac{t_{oxi}^2}{B} \right] = t$$

$$\frac{t_{ox}}{B/A} + \frac{t_{ox}^2}{B} = t + \tau \quad \text{where} \quad \tau = \frac{t_{oxi}}{B/A} + \frac{t_{oxi}^2}{B}$$

$\tau$  represents the additional time that would have been needed to grow the layer of oxide that was already on the surface of the wafer. This is simply a redefinition of the initial oxide from a thickness into an equivalent oxidation time.

Use this equation when you know how much oxide you would like to grow and need to determine the amount of time required. If there is an initial oxide on wafer, you must determine the value of  $\tau$  and include that in the growth time.

Note that is a non-linear equation, and you cannot simply add times or thicknesses like you would for a linear relationship – doubling the oxidation time does not double the thickness.

A number of example problems are given in a separate set of notes.

When you know the oxidation time and need to find the resulting thickness, you can use the inverted form of the equation. This is a simple application of the quadratic formula.

$$t_{ox} = \frac{A}{2} \left[ \sqrt{1 + \frac{4B}{A^2} (t + \tau)} - 1 \right] \quad (\text{Check it for yourself. Note the } -1 \text{ term is outside the square-root.})$$

Since we work with the linear and parabolic coefficients  $B/A$  and  $B$ , we might rewrite the above equation to use those coefficients directly.

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

# The linear and parabolic coefficients

Finally, in order to come with numbers for our designs, we need the values of the linear and parabolic coefficients.

$$A = \frac{2D}{k_S}$$

$$B = \frac{2DN_S}{M}$$

$$\frac{B}{A} = \frac{N_S k_S}{M}$$

parabolic

linear

The values of the quantities above is different depending on whether it is oxygen or water vapor being used in the oxidation.

As we saw earlier,  $M$  is a constant. Also, we will treat  $N_S$  as a constant, although doing so requires a bit of justification.

Note that linear term depends on  $k_S$  (and not  $D$ ) so it describes only the reaction, and the parabolic term depends only on  $D$  (and not  $k_S$ ) so that it describes only the diffusion. Both of these are strongly temperature dependent, with a relationship given by the *Arrhenius equation*.

# Arrhenius relationship

The Arrhenius relationship describes the temperature dependence of many thermally induced processes, like: chemical reactions, particle diffusion, evaporation rates, lattice vibrations, defects in crystals (including electrons and holes), and many other things in chemistry and physics. (You may have seen the Arrhenius equation in your freshman chemistry class or the thermodynamics part of physics.)

The Arrhenius equation says that a given quantity (or rate),  $\alpha$ , has an exponential dependence on temperature,

$$\alpha(T) = A_0 \exp\left(-\frac{E_A}{k_B T}\right)$$

where  $A_0$  is a pre-factor and  $E_A$  is the *activation energy* for the process. Because it is inside the exponential, the activation energy is much more important than the pre-factor in determining the value of  $\alpha$ .

The activation energy represents the energy that must be overcome in order for a reaction to occur.

$$\alpha(T) = A_0 \exp\left(-\frac{E_A}{k_B T}\right)$$

The quantity  $k_B T$  is the thermal energy available to induce the reaction to occur. If the available thermal energy is small compared to the activation energy, then  $\alpha$  will be small. If the temperature is raised so that there is more thermal energy available, then  $\alpha$  will increase.

Rule of thumb: Increasing the temperature by  $10^\circ\text{C}$  will cause  $\alpha$  to double.

As you may recall from thermodynamics,  $k_B$  is Boltzmann's constant:  
 $k_B = 1.38 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$ .

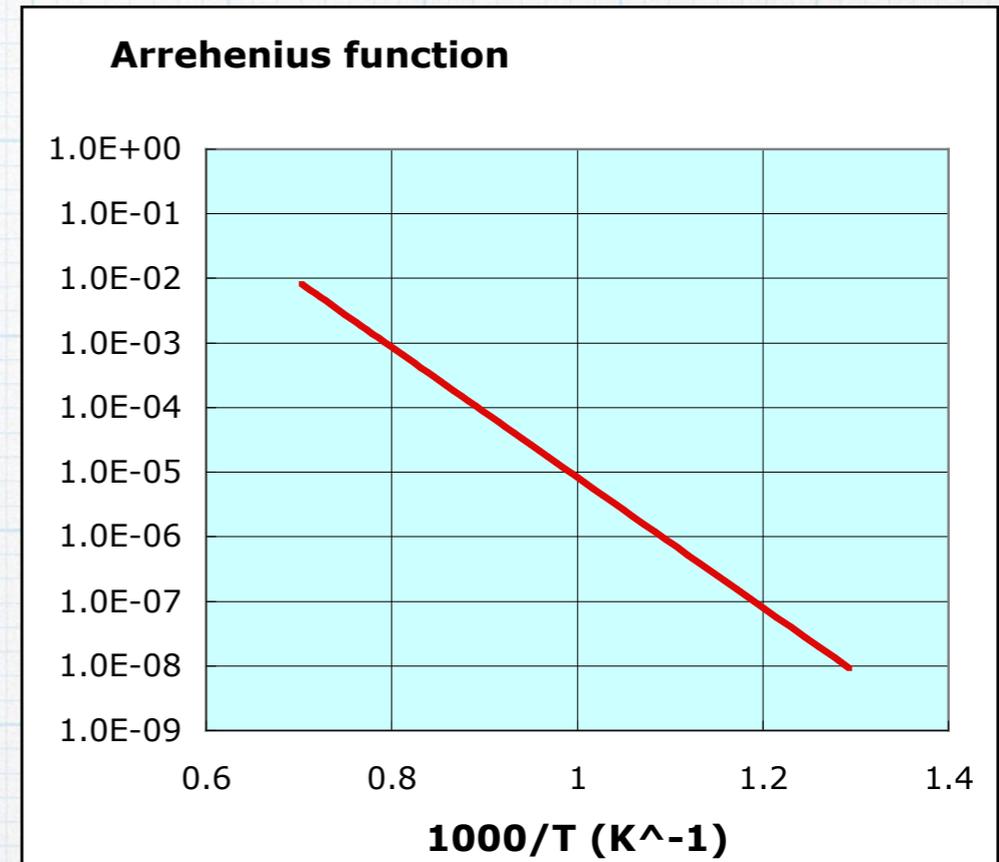
$T$  is the absolute temperature, expressed in degrees Kelvin. The temperature in Kelvin is the temperature in Celsius + 273. ( $0^\circ\text{C} = 273 \text{ K}$ ,  $27^\circ\text{C} = 300 \text{ K}$ ,  $1000^\circ\text{C} = 1273 \text{ K}$ , etc.)

$$\alpha(T) = A_o \exp\left(-\frac{E_A}{k_B T}\right)$$

$$\ln(\alpha) = \ln(A_o) - \frac{E_A}{k_B T}$$

Straight-line on plot of  $\ln(\alpha)$  vs.  $T^{-1}$ .

Slope is  $E_A/k_B$ .



Since both reaction-rate,  $k_s$ , and diffusion coefficient  $D$  are Arrhenius-type quantities, the linear and parabolic oxidation coefficients will be given by Arrhenius equations.

An oxidation process is then characterized by temperature and time. The temperature sets the values of the linear and parabolic coefficients (the rates) and the time is how long growth occurs.

# About $N_s$

- $N_s$  is the concentration of the oxygen or water molecules at the surface of the oxide.
- In general, we would expect the value to depend on the pressure of the incident gas and the temperature.
- Most oxidation systems are operated at atmospheric pressure. In that case,  $N_s$  will be at the *solid solubility limit* of the concentration of molecules in the oxide – the oxide is holding as many of the molecules as possible.
- This limit is not strongly dependent on temperature, so we can treat  $N_s$  as a simple constant. Since it is included in the of the Deal-Grove  $B$  parameter, we don't need to know its exact value.
- $N_s$  for water in  $\text{SiO}_2$  is much bigger than that for oxygen in  $\text{SiO}_2$  (more than 1000x).
- It is possible to carry out oxidations at higher pressure (HIPOX). This would have the effect of increasing  $N_s$  and hence increasing the oxidation rate. However, HIPOX is not a routinely used, since it requires more complex equipment.

# The linear and parabolic coefficients

Deal and Grove determined the  $B/A$  and  $B$  (linear and parabolic) coefficients by doing a number of oxidations under differing conditions and then fitting the results to the Deal-Grove rate equation.

$$\left(\frac{B}{A}\right)_{wet} = \left(9.70 \times 10^7 \frac{\mu m}{hr}\right) \exp\left(-\frac{2.05eV}{kT}\right)$$

$$B_{wet} = \left(386 \frac{\mu m^2}{hr}\right) \exp\left(-\frac{0.78eV}{kT}\right)$$

With  $H_2O$   
(wet oxidation)

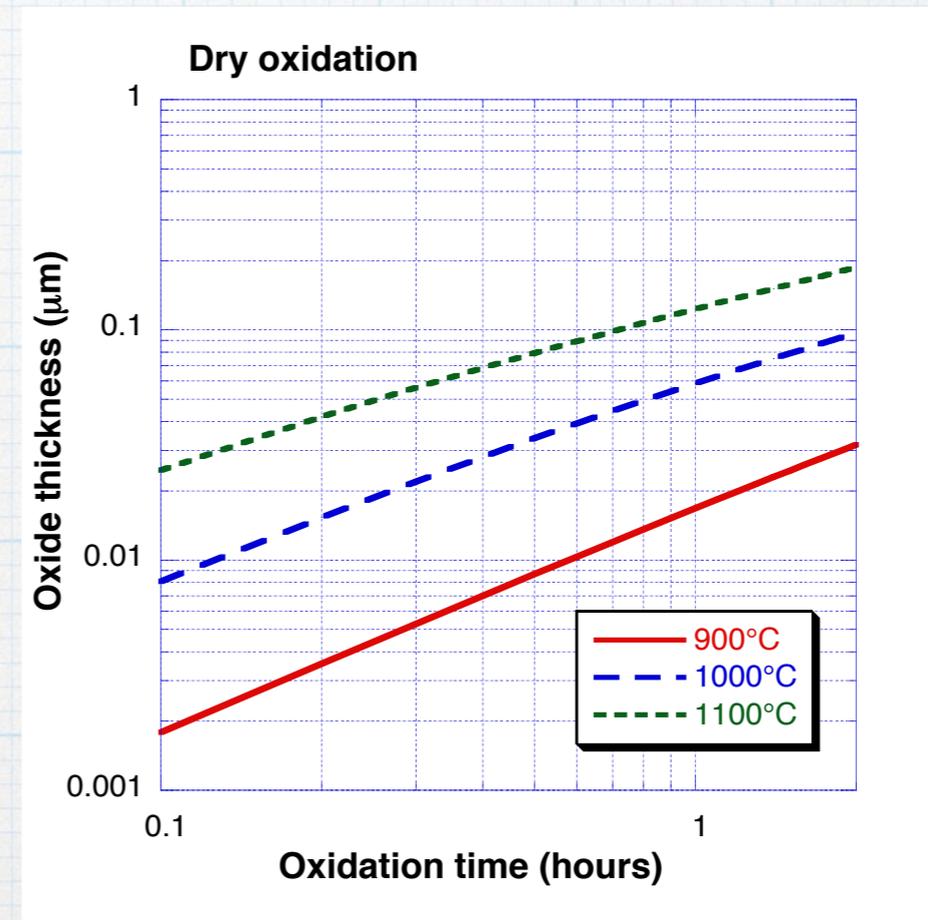
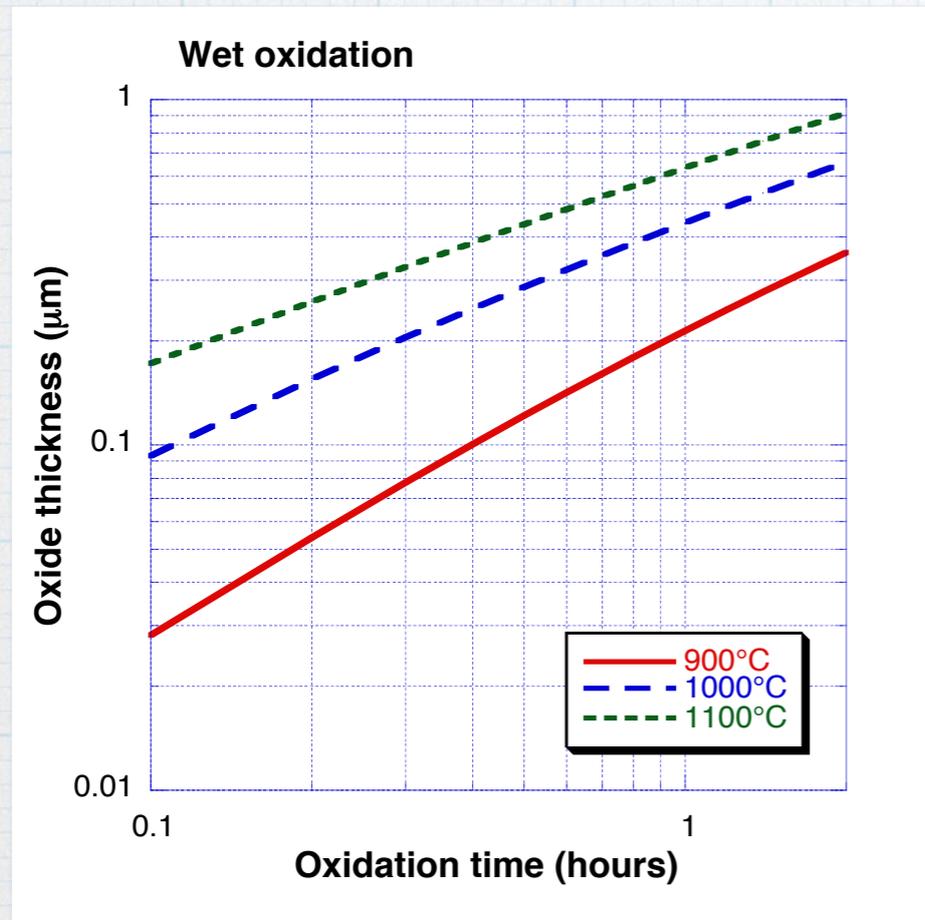
$$\left(\frac{B}{A}\right)_{dry} = \left(3.71 \times 10^6 \frac{\mu m}{hr}\right) \exp\left(-\frac{2.00eV}{kT}\right)$$

$$B_{dry} = \left(772 \frac{\mu m^2}{hr}\right) \exp\left(-\frac{1.23eV}{kT}\right)$$

With  $O_2$   
(dry oxidation)

The numbers tell us that wet oxidation will always be faster than dry oxidation. This is because of the differences in  $D$ ,  $k_s$ ,  $M$ , and  $N_s$  for the reactions of the two types of molecules. Don't be fooled by the pre-factors in the Arrhenius functions. The exponential dependance always gives dominance to the activation energy – a smaller activation energy leads to a larger coefficient.

Plotting oxidation thickness as function of oxidation time shows that wet oxidation is definitely faster. The plots below are for (100)-oriented silicon.



Since we have the equations, it's better to calculate the times or thicknesses directly, rather than trying to read them from a log-log plot.