Among the various oxidation methods for semiconductors, thermal oxidation is by far the most important for silicon and silicon carbide devices. The kinetic model of Si oxidation that is most often taken as a reference is the one so-called Deal-Grove model proposed by Deal and Grove. Deal-Grove model was published in 1965[1]. However, this model with slight modification was used here.

The following chemical reactions describe the thermal oxidation of silicon and silicon carbide.

**Dry Oxidation:**

\[
\text{Si(Solid)} + \text{O}_2(\text{Gas}) \rightarrow \text{SiO}_2(\text{Solid})
\]

\[
\text{SiC(Solid)} + 1.5\text{O}_2(\text{Gas}) \rightarrow \text{SiO}_2(\text{Solid}) + \text{CO}
\]

**Pyrogenic Oxidation:**

\[
\text{Si(Solid)} + 2\text{H}_2(\text{Gas}) + \text{O}_2(\text{Gas}) \rightarrow \text{Si(Solid)} + 2\text{H}_2\text{O}(\text{Gas}) \rightarrow \text{SiO}_2(\text{Solid}) + 2\text{H}_2(\text{Gas})
\]

\[
\text{SiC(Solid)} + 3\text{H}_2(\text{Gas}) + 1.5\text{O}_2(\text{Gas}) \rightarrow \text{SiC(Solid)} + 3\text{H}_2\text{O}(\text{Gas}) \rightarrow \text{SiO}_2(\text{Solid}) + \text{CO}(\text{Gas}) + 2\text{H}_2(\text{Gas})
\]

Dry oxidation and pyrogenic oxidation are typical methods for silicon and silicon carbide oxidation. However, we have been found empirically that the pyrogenic oxidation has been the best oxidation method of all kind of oxidation methods. These oxidation reaction occurs at surface of silicon (or silicon carbide), so that silicon (or silicon carbide) - dioxide interface move into the silicon (or silicon carbide) during the oxidation process (Fig.1).

Since oxidation area is fixed, oxide thickness is proportional to oxide volume. If we know the volume of 1 mol of the silicon and silicon dioxide, we can calculate the thickness of silicon being consumed.

![Figure 1](image)

The molecular weight of Si is 28.9 g/mol, and the density of Si is 2.33 g/cm$^3$. The corresponding values for SiC and SiO$_2$ are 40.10 g/mol – 3.21 g/cm$^3$ and 60.08 g/mol –2.21 g/cm$^3$.

The volume of 1 mol of silicon and silicon carbide are:

\[
\frac{28.9 \text{ g/mol}}{2.33 \text{ g/cm}^3} = 12.40 \text{ cm}^3/\text{mol} \quad \frac{40.10 \text{ g/mol}}{3.21 \text{ g/cm}^3} = 12.49 \text{ cm}^3/\text{mol}
\]
and the volume of 1 mol of silicon dioxide is:

\[
\frac{60.08 \, g/mol}{27.18 \, g/cm^3} = 27.18 \, cm^3/mol
\]

Since 1 mol of silicon and silicon carbide are converted to 1 mol of silicon dioxide:

\[
\frac{\text{Thickness of Si}}{\text{Thickness of SiO}_2} = \frac{12.40}{27.18} = 0.4562 \approx 0.46 \quad \text{Thickness of SiC} = \frac{12.49}{27.18} = 0.4596 \approx 0.46
\]

Thickness of Si \(\approx 0.46 \times \) Thickness of SiO\(_2\) \quad \text{Thickness of SiC} \approx 0.46 \times \text{Thickness of SiO}_2

For example, in case of silicon carbide, to grow a silicon dioxide layer of 100 Å, a layer of 46 Å of silicon carbide is consumed. The theory of thermal oxidation of silicon can be studied using Deal-Grove model illustrated in Fig. 2, where \(C_O\) is the concentration of the oxidant adjacent to the oxide surface, and \(C_S\) is the concentration at silicon surface. The flux \(F_1\) can be written as

\[
F_1 = D \frac{dC}{dx} \approx \frac{D(C_O - C_S)}{x}
\]

where \(D\) is the diffusion coefficient of the oxidant and \(x\) is the thickness of the oxide layer already present.

At the silicon surface, the oxidant reacts chemically with silicon. Assuming the rate of reaction is proportional to the concentration of the oxidants at the silicon surface, the flux \(F_2\) is given by

\[
F_2 = kC_S
\]
where \( k \) is the surface reaction rate constant for the oxidation. At the steady state, \( F_1 = F_2 = F \). Then we can transform these equations as follows.

\[
F = D \frac{(C_0 - C_s)}{x} \quad (1-1), \quad F = k C_s \quad (1-2)
\]

\[
xF = D(C_0 - C_s) \quad (1-3), \quad C_s = \frac{F}{k} \quad (1-4)
\]

Combining the equations 3 and 4 gives

\[
xF = D \left( C_0 - \frac{F}{k} \right) \rightarrow xF + D \frac{F}{k} = DC_0 \rightarrow F \left( x + \frac{D}{k} \right) = DC_0 \therefore F = \frac{DC_0}{x + \frac{D}{k}} \quad (1-5).
\]

Here, Let \( C_1 \) is a concentration of the consumed oxidant in the Oxide. Then, the flux \( F \) divided by \( C_1 \) gives the growth rate of the oxidation layer thickness. It will be easy to understand this, if we use the dimensional analysis.

\[
\frac{[F]}{[C_1]} = \frac{\text{number}}{\text{cm}^2 \cdot \text{sec}} = \frac{\text{cm}}{\text{sec}}.
\]

Since \( \text{cm/sec} \) is dimension of speed, \( F/C_1 \) becomes the growth rate of the oxidation layer thickness. Hence

\[
\frac{dx}{dt} = \frac{F}{C_1} = \frac{DC_0}{(x + \frac{D}{k}) C_1}.
\]

This equation is a linear ordinary differential equation with variable separation\(^3\).

\[
\left( x + \frac{D}{k} \right) dx = \frac{DC_0}{C_1} dt
\]

We can easily solve this.

\[
\int_{d_0}^{x} \left( x + \frac{D}{k} \right) dx = \int_{0}^{t} \frac{DC_0}{C_1} dt
\]

\[
\frac{1}{2} x^2 + \frac{D}{k} x - \frac{1}{2} d_0^2 - \frac{D}{k} d_0 = \frac{DC_0}{C_1} t
\]

\[
x^2 + \frac{2D}{k} x = \frac{2DC_0}{C_1} t + d_0^2 + \frac{2D}{k} d_0 = \frac{2DC_0}{C_1} \left( t + \frac{C_1}{2DC_0} \left( d_0^2 + \frac{2D}{k} d_0 \right) \right)
\]

where \( d_0 \) is the initial condition of oxide thickness \( x \). And we define \( \tau \) as follows.

\[
\tau = \frac{C_1}{2DC_0} \left( d_0^2 + \frac{2D}{k} d_0 \right)
\]

then

\[
x^2 + \frac{2D}{k} x = \frac{2DC_0}{C_1} (t + \tau) \quad (1-6)
\]

Even if we were not able to remember the quadratic formula, we could solve this equation easily. First we add \( D^2/k^2 \) to both side of equation 6.

\[
x^2 + \frac{2D}{k} x + \frac{D^2}{k^2} = \frac{2DC_0}{C_1} (t + \tau) + \frac{D^2}{k^2} \quad (1-7)
\]

Transforming this equation as follows
\[
(x + \frac{D}{k})^2 = \frac{D^2}{k^2} \left( 1 + \frac{2C_0 k^2 (t + \tau)}{DC_1} \right)
\]

\[
x + \frac{D}{k} = \pm \frac{D}{k} \sqrt{1 + \frac{2C_0 k^2 (t + \tau)}{DC_1}}
\]

\(x\) should be a positive number so that

\[
x + \frac{D}{k} = \frac{D}{k} \sqrt{1 + \frac{2C_0 k^2 (t + \tau)}{DC_1}}
\]

The oxide thickness after an oxidation time \(t\) is given by

\[
x = \frac{D}{k} \left( \sqrt{1 + \frac{2C_0 k^2 (t + \tau)}{DC_1}} - 1 \right)
\]

In the case of Deal-Grove model, formula 6 is written in a more compact form:

\[
x^2 + Ax = B(t + \tau) \quad (1-8)
\]

where \(A = 2D/k; B = 2DC_0/C_1\).

For small values \(t\), it becomes \(x^2 \ll x\), equation 7 reduces to

\[x = \frac{B}{A}(t + \tau)\]

And for larger values of \(t\), it becomes \(x^2 \gg x\), it reduce to

\[x^2 = B(t + \tau)\]

According to reference [1], \(B/A\) is referred to as linear rate constant and \(B\) is referred to as parabolic rate constant.

To inspect the equation 7, oxidation experiment were implemented. Fig.3 shows experimental results for silicon dioxide reaction time as a function of thickness. Where Si_f is (0001)face of 4H-SiC(Si face), C_f is (0001)face of 4H-SiC (C face), and Si is (100)face of silicon. Very interesting results were indicated on the graph. All of approximate curves forms \(t = \frac{1}{B}x^2 + \frac{A}{B}x\) and no \(\tau\) (or \(\tau = 0\)), and \(R^2\) is very close to 1. It means that our experimental formula

\[x^2 + Ax = Bt \quad (1-9)\]

is precisely meet the theory.

According to equation 8, oxide thickness will be 0 when reaction time is 0. This result seems quite reasonable.

Another oxidation experiment was done to inspect in more detail. Fig.4 shows experimental results for silicon dioxide thickness as a function of reaction time. Pyrogenic oxidation temperature was 850 ºC. Substrate was silicon (100) only. The oxide thicknesses already exceed 2nm after oxidation start in 30 seconds, and the oxide thickness does not grow up that much until 120 seconds (approximately thickness was 2nm). After that the oxide thickness grows up in proportion to time. 2nd oxidation experiment shows that equation 8 or Modified Deal-Grove Model is valid for Oxide films which are thicker than 2nm.
Now, can this 2nm Oxide be used for Gate oxide of MOSFETs? To answer this question, we made n-channel MOSFETs which oxide thickness was 2.13nm, channel length was 0.4μm, and channel width was 20μm. Fig. 5 indicates the $\tau_I - \tau$ characteristics of this n-MOSFETS. To find the threshold voltage ($V_{th}$), we extrapolated from maximum point of transconductance ($G_m$). $V_{th}$s were less than 0.1V, but these results were quite reasonable for 2nm thickness level of gate oxide film. The $I_D-V_D$ characteristics were shown in Fig. 6. Thus the modified Deal-Grove model is effective in which thickness of silicon dioxide is more than 2nm. What is more, 2nm thin oxide film can be used for Gate oxide film.
Reference

