

# THERMAL OXIDATION OF SILICON

DENNIS W. HESS  
 University of California  
 Berkeley, CA 94803

FOR NEARLY THIRTY years, silicon has been the semiconductor material of choice for the fabrication of microelectronic devices and integrated circuits (ICs). This situation has arisen and continues today despite the fact that silicon is not the best semiconductor material from the standpoint of device speed (*i.e.*, the electron mobility is not as high as in materials such as gallium arsenide and indium antimonide). However, in order to fabricate solid state devices and ICs in the surface of a semiconductor, it is necessary to greatly reduce the number of unsatisfied orbitals ("dangling bonds" or surface electronic states); otherwise, the electron (or hole) concentration at the semiconductor surface cannot be reproducibly established and controlled. A reduction in "dangling bond" density was demonstrated in the late 1950s by merely exposing the silicon surface to air so that a thin "native oxide" layer formed [1]. Subsequent studies showed that a further reduction could be achieved if intentional oxidation of the silicon surface was performed at high (> 600°C) temperature [2]. Currently, no other semiconductor/insulator solid state structure can achieve the low level of surface or interface states that is obtained in the Si/SiO<sub>2</sub> interface system. Furthermore, other formation methods (such as chemical vapor deposition) for SiO<sub>2</sub> do not yield the excellent interfacial properties that exist in the thermal growth of SiO<sub>2</sub> on Si. Finally, amorphous SiO<sub>2</sub> films thermally grown on Si are unparalleled in their dielectric properties, and can serve as diffusion barriers for common dopants (*e.g.*, boron, phosphorus, arsenic) in silicon IC process technology [3]. These facts have led to the extensive use of thermal SiO<sub>2</sub> in device components, device isolation, and as a passive insulator and a mechanical and chemical protection (passivation) layer. As a result, a large number of silicon oxidation studies have been performed since the early 1960s [4-7]. The investigations have yielded a reasonable description of the kinetics of silicon oxidation. However, a detailed atomistic model is still lacking. Therefore, fundamental research efforts in silicon oxidation continue [8-10].

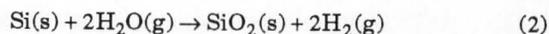
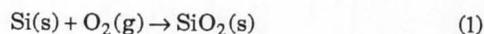
Dennis W. Hess is professor and vice chairman of the chemical engineering department at the University of California, Berkeley. He received his BS in chemistry from Albright College and his MS and PhD in physical chemistry from Lehigh University. Prior to joining the Berkeley faculty in 1977 he was a member of the research staff and manager of process development at Fairchild Semiconductor. His research efforts involve thin film science and technology and rf glow discharge (plasma) processes, as applied to the fabrication of electronic materials and microelectronic devices.



The fabrication of silicon ICs consists of a number of individual steps ("unit operations") that are carefully sequenced to yield an overall process. For instance, since ICs are built up of layers of thin films, various means of forming thin film materials (*e.g.*, chemical vapor deposition, sputtering, evaporation, oxidation) are needed. In addition, precise patterns must be established in these layers (lithography) and selective regions of the silicon doped (solid state diffusion) to control the resistivity level and type (n or p). Of these various process steps, silicon oxidation has probably been the most extensively studied. Furthermore, since the chemistry and chemical engineering principles behind silicon oxidation have been covered by the time a materials and energy balance course has been completed, this "unit operation" can serve as an elementary example of a process step in a non-traditional field.

## OXIDATION PROCESS

Silicon is oxidized by exposure to oxygen or water vapor at elevated (> 700°C) temperatures. For these oxidants, the overall oxidation reactions to form amorphous SiO<sub>2</sub> can be written



Oxidant species diffuse through the growing SiO<sub>2</sub> film to the Si/SiO<sub>2</sub> interface where they react with Si. Therefore, Si is consumed and the Si/SiO<sub>2</sub> interface moves into the bulk Si as oxidation proceeds. It can be shown from the densities and molecular weights of Si and SiO<sub>2</sub>, that if a thickness of SiO<sub>2</sub>, X<sub>o</sub>, is formed, 0.45 X<sub>o</sub> silicon is consumed.

Thermal oxidation of Si is generally performed in a tubular quartz reactor contained in a resistance heated furnace. Silicon substrates are placed upright in slotted quartz carriers or boats, and pushed into the reactor. The oxide thickness is established by precise control of temperature, oxidant partial pressure, oxidation ambient, and oxidation time.

### MODEL FOR SILICON OXIDATION

A general kinetic relationship describing the oxidation of silicon was proposed over twenty years ago [12]. Although the mechanistic details of the oxidation process have not been firmly established, the overall form of the rate expression that results from this model can assimilate data generated by numerous investigators over a wide range of temperature, silicon crystal orientation, oxide thickness, and oxidation ambient. As described in Figure 1, the approach to model formulation for silicon oxidation considers three fluxes that could control oxidation rate [12]. Oxidant (generally  $O_2$ ,  $H_2O$ , or both) is transported ( $F_1$ ) to the surface of the growing  $SiO_2$  film and is subsequently incorporated. Since nearly two orders of magnitude change in gas flow rate has no effect on silicon oxidation rate, these steps are considered rapid and thus are not rate limiting under normal conditions. Oxidant species then diffuse across the growing oxide ( $F_2$ ) to the  $SiO_2/Si$  interface, where they react with Si ( $F_3$ ) to form  $SiO_2$ . The overall oxidation rate can be derived by writing analytical expressions for each flux,  $F$ , equating them, since steady state conditions apply, and determining oxide thickness as a function of time. The following formulation of this problem parallels the

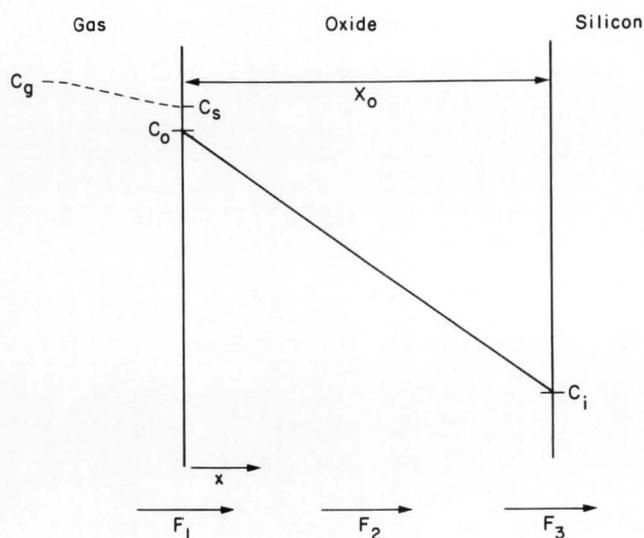


FIGURE 1

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original derivation of an expression for the oxidation rate of silicon [12, 13].

Referring to Figure 1, the gas phase flux  $F_1$  is assumed to be proportional to the difference between the oxidant concentration in the bulk gas ( $C_g$ ), and that near the oxide surface ( $C_s$ ). The proportionality constant is defined as the gas phase mass transfer coefficient,  $h_g$

$$F_1 = h_g(C_g - C_s) \quad (3)$$

In order to estimate the concentration of oxidant in the oxide (solid) surface, we assume that Henry's Law holds. Thus

$$C_o = k_{HL}P_s \quad (4)$$

where the concentration of oxidant in the outer surface of the oxide,  $C_o$ , is proportional to the partial pressure of the oxidant next to the oxide surface,  $P_s$ , and the proportionality constant is Henry's Law constant,  $k_{HL}$ . Finally, the oxidant concentration,  $C^*$ , that would be in equilibrium with the partial pressure in the bulk gas,  $P_g$ , can be written

$$C^* = k_{HL}P_g \quad (5)$$

If ideal gas behavior is assumed, the concentration of oxidant in the bulk gas and near the oxide surface can be written

$$C_g = \frac{P_g}{kT} \quad (6)$$

and

$$C_s = \frac{P_s}{kT} \quad (7)$$

Combining Eqs. (3) to (7),

$$F_1 = h(C^* - C_o) \quad (8)$$

where  $h = h_g/(k_{HL}kT)$ , and represents a gas phase mass transfer coefficient written in terms of oxidant concentration in the solid. Thus, Eq. (8) defines the flux of oxidant from the gas to the oxide surface.

The flux of oxidant across the growing oxide layer is given by Fick's First Law

$$F_2 = -D_{eff} \frac{dc}{dx} \quad (9)$$

where the effective diffusion coefficient,  $D_{eff}$ , is used

because at present it is not clear what *the* diffusing species is (probably O<sub>2</sub>, but O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, and O have also been proposed), and x represents the distance into the oxide film from the SiO<sub>2</sub> surface. If quasi-steady state oxidation is assumed (*i.e.*, no accumulation of oxidant in the oxide), F<sub>2</sub> must be the same at any point in the oxide layer, so that dF<sub>2</sub>/dx = 0. Therefore, Eq. (9) can be written

$$F_2 = D_{\text{eff}} \left( \frac{C_o - C_i}{X_o} \right) \quad (10)$$

where X<sub>o</sub> represents the oxide thickness.

Finally, the flux of oxidant due to the oxidation reaction at the SiO<sub>2</sub>/Si interface is assumed to be proportional to the concentration of oxidant at the interface, C<sub>i</sub>. The proportionality constant is the surface reaction rate coefficient for oxidation, k<sub>s</sub>

$$F_3 = k_s C_i \quad (11)$$

Under steady state conditions, F<sub>1</sub> = F<sub>2</sub> = F<sub>3</sub> = F; therefore, we can develop an expression for the concentration of oxidant reaching the silicon surface. The flux is

$$F_3 = F = \frac{k_s C^*}{1 + \frac{k_s}{h} + \frac{k_s X_o}{D_{\text{eff}}}} \quad (12)$$

The growth rate can now be described if the number of oxidant molecules incorporated into a unit volume of oxide is known. If this quantity is defined by θ, then the oxidation rate is

$$\frac{dX_o}{dt} = \frac{F_3}{\theta} = \frac{k_s C^* / \theta}{1 + \frac{k_s}{h} + \frac{k_s X_o}{D_{\text{eff}}}} \quad (13)$$

This differential equation can be solved if an initial condition is specified. To formulate the initial condition, it is useful to consider X<sub>o</sub> consisting of two parts: an initial oxide layer X<sub>i</sub> that might have been present on the silicon surface prior to the present oxidation step, and the additional oxide grown during the oxidation cycle. Such an approach makes the model general to multiple oxidations. The initial condition used is therefore X<sub>o</sub> = X<sub>i</sub> at t = 0.

Solution of Eq. (13) yields the general relationship for the thermal oxidation of silicon

$$X_o^2 + AX_o = B(t + \tau) \quad (14)$$

$$A \equiv 2 D_{\text{eff}} \left( \frac{1}{k_s} + \frac{1}{h} \right) \quad (14a)$$

$$B \equiv 2 D_{\text{eff}} \frac{C^*}{\theta} \quad (14b)$$

$$\tau \equiv \frac{X_i^2 + AX_i}{B} \quad (14c)$$

where τ is a constant (time units) that corrects for the presence of an initial oxide layer, X<sub>i</sub>, or for an initial "rapid oxidation rate" in dry oxygen [6-12]. Eq. (14) can also be solved for X<sub>o</sub> as a function of oxidation time, t.

$$\frac{X_o}{A/2} = \left( 1 + \frac{t + \tau}{A^2/4B} \right)^{1/2} - 1 \quad (15)$$

It is useful to consider this expression in two limiting forms. At relatively long oxidation times or thick oxides, Eq. (15) reduces to

$$X_o^2 \equiv Bt \quad (16)$$

This represents the parabolic oxidation regime wherein the oxidation rate depends upon diffusion of oxidant through the growing oxide; B is the parabolic rate coefficient. For relatively short oxidation times or thin oxides, Eq. (15) becomes

$$X_o \equiv \frac{B}{A}(t + \tau) \quad (17)$$

Eq. (17) describes the linear or surface reaction rate controlled regime; B/A is the linear rate coefficient. As a result, Eq. (14) is often referred to as a linear-parabolic oxidation law.

Using the definitions (14a) and (14b), the semiquantitative dependence of the rate coefficients B and B/A on temperature (through h, k<sub>s</sub>, and D<sub>eff</sub>) and pressure (through C\*) can be considered. Furthermore, the activation energy for the linear rate coefficient (B/A) at temperatures of 1000°C and above is ~2.0 eV for both dry O<sub>2</sub> and steam oxidation [1, 6]. This value is approximately equal to the Si-Si bond energy, which is consistent with the linear kinetics

TABLE 1

Oxidation Time (hr)	Oxide Thickness (μm)	
	(100)Si	(111)Si
1	0.0490	0.0700
2	0.0780	0.1050
4	0.1235	0.1540
7	0.1800	0.2120
16	0.2980	0.3390

regime controlling the oxidation by breaking a Si-Si bond on the silicon surface. By comparison, the activation energy for the parabolic rate coefficient B [1, 6] is higher for dry O<sub>2</sub> (~1.2 eV) than for steam (~0.8 eV). These results are consistent with values reported for diffusion of O<sub>2</sub> and H<sub>2</sub>O through fused silica and suggest that the rate controlling step in the parabolic oxidation regime is diffusion of oxidant through the oxide film.

Although the above model is extremely useful for most oxidation regimes, it appears inadequate to describe the initial "rapid" oxidation rate observed in dry O<sub>2</sub> and the curvature of Arrhenius plots at temperatures below 1000°C. As a result, new models are being formulated, and additional experimental data are being generated [7-11].

### EXAMPLE

A simple example can be used as a homework problem or can be incorporated into lectures or discussion sections to demonstrate the use of the general relationship for the thermal oxidation of silicon (Eq. 14).

Silicon wafers are thermally oxidized in dry oxygen at 1000°C, and the kinetic data shown in Table 1 are obtained by measuring the SiO<sub>2</sub> thickness grown on (100) and (111) crystal orientations of silicon.

- a. From the data in Table 1, determine the parabolic (B) and linear (B/A) rate constants via a graphical method for (100) and (111) silicon
- b. Discuss the comparison of the rate constants for these two orientations of silicon.

### Solution

- a. Dividing Eq. (14) by X<sub>o</sub> and rearranging yields

$$X_o = B \left( \frac{t + \tau}{X_o} \right) - A \quad (18)$$

This is the equation of a straight line; thus if X<sub>o</sub> is plotted versus (t + τ)/X<sub>o</sub>, the slope of the line is B and the intercept is -A. The parabolic (B) and linear (B/A) rate constants can therefore be determined by linear regression analysis. First, however, we need a value for τ, a correction factor for the initial "rapid oxidation rate" in dry O<sub>2</sub>. Evaluation of τ is performed by extrapolating a plot of X<sub>o</sub> versus t to zero oxide thickness. For these data, the extrapolation crosses the time axis at ~ -0.35 hr, so that τ is defined as 0.35 hr (this value can be given to the student as a constant).

Linear regression analysis of the oxidation rate data in the form of Eq. (18) gives

For (100) orientation

$$A = 0.196 \mu\text{m}, \quad B = 9.07 \times 10^{-3} \mu\text{m}^2/\text{hr}$$

so that

$$B = 0.0091 \mu\text{m}^2/\text{hr} \quad \text{and} \quad B/A = 0.0463 \mu\text{m}/\text{hr}$$

For (111) orientation

$$A = 0.105 \mu\text{m}, \quad B = 9.19 \times 10^{-3} \mu\text{m}^2/\text{hr}$$

so that

$$B = 0.0092 \mu\text{m}^2/\text{hr} \quad \text{and} \quad B/A = 0.0874 \mu\text{m}/\text{hr}$$

b. The two orientations of Si have essentially the same parabolic rate constant. Since B relates to the diffusion of oxidant through the amorphous SiO<sub>2</sub> layer, there should be no effect of B on silicon surface orientation provided that the oxide is the same in both cases.

The linear rate constant is larger for (111) than for (100) orientation. This observation correlates with the higher packing density of the Si (111) plane. Since the linear rate constant appears to be controlled by the reaction of oxidant with the Si surface, such differences are consistent with the atom density in the different planes.

### SUMMARY

Thermal oxidation of silicon is an important step in the manufacture of silicon devices and integrated circuits. A general relationship describing the thermal oxidation process can be derived easily by considering fundamental chemical engineering principles. This expression can be used as an example to demonstrate the reduction of kinetic data obtained for silicon oxidation in undergraduate core chemical engineering courses.

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