W. A. Pliskin

Separation of the Linear and Parabolic Terms in the Steam Oxidation of Silicon*

Abstract: Using accurate film thickness measurements, it was found possible to separate linear and parabolic terms in the steam oxidation of silicon, and thus obtain much more precise expressions for the thermal oxidation under different conditions. The combined linear-parabolic relation was found to be applicable to various crystallographic orientations. The pure parabolic "constant" obtained from this relation was the same for different crystal orientations, but the linear term in the relation was found to be very surface sensitive. By these techniques, more accurate parabolic rate "constants" can be obtained and the linearity of the log k vs $1/T$ plot can be extended to much lower temperatures. The activation energy of the parabolic term for steam oxidation was found to be only 16 kcal/mole. The effect of neglecting the linear term in various methods of computing the parabolic rate is discussed.

Introduction

Many papers have been written in recent years on the thermal oxidation of silicon.[1–27,32] At steam pressures of an atmosphere or less, the oxidation is said to follow a parabolic growth law providing the temperature is sufficiently high ($\geq$1000°C or 1100°C, depending on the author) or sufficiently thick (>3000 Å). The earlier work is covered quite thoroughly by Thurston et al.[4,12] Evitts, Cooper and Flaschen[19] have shown that the rate is parabolic on ⟨111⟩ silicon surfaces for temperatures $\geq$1100°C. Similar results have been obtained by Fuller and Strieter[23] with best fits of their data to the empirical equation $X = At^n$, with n approaching 0.5 at the higher temperatures.

Zaininger and Revesz[18] consider the steam oxidation at 1000°C to be diffusion controlled; i.e., parabolic, for films thicker than 3000 Å, claiming "that diffusion is the controlling mechanism only if the oxide thickness is larger than the space charge region." Similarly Lieberman and Averkiou[24] claimed parabolic rates for films thicker than 3000 Å in the 900°C to 1200°C temperature range and for water vapor pressures from 13 mm to 140 mm of Hg. Deal[15] had suggested the possibility that below 1000°C the oxidation can be represented by a combined parabolic-linear type reaction of the form

$$X^2 + k_1 X = k_2 t, \qquad (1)$$

where X is the film thickness, k_1 and k_2 are constants, and t is the time of oxidation. Normally, as was recognized by Deal,[15] it would be difficult to separate the variables of such a mixed reaction. However, by using very accurate film thickness measuring techniques,[29,30] we find that the oxidation of silicon can be best described at all temperatures ($\geq$910°C) and thicknesses by this parabolic-linear relation. The applicability of this relation was shown most strongly during a detailed study of the oxidation of silicon wafers cut along primary crystal planes. Since no differences could be detected in the nature of the SiO_2 formed on the different crystal planes, and since it is recognized that the oxidizing species diffuses through the oxide to react at the silicon interface,[6,9,13,14,20,21] one should obtain the same parabolic constant for the different crystal planes even though the apparent oxidation rate is different. This will be shown to be true even at temperatures as low as 910°C. As will be shown later, there is some variability in the value of k_1 and a lesser variability in the value of k_2, but for all practical purposes the oxidation can still be described very accurately by assuming these parameters to be constant depending only on temperature in the case of k_2 and temperature and surface in the case of k_1. Since presentation and submission of this paper, Deal and Grove[32] have published a paper on the oxidation behavior of mechanically polished ⟨111⟩ oriented silicon in both dry and wet oxygen. They also conclude that the steam oxidation follows a parabolic-linear oxidation, but for dry oxygen they found, in addition, a fast initial reaction. Recently, Burkhardt and Gregor[26] studied the oxidation of silicon in ultra dry oxygen. Over a wide thickness range they conclude their data fit the equation $X = At^n$ (with $n > 0.5$) better than

* Presented in part at the Meeting of the Electrochemical Society, Buffalo, New York, October 13, 1965. See *J. Electrochem. Soc.* **112**, 259 C (1965).

the parabolic-linear relation. In a recent investigation of the kinetics of thermal growth of silicon dioxide films in water vapor over a wide temperature range, Nakayama and Collins[27] obtained first-order pressure dependency only at lower pressures.

Theory

Equation (1) was derived quite simply by considering both the diffusion of the oxidizing species through a film of thickness X and the reaction of the oxidizing species at the oxide-silicon interface, as has been done by Evans.[28] The flux of the diffusing species at a point x through the oxide is given by

$$J_x = -D\frac{\partial C}{\partial x},$$

where D is the diffusion constant and C is the concentration of oxidizing species at x. In a steady state process J_x is constant and therefore

$$J_x = D\frac{C_0 - C_i}{X},$$

where C_0 is the concentration of the oxidizing species at the outer surface, C_i at the inner surface, and X the oxide thickness. This above relation can be easily given in terms of growth rate by

$$\frac{dX}{dt} = \frac{nM}{2N_0\rho}J_x = \frac{nM}{2N_0\rho}D\frac{C_0 - C_i}{X} = k_p\frac{C_0 - C_i}{X}, \tag{1a}$$

where n is the number of oxygen atoms in the diffusion species, M the gram-molecular weight of the oxide, N_0 Avogadro's number, and ρ the density of the oxide. The value k_p can be considered a diffusion type "constant." The rate of reaction at the oxide-silicon interface is given by

$$\frac{dX}{dt} = k_c C_i, \tag{1b}$$

where k_c is a chemical reaction rate "constant."

Eliminating C_i one obtains

$$\frac{dX}{dt} = \frac{k_p k_c C_0}{k_c X + k_p}, \tag{1c}$$

which on integration becomes

$$X^2 + \frac{2k_p}{k_c}X = 2k_p C_0 t, \quad \text{or} \tag{1d}$$

$$X^2 + k_1 X = k_2 t, \tag{1}$$

where

$$k_1 = \frac{2k_p}{k_c}, \qquad k_2 = 2k_p C_0.$$

Thus in Eq. (1) the parabolic rate "constant" k_2 depends on the diffusion constant and the oxide surface concentration of oxidizing species, which is pressure dependent.

On the assumption of a simplified parabolic oxidation, we have

$$X^2 = k_2' t, \tag{2}$$

where k_2' is the apparent parabolic constant. If a film of initial thickness X_i is oxidized in time t to a thickness X_f then

$$k_2' = \frac{X_f^2 - X_i^2}{t}. \tag{3}$$

From Eqs. (1) and (3), we obtain

$$k_2 = \frac{X_f^2 - X_i^2}{t} + k_1\frac{X_f - X_i}{t}$$

$$= k_2' + k_1\frac{X_f - X_i}{t}, \tag{4}$$

and thus if one oxidizes a wafer with at least two different oxide thicknesses, then at least two equations corresponding to Eq. (4) will be obtained and k_1 and k_2 can be determined. To accomplish this, it is necessary to have the very accurate film thickness measuring techniques which are possible with VAMFO.[29,30]

Experiment

At any particular temperature, the easiest technique is to prepare a silicon wafer with various accurately measured initial oxide thicknesses (X_i) (including bare portions on the same wafer), oxidize in steam at atmospheric pressure over a definite time interval, re-measure the oxide film thicknesses, apply Eq. (4) for various pairs of points, and finally average the determined k_1 and k_2 for the best fit. The validity of the technique is supported by the agreement obtained between the k_1 and k_2 for various pairs of points and the agreement among the k_2 for various crystallographic orientations, since k_2 should depend only on the nature of the oxide, the temperature, and ambient pressure, and not on the crystallographic orientation.

To eliminate the difficulty with regard to temperature rise times, the wafers were inserted in the hot tube furnace and preheated in an atmosphere of dry oxygen or dry nitrogen for times ranging from four to ten minutes. In those cases for which dry oxygen was used, corrections were made to the total steam oxidation time to correct for the slight oxidation due to the exposure to oxygen. These corrections were based on the known relative oxidation rates in steam and oxygen and amounted to at most one minute. The preliminary data were obtained with the dry oxygen-steam combinations using wafers which had oxide stripes of four different initial thicknesses on the "top" or examining side and were bare on the back side.

Table 1 Atmospheric steam oxidation at 1097°C (preheat in O_2, corrected oxidation time—61 minutes).

Wafer orientation	*pt*	X_i	X_f (*meas.*)	*Eq. (3); parabolic** X_f (*calc.*)	ΔX_f	*Eq. (4); linear-parabolic** X_f (*calc.*)	ΔX_f
⟨111⟩	1	4998 Å	8800 Å	8812 Å	− 12 Å	8801 Å	− 1 Å
⟨111⟩	2	5874	9336	9336	0	9339	− 3
⟨111⟩	3	5583	9147	9156	− 9	9155	− 8
⟨111⟩	4	0	7076	7257	−181	7081	− 5
⟨100⟩	1	4977	8674	8688	− 14	8663	+11
⟨100⟩	2	5892	9243	9243	0	9238	+ 5
⟨100⟩	3	5647	9082	9088	− 6	9078	+ 4
⟨100⟩	4	0	6784	7121	−337	6778	+ 6

* Parameters used:
For Eq. (3): ⟨111⟩, $k'_2 = 0.8632 \times 10^6$ Å²/min.
⟨100⟩, $k'_2 = 0.8314 \times 10^6$ Å²/min.
For Eq. (4): ⟨111⟩, $k_1 = 715$ Å
⟨100⟩, $k_1 = 1366$ Å
⟨111⟩ & ⟨100⟩, $k_2 = 0.9049 \times 10^6$ Å²/min.

After establishing the validity of the linear-parabolic theory by this technique, the dry nitrogen-steam combination was used. Unless specifically stated otherwise, all experiments which will be quoted here involve nitrogen preheating. In one set of these experiments striped oxide wafers were used with initial oxide thicknesses of approximately 5500 Å, 3300 Å, and bare regions on the "top" side and 3300 Å on the "back" side. The wafers were then oxidized for times sufficient to obtain thicknesses of about 8000 to 9000 Å on the thickest region. During the course of this study it was found that the strain induced by an oxide stripe was sufficient to affect the oxidation rate of the adjacent bare region. Therefore in the final set of experiments only uniform wafers were used. With the uniform films similar thickness ranges were used in addition to some oxidations for which the initial thicknesses were about 7500 Å and the final thicknesses were about 11,000 Å.

The wafers used were chemically polished except for one oxidation at 980°C involving a ⟨111⟩ oriented mechanically polished wafer. No significant difference was seen in this particular case. No significant difference was seen between float zone and pulled crystals, or between *n*- and *p*-type material, providing the resistivities were sufficiently high. The resistivities of the materials used were greater than 2 Ω/cm except for two special experiments involving silicon highly doped with phosphorus or with boron.

Temperatures were periodically and manually measured during oxidation with a Pt–Pt, 10% Rh thermocouple imbedded in the quartz boat upon which the wafers had been placed. The thermocouple in the boat was then calibrated against a standardized thermocouple placed in the position normally occupied by the silicon wafers. The reference junction was maintained at 0°C in an ice bath.

For the determination of oxide thicknesses to a very high degree of accuracy (~0.1% and better), measurements were made using VAMFO[29,30] on a step of 100 Å depth formed by etching with "*P*" etch.[20] The "*P*" etch rate was determined for the various oxides. The etch rate of steam grown oxides is slightly faster (5 to 10%) than that of oxides grown in dry oxygen or steam-grown oxides which have been dried. Also the higher temperature (1200°C) oxides etch about 15% faster than the lower temperature oxides (900–1000°C). Half of the step depth was added to the measured thickness to obtain the final thickness. On freshly etched wafers this correction was 50 Å and on re-oxidized wafers the correction was $50X_{im}/X_{fm}$ where X_{im} and X_{fm} are the uncorrected initial and final oxide thicknesses. Time zero was taken as five seconds after the introduction of steam into the furnace tube. This was based on the fact that the elapsed time from the introduction of the steam to the condensation of the steam at the exit tube was approximately ten seconds, and the wafers were near the center of the furnace tube.

Results and discussion

• *Comparison of thicknesses calculated by a parabolic law and by a linear-parabolic law (1097°)*

In Table 1, data are listed for oxidation in steam at atmospheric pressure and 1097°C. The differences between the thicknesses determined by Eqs. (3) and (4) are not as great as that obtained by applying the same methods for lower temperature oxidations. The reason is that the decrease in the k_1 factor with increased temperature results in an oxidation which is more nearly parabolic. The data in Table 1 show that even at 1097°C the linear-parabolic relation gives a much better fit to the experimental data than does a pure parabolic relation. It should be noted that in calculating X_f by Eq. (4) we have used the same parabolic "constant" for both the ⟨111⟩ and ⟨100⟩ orientations. The ΔX_f shown in the last column are approximately equal to the experimental error.

Table 2 Atmospheric steam oxidation rate parameters of silicon wafers (preheat in nitrogen).

Temperature (°C)	k_1 ⟨111⟩ (Å)	k_1 ⟨100⟩ (Å)	k_2 ⟨111⟩ (Å²/*min.*)	k_2 ⟨100⟩ (Å²/*min.*)	$k_{2\,avg}$ (Å²/*min.*)
Striped oxide films:					
1202	—	200	1.444×10^6	1.450×10^6	1.447×10^6
1098	610	1450	0.912	0.933	0.922
980	3020	5120	0.529	0.532	0.530
917	6010	9570	0.379	0.376	0.377
Uniform oxide films:					
1202	170	280	1.457	1.452	1.454
1094	830	1570	0.909	0.917	0.913
973	3550	6080	0.520	0.514	0.517
912	6860	10,990	0.384	0.386	0.385

• *Activation energy of the parabolic term*

The values of the rate parameters at various temperatures determined from wafers with striped oxide films and from uniform oxide wafers are shown in Table 2. These data show, as in Table 1, that the parabolic "constants" k_2 are independent of crystal orientation. Furthermore, the difference between the k_2 term for the striped oxide films and uniform oxide films shown in Table 2 is insignificant. This is more readily seen in Fig. 1 where we have made a logarithmic plot of the parabolic "constant" k_2 against $10^4/T$, where T is the absolute temperature. From this plot the activation energy for the parabolic "constant" was found to be 16.0 kcal/mole.*

The two conditions, as exemplified in Fig. 1, are considered more accurate than our earlier value for three reasons: (1) There was no need for any dry oxygen oxidation correction term; (2) the wafers were less strained since the striped as well as the uniform oxide wafer had oxide on the "back" side of the wafer; and (3) with the more recent data, barometric pressure readings were taken and corrections were made to the calculated k_2 term on the valid assumption that it is directly proportional to the steam pressure which corresponds to the barometric pressure in this experiment. The experimental error of k_2 is estimated to be about 1%. The experimental error of k_1 can be given more consistently in terms of an absolute error of about 100 Å.

* This value is slightly less than that determined from our preliminary measurements in which case we had calculated a value of 16.6 kcal/mole covering a temperature range from 910 to 1196°C with excellent linearity.

Figure 1 Parabolic rate constant k_2 for steam oxidation of silicon as a function of the absolute temperature T.

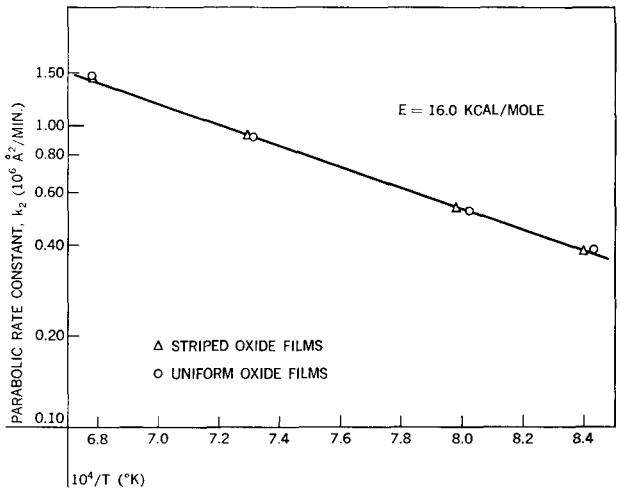
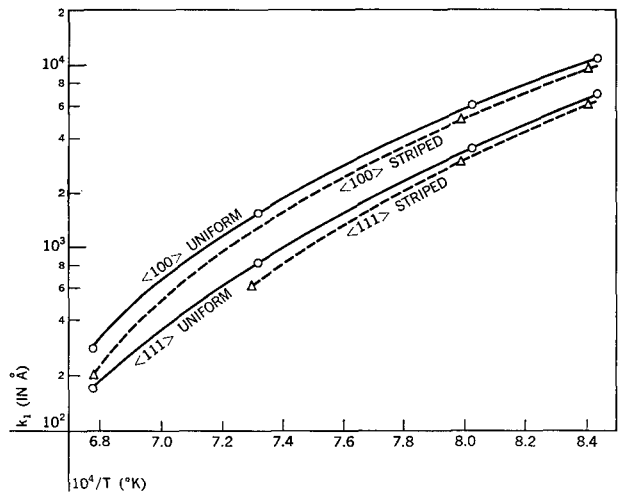


Figure 2 Variation of steam oxidation parameter k_1 with temperature.



• *Surface sensitivity of the k_1 term*

The sensitivity of the k_1 term to surface conditions is shown in Table 2 and in Fig. 2. It is obvious that the most pronounced difference is due to crystal orientation, but there is a significant difference at the lower temperatures between the uniform oxide films and the striped oxide films. This could be due to the effect of strain on the wafers. This was shown most markedly by the steam oxidation of a wafer which was bare except for a single oxide stripe approximately 200 mils wide. The new oxide formed on the region immediately adjacent to the stripe was 40 to 50 Å thicker than regions 100 to 200 mils away from the edge of the stripe (5650 Å compared to 5600 Å). The "fall-off" is most pronounced in the first 100 mils. This apparent increase in the oxidation of the bare regions due to proximity of the initial oxide stripe will result in a lower k_1 term, as is observed with the striped films.

• *Oxidation on ⟨311⟩ and ⟨110⟩ silicon surfaces*

The oxidations on ⟨111⟩ and ⟨100⟩ crystal orientations were chosen for detailed discussion because they represent the extremes of relatively fast and slow oxidation rates for common orientations. The steam oxidation parameters at 971°C for ⟨110⟩ and ⟨311⟩ orientations were determined. The k_1 terms were 4090 Å for the ⟨110⟩ orientation and 4890 Å for the ⟨311⟩ orientation. The calculated k_2 terms were 0.510×10^6 and 0.512×10^6 Å^2/min which are essentially the same as for the ⟨111⟩ and ⟨100⟩ orientations as expected. Thus the relative rates of oxidation for common surface orientations can be listed in order of increasing rate as ⟨100⟩, ⟨311⟩, ⟨110⟩, and ⟨111⟩. This sequence differs from the observation of Ligenza[8] who made high pressure steam oxidations at lower temperatures. This difference cannot be resolved until lower pressure steam oxidations can be made at corresponding temperatures.

• *Oxidation of highly doped silicon*

For the investigation of the steam oxidation kinetics of highly doped silicon, ⟨111⟩ wafers were oxidized at 978°C using striped oxide films. For comparative purposes it is simpler to use wafers with striped oxide films of different thicknesses. The results shown in Table 3 indicate the reason for the differences observed between the oxidation characteristics of silicon highly doped with phosphorus and of silicon highly doped with boron. Deal and Sklar[22] have shown that boron-doped degenerate silicon oxidizes much faster at 920°C to 1200°C than does high-resistivity silicon. On the other hand, with highly doped phosphorus samples, the oxidation rate is much faster at temperatures below 1100°C, while at 1200°C, the oxidation rates of highly doped phosphorus samples are not much different from that of high resistivity silicon samples. Note in Table 3 that in the case of highly doped phosphorus samples, the k_1 term is significantly less than the k_1 term for high resistivity samples, but the parabolic "constant" k_2 is practically the same. Therefore, one can see that at lower temperatures where the k_1 term has an appreciable effect on the oxidation, the oxidation rate is significantly faster for the highly doped phosphorus silicon; but at higher temperatures, where the k_1 term for the high resistivity samples is already small, the effect of highly doped phosphorus will be insignificant. In the case of highly doped boron samples, the k_1 term is only slightly smaller than that of high resistivity samples, but the k_2 term is much larger. This is attributed to the segregation of boron in the oxide. Because of the boron present in the oxide, the oxidizing species diffuses much more rapidly through this slightly doped SiO_2 than it diffuses through regular SiO_2. At higher temperatures, where the k_1 term is small, the effect of the k_2 term is completely dominant. Since the k_2 term is significantly larger for the highly doped boron samples due to diffusion effects, it should be significantly larger at 1200°C as well as at 978°C; consequently the oxidation rates at 1200°C will be larger for the highly doped boron samples than for the high resistivity samples.

• *Oxidation at low water vapor pressure*

In Table 4 the results of oxidation at low vapor pressures show that the parabolic term k_2 is for all practical purposes directly proportional to the pressure. On a simple basis this is expected since $k_2 = 2k_pC_0$. C_0 should be directly proportional to the pressure and on the assumption of a constant k_p, k_2 would be directly proportional to the pressure. This may not be strictly correct as will be discussed later. In practice, we can write the equation:

$$\frac{k_{2p}}{k_{2p'}} = \left(\frac{p}{p'}\right)^n. \tag{5}$$

If k_2 were directly proportional to the pressure, than n in the above equation would be equal to 1. From the data given in Table 4, n was found to be 1.01. For all practical purposes, one could say that the k_2 term is directly proportional to the pressure, since this difference from 1.00 is within experimental error. However, it is felt that this

Table 3 Oxidation rate parameters k_1 and k_2 for highly doped silicon (⟨111⟩ surface, 978°C; striped oxide films).

Dopant	*Initial* C_0	k_1 (Å)	k_2 (Å^2/*min.*)
Phosphorus	4.9×10^{20}	1540	0.521×10^6
Boron	4×10^{20}	2970	0.574×10^6
	High Resistivity	3100	0.528×10^6

Table 4 Oxidation at low water vapor pressure* (stripped oxide films).

Oxidation temp. (°C)	*Pressure* (*mm Hg*)	k_1 ⟨111⟩ (Å)	k_1 ⟨100⟩ (Å)	k_2 (Å²/*min.*)	k_2 *ratio*	*Pressure ratio*	*n*
978°C	760	3100	5200	528,000	28.2	27.3	1.01
978°C	27.9	1950	—	18,700			
974°C	760	3200	5400	520,000	174.5	165.9	1.01
974°C	4.58	1730	3040	2,980			

* A water vapor pressure of 4.58 mm of Hg was obtained by bubbling nitrogen (1.3ℓ/min.) through two water traps in series, maintained at 0°C. The 27.9 mm water vapor pressure was obtained by maintaining the traps at 27.7°C and the lead lines from the traps at temperatures greater than 27.7°C.

difference might be real. It could be explained in terms of the k_p term being pressure sensitive. With increased water vapor pressure, the hydroxyl content in the silicon dioxide increases, modifying the SiO_2 structure such that the diffusion "constant" k_p of the oxidizing species, presumably OH, increases. This results in a larger value for k_2 at higher pressures than at lower pressures. To test this hypothesis, wafers were oxidized to different film thicknesses. The idea here is that for very thick oxide films, the average concentration of hydroxyl through the oxide would be significantly less than for thinner oxide films. Therefore, the calculated k_2 term would be smaller for the thicker oxide films because the k_p term is smaller. The results shown in Table 5 appear to verify that a few percent difference in the k_2 term can occur because of variation in the average hydroxyl content. The increased diffusion rate with increased concentration of hydroxyl groups in silica has been observed previously by Drury and Roberts[31] in their examination of silica glass subjected to tritiated water vapor.

(In view of the first power dependence of the parabolic k_2 term on steam pressure, the author was questioned with regard to the hydroxyl group as the presumed diffusing species on the basis of a surface reaction,

$$Si - O - Si + H_2O \rightarrow 2\ SiOH,$$

from which one would expect a half-power dependence of the k_2 term on steam pressure, rather than the observed first-power dependence. It should be emphasized that in steam oxidation the surface is covered with silanol groups and if silanol groups are the diffusing species, the reaction can be better represented in two steps

$$SiOH \rightarrow Si + OH \text{ (into oxide)},$$

$$2\ H_2O + 2\ Si \rightarrow 2\ SiOH + H_2,$$

for which a first power dependence would be expected. With this model hydrogen would be released both at the gas-oxide interface and at the oxide-silicon interface.)

In Table 5 the bare silicon surfaces were indicated by "0." Actually, the so-called bare surfaces have a native oxide film of the order of 10 Å thick. The results of calculations based on such a native oxide thickness were insignificantly different from those based on a zero oxide thickness, and therefore it was not necessary to include the actual native oxide thickness for determining k_1 and k_2.

Both Table 4 and Table 5 show that the k_1 term is smaller at slower oxidation rates. This may be due to the existence of more than one type of oxidation site at the oxide-silicon interface. The k_1 term is given by $k_1 = 2k_p/k_c$. The variation of k_p is only a few percent as indicated by the variation of k_2. The chemical reaction rate constant k_c will be dependent on the oxidation sites available at the oxide-silicon interface. If, for example, there are two types of sites with relative concentrations θ_a and θ_b where $\theta_a + \theta_b = 1$, then $k_c = \theta_a k_{ac} + \theta_b k_{bc}$. Now if the rate of formation of one type site is less than the other, then the observed k_1 will depend on the overall oxidation rate. Therefore at various temperatures of oxidation one may not get the same surface distribution of types of oxidation sites. The distribution at various temperatures will be

Table 5 Effect of large oxidation rate differences on k_1 and k_2 (⟨111⟩ surface, 971–972°C, uniform thickness oxide films).

Film thickness range (Å)	*Avg. growth rate* (Å/*min.*)	k_1 (Å)	k_2 (Å²/*min.*)
5180–7644	45	3740	0.517×10^6
"0"–4787			
7644–11420	34	3360	0.507
"0"–7675			
11420–15350	20	2440	0.480
5849–11610			

more similar if the oxidation rate is relatively slow due to thick films or low vapor pressure.

Although k_1 and k_2 were found to decrease with film thickness, we do find an excellent experimental fit out to 15,000 Å using the k_1 and k_2 values determined from the thickness range up to 11,000 Å, as shown in Fig. 4. It appears that the effect of the decrease of k_1 with film thickness is at least partially offset by a decrease in k_2.

• *Effect of neglecting the linear term*

The effect of neglecting the linear term can be shown mathematically by combining Eqs. (1) and (2) to obtain

$$k_2' = k_2 - k_1(X/t). \tag{6}$$

Solving for t in Eq. (2) and substituting into Eq. (6), we obtain

$$k_2' = k_2[X/(X + k_1)]. \tag{7}$$

Equation (7) shows that the thinner the films or the greater the value of k_1, the greater will be the discrepancy of the apparent parabolic rate constant k_2' from the actual rate "constant" k_2. Equation (7) is applicable to bare wafers which are oxidized for time t to an oxide film thickness X. If a wafer with an initial oxide film thickness X_i is oxidized for time t to a film thickness X_f, we have from Eq. (4)

$$k_2' = k_2 - k_1\left[\frac{X_f - X_i}{t}\right]. \tag{8}$$

Solving for t in Eq. (3) and substituting into Eq. (4) or (8), we obtain

$$k_2' = k_2\left[\frac{X_f + X_i}{X_f + X_i + k_1}\right]. \tag{9}$$

Thus, when one oxidizes a wafer with an initial oxide film rather than a bare wafer, the apparent parabolic rate constant, k_2', determined by Eq. (3) rather than Eq. (2), is closer to the actual parabolic rate "constant" k_2 as can be seen by comparing Eq. (9) with Eq. (7).

The relation between the apparent parabolic rate constant and pure parabolic rate "constant" can also be given in terms of the time of oxidation, t, by solving for X in Eq. (2) and substituting into Eq. (6) to obtain

$$k_2' = k_2 - \frac{k_1}{2t}(\sqrt{k_1^2 + 4k_2t} - k_1). \tag{10}$$

This relation shows that the greater the time of oxidation, the smaller will be the difference between k_2 and k_2', but with increasing k_1 (as occurs with a decrease in temperature), the difference between k_2 and k_2' is increased.

The differences between the apparent parabolic rate constant k_2' computed under different conditions and the actual parabolic rate "constant" k_2 is shown in Fig. 3 for the ⟨111⟩ crystallographic orientation. Case I was computed from Eq. (7) for oxidation of bare wafers to films 5000 Å thick. Case II is based on Eq. (9) and was computed on the basis of oxidizing wafers with initial film thicknesses of 5000 Å to film thicknesses of 10,000 Å. Case III is for uniform oxidation times of 120 minutes. These results show that, at the higher temperature, there is little difference between the apparent and true parabolic rate "constants," but at the lower temperatures, the apparent parabolic rate is significantly less than the true parabolic rate. This plot shows that neglect of the k_1 factor will lead to incorrect activation energies. Thus one might conclude that at lower temperatures, the activation energy is greater than at higher temperatures, whereas the k_2 plot shows the activation energy is constant in this temperature range. Figure 3 explains the discrepancies appearing in the literature for the activation energy of the steam oxidation of silicon for which we obtained 16.0 kcal/mole.

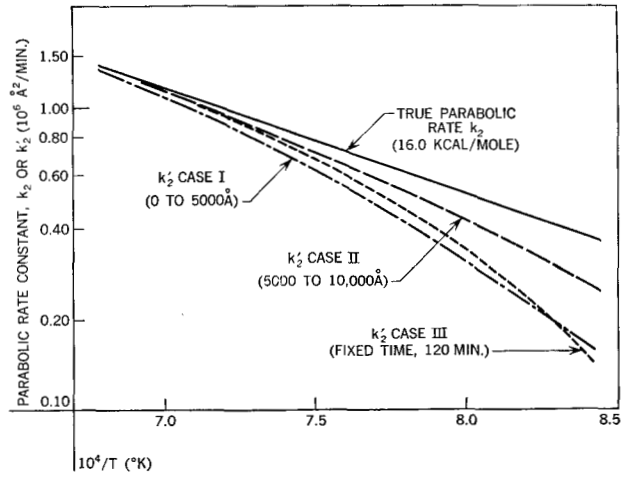


Figure 3 Comparison of "parabolic" atmospheric steam oxidation rates determined by various methods (⟨111⟩ surface).

• *Comparison of parabolic, linear-parabolic, and linear oxidations*

From Eq. (1), we obtain

$$X = (-k_1 + \sqrt{k_1^2 + 4k_2t})/2. \tag{11}$$

The oxide thicknesses obtained on basis of Eq. (11) for ⟨111⟩ and ⟨100⟩ silicon surfaces oxidized at 972°C at a steam pressure of 752 mm Hg (average pressure for the experimental points) are compared with a pure parabolic oxidation ($k_1 = 0$) in Fig. 4. The excellent experimental fit and the approach to a parabolic slope as the oxidation time increases is evident.

At low temperatures or short oxidation times where $k_1 \gg 4k_2t$, Eq. (11) reduces to

$$X = (k_2/k_1)t = k_eC_0t, \tag{12}$$

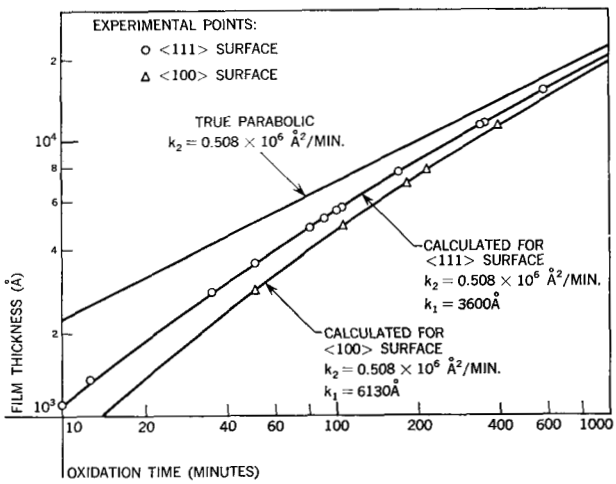
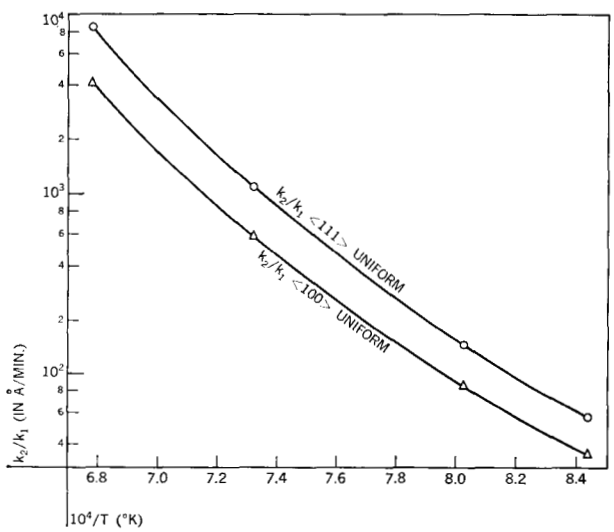


Figure 4 Steam oxidation of ⟨111⟩ and ⟨100⟩ silicon surfaces compared with a true parabolic oxidation (at 752 mm of Hg and 972°C—average pressure and temperature for the experimental points).

Figure 5 "Linear" steam oxidation rate k_2/k_1 for ⟨111⟩ and ⟨100⟩ silicon surfaces.



where k_2/k_1 is the linear oxidation rate. A plot of the linear oxidation rate k_2/k_1 vs $1/T$ is given in Fig. 5 for ⟨111⟩ and ⟨100⟩ silicon surfaces. As previously discussed, the k_1 term is dependent on the overall oxidation rate and therefore one does not expect a straight line.

Conclusions

As a result of this investigation the following conclusions can be made:

(1) The same parabolic rate "constant" is obtained for ⟨100⟩ wafers as for ⟨111⟩ wafers, even at temperatures as low as 910°C;

(2) the incorrect assumption of a pure parabolic oxidation leads to an apparent higher activation energy, especially at lower temperatures;

(3) a plot of the parabolic rate "constant" vs $1/T$ remains linear down to lower temperatures (910°C) than previously reported;

(4) the activation energy so obtained is 16.0 kcal/mole which is in agreement with the recently reported activation energy of 16.3 kcal/mole for oxygen saturated with water vapor[32] at 95°C;

(5) much better agreement is obtained between actual and calculated film thicknesses than that obtained on basis of a pure parabolic law;

(6) the k_1 "constant" in Eq. (1) is very surface sensitive;

(7) with very highly doped silicon the primary effect on the oxidation rate is due to an increase of k_2 when boron doped and a decrease of k_1 when phosphorus doped; and

(8) for all practical purposes the parabolic "constant" k_2 is directly porportional to the water vapor pressure.

Acknowledgments

The author appreciates the interest shown in discussions by Dr. J. A. Perri, Dr. R. M. Valletta, V. J. Lyons, and H. S. Lehman and would like to thank R. P. Esch for help with the experimental work.

References

1. M. B. Brodsky and D. Cubicciotti, *J. Am. Chem. Soc.* **73**, 3497 (1951).
2. J. T. Law, *J. Phys. Chem.* **61**, 1200 (1957).
3. M. M. Atalla, E. Tannenbaum, E. J. Scheibner, *Bell System Tech. Journ.* **38**, 749 (1959).
4. D. Kahng and M. O. Thurston, *ASTIA Report 218842*, Ohio State University Research Foundation (1959).
5. M. M. Atalla and E. Tannenbaum, *Bell System Tech. Journ.* **39**, 933 (1960).
6. J. R. Ligenza and W. G. Spitzer, *J. Phys. Chem. Solids* **14**, 131 (1960).
7. W. G. Spitzer and J. R. Ligenza, *J. Phys. Chem. Solids* **17**, 196 (1961).
8. J. R. Ligenza, *J. Phys. Chem.* **65**, 2011 (1961).
9. M. M. Atalla, *Metallurgical Society Conferences*, H. C. Gatos, Editor, Interscience Publishers, Inc., New York, Vol. V, p. 163 (1963).
10. J. R. Ligenza, *J. Electrochem. Soc.* **109**, 73 (1962).
11. T. H. Yeh, *J. Appl. Phys.* **33**, 2849 (1962).
12. M. O. Thurston and K. D. Kang, *ASTIA Report 294657*, Ohio State University Research Foundation (1962).
13. P. J. Jorgensen, *J. Chem. Phys.* **37**, 874 (1962).
14. N. Karube, K. Yamamoto, M. Kamiyama, *Jap. J. Appl. Phys.* **2**, 11 (1963).
15. B. E. Deal, *J. Electrochemical Society* **110**, 527 (1963).
16. P. S. Flint, *Abstract No.* **94** of paper presented at the *Los Angeles Meeting of the Electrochemical Society*, May, 1962.
17. B. H. Claussen and M. Flowers, *J. Electrochem. Soc.* **110**, 983 (1963).

18. K. H. Zaininger and A. G. Revesz, *J. de Physique* **25**, 66 (1964).
19. H. C. Evitts, H. W. Cooper, and S. S. Flaschen, *J. Electrochem. Soc.* **111**, 688 (1964).
20. W. A. Pliskin and R. P. Gnall, *J. Electrochem. Soc.* **111**, 872 (1964).
21. P. Balk, C. Aliotta, and L. V. Gregor, *Trans. Metall. Soc. AIME* **233**, 533 (1965).
22. B. E. Deal and M. Sklar, *J. Electrochem. Soc.* **112**, 430 (1965).
23. C. R. Fuller and F. J. Strieter, *Abstract No. 74* of paper presented at the *Toronto Meeting of the Electrochem. Soc.*, May, 1964.
24. M. A. Lieberman and G. Averkiou, *Abstract No. 91* of paper presented at the *San Francisco Meeting of the Electrochem. Soc.*, May, 1965.
25. F. Lukeš and E. Schmidt, *J. Phys. Chem. Solids* **26**, 1353 (1965).
26. P. J. Burkhardt and L. V. Gregor, *Trans. Metall. Society AIME*, to be published.
27. T. Nakayama and F. C. Collins, to be published.
28. U. R. Evans, *The Corrosion and Oxidation of Metals*, Edward Arnold Ltd., London, 1960, p. 826.
29. W. A. Pliskin and E. E. Conrad, *J. de Physique* **25**, 17 (1964) and *IBM Journal* **8**, 43 (1964).
30. W. A. Pliskin and R. P. Esch, *J. Appl. Phys.* **36**, 2011 (1965).
31. T. Drury and J. P. Roberts, *Physics and Chemistry of Glasses* **4**, 79 (1963).
32. B. E. Deal and A. S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).

Received December 15, 1965.