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A STUDY OF THE GROWTH OF
SILICON DIOXIDE DURING REOXIDATION

by

Stewart E. Rauch, III

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Electrical Engineering

Lehigh University

1976

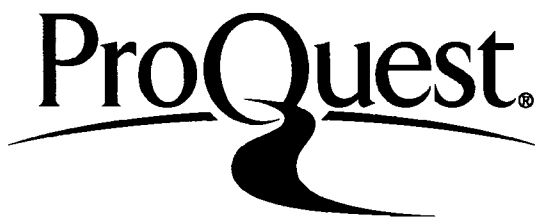
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This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

Sept. 15, 1976
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Professor in Charge

Chairman of Department

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ABSTRACT

Silicon dioxide films thermally grown in dry oxygen at 925°C and 1125-1250°C have been reoxidized at 925°C. It is found that the oxides initially formed at the higher temperature range (1125-1250°C) grow faster during the 925°C reoxidation than the control samples which were initially grown at 925°C. The growth data have been fitted to a quadratic equation of the form

$$t = a_0 + a_1 x + a_2 x^2$$

Whereas the control samples' growth yields values of a_1 and a_2 consistent with published data, a_1 becomes negative for the oxides which were initially grown at the higher temperature.

These results, which have not been previously reported in the literature, can not be explained on the basis of the presently accepted oxidation theory of Deal and Grove. A modification of this theory is explored by assuming that oxides grown at different temperatures have different physical parameter associated with the oxidation process. The resulting two-layer oxide model yields a negative a_1 coefficient.

1.0 INTRODUCTION

The growth of silicon-dioxide on the silicon surface by heating at 700-1250°C in an oxygen or water vapor ambient is an important process in the semiconductor and microelectronics industries. Such layers are used to mask selected areas during the diffusion of dopant impurities, to passivate the silicon surface against unwanted changes in characteristics during use caused by contamination from its working environment, and as an insulating film in MOS and tunnelling devices (1).

There still exist many questions regarding certain properties of SiO₂ on Si which are important in device manufacture and performance, but the theory of the growth rate of the SiO₂ layer during thermal oxidation was worked out in 1965 by Deal and Grove (2), yielding excellent agreement with experimental data, and is generally thought to be well understood.

However, this study presents a situation in which their theory does not hold. Silicon samples were oxidized in dry oxygen at 1125°C, 1200°C, and 1250°C. These samples were then reoxidized in dry oxygen at 925°C. The resulting growth rate is shown to be faster than normal oxide growth at 925°C, and although the growth data can be fitted by the quadratic curve,

$$t = a_2x^2 + a_1x + a_0$$

(where t = time and x = oxide thickness), as called for in the theory of Deal and Grove, the a_1 coefficient proved to be negative whereas a_1 must be positive in the Deal and Grove theory.

The model presented here to explain this discrepant behavior assumes that the 1125-1250°C oxidation and the 925°C oxidation form oxides with slightly different properties. Thus there are two layers of oxide to be considered by the mathematical theory. This model indeed yields negative values for the a_1 coefficient.

2.0 SILICON OXIDATION

2.1 Oxidation Theory of Deal and Grove

The theory proposed by B.E. Deal and A.S. Grove (2) in 1965 first satisfactorily explained high temperature thermal oxidation of silicon. Qualitatively their model shown in Fig. 1 assumes the following sequential steps: The oxidizing species, which for oxidation in an O_2 ambient are shown to be neutral or singly charged O_2 molecules, enter the oxide surface from the gas phase, diffuse through the oxide layer (this fact had already been established by several previous authors, see reference [9]), and react with excess Si at the SiO_2 - Si interface.

In connection with this model the following assumptions were made:

1. The concentration profile of the oxidizing species is in quasi-steady state (i.e., is approximately a straight line) which occurs when $Dt \gg X^2$, where D = effective diffusion constant, t = time from the start of the oxidation, and X = oxide thickness. Under this assumption the diffusion equation,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}$$

where C = concentration of oxidizing species, greatly simplifies to,

$$0 = D \frac{\partial^2 C}{\partial X^2}$$

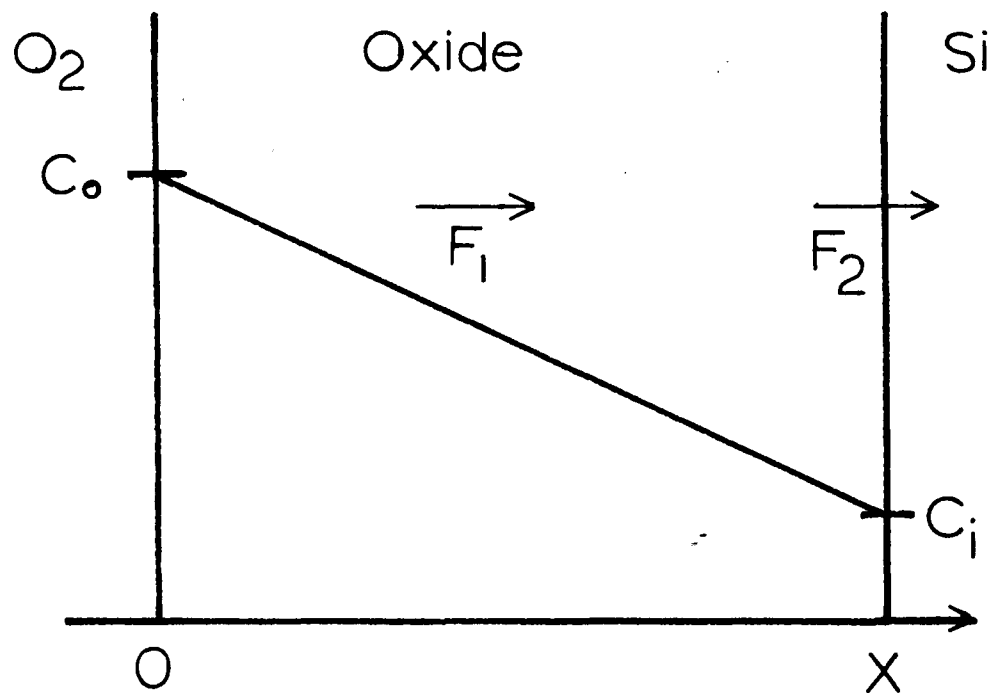


Fig. 1 Interstitial O_2 concentration profile in Deal and Grove model.

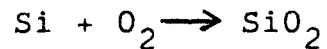
Thus the diffusion flux of the oxidizing species, is given by Fick's first law,

$$F_1 = D \frac{\Delta C}{\Delta X} ,$$

since the flux is everywhere the same. This assumption was shown to be valid by the experimental work of Deal and Grove, and other researchers.

2. The concentration of oxidizing species at the SiO_2 outer surface (C_o) is equal to its solid solubility. (The solubility of O_2 in bulk SiO_2 had previously been determined along with its diffusion constant by Norton (10))

3. The rate of the reaction



occurring at the Si - SiO_2 interface is proportional to the concentration of the oxidizing species there. Stated mathematically,

$$F_2 = KC_i$$

where F_2 = flux of reacting O_2 , C_i = concentration of O_2 at Si- SiO_2 interface.

The assumption of steady state (no. 1) also implies that

$$F_1 = F_2$$

Therefore

$$F = D \frac{C_o - C_i}{X} = KC_i \quad .$$

Eliminating C_i ,

$$F = \frac{C_o}{1/k + x/D}$$

and since the flux is related to the growth rate by

$$F = N \frac{dx}{dt}$$

(where N = number of O_2 molecules incorporated into a unit volume of SiO_2), we have

$$\frac{dx}{dt} = \frac{C_o}{N} \frac{1}{1/k + x/D} \quad ,$$

whose solution is

$$t = \left(\frac{N}{2DC_o}\right) X^2 + \left(\frac{N}{kC_o}\right) X + t_o \quad ,$$

where t_o is an integration constant.

This equation is of the form

$$t = a_o + a_1 X + a_2 X^2$$

or

$$x = \frac{-a_1 + \sqrt{a_1^2 + 4 a_2 (t - a_o)}}{2a_2}$$

2.2 Growth Convergence

If two samples with different SiO_2 thicknesses x_1 and

x_2 are reoxidized together for a time t , and are assumed to obey the oxidation equation with the same a_1 and a_2 values, then

$$x_1 = \frac{-a_1 + \sqrt{a_1^2 + 4a_2(t-t_1)}}{2a_2}$$

$$x_2 = \frac{-a_1 + \sqrt{a_1^2 + 4a_2(t-t_2)}}{2a_2}$$

Therefore, the difference in thickness between the two layers is

$$\Delta \equiv x_1 - x_2 = \frac{\{a_1^2 + 4a_2(t-t_1)\}^{1/2} - \{a_1^2 + 4a_2(t-t_2)\}^{1/2}}{2a_2}$$

squaring both sides, this becomes

$$\Delta^2 = \frac{2a_1^2 + 4a_2(t-t_1) + 4a_2(t-t_2)}{4a_2^2}$$

$$- \frac{1}{2a_2^2} \left[\{a_1^2 + 4a_2(t-t_1)\} \{a_1^2 + 4a_2(t-t_2)\} \right]^{1/2}$$

For small Δ ,

$$\Delta^2 \approx \frac{(t_1 - t_2)^2}{a_1^2 + 4a_2 \frac{t_1 + t_2}{2}}$$

or,

$$\Delta^2 \approx \frac{(t_1 - t_2)^2}{a_1^2 - 2a_2(t_1 + t_2)} \cdot \frac{1}{1 + \frac{4a_2 t}{a_1^2 - 2a_2(t_1 + t_2)}}$$

or

$$\Delta \approx \Delta_0 \{1 + t/\tau\}^{-1/2}$$

where $\Delta_0 = \Delta(t = 0) = x_1(0) - x_2(0)$,

$$= \frac{a_1^2 - 2a_2(t_1 + t_2)}{4a_2}$$

Since,

$$t_1 = -a_2 x_1^2(0) - a_1 x_1(0)$$

$$t_2 = -a_2 x_2^2(0) - a_1 x_2(0)$$

$$\tau = \frac{a_1^2 + 2a_2 \left[a_2 \{x_1^2(0) + x_2^2(0)\} + a_1 \{x_1(0) + x_2(0)\} \right]}{4a_2}$$

Let

$$x_a \equiv \frac{x_1(0) + x_2(0)}{2}$$

Then,

$$\tau \approx \frac{(a_1 + 2a_2 x_a)^2}{4a_2}$$

For $\Delta_0/x_a \leq 25\%$, and $x_a \leq 100 a_1/a_2$

(For the purposes of this paper we are concerned with values of x_a on the same order of magnitude as a_1/a_2 .)

These approximations for $\Delta(t)$ are accurate to better than 0.25%.

3.0 EXPERIMENTAL DETAILS

3.1 Sample Processing

Prior to the first oxidation each wafer was subjected to a cleaning procedure as described in Appendix A. The oxidations were carried out in a Lindberg three zone resistance heated furnace with a single-walled quartz tube and mullite liner. The temperatures quoted were based on thermocouple (Pt-Pt-Rd 13%) readings. All oxidations were performed in dry O_2 using gases from Air Products and Chemicals Inc., Allentown, Pa. passed through Matheson molecular sieve filters (model 451).

The ellipsometric measurements were made on a Rudolph Ellipsometer (model 432A4) by an averaging technique and measuring P and A values (The angles of the polarizer and analyzer, respectively) in two quadrants. All thickness measurements were reproducible to approximately $\pm 10 \text{ \AA}$ except where noted. Error limits on some samples which had a noticeable color gradient (indicating a thickness gradient across the wafer) were determined by making several measurements across the wafer. A computer program (6) was used to perform the data reduction.

Between oxidations the samples were stored in a desiccator containing silica gel under partial vacuum ($\sim .5 \text{ atm}$). Before placing the samples in the furnace, N_2 was blown across the surface to remove any dust.

3.2 Run A

After subjecting 10 half-wafers ($2.0-3.5\ \Omega\text{-cm.}$, phosphorus-doped [n-type], 10 mils thick, 1.5" diameter, chem-mechanically polished $\langle 100 \rangle$ surface) to the cleaning procedure, 5 were oxidized at 1125°C for one hour with a O_2 gas flow of 500 cc/min and 5 were oxidized at 925°C (O_2 flow 300 cc/min) for 810 minutes.

The samples were then reoxidized for various times in pairs (one from each group of 5) at 925°C with a flow rate of O_2 of 300 cc/min, and ellipsometric measurements made.

3.3 Run B

Ten half wafers ($8-12\ \Omega\text{-cm}$, P-doped [n-type], 10 mils, 1.75" diameter, chem-mechanically polished $\langle 100 \rangle$ surface) were cleaned and oxidized at 1125°C in dry O_2 (500 cc/min) for one hour, then reoxidized at 925°C (300 cc/min O_2) for various times. Measurements were taken as before.

3.4 Run C

Sixteen half-wafers ($8-12\ \Omega\text{-cm}$, P-doped, [n-type], 12-14 mils thick, 1.75" diameter, chem-mechanically polished $\langle 100 \rangle$ surface) were prepared as before.

Eight were oxidized at 1200°C (750 cc/min O_2) for 34 min, and eight were oxidized at 1250°C (750 cc/min O_2)

for 23 min. All were reoxidized at 925°C (300 cc/min O₂), and measurements made on the ellipsometer.

4.0 EXPERIMENTAL RESULTS

4.1 Run A

Run A was performed in an attempt to verify unambiguously the dependence of growth rate on the previous oxidation treatment.

Ellipsometric determinations of thickness were made assuming n_s (index of refraction of the Si substrate) = $4.0517 - i .028$, n_f (index of refraction of the oxide film) = 1.455 (3) and rounded to the nearest 5 \AA to eliminate insignificant precision in the computer answers ($.1\text{\AA}$).

The deviation of growth rates was shown by subtracting the thickness of the "cold" (925°C - 925°C) oxides from that of the "hot" (1125 - 925°C) oxides to obtain a thickness difference (see Fig. 2). It is seen that (t) increases with time while the theoretical expression for (t) set forth in section 2.2 (also shown in Fig. 2) decreases with time.

The thickness data were also fit to a curve of the form

$$t = a_0 + a_1x + a_2x^2$$

by a least mean square procedure using a computer routine written by the author. The resulting a_1 and a_2 values and their confidence limits are summarized in Table 1, along with values obtained from references (2) and (4) for similar conditions. For an explanation of the meaning of "confidence level" see Appendix B.

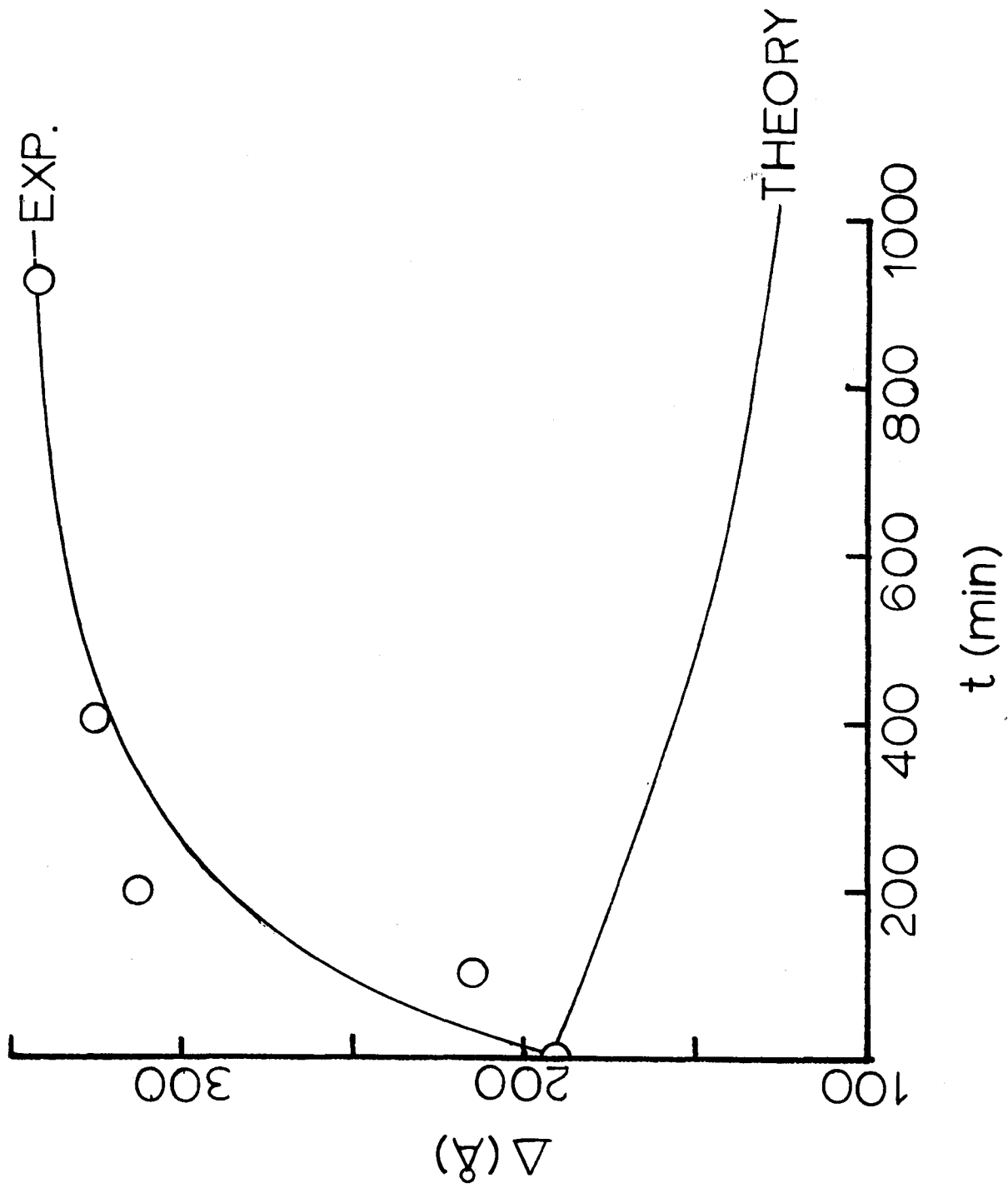


Fig. 2 Variation of theoretical and experimental thickness difference (Δ) with time.

Table 1. Summary of a_1 and a_2 values found for growth of samples in Run A.

	<u>50% Confidence</u>	<u>90% Confidence</u>
"Cold"	$a_1 = 0.32 \text{ min}/\text{\AA} \pm 0.16 \text{ min}/\text{\AA}$	$\pm 1. \text{ min}/\text{\AA}$
	$a_2 = 1.8 \times 10^{-4} \text{ min}/\text{\AA}^2 \pm 4 \times 10^{-5} \text{ min}/\text{\AA}^2$	$\pm 2.5 \times 10^{-4} \text{ min}/\text{\AA}^2$
"Hot"	$a_1 = - .91 \text{ min}/\text{\AA} \pm .24 \text{ min}/\text{\AA}$	$\pm 0.86 \text{ min}/\text{\AA}$
	$a_2 = 4.05 \times 10^{-4} \text{ min}/\text{\AA}^2 \pm 5.5 \times 10^{-5} \text{ min}/\text{\AA}^2$	$\pm 2.0 \times 10^{-4} \text{ min}/\text{\AA}^2$
5 Ref. 2	$a_1 = 0.29 \text{ min}/\text{\AA}$ (at 920°C)	
	$a_2 = 1.2 \times 10^{-4} \text{ min}/\text{\AA}^2$	
Ref. 4	$a_1 = 0.19 \text{ min}/\text{\AA}$ (at 927°C)	
	$a_2 = 2.3 \times 10^{-4} \text{ min}/\text{\AA}^2$	

In addition, plots were made of x^2 VS $t - a_1 \cdot (x - x(0))$ ($t = 0$ being the start of the reoxidation) in order to obtain linear growth curves. (See Figures 3 and 4) demonstrating the agreement between the experimental data and the fitted quadratic, growth equation.

While the a_1 and a_2 numbers obtained for the "cold" oxides agree favorably with those reported in references (2) and (4), note that the value of a_1 for the "hot" oxides is negative, an impossibility under the theory of Deal and Grove for Si oxidation rates.

4.2 Run B

Since the determination of a_1 and a_2 was somewhat imprecise due to the small number of points used in the LMS procedure, another 1125-925°C run was performed using a larger number of samples (ten as opposed to five for Run a). It was deemed unnecessary to repeat the 925-925°C experiment because of the general agreement between our data and published values for the growth constants at this temperature.

In this case, also, the least mean square routine yielded a negative a_1 , as can be seen in Table 2.

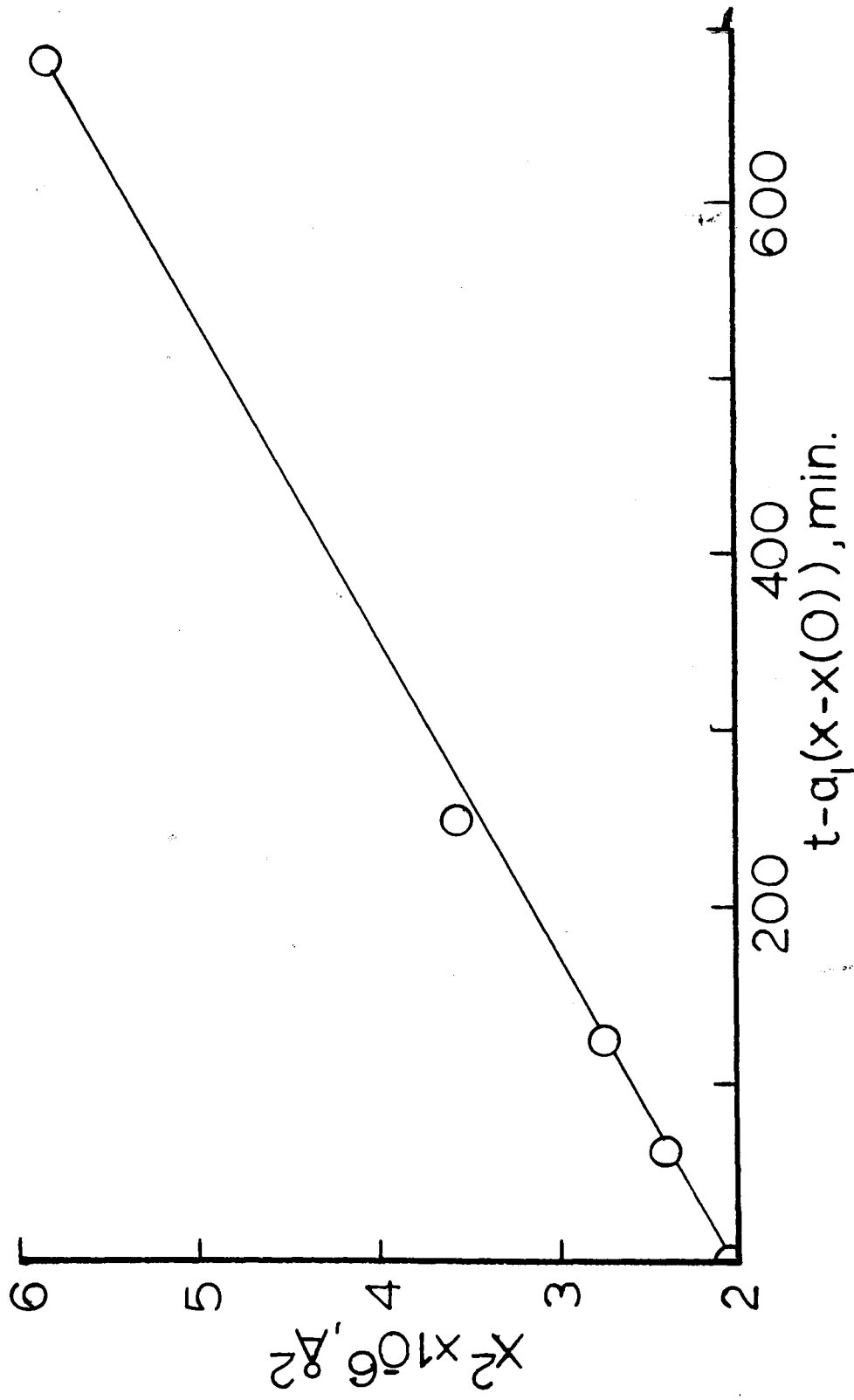


Fig. 3 Variation of thickness of "cold" oxides of Run A with reoxidation time.

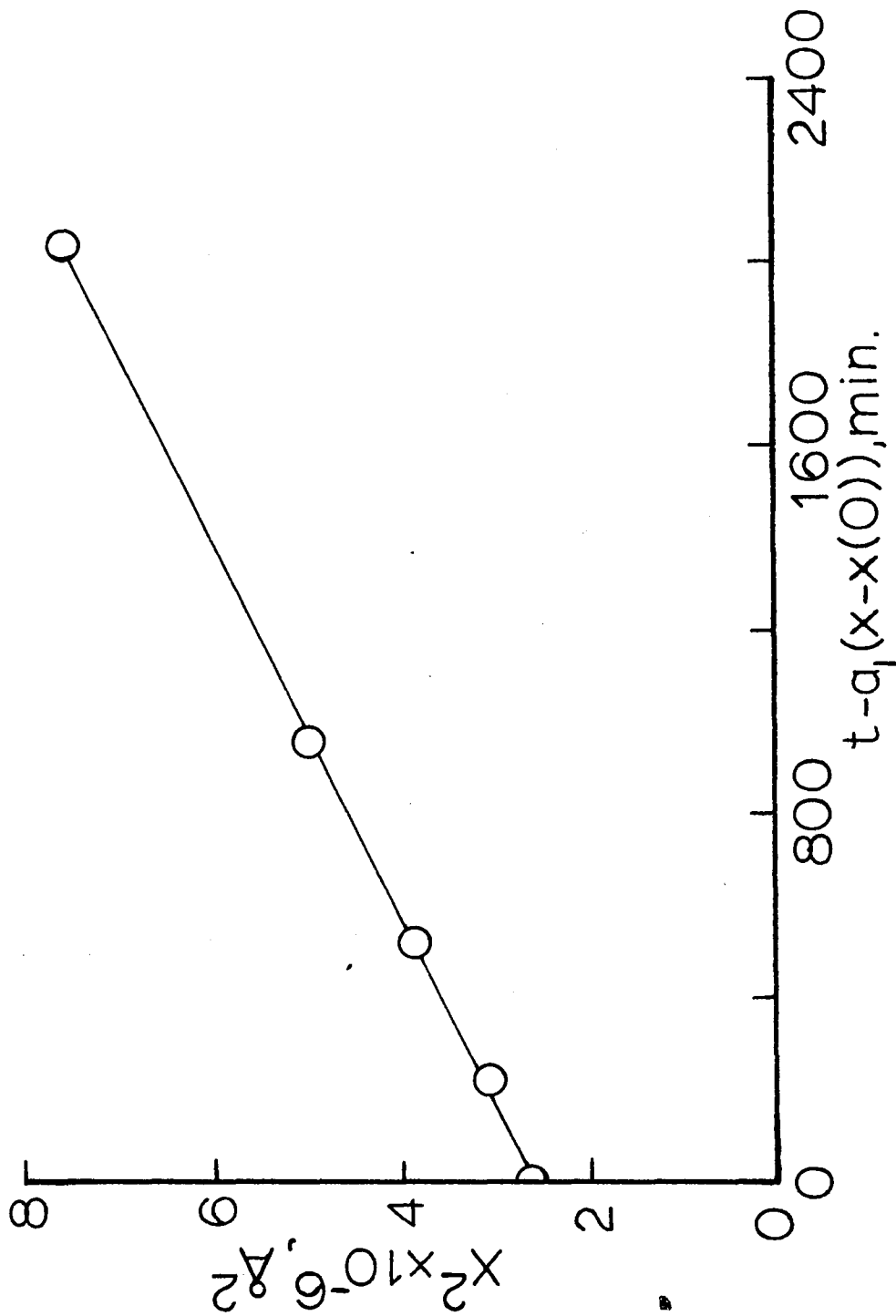


Fig. 4 Variation of thickness of "hot" oxides of Run A with reoxidation time.

Table 2. Summary of a_1 and a_2 values found for growth of samples in Run B.

	<u>50% Confidence</u>	<u>90% Confidence</u>
$a_1 = -0.21 \text{ min}/\text{Å} \pm 0.04 \text{ min}/\text{Å}$		$\pm 0.10 \text{ min}/\text{Å}$
$a_2 = 2.74 \times 10^{-4} \text{ min}/\text{Å}^2 \pm 9 \times 10^{-6} \text{ min}/\text{Å}^2$		$\pm 2.4 \times 10^{-5} \text{ min}/\text{Å}^2$

The quadratic curve provided an excellent fit to the thickness data (see Fig. 5), except for the last point, which was considered an outlier, and eliminated from the set of data points used for the binomial regression.

As seen in Table 2, the value of a_1 is negative inside the 90% confidence interval. Computation proved it to be negative to a 99.4% confidence level.

4.3 Run C

Run C was performed in order to see the effect of a first oxidation at higher than 1125°C prior to the 925°C reoxidation.

After the 925°C oxidation color gradients were observed on several of the Si wafers, and so ellipsometric measurements were made at the middle of the slice (this was used as the thickness value) and at the color extremes (to determine error limits for the thickness).

The results of the binomial regression are shown in Table 3 and plotted along with the data points in Figure 6.

Although the results are far less precise than those of Run B, they still indicate a negative a_1 .

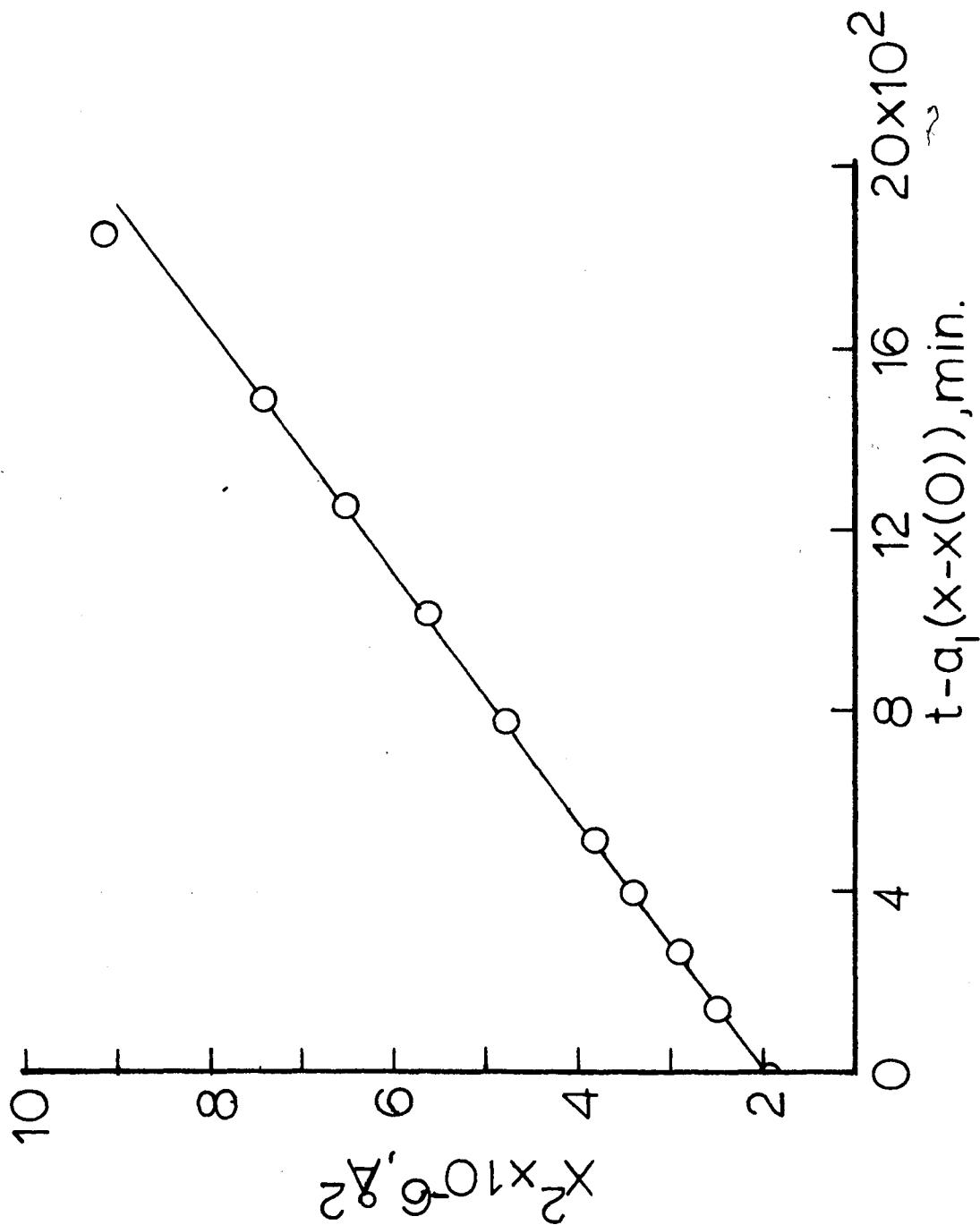


Fig. 5 Variation of thickness of oxides of Run B with reoxidation time.

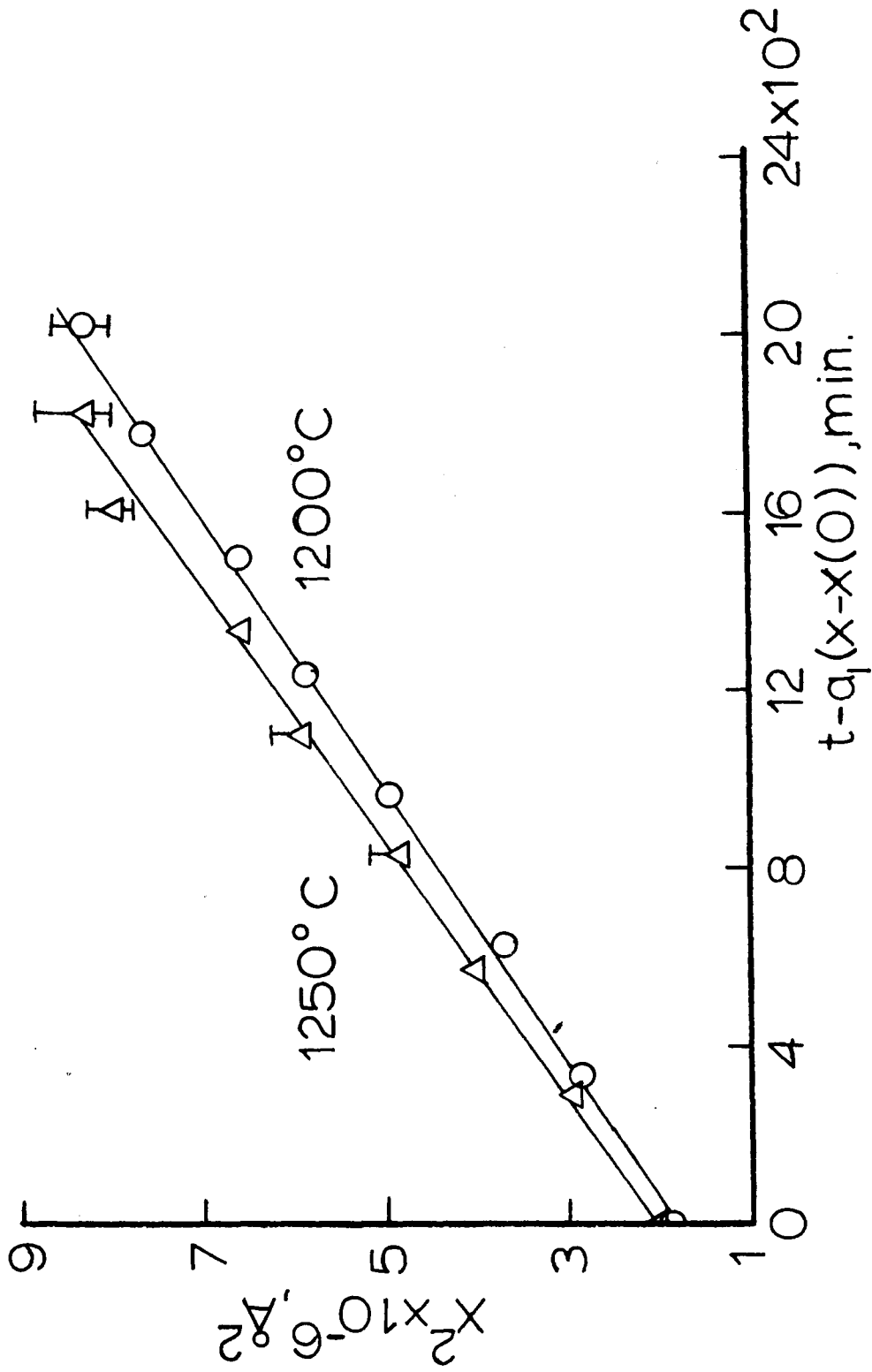


Fig. 6 Variation of thickness of oxides of Run C with reoxidation time.

Table 3. Summary of a_1 and a_2 values found for growth of samples in Run C.

	<u>First Oxidation</u>	<u>50% Confidence</u>	<u>90% Confidence</u>
1200°C	a_1	$= -0.41 \text{ min}/\text{\AA} \pm 0.12 \text{ min}/\text{\AA}$	$\pm 0.34 \text{ min}/\text{\AA}$
	a_2	$= 3.2 \times 10^{-4} \text{ min}/\text{\AA}^2 \pm 3 \times 10^{-5} \text{ min}/\text{\AA}^2$	$\pm 8 \times 10^{-5} \text{ min}/\text{\AA}^2$
1250°C	a_1	$= -0.29 \text{ min}/\text{\AA} \pm 0.14 \text{ min}/\text{\AA}$	$\pm 0.43 \text{ min}/\text{\AA}$
	a_2	$= 2.8 \times 10^{-4} \text{ min}/\text{\AA}^2 \pm 3 \times 10^{-5} \text{ min}/\text{\AA}^2$	$\pm 1.0 \times 10^{-4} \text{ min}/\text{\AA}^2$

4.4 Index of Refraction Determination

The ellipsometric program was used to determine the refractive index of the "cold" oxides of Run A and the "hot" oxides of Runs A and B. Unfortunately, the computed indices became increasingly inaccurate due to systematic errors as the thickness approached 2460\AA . (The P and A values, which are periodic functions of thickness, become very insensitive to index of refraction near $x = 0$ and $x = n \cdot 2460\text{\AA}$ [7, 8])

However, when the computed indices of refraction were plotted against oxide thickness for these samples (see Fig. 7) a pattern emerged, and it could clearly be seen that the index of the "hot" oxides was initially lower than that of the "cold" oxides and that it approached the "cold" value.

Note that the indicated refractive indices per se are not significant, but rather the difference between the indicated values for "hot" and "cold" oxides.

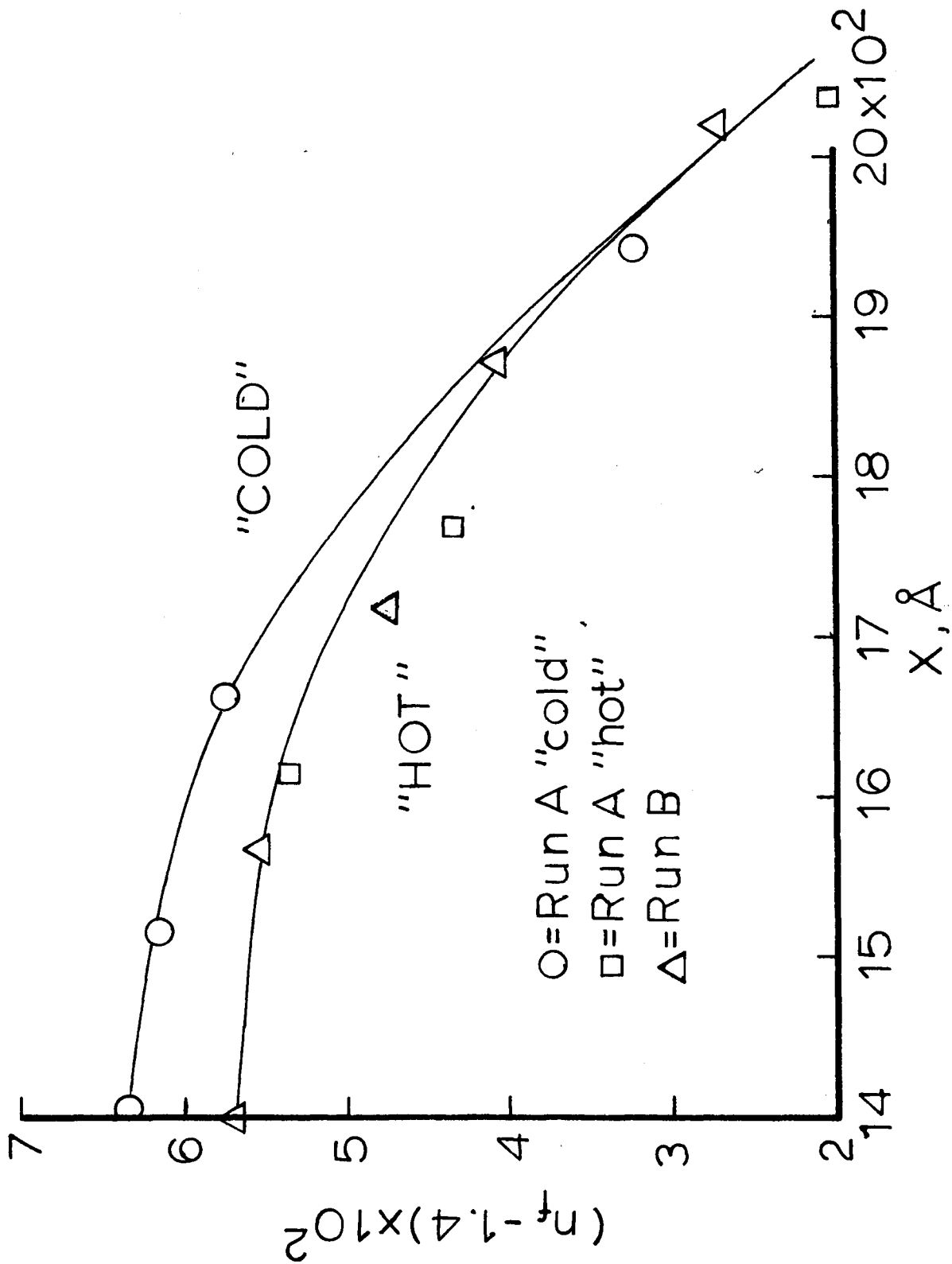


Fig. 7 Variation of observed index of refraction (n_f) of "hot" and "cold" oxides with observed thickness.

5.0 THEORETICAL CONSIDERATIONS

The fact that the "hot" oxides grew faster than the "cold" oxides in Run A implies the existence of some sort of memory inherent in the oxidation process. At first thought, it seems that a certain O_2 concentration profile could be produced in the oxide by oxidizing at 1125°C , whose effects would persist during the 925°C oxidation, thus yielding a different growth rate for a time. A simple calculation shows this idea to be erroneous, however (for the same reason that Deal and Grove were correct in assuming steady state conditions in the oxide). Suppose that all of the oxygen "stored" in the oxide during the 1125°C oxidation was converted into extra oxide during the 925°C oxidation. The extra thickness would be,

$$\Delta X \propto \frac{C_o x}{N}$$

Since $C_o = 5 \times 10^{16} \text{ cm}^{-3}$ (10), $N = 2.3 \times 10^{22} \text{ cm}^{-3}$ (2), and $x = 1500 \text{ \AA}$ for Run A,

$$\Delta X \approx 3 \times 10^{-3} \text{ \AA}$$

as compared to $\Delta - \Delta$ approaching 150 \AA (see Fig. 2) in Run A.

It would also be difficult to envision that the higher growth rate could be caused by a faster interfacial reaction, since there is no reason to expect the oxide forming at 925°C at the interface, (and hence the interface itself) to be any different because the oxide above it was

formed at a higher temperature.

The simplest hypothesis which appears to be left is that the memory is in the 1125°C oxide itself. Deal and Grove's theory implicitly assumes a homogeneous oxide, so that any inhomogeneity would cause a departure from their theory. Because SiO₂ as grown on Si is amorphous (2) a difference of structure could exist between the oxide formed at 1125°C and that formed at 925°C. Deal (5) noted a density difference between dry and steam grown oxides (2.27 gm/cm³ and 2.08 gm/cm³ respectively) and a faster growth rate of steam grown oxides than that of dry oxides when reoxidized in steam, as well as an apparently lower diffusion coefficient of phosphorus in denser oxides.

Our observation of different refractive indices for the "hot" and "cold" oxides (see Section 4.4) also supports the hypothesis that their structures (density, and/or perhaps average number of atoms per ring, etc.) are not exactly the same.

5.1 Model

Since a dissimilarity is indicated between the "hot" and "cold" SiO₂ layers, the following model is proposed (see Fig. 8). In the experiments reported here, a "cold" oxide layer grows under a "hot" layer. Classical oxidation theory (Deal and Grove) was followed, with the exceptions

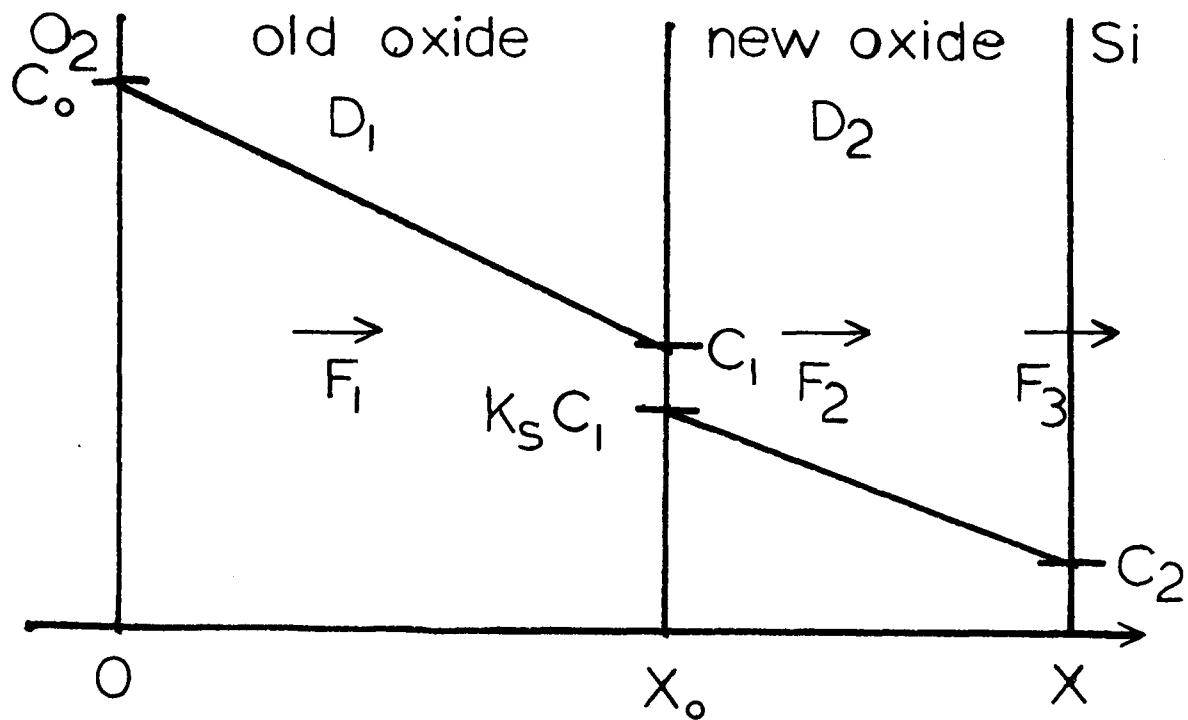


Fig. 8 Interstitial O_2 concentration profile in two-layer oxide model.

that the two oxide layers have different effective diffusion constants for O_2 , and that a segregation coefficient for O_2 exists at the interface between the two layers.

Equating the flux of O_2 in the three regions,

$$F = D_1 \frac{C_0 - C_1}{X_0} = D_2 \frac{K_s C_1 - C_2}{X - X_0} = KC_2 .$$

Eliminating C_1 and C_2 yields,

$$F = \frac{D_1 C_0}{X_0} \left\{ 1 - \frac{1}{1 + \frac{X_0 K K_s}{D_1 \left[1 + (x - x_0) (K/D_2) \right]}} \right\}$$

So,

$$N \frac{dx}{dt} = \frac{C_0 K_s K}{1 + (x - x_0) (K/D_2)} \frac{1}{1 + D_1 \left\{ 1 + (x - x_0) (K/D_2) \right\}}$$

or,

$$\frac{dx}{dt} = \frac{K_s K C_0}{N} \cdot \frac{1}{1 + \frac{(x - x_0) K}{D_2} + \frac{x_0 K_s K}{D_1}}$$

Collecting terms in x in the denominator,

$$\frac{dx}{dt} = \frac{K_s K C_0}{N} \cdot \frac{1}{1 + Kx_0 \left\{ \frac{K_s}{D_1} - \frac{1}{D_2} \right\} + \frac{K}{D_2} x}$$

whose solutions is,

$$t + t_0 = \frac{N}{K_s K C_0} \left[\left\{ 1 + \frac{Kx_0}{D_2} \left(K_s \frac{D_2}{D_1} - 1 \right) \right\} x + \frac{K}{2D_2} x^2 \right]$$

This equation is of the form,

$$t = a_0 + a_1 x + a_2 x^2$$

with,

$$a_1 = \frac{N}{K C_o} \left\{ \frac{1}{K_s} + \frac{K x_o}{D_2} \left(\frac{D_2}{D_1} - \frac{1}{K_s} \right) \right\}$$

$$a_2 = \frac{N}{2D_2 C_o} \left(\frac{1}{K_s} \right)$$

or.

$$a_1 = a_{10} \left\{ \frac{1}{K_s} + \frac{K x_o}{D_2} \left(\frac{D_2}{D_1} - \frac{1}{K_s} \right) \right\}$$

$$a_2 = a_{20} \left(\frac{1}{K_s} \right)$$

where a_{10} and a_{20} are the coefficients derived by the Deal and Grove theory with only the "cold" layer (see Section 2.1).

It is seen that a negative a_1 is indeed possible in this two layer model.

Several variants of this model are allowable:

Table 4 indicates the values for D_2/D_1 and K_s needed to fit the observed a_1 and a_2 numbers for the oxides of Runs B and C if C_o is assumed constant.

Table 4. Approximate values of the ratio of diffusion coefficients D_2/D_1 and the segregation coefficient k_s predicted by the experimental data (assuming $a_{10} = .25 \text{ min/A}$, $a_{20} = 2 \times 10^{-4} \text{ min/A}^2$ C_o constant)

<u>Run</u>	<u>Temperature</u>	<u>D_2/D_1</u>	<u>K_s</u>
B	1125°C	0.4	0.7
C	1200°C	0.5	0.6
C	1250°C	0.5	0.7

We can let $K_s = 1$ if we also allow C_o to be different in hot and cold oxides. The values for $C_o(\text{hot})/C_o(\text{cold})$ and D_2/D_1 needed under these assumptions are listed in Table 5.

Table 5. Approximate values of the ratio of the diffusion coefficients D_2/D_1 , and O_2 solid solubilities $C_o(\text{hot})/C_o(\text{cold})$ predicted by the experimental data (assuming $a_{10} = .25 \text{ min/A}$, $a_{20} = 2 \times 10^{-4} \text{ min/a}^2$, $K_s = 1$)

<u>Run</u>	<u>Temperature</u>	<u>D_2/D_1</u>	<u>$C_o(\text{hot})/C_o(\text{cold})$</u>
B	1125°C	0.3	0.7
C	1200°C	0.3	0.6
C	1250°C	0.3	0.7

Note that in either case D_2/D_1 is essentially constant for first oxidation temperatures from 1125°C to 1250°C.

Of course a mixture of the above two hypothesis is possible ($K_s \neq 1$ and $C_o(\text{hot})/C_o(\text{cold}) \neq 1$).

6.0 Conclusions

1. A "hot" oxide grown in the temperature range 1125°C-1250°C in dry oxygen grows faster than a "cold" oxide grown at 925°C in dry oxygen when both are reoxidized at 925°C in dry oxygen. The growth of these oxides during the reoxidation does not obey the oxidation theory of Deal and Grove since the difference in thickness between the "hot" and the "cold" oxide tended to increase with re-oxidation time, whereas the theory of Deal and Grove predicts a decrease (That is, the thickness of the hot oxide and that of the cold oxide should have approached each other, but they diverged).

2. The growth data for both the "hot" and the "cold" oxide can be fit to a quadratic curve of the form

$$t = a_2x^2 + a_1x + a_0$$

where t = time and x = oxide thickness. Such a quadratic growth curve was predicted by Deal and Grove. Although the values of the a_1 and a_2 coefficients found for the "cold" oxide agreed with published data, the value of a_1 for the "hot" oxides was found to be negative, whereas it is always positive in the Deal and Grove theory.

3. The model proposed here, which assumes two different layers of oxide (one formed at 1125-1250°C, one at 925°C), can explain the negative value of a_1 if the two layers have different diffusion constants for O_2 (perhaps because of a density difference).

Appendix A

Wafer Cleaning Procedure:

1. Boiling trichloroethylene
2. Boiling acetone
3. Boiling methanol
4. Boiling DIW (de-ionized water)
5. DIW rinse
6. Solution of H_2SO_4 and H_2O_2 (20%) at $150^\circ C$
7. DIW rinse
8. HF + DIW etch
9. Oxide layer grown on samples by wet oxidation at $1125^\circ C$ for one hour (300 cc/min O_2 , $95^\circ C$ H_2O)
10. HF + DIW etch

Appendix B

The Meaning of "Confidence Limit"

The least mean square procedure is based on the assumption that the random errors in experimental data are normally distributed (fall on the well-known "bell-shaped" curve). Since these random errors are unavoidable any fit to the data is necessarily not exactly precise. The values for a_1 and a_2 computed are the most probable values for the true values given these specific data. If the same experiment is repeated the next week however, different data would result, and a_1 and a_2 values would be different. How then can one say quantitatively how much accuracy a determined value has?

If the same experiment were repeated many times a distribution of a_1 and a_2 values would result and a "90% confidence interval for a_1 " could be defined as an interval (It need not center on the average value) in which 90% of the determinations of a_1 fall.

It turns out that a confidence interval can be computed given only one set of data. Then a "90% confidence interval" can be taken to mean that 90% of such experiments are expected to yield a result in this interval. (11)

REFERENCES

1. S.K. Ghandi, The Theory and Practice of Micro-electronics, John Wiley and Sons, Inc., New York, 1968, p. 139.
2. B.E. Deal and A.S. Grove, J. Appl. Phys., 36, 3770 (1965).
3. K. Vedam, et. al., J. Opt. Soc. of Amer., 59, 64 (1969).
4. E.A. Irene, J. Electrochem. Soc., 121, 1613 (1974).
5. B.E. Deal, J. Electrochem. Soc., 110, 527 (1963).
6. F.L. McCrackin, NBS Technical Note 479 (1969).
7. A.N. Saxena, J. Opt. Soc. of Amer. 55, 1061 (1965).
8. Y.J. van der Meulen, J. Electrochem. Soc., 119, 530 (1972).
9. J.R. Ligenza, and W.G. Spitzer, J. Phys. Chem. Solids 17, 196 (1960); N. Karube, et. al., Japan J. Appl. Phys., 2, 11 (1963); W.A. Pliskin and R.P. Grall, J. Electrochem. Soc., 111, 872 (1964).
10. F.J. Norton, Nature, 171, 701 (1961).
11. A.S.C. Ehrenberg, Data Reduction, Analysing and Interpreting Statistical Data, John Wiley and Sons, Inc., New York, 1975, pp. 315-318.

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