

Thermal oxidation of Silicon - development of the Deal-Grove model for dry thermal oxidation

Richard K. Herz, rherz@ucsd.edu

SiO₂ layers are grown over Si wafers in order to form electrically insulating regions during integrated circuit manufacturing. Wikipedia has good overviews of SiO₂ deposition methods. The methods available are:

- Thermal oxidation - oxidation of the silicon wafer itself (800-1200 °C)
 - Dry thermal oxidation using O₂:
$$\text{Si (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{SiO}_2 \text{ (s)}$$
 - Wet thermal oxidation using H₂O: $\text{Si (s)} + 2 \text{H}_2\text{O (g)} \rightarrow \text{SiO}_2 \text{ (s)} + 2 \text{H}_2 \text{ (g)}$
- CVD - chemical vapor deposition by reaction to add SiO₂ over the wafer
 - using silane: $\text{SiH}_4 \text{ (g)} + 2 \text{O}_2 \text{ (g)} \rightarrow \text{SiO}_2 \text{ (s)} + 2 \text{H}_2\text{O (g)}$ (300-500 °C)
 - using dichlorosilane: $\text{SiCl}_2\text{H}_2 \text{ (g)} + 2 \text{N}_2\text{O} \rightarrow \text{SiO}_2 \text{ (s)} + 2 \text{N}_2 \text{ (g)} + 2 \text{HCl (g)}$ (900 °C)
 - using tetraethoxysilane (TEOS): $\text{Si(OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 \text{ (s)} + \text{byproducts}$ (650-750 °C)

The dry thermal oxidation process is considered here. Typical conditions are 1 atm of dry O₂ at 1200 K. The final goal here is to get a kinetic model that explains experimental measurements of the thickness of the SiO₂ layer vs. reaction time.

Most reactions encountered in materials science and engineering involve reactions at a solid surface or interface and involve mass transfer steps coupled with chemical reaction. In thermal oxidation of Si, O₂ reacts with Si at the Si-SiO₂ interface, and the rate of this reaction is directly affected by the rate at which O₂ can diffuse through the SiO₂ layer. As the thickness of the layer increases, the rate of reaction decreases.

Experiments and theory have shown that the diffusing oxygen species is O₂ and that diffusion occurs via "percolation" through the disordered SiO₂ layer. This layer is less dense than fused silica (quartz). See A. Bongiorno and A. Pasquarello, DOI: 10.1103 / PhysRevLett.88.125901 (2002).

In class, we came up with several ways in which the thickness of the SiO₂ layer might be determined at a given time of reaction during experiments, including:

- * measure change in O₂ partial pressure in gas flowing in and out of the reaction chamber (proportional to the growth rate), or measure the partial pressure of O₂ vs. time in a batch reaction
- * bounce light off the wafer: ellipsometry, interferometry
- * weigh the wafer: gravimetric measurement
- * cut the wafer and use microscopy to measure the SiO₂ thickness
- * measure resistance across SiO₂ layer

After brainstorming, the next step would evaluate the advantages and disadvantages of the methods to select which one(s) to use. Note most of these methods do not directly give us readings of reaction rate, so we must use additional information about the system and may have to differentiate data in order to determine reaction rates.

Experiments would give us data for the thickness of the SiO₂ layer, Z, vs. time, t. Now we want to come up with a model of the system that fits the data. Also see Chapter 8 in Middleman and

Hochberg, "Process Engineering Analysis in Semiconductor Device Fabrication," McGraw-Hill (1993).

Balance on O₂ in SiO₂ layer over the control volume ($A\Delta z$) from z to $z + \Delta z$:

rate of accumulation = in - out + generation by rxn

$$\frac{dN}{dt} = A\Delta z \frac{dC}{dt} = A \left(-D \frac{dC}{dz} \Big|_z \right) - A \left(-D \frac{dC}{dz} \Big|_{z+\Delta z} \right) + 0$$

where N = number of moles of O₂ in control volume, A = area of Si wafer, D = diffusion coefficient of O₂ in SiO₂ layer, C = molar concentration of O₂ in SiO₂ layer, lower-case z = distance from gas-SiO₂ interface into SiO₂ layer toward wafer. No reaction occurs within the SiO₂ layer (only at the Si-SiO₂ interface), so the reaction term is zero.

Divide by $A\Delta z$ and taking the limit as Δz approaches zero:

$$\frac{dC}{dt} = D \left(\frac{\frac{dC}{dz} \Big|_{z+\Delta z} - \frac{dC}{dz} \Big|_z}{\Delta z} \right)$$

$$\frac{dC}{dt} = D \frac{d^2C}{dz^2}$$

The characteristic time for diffusion through a 1 μm SiO₂ layer is small:

$$\tau_{diffusion} = \frac{Z^2}{D} = \frac{(0.1 \mu\text{m})^2}{1 \times 10^3 (\mu\text{m})^2/\text{h}} = 1 \times 10^{-5} \text{ h}$$

where $z = Z$ is the position at the Si-SiO₂ interface, and Z is the thickness of the SiO₂ layer. In contrast, the characteristic time of the overall process to produce a 0.1 μm SiO₂ layer is much larger, roughly 10 h.

Because the characteristic time of O₂ diffusion in the SiO₂ layer is much less than the overall time scale of the process, we can specify quasi-steady-state conditions for the diffusion process:

$$0 \approx \frac{dC}{dt} = D \frac{d^2C}{dz^2}$$

$$\frac{d^2C}{dz^2} = 0 \quad \text{with boundary conditions} \quad C(0) = C_S \quad \text{and} \quad C(Z) = C_Z$$

C_S is the concentration of O₂ dissolved in the SiO₂ layer at the gas-SiO₂ interface. We assume that the O₂ in the SiO₂ and in the gas at the interface are in equilibrium with each other, and that mass transfer resistance in the gas phase is negligible.

Integrating, we get the linear concentration profile that we expect for quasi-steady-state diffusion through a layer in which no reaction is occurring:

$$C(z) = C_s - \left(\frac{C_s - C_z}{Z} \right) z$$

The rate of reaction at the Si-SiO₂ interface is specified to be first-order in O₂

$$r_{O_2} = -kC_z$$

where r_{O_2} is the rate of generation of O₂ per unit area of wafer. Since O₂ is a reactant, r_{O_2} has a negative value. If model predictions do not fit the data, then we would have to propose and test a different rate expression.

At the Si-SiO₂ interface, we also know that the flux of O₂ diffusing from the SiO₂ layer equals the rate per unit area at which O₂ is being consumed by reaction.

$$-D \frac{dC}{dz} \Big|_{z=Z} = -r_{O_2} = kC_z$$

Substitute the expression obtained above for $C(z)$ into the derivative term on the left hand side:

$$-D \frac{dC}{dz} = D \left(\frac{C_s - C_z}{Z} \right) = kC_z$$

Solving for C_z we get:

$$C_z = \frac{C_s}{1 + (kZ/D)}$$

Now we know how C_z varies with Z in this model. The rate of change of the SiO₂ layer thickness can be related to the rate of reaction at the Si-SiO₂ interface:

$$\frac{1}{v} \frac{dZ}{dt} = kC_z \left[\frac{\text{mol O}_2}{\text{m}^2 \text{ s}} \right]$$

where v is the molar volume (m³/mol) of SiO₂. Using the result for C_z obtained above:

$$\frac{dZ}{dt} = \frac{vkC_s}{1 + (kZ/D)} \quad \text{I.C.: at } t = t_0 \quad Z = Z_0$$

This model does not apply to the time before t_0 when a thin layer of oxide forms rapidly by a process that has to be described by a different rate expression.

Integrating, we get an equation which is called the "Deal-Grove model" of thermal Si oxidation:

$$t - t_0 = \frac{Z - Z_0}{k_{LIN}} + \frac{Z^2 - Z_0^2}{k_{PAR}} \quad \text{where } k_{LIN} \equiv vkC_S \quad \text{and } k_{PAR} \equiv 2vDC_S$$

When diffusion is fast relative to reaction (relatively large D , or small Z), the parabolic term becomes negligible, and this limit is called "reaction rate limited." This happens at early reaction times for constant k and D . When diffusion is slow relative to reaction (relatively large k , or large Z), the linear term becomes negligible and this limit is called "diffusion limited." This happens at longer reaction times for constant k and D . This equation can be rearranged to solve for $Z = f(t)$, which is a quadratic solution.

This model can now be tested by determining the values of the two parameters, k_{LIN} and k_{PAR} , which provide the best fit of the model to experimental data. If we get a reasonable fit, then we conclude that the assumptions used in development of the model were reasonable.

There are two options to find values for k_{LIN} and k_{PAR} .

The first option is to use the "integral method" of kinetic analysis. Fitting data to the integrated form of a rate equation is called the integral method. This problem is linear in the unknown values ($1/k_{LIN}$) and ($1/k_{PAR}$), so linear least-squares fitting can be used to minimize the sum of the squared errors (e.g., sum of $(t_{calc} - t_{expl})^2$ at each Z).

The second option is to use the "differential method" of kinetic analysis. Fitting experimental rate data to the differential form of a rate equation is called the "differential method." In this method, experimental measurements of Z vs. t are differentiated in order to determine the growth rate, (dZ/dt) . This process will increase the relative scatter in the data plot and will require more data points than the integral method. A plot of the data for inverse of the growth rate vs. Z is linear if the model fits the data.

$$\left(\frac{dZ}{dt}\right)^{-1} = \frac{1}{k_{LIN}} + \frac{2}{k_{PAR}}Z$$

where k_{LIN} and k_{PAR} can be determined from the intercept and slope of the best-fit straight line through the points.

Below are excerpts of Deal and Groves' 1965 paper

<http://scitation.aip.org/content/aip/journal/jap/36/12/10.1063/1.1713945>

<u>Deal & Grove</u>	<u>here</u>
t	$t - t_0$
x_0	$Z - Z_0$
B	k_{PAR}
B/A	k_{LIN}

Note: see the last page of these notes for an interesting use of this analysis for a completely different problem - rate of ice freezing over a lake!

General Relationship for the Thermal Oxidation of Silicon

B. E. DEAL AND A. S. GROVE

Fairchild Semiconductor, A Division of Fairchild Camera and Instrument Corporation, Palo Alto, California

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The thermal-oxidation kinetics of silicon are examined in detail. Based on a simple model of oxidation which takes into account the reactions occurring at the two boundaries of the oxide layer as well as the diffusion process, the general relationship $x_0^2 + Ax_0 = B(t + \tau)$ is derived. This relationship is shown to be in excellent agreement with oxidation data obtained over a wide range of temperature (700°–1300°C), partial pressure (0.1–1.0 atm) and oxide thickness (300–20 000 Å) for both oxygen and water oxidants. The parameters A , B , and τ are shown to be related to the physico-chemical constants of the oxidation reaction in the predicted manner. Such detailed analysis also leads to further information regarding the nature of the transported species as well as space-charge effects on the initial phase of oxidation.

1. INTRODUCTION

OWING to its great importance in planar silicon device technology, the formation of silicon dioxide layers by thermal oxidation of single-crystal silicon has been studied very extensively in the past several years.^{1–16} Now, with the availability of large amounts of experimental data, it appears that there is much contradiction and many peculiarities in the store of knowledge of silicon oxidation. For instance, reported

contain a summary of data obtained in these laboratories which are in good general agreement with the corresponding data of Fuller and Strieter¹⁴ and of Evitts, Cooper, and Flaschen.¹³ (The experimental methods are dealt with in detail later.) The plots are logarithm of oxide thickness vs the logarithm of oxidation time for dry and wet oxygen (95°C H₂O) at various temperatures. The slope of the lines corresponds to the exponent n in the above power law. These values are indicated at the limiting position of some of the curves. In the

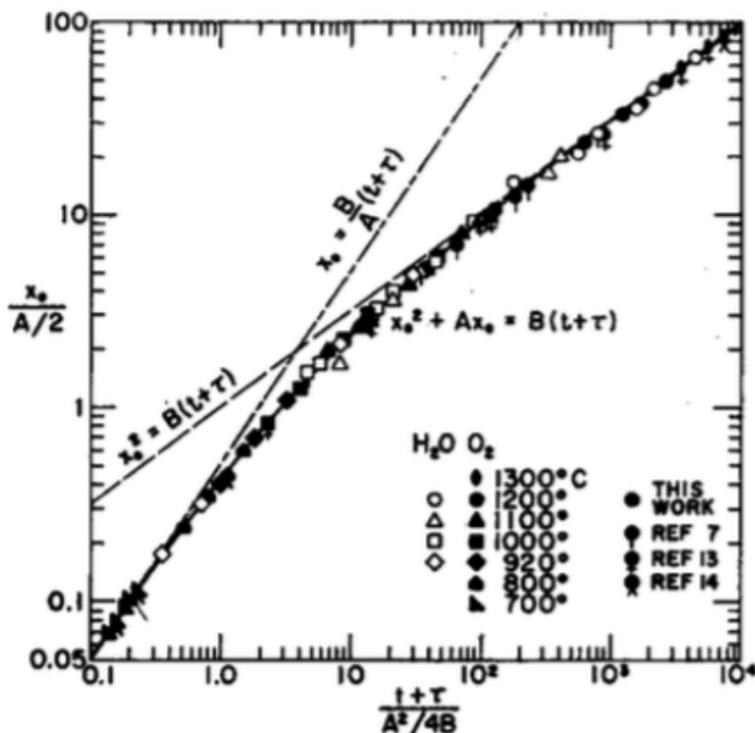


FIG. 12. General relationship for thermal oxidation of silicon. The solid line represents the general relationship, the dotted lines its two limiting forms. Experimental data were reduced using values of A and B determined from Figs. 8, 9, and 11. The values of τ correspond to $x_i = 0$ and 200 Å for wet and dry oxygen, respectively.

Your goal at the university is to learn the fundamentals of how to solve important problems so that you can apply these fundamentals to other problems - sometimes completely different problems!

This is important because the pace of change in the world today is increasing and you can't count on having the same job, solving the same problems, for very long.

Here is an example of two apparently very different problems that can be solved by the same approach. The mathematical approach used to determine the rate of thermal oxidation of a silicon wafer can be applied to determining the rate of ice freezing over the surface of a lake!

This ice problem relates historically to cutting lake ice and storing it in ice houses for food preservation through the summer. Cutting and storing lake ice was common through the early 1900's in this country. I thought of this when I remembered the description of cutting lake ice in Thoreau's "Walden Pond"

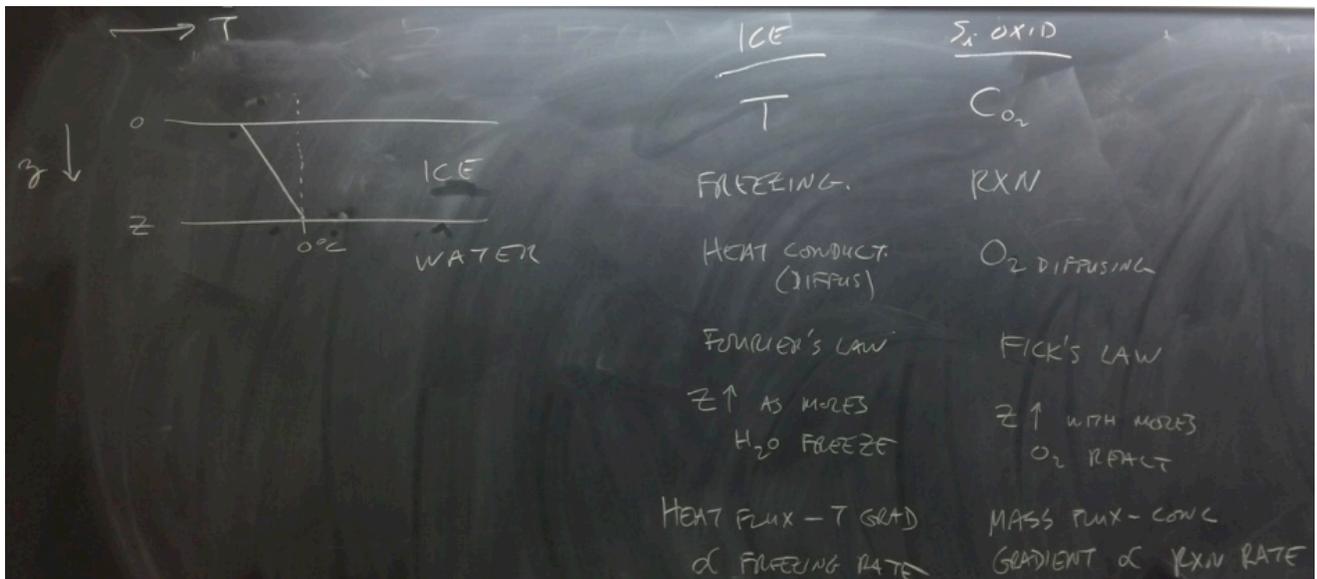
"They stacked up the cakes thus in the open air in a pile thirty-five feet high on one side and six or seven rods square, putting hay between the outside layers to exclude the air; for when the wind, though never so cold, finds a passage through, it will wear large cavities, leaving slight supports or studs only here and there, and finally topple it down. At first it looked like a vast blue fort or Valhalla..."

from "The Pond in Winter" chapter in "Walden Pond" by Henry David Thoreau
<http://thoreau.eserver.org/walden16.html>

google search for images of ice cutting

https://www.google.com/search?q=ice+cutting&hl=en&btnG=Search+Images&tbm=isch&gws_rd=ssl

Your first impression might be that these are completely different and totally unrelated. However, think of the parallels:



Water freezing at the ice-water interface releases the "heat of fusion" of water. This thermal energy must be carried away from the interface by heat conduction through the ice to the colder air. Can you write and solve the equations? Yes, of course you can!