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DIFFUSION OF IMPURITIES INTO SILICON
THROUGH AN OXIDE LAYER

M. O. Thurston, J.C.C. Tsai and K. D. Kang

March 1961

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Investigation of: Diffusion of Impurities into Silicon Through
an Oxide Layer

Subject or Report: DIFFUSION OF IMPURITIES INTO SILICON
THROUGH AN OXIDE LAYER

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FOREWORD

This report was prepared by J. C. C. Tsai, K. D. Kang, and M. O. Thurston of the Electron Device Laboratory, Department of Electrical Engineering, The Ohio State University. It was prepared under a contract between The Ohio State University Research Foundation and the United States Army Signal Supply Agency, Laboratory Procurement Office, Fort Monmouth, New Jersey; Contract DA-36-039-SC-83874, File No. 19032-PM-59-93-93, "Diffusion of Impurities into Silicon Through an Oxide Layer."

Appreciation is also expressed for the contributions to this research by many other members of the laboratory staff.

ABSTRACT

Theoretical studies have been made of the diffusion of impurities into silicon through an oxide film. In one case the silicon was assumed to be initially free of oxide and to oxidize parabolically during the diffusion. In the second case the initial oxide film on the silicon was assumed to be sufficiently thick and the diffusion time sufficiently short that a linear approximation for the oxide growth could be used.

Experimental results consistent with the analysis have been obtained using the box method of D'Asaro with phosphorus, boron, and antimony as diffusants. The diffusivities in the oxide layer for these three doping agents have been determined experimentally in the temperature range from 1150 to 1350°C and for various concentrations. All diffusions were done in air.

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DIFFUSION OF IMPURITIES INTO SILICON THROUGH AN OXIDE LAYER

1.0 PURPOSE

The contractor shall make a theoretical and experimental study of the diffusion of impurities, both donors and acceptors, into silicon through an oxide layer. The theoretical and experimental investigation to be conducted under this specification shall cover the following.

a) A study to determine the mechanism of oxidation of silicon in sufficient detail to clarify the formulation of the diffusion problem. Radioactive tracer techniques in addition to other methods may be used.

b) A mathematical study of the oxide-diffusion problem taking into account the rate of increase in thickness of the oxide layer with consideration of both preoxidized and initially oxide-free silicon.

c) An experimental investigation of the validity of the mathematical results of the study specified in (b) including evaluation of the diffusion constant in the oxide and the distribution coefficient at the oxide-silicon interface. This shall be done for various important donors and acceptors at various temperatures and with various atmospheres.

d) The preparation of design charts to predict junction depth, surface concentration of impurities, resistivity and other important quantities for diffusion conditions.

2.0 PUBLICATIONS AND REPORTS

Dawon Kahng, "Phosphorus Diffusion into Silicon Through an Oxide Layer," presented as a Ph. D. Dissertation at The Ohio State University; 1959.

Ki Dong Kang, "Studies of the Masking of Boron in Fabricating Silicon P-N Junction Devices," presented as an M. Sc. Thesis at The Ohio State University; 1960.

Hsing-San Lee, "Antimony Diffusion into Silicon Through an Oxide Layer," presented as an M. Sc. Thesis at The Ohio State University; 1960.

D. Kahng and M. O. Thurston, "Diffusion of Phosphorus into Silicon Through an Oxide Layer," presented at the Fall Meeting of the Electrochemical Society; October 1959.

The following quarterly reports have been submitted:

No. 1. D. Kahng and M. O. Thurston, "Phosphorus Diffusion into Silicon Through an Oxide Layer"; May 1959.

No. 2. D. Kahng and M. O. Thurston, "Oxidation of Silicon in Steam, and Snow Plow Effect"; July 1959.

No. 3. J. C. C. Tsai and M. O. Thurston, "The Diffusion of Boron into Silicon Through Silicon Dioxide for 0.1 Per Cent Source Strength"; November 1959.

No. 4. J. Tsai and M. O. Thurston, "The Silicon Oxidation Mechanism in the Diffusion Atmosphere, and Antimony Diffusion into Silicon Through an Oxide Layer"; January 1960.

No. 5. Hsing-San Lee and M. O. Thurston, "Antimony Diffusion Into Silicon Through an Oxide Layer"; April 1960.

No. 6. J. Tsai, K. D. Kang and M. O. Thurston, "A Theoretical Study of the Simultaneous Diffusion of Two Impurities into Silicon Through an Oxide Layer, and The Diffusion of Boron Into Silicon Through Dioxide for 0.001 Per Cent Source Strength of Boron"; August 1960.

No. 7. Thurston, Pratinidhi, Fell, and Cornet, "Studies Concerning the Oxidation of Silicon"; October 1960.

3.0 FACTUAL DATA

3.1 Introduction The objectives of this research, as outlined in Section 1.0, grew out of the need for a more basic understanding of the oxide masking process used in the fabrication of silicon devices by diffusion. The masking technique has become one of the more widely used methods of producing very small or very intricate junction structures. It can be, and commonly is, used quite successfully in an empirical way without detailed knowledge of the mechanisms involved. Nevertheless, it might be anticipated that a thorough understanding of the diffusion of impurities through the oxide layer on the surface of silicon would lead to useful and novel techniques for controlling junction depths, surface concentrations, and in general the impurity distributions.

In the simplest view, one might think of overall process as consisting of two stages of diffusion: the first in the oxide layer and the second in the silicon itself. The steps in studying this process would be first to show qualitatively that this diffusion process in fact occurs: and second to elaborate the quantitative details involved.

That oxide masking is essentially a diffusion process has been verified by many experiments here and elsewhere. Evidence for this, as well as cases in which other processes dominate will be discussed later. The details of the diffusion process are in general quite complex, and only certain special cases have been studied. The complications arising from the simultaneous increase in thickness of the oxide layer during the diffusion operation will be discussed in Section 3.3.

In the experimental studies of masking and diffusion through oxides the box method of diffusion first proposed by L. A. S'Asaro has been used. Although this method has not provided the theoretical simplicity originally hoped for, it has been experimentally convenient and has been interesting in its own right. Experimental experience with the box method is presented in Section 3.3 together with the details of sample preparation, oxide measurements, junction measurements, and related matters.

The experimental results of the diffusion studies are given in Section 3.4 and supporting work on oxidation of silicon is summarized in Section 3.5.

3.2 Theory of Diffusion Through Oxides Diffusion equations for the box system were first solved for two cases: namely, the case without an initial oxide layer and the case with an initial oxide layer of thickness a_0 but with a diffusion time short enough so that the oxide growth is approximately linear with time. The applicability of the solutions for the second case was limited by the stringent condition that the initial oxide thickness must be much greater than the increase in the thickness during the diffusion. This is not usually met in practice for low temperature diffusions, say less than 1150°C in air. Therefore, another approach which will be applicable to long diffusion time for both low and high temperatures has been attempted. In addition, solutions for the simultaneous diffusion of two impurities were obtained for the case of a thick initial oxide layer and a short diffusion time. A summary of these studies is given in the following sections.

3.21 Solutions of the diffusion equations for the case of initial oxide layer on the silicon sample. In this derivation the following assumptions were made:

- a) The diffusion equations take the one dimensional form.
- b) The diffusivities of the impurity atoms in both SiO_2 and Si do not depend on the impurity concentration. Fick's law then has the following simple form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

- c) The oxide thickness increases during diffusion according to the parabolic law, that is,

$$a = (a_0^2 + \sigma^2 t)^{\frac{1}{2}} \quad (2)$$

where σ is the oxide growth constant.

- d) The reference for the coordinate systems has been taken as the silicon-oxide interface. One needs, however, two coordinate systems in establishing the problem, one for the oxide region and one for the silicon region. These two coordinate systems are related as follows:

$$x = y - \frac{\frac{1}{\sigma t^{\frac{1}{2}}}}{r} \quad (3)$$

These quantities are related as shown in Fig. 1.

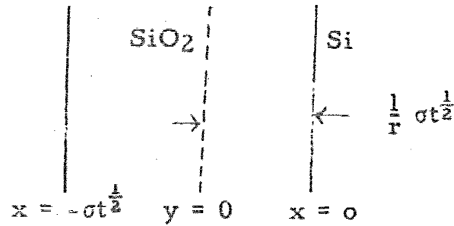


Fig. 1. The Relation Between the Coordinate Systems

e) The impurity concentrations in the source and the vapor state are constant throughout the diffusion period.

f) There is no discontinuity of the impurity concentration at the silicon-oxide interface. There is considerable evidence to indicate that this is a poor assumption! However, experiments here on the impurity distribution in silicon dioxide using the radioactive tracer technique indicate that the distribution of phosphorus across the oxide-silicon interface is continuous.

g) That oxidation takes place at the oxide surface.

Assumptions (a) and (b) simplify the mathematics involved. The assumption (c) is derived from experiment. More discussion of assumption (g) will be given in the experimental section.

The diffusion equations with initial and boundary conditions which satisfy the assumptions given above are

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} \quad (4)$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial y^2} \quad (5)$$

$$C_2(y, 0) = 0 \quad (6)$$

$$C_1(-\sigma t^{\frac{1}{2}}, t) = C_0 \quad (7)$$

$$C_2(\infty, t) = 0 \quad (8)$$

$$C_1(0, t) = C_2\left(\frac{1}{r} \sigma t^{\frac{1}{2}}, t\right) \quad (9)$$

$$-D_1 \left[\frac{\partial C_1}{\partial x} \right]_{x=0} = \left[-D_2 \frac{\partial C_2}{\partial y} - \frac{\sigma}{2r} \frac{1}{t^{\frac{1}{2}}} C_2 \right]_{y=\frac{1}{r} \sigma t^{\frac{1}{2}}} \quad (10)$$

The solution of the Eqs. (4) and (5) with the boundary conditions satisfied take the form

$$C_1(x, t) = \frac{C_0}{1 + \eta RF(h)} \left[1 - RF(h) \operatorname{erf} \frac{x}{2(D_1 t)^{\frac{1}{2}}} \right]$$

$$C_2(y, t) = \frac{1}{\lambda} \frac{C_0}{1 + \eta RF(h)} \operatorname{erfc} \frac{y}{2(D_2 t)^{\frac{1}{2}}}$$

If the assumption (g) is replaced by an assumption that oxidation takes place at the oxide-silicon interface and the coordinate origin is changed to the oxide surface, the solutions of a set of diffusion equations similar to the above equations will be

$$C_1 = C_0 \left[1 - \frac{RF(h)}{e^{-\rho^2} + \eta RF(h)} \operatorname{erf} \frac{x}{2(D_1 t)^{\frac{1}{2}}} \right] \quad (13)$$

$$C_2(y, t) = \frac{1}{\lambda} \frac{e^{-\rho^2} C_0}{e^{-\rho^2} + \eta RF(h)} \operatorname{erfc} \frac{y}{2(D_2 t)^{\frac{1}{2}}} \quad (14)$$

One may view the above two sets of solutions as the two extreme cases, one is for the case of oxidation at the oxide surface while the other is for oxidation at the oxide-silicon interface. However, in an actual diffusion the oxidation may take place at an intermediate position, depending on the temperature and the oxygen pressure. For the diffusion of phosphorus, experimental results indicated that the oxidation most likely takes place at the oxide surface.

3.22 Solutions for the diffusion equations for the case where there is an initial oxide layer on the silicon surface and linear oxide growth. In this derivation all the assumptions in Section 4.1 remain the same except that the oxide growth rate follows a linear law instead of the parabolic law, that is,

$$a = a_0 + bt \quad (15)$$

This assumption imposes a limit on the oxide layer thickness after diffusion to be $a_0^2 \gg \sigma^2 t$. In actual diffusion in air this condition is often violated. However, for diffusion in some special gas atmospheres this derivation can be used. The coordinate system is shown in Fig. 1-a.

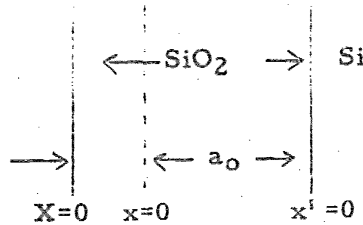


Fig. 1-a. The Coordinate System for Diffusion Through an Oxide Layer

It is assumed that the oxide layer is semi-infinite in extent. Then the diffusion equation in the region $x = 0$ to $x = -bt$ is solved under boundary conditions (Eqs. (17) and (18)).

$$\frac{\partial C_g}{\partial t} = D_1 \frac{\partial^2 C_g}{\partial x^2} \quad (16)$$

$$C_g(-bt, t) = C_0 \quad (17)$$

$$C_g(\infty, t) = 0 \quad (18)$$

$$X = x + bt \quad (19)$$

The solution is of the form

$$C_g(X, t) = \frac{C_0}{2} \left[\operatorname{erfc} \frac{X-bt}{2(D_1 t)^{\frac{1}{2}}} + e^{\frac{b}{D_1} X} \operatorname{erfc} \frac{X+bt}{2(D_1 t)^{\frac{1}{2}}} \right] \quad (20)$$

Then it is assumed that the diffusion for the rest of the system takes place from $x = 0$ to $x = a_0$, a region of SiO_2 , and from $x = a_0$ to $x = \infty$, in a region of Si. However, the surface concentration at $X = bt$ varies with time as

$$C_{10}(t) = C_g(-a_0, t) = \frac{C_0}{2} \left[1 + e^{\frac{b^2 t}{D_1}} \operatorname{erfc} b \left(\frac{t}{D_1} \right)^{\frac{1}{2}} \right] \quad (21)$$

Finally, by Duhamel's method one will get (Duhamel's method can be interpreted as the convolution integral which gives the response of a system as the integral of the product of the excitation function and time derivative of the unit step response function of the system. For a more detailed discussion see Quarterly Report No. 5).

$$C_1(x', t) = \frac{C_0}{2} \left\{ \operatorname{erfc} \frac{a_0 + x'}{2(D_1 t)^{\frac{1}{2}}} + e^{\frac{b}{D_1} (a_0 + x' + bt)} \operatorname{erfc} \frac{a_0 + x' + 2bt}{2(D_1 t)^{\frac{1}{2}}} \right. \\ \left. - \frac{R-1}{R+1} \left[\operatorname{erfc} \frac{a_0 - x'}{2(D_1 t)^{\frac{1}{2}}} + e^{\frac{b}{D_1} (a_0 - x' + bt)} \operatorname{erfc} \frac{a_0 - x' + 2bt}{2(D_1 t)^{\frac{1}{2}}} \right] \right\} \quad (22)$$

$$C_2(x', t) = \frac{C_0}{R+1} \left[\operatorname{erfc} \frac{R a_0 + x'}{2(D_2 t)^{\frac{1}{2}}} \right. \\ \left. + e^{\frac{b(R a_0 + x' + bt)}{D_1 D_2}} \operatorname{erfc} \left(\frac{R a_0 + x'}{2(D_2 t)^{\frac{1}{2}}} + b \sqrt{\frac{t}{D_1}} \right) \right] \quad (23)$$

Eq. (20) differs from the Eq. (73) of Quarterly Report No. 1, page 26, only in the replacement of x' by $X - (a_0 + bt)$. The x_s' of Eqs. (73), (75), and (76) should be x' for the coordinate system shown in Fig. 2 of this report). Since Eq. (22) was derived by assuming a reflection from the oxide-silicon interface, this equation cannot be applied to the region $x' < -a_0$, that is, the oxide layer grown during diffusion. The solution for the region $x' < -a_0$ (or $x < 0$) is given by Eq. (20) upon replacing x' by $x - a_0$. If the arguments of the complementary functions are greater than 2, one can use the approximation

$$\operatorname{erfc} y \approx \frac{e^{-y^2}}{\sqrt{\pi} y} \quad (24)$$

$$C_2(x', t) \approx \frac{C_0}{R+1} \left[1 + \frac{Ra_0 + x'}{R(2a - a_0) + x'} \right] \operatorname{erfc} \frac{Ra_0 + x'}{2(D_2 t)^{\frac{1}{2}}} \quad (25)$$

at $x' = 0$

$$C_2(0, t) = \frac{C_0}{R+1} \left[1 + \frac{a_0}{2a - a_0} \right] \operatorname{erfc} \frac{a_0}{2\sqrt{D_1 t}} \quad (26)$$

or

$$C_2(0, t) = \frac{C_0}{R+1} \left[1 + \frac{a_0}{a} \right] \operatorname{erfc} \frac{a_0}{2(D_1 t)^{\frac{1}{2}}} \quad (27)$$

if $a \approx a_0$. Equation (27) was used for determining D_1 for most of the cases. Several corrections were obtained for the particular cases concerned; however, these corrections would modify the D_1 obtained from Eq. (27) only slightly. Owing to the experimental difficulties in measuring the surface resistances and the junction depths for shallow junctions, the applicability of Eq. (27) is limited to high temperature and short time diffusions in air. An attempt to remove this restriction has been tried, but no definite result was found. This is discussed in the following section.

3.23 Solutions for the diffusion equations for the case where there is an initial oxide layer on the silicon surface and the oxide growth is parabolic. In Dr. Kahng's original derivation he assumed that the oxide layer growing during diffusion can be approximated by a linear relationship,

$$a = a_0 + bt. \quad (28)$$

This approximation is limited in application to short time diffusions, that is, when a_0 remains larger than bt . However, in an actual diffusion one often has the opposite case, $a \gg a_0$. For instance, if one wants to determine D_1 at 1000°C for phosphorus, the final oxide layer may be six times thicker than a_0 before the silicon surface is converted. The linear approximation for the oxidation during diffusion is thus violated. Figure 2 shows the relationship between the oxide layer thickness and the diffusion time obtained from phosphorus diffusion at

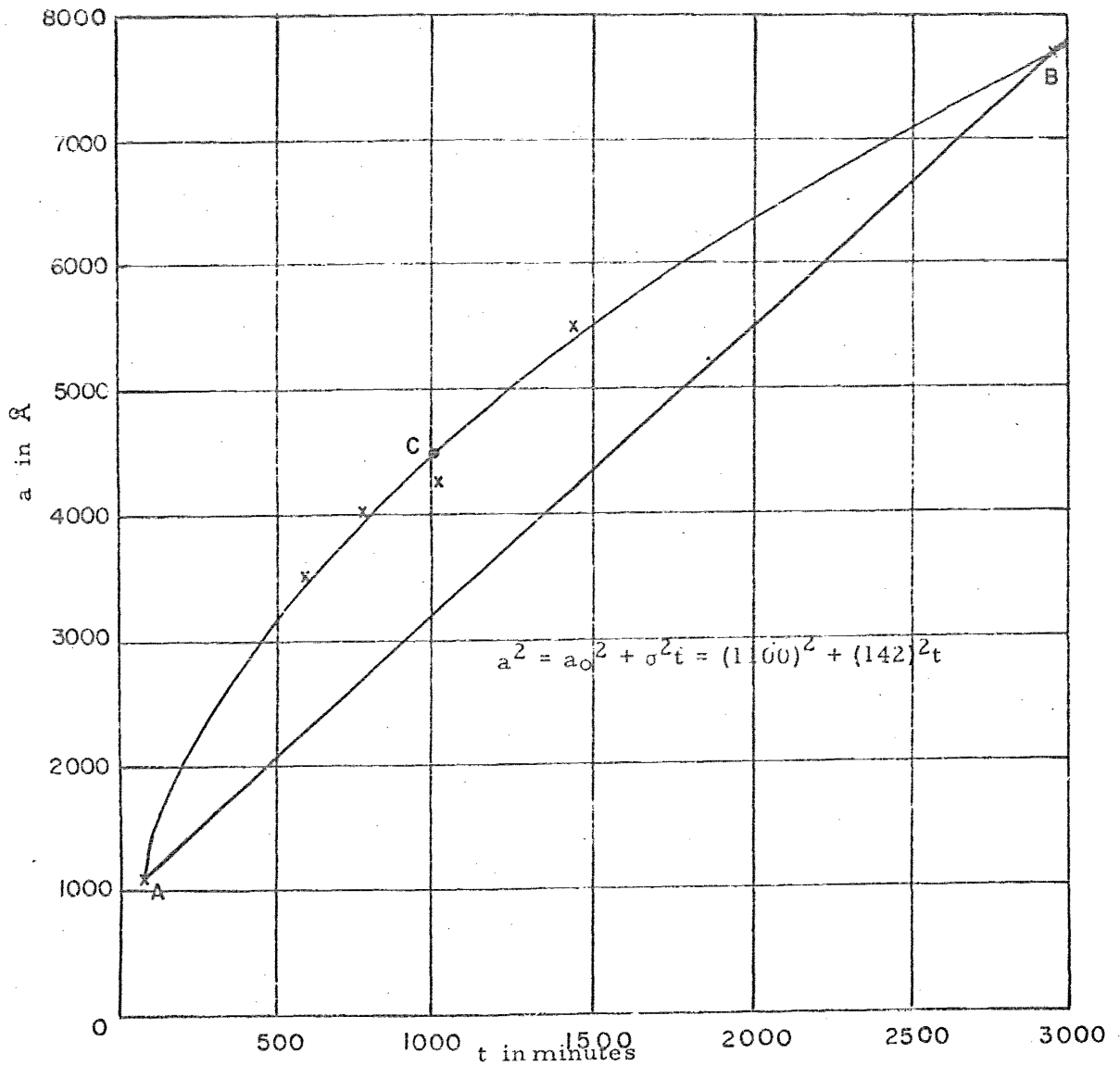


Fig. 2. Oxide Layer Thickness Versus Diffusion Time

1005°C. Point A represents the initial oxide layer thickness. Point B represents the thickness after a diffusion for 49 hours and 27 minutes. From this curve it is easy to see that the linear approximation to the true oxidation is quite poor for this case. The calculated value of D_1 based on Eq. (27) is $4.3 \times 10^{-14} \text{ cm}^2/\text{sec}$. This value is too high for phosphorus at that temperature. Several other diffusion times have been tried, but reliable junction depth measurements could not be obtained. The diffusion times were 10, 13, 17, and 24 hours. This indicates that one cannot use Kahng's formula to determine the diffusion constant of impurities in SiO_2 at a temperature lower than, say, 1100°C.

It is found experimentally that the oxidation during diffusion follows closely a parabolic law of the form

$$a^2 = a_0^2 + \sigma^2 t \quad (29)$$

If one uses this relationship to set up the differential equation for diffusion with a moving boundary, one may proceed as follows. The coordinate systems are shown in Fig. 3.

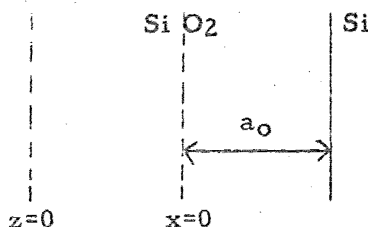


Fig. 3. The Coordinate Systems Used in Deriving the Diffusion Equation

Fick's law with the fixed coordinate reference is

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial x^2} \quad (30)$$

The moving SiO_2 surface is related to the x-coordinate axis by

$$z = x - a_0 + (a_0^2 + \sigma^2 t)^{\frac{1}{2}} \quad (31)$$

(It is assumed that oxide layer grows at the oxide surface).

After change of variable one will have

$$\frac{\partial^2 C}{\partial z^2} - \frac{\sigma^2}{2D_1(a_0^2 + \sigma^2 t)^{\frac{1}{2}}} \frac{\partial C}{\partial z} - \frac{1}{D_1} \frac{\partial C}{\partial t} = 0. \quad (32)$$

This can be reduced to a simpler form by the following transformation.*
Let

$$\Theta = \int_0^z \alpha \, dz \quad (33)$$

where

$$\alpha = \frac{-\sigma^2}{4D_1(a_0^2 + \sigma^2 t)^{\frac{1}{2}}} \quad (34)$$

$$\text{then let } C' = e^{\Theta} C. \quad (35)$$

Substitution of Eq. (35) into Eq. (32) yields

$$\frac{\partial^2 C'}{\partial z^2} - \frac{1}{D_1} \frac{\partial C'}{\partial t} - \frac{\sigma^4 C'}{16D_1^2(a_0^2 + \sigma^2 t)} + \frac{\sigma^4 z C'}{8D_1^2(a_0^2 + \sigma^2 t)^{3/2}} = 0. \quad (36)$$

One can rather easily find a particular solution of Eq. (36) of the form

$$C_p' = e^{\frac{-\sigma^2 z}{4D_1(a_0^2 + \sigma^2 t)^{\frac{1}{2}}}} \quad (37)$$

This gives $C = \text{constant}$. This one may consider as the steady state case, that is, when there is no concentration gradient inside the oxide layer. There is no simple method to find the general solution of this parabolic form. However, the form of the last term of Eq. (36) suggests the use of a series of the following type as a trial solution.

$$C'(z, t) = \sum_{n=0}^{\infty} b_n(t) \frac{z^n}{(a_0^2 + \sigma^2 t)^n} \quad (38)$$

Substituting Eq. (38) into Eq. (36) leads to a recursion relation for the coefficients $b_n(t)$.

*A. R. Forsyth, "Theory of Differential Equations," Sec. 206, p. 97, Vol. 6.

$$b_{n+2}(t) = \left\{ \frac{1}{(n+1)(n+2)} - \frac{\sigma^2}{D_1} \left(n - \frac{\sigma^2}{16D_1} \right) (a_0^2 + \sigma^2 t) b_n(t) \right. \\ \left. - \frac{\sigma^4}{8D_1^2} (a_0^2 + \sigma^2 t)^{3/2} b_{n-1}(t) + \frac{(a_0^2 + \sigma^2 t)^2}{D_1} b_n'(t) \right\} . \quad (39)$$

Then the solution for $C(z, t)$ will be

$$C(z, t) = e^{-\frac{\sigma^2 z}{4D_1(a_0^2 + \sigma^2 t)^{1/2}}} \sum b_n(t) \frac{z^n}{(a_0^2 + \sigma^2 t)^n} . \quad (40)$$

One can find $b_0(t)$ by applying the boundary condition that

$$C(0, t) = C_0 = b_0(t) . \quad (48)$$

Thus

$$b_0'(t) = 0 \quad (49)$$

and

$$b_2(t) = \frac{\sigma^4}{32D_1^2} (a_0^2 + \sigma^2 t) C_0 . \quad (50)$$

The other unknown is $b_1(t)$. It can be found if one knows

$$\left. \frac{\partial C}{\partial z} \right|_{z=0} = \frac{\sigma^2}{4D_1(a_0^2 + \sigma^2 t)^{1/2}} b_0(t) + b_1(t) \frac{1}{(a_0^2 + \sigma^2 t)} . \quad (51)$$

From the physical set-up of the closed box diffusion system it is very

hard to determine $\left. \frac{\partial C}{\partial z} \right|_{z=0}$. Physically $-D_1 \left. \frac{\partial C}{\partial z} \right|_{z=0}$ represents the flow of the impurity atoms into SiO_2 . However, if one can find the distribution of impurity in silicon dioxide experimentally, one can

find the slope of this distribution curve at $z = 0$ as a function of time. A solution of this differential equation is thus found for the oxide region. Then by applying the boundary condition at the silicon-silicon oxide interface to the solution of the diffusion equation in the silicon region one can solve the moving boundary problem and D_1 may be determined. If one considers only the case where z varies from zero to $(a_0^2 + \sigma^2 t)^{\frac{1}{2}}$, that is, from the oxide surface to the silicon-oxide interface, there is no question that this series expansion is convergent. This is true because the assumed form of solution is a convergent series if the

coefficients are convergent. If $\left. \frac{\partial C}{\partial z} \right|_{z=0}$ is determined experimentally,

$b_1(t)$ will surely be a convergent function of time. Actually, one can

even guess the change of $\left. \frac{\partial C}{\partial z} \right|_{z=0}$ from the physical picture of diffu-

sion. At $t = 0$, $\left. \frac{\partial C}{\partial z} \right|_{z=0}$ will be very large, because at the interface

there is a big change in impurity concentration. When t becomes

large $\left. \frac{\partial C}{\partial z} \right|_{z=0}$ will be small and finally go to zero as t goes to

infinity. However, this series solution may not be applicable to the case for which the oxide layer is considered to be of semi-infinite extent.

Since this diffusion equation is not solved, the above discussion gives only a plausible avenue for further study. Other methods for determining D_1 from data obtained during low temperature diffusions have been considered.

As shown in Fig. 2, the assumed linear function for the oxide layer thickness deviates from the parabola too much. However, one may select a straight line portion from the curve shown, for instance between points C and B. Then considering point C as the time for the initial oxide layer, the diffusion time is CB of Fig. 2. Since C_{N0} is independent of t , while C_{ox} can be found experimentally by doing several long time diffusions, one can use Kahng's Eq. (85) to calculate D_1 . There is a question, however, whether the surface layer will be converted for such a thick a_0 and a diffusion time t_{BC} . This has to be answered experimentally. Experiments at 1005°C for 3 per cent phosphorus were not successful. Diffusion times of 10, 13, 17, 24 and 49 hours were tried, and only the last one gave a measurable

junction depth for $a_0 = 1100\text{\AA}$.

Another possible method of measuring D_1 at low temperature depends on reducing the oxidation rate during diffusion by filling the capsule with a mixture of air and an inert gas. Several experiments have been conducted with boron as diffusant in a helium atmosphere. The oxidation rate could be reduced. Further investigations are in progress.

3.3 Experimental Methods

3.31 Principles and Techniques of the Box Method of Diffusion

The box method of diffusion, developed by D'Asaro (ref. 2), was selected at the outset of these experiments because it appeared to offer independent control of surface concentration and temperature. The essential part of the technique is to place the test samples and a diffusant source consisting of the impurity oxide dissolved in SiO_2 together into a rather tightly closed container. An oxidizing atmosphere is used, and the diffusant in the source may be expected to come to equilibrium with the diffusant in the surface of the oxide on the sample after the system is raised to a stable high temperature. The principal advantage of the method, provided the surface area of the source is much greater than the surface area of the sample, was presumed to be an equilibrium surface concentration of diffusant in the oxide that would be independent of temperature over the ordinary diffusion range. In the simplest view the surface concentration in the oxide layer of the test sample would be the same as the bulk concentration of diffusant in the source mixture.

In early experiments the box was made of thin platinum sheet and had a cover that was designed to provide a long leakage path for the diffusant while allowing the pressure to equalize readily. The source mixture was prepared by drying a slurry of colloidal silica and a solution of the diffusant oxide (P_2O_5 , B_2O_3 , etc.). The system was not satisfactory, however, because the source concentration decreased very rapidly at diffusion temperatures. This was checked by comparing the sheet resistances of a series of samples diffused in succession for short times using the same source.

An improved box was then made of fused silica in the form of a capsule. Platinum foil was used to improve the seal and to prevent the two silica caps fusing together. The depletion of the source material was found to be slight even for diffusions of the order of twenty-four hours.

3.32 The Bake-out Effect Another difficulty was observed, however, with the tighter box. When a series of short diffusion runs was made with the same source material and capsule, it was found that the surface concentration on successive test samples increased for a while and then remained constant. The time required to reach a stable constant concentration was a few hours. This bake-out time depended on source strength, the type of diffusant, and the diffusion temperature.

Several experiments were done in an attempt to determine the origin of the bake-out effect. In one, a much tighter platinum box was used instead of the silica capsule. It was found that the bake-out time was the same as in quartz. This result would appear to rule out any explanation of the bake-out effect based on saturation of the box.

The same conclusion was reached from experiments in which the same silica capsule was used for a long time. Each time new source material was used in the old capsule the same bake-out time was observed.

The possibility of a slow change of surface conditions in the source was next considered. One method of modifying surface conditions is discussed next.

Fresh mixtures of SiO_2 and P_2O_5 made from mixing silicic acid and phosphoric acid were heat-treated at 1237°C for $4\frac{1}{2}$ hours in a platinum container with a tight quartz cover. A few diffusions were carried out during this process for checking the rise of surface concentration. Then the source and the container were boiled for an hour with distilled water. After driving out most of the moisture in the source, several diffusions were done. This process was repeated three times with boiling water for one hour, 30 minutes, and 3 hours respectively. The results are shown in Table 1. It is rather consistent that there is a drop in surface concentration for the diffusion after each boiling process. Each time the concentration built up gradually but took a shorter time than for the first bake-out time period. From the oxidation rate for each sample after the boiling process the indication is that the drop in surface concentration was not due to fast oxidation in the presence of moisture during diffusion.

A test for phosphorus content in the distilled water after each boiling process gave no indication of phosphorus. However, from the change in surface concentration there was a decrease in phosphorus concentration in the source after each boiling. It is possible that the amount of phosphorus dissolved was too small to be detectable.

TABLE I

No.	T °C	t min	a _o Å	ρ _s ohm	x _j micron	C _o atoms/cm ³	Remarks
1.	1237	30	2100	8.94	5.17	3.3 x 10 ¹⁹	source saturated for another hour
2.	1237	30	2050	6.96	4.52	5.1 x 10 ¹⁹	
3.	1239	30		8.09	5.06	3.8 x 10 ¹⁹	boiled for one hour
4.	1238	12	1000	67.7	1.53	1.4 x 10 ¹⁹	
5.	1240	30	2200	4.95	4.96	3.8 x 10 ¹⁹	
6.	1238	30	2200	5	5.19	5.8 x 10 ¹⁹	boiled for 30 min.
7.	1240	12	1200	115	1.86	6.8 x 10 ¹⁸	junction irregular
8.	1240	30	2200	6.82 8.23	5.06	4.6 x 10 ¹⁹	
9.	1240	30		8.23	4.5	4.1 x 10 ¹⁹	
10.	1240	30		7.7	4.72	4.15 x 10 ¹⁹	
11.	1240	21	1720	9.06	4.02	4.1 x 10 ¹⁹	boiled for 3 hours
12.	1241	15	1400	19.5	2.78	2.8 x 10 ¹⁹	
13.	1241	16	1500	15.62	3.24	3 x 10 ¹⁹	
14.	1241	15	1430	16.2	3.1	3.1 x 10 ¹⁹	
15.	1241	30	2110	8.94	4.72	3.7 x 10 ¹⁹	

Experimental Results of Boiling Phosphorus Source Material

One possible explanation for this experiment would be that under the bake-out period there is a redistribution of impurity oxide molecules in the silicon dioxide. There is a tendency for the concentration of phosphorus atoms to reach an equilibrium value at the surface of the silicon dioxide clusters. Although one may consider it as a solid solution, conditions at the surface may be quite different from those in the bulk. Since the silica is colloidal, surface conditions dominate. This mixture forms rather tight structures and water will

dissolve it only superficially. The source material (3% phosphorus) forms a porous but coherent solid after few hours heat treatment. In view of this nature of the source material it seems that the rapid increase of surface concentration after each boiling may come from migration of impurity atoms from the inside of the source mixture to the surface of the porous clusters. Similar experiments for a 15% phosphorus source which melts to a glassy form, have been attempted. No bake-out time has been observed. The fact that a liquid source does not exhibit the bake-out effect again suggests that the effect is associated with the colloidal structure of the source.

There are occasions when using a source material at a temperature which differs from its previous heat treatment would give a surface concentration for the first diffusion different from the next one. If the source has been used at a high temperature before, when it is used at a lower temperature the first sample usually has a higher surface concentration than the constant surface concentration for this low temperature. This may indicate the temperature dependence of the source condition. This may also give an indication of the peculiar behavior of the impurity atoms in the source surface layer. The rearrangement takes less time than the first bake-out period, but it is hard to determine experimentally how long it will take to reach the stable condition. This is because the effect is observed from the change of surface concentration obtained. At low temperature one has to conduct the diffusion for a rather long period of time in order to obtain measurable junction depth; thus, this prevents a determination of the time required for rearrangement of source mixture.

The difficulties with source depletion and bake-out effects call attention to what may be a fundamental problem with the box method. If the box is made tight enough to prevent source depletion, it will also reduce the transfer of moisture out of the box and the transfer of oxygen into the box. Since there is always some variation of tightness of the box from one run to the next there will be uncertainty about the partial pressures of oxygen and water vapor. This in turn will lead to variations in oxidation rate and consequently to variations in diffusion. Fortunately, the observed oxide growths during diffusion have been fairly predictable. There is always the possibility, however, that brief changes in oxidation rate may lead to scatter in the diffusion data.

3.33 Junction Measurements and Calculations Sheet resistances were measured by the conventional four-point probe method, and junction depths were estimated by the angle lapping and staining techniques. Measurements of this type are difficult to make under the

conditions encountered in many of these diffusion studies. The critical cases, in which masking is marginal, are of great interest theoretically but result either in no junction or a very shallow junction. When the diffusion is performed through an oxide, it is found experimentally that very shallow junction depths and junction irregularities are often associated. The sheet resistance is high and varies across the sample, making probe measurements less reproducible. On the other hand, if the junction depth is more than a micron or two the measurements are readily made.

The surface concentrations were calculated using the method given by Backenstoss (ref. 3).

3.34 Oxide Layer Measurement The oxide layer thickness was measured by comparing the interference color on the oxide surface with a series of standard samples under a microscope. The standard samples were prepared by controlled etching of oxidized samples in diluted HF. They cover a range of thickness from 500 to 10,000 Å at intervals of about 100 Å. The oxide layer thicknesses can be interpolated within about ± 30 Å, except at thicknesses less than 800 Å. In this range the uncertainty is larger, partly because there is more uncertainty in the interference fringe technique used for calibration. Fortunately, however, most thicknesses to be measured were greater than 1000 Å. Details of the preparation of these standard samples are presented in the appendix of this report.

3.35 Procedures of Sample Preparation Single crystal with the proper initial doping was cut into rectangles of size 1/4 by 1/8 inch and from 10 to 15 mils thick. The broad surface was a (111) plane. One side of the sample was polished with Linde A abrasive to mirror-like smoothness. The samples were then degreased with alcohol, trichloroethylene, and acetone. The samples were then etched in HF, rinsed in deionized distilled water and stored in acetone before the diffusion. The acetone protects the surface and evaporates readily at room temperature.

At first it was thought that a useful way to remove the surface damage due to polishing might be to oxidize the sample heavily in steam. After removal of the oxide with HF the surface remains smooth and polished. It was found by King, however, (discussed in the Second Quarterly Report) that under these conditions the "snow plow" effect could make serious changes in the surface concentration and hence might lead to errors in the diffusion experiments. Consequently this technique was not used for surface preparation in later experiments.

3.36 Source Material Preparation and Calculations of Source Strengths Source materials were prepared from the oxide of the diffusant mixed with silicic acid in distilled water in predetermined proportion. The resulting slurry was dried to powder form and then heated in a loose capsule for from 10 to 15 minutes at a temperature around 300°C to drive off additional moisture and finally sintered at 1000°C from 3 to 5 minutes before being used for diffusion. The source strengths quoted later are in terms of percent by weight of phosphorus or boron relative to the total weight of the source powder.

3.37 Experimental Diffusion Methods for the Closed Box System Quartz capsules mostly of the type shown in Fig. 4 were used for the diffusion studies. Tightness of the capsule is essential for consistent experimental results and is maintained by means of platinum foil between the two halves of the capsule. Before use the quartz capsule and the platinum foil were cleaned in HF from 10 to 15 minutes and then thoroughly rinsed.

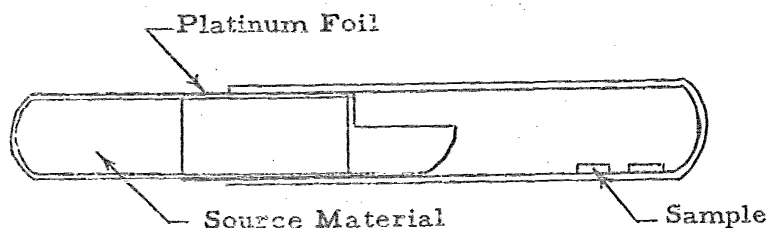


Fig. 4. Quartz Capsule for Closed-Box Diffusion

For fresh source material the bake-out time was first established so that consistent surface concentrations could be obtained. Then the time dependence of surface concentration was checked with control samples to be sure that the source did not deplete. The temperature dependence of surface concentration, the oxide masking effect, and the determination of D_1 were studied next. This was done by placing four to five samples with different initial oxide layer thicknesses for diffusion at a fixed temperature and an estimated length of diffusion time. These experiments were repeated for various temperatures. Considerable cut-and-try was involved in establishing suitable combinations of

oxide thickness and time since D_1 has to be determined under the condition that the final oxide layer is not very much thicker than the initial oxide layer and a measurable x_j must be obtained. The lower limit chosen for the evaluation of D_1 was $a_o/a = 0.4$. Usually the D_1 was calculated for a_o/a ranging from 0.4 to 0.65. This imposed a severe limitation on the use of Eq. (27) to determine D_1 at temperatures lower than 1150°C when the diffusion was in air.

3.4 Experimental Diffusion Studies

3.41 Experimental Results for Diffusion of Phosphorus Into Silicon in an Oxidizing Atmosphere. It is now well established that the process responsible for oxide masking in the case of phosphorus diffusion into silicon is the slow diffusion of phosphorus through the oxide layer. This effect was made qualitatively very clear by the observation of the distribution of radioactive phosphorus in the oxide using standard tracer techniques as discussed in earlier reports.

The objectives of the remainder of the experimental work were to evaluate the adequacy of the theory presented in Section 3.2 and to determine the magnitudes of the constants in the appropriate equations. The measured quantities were the sheet resistance of the diffused layer in silicon, the junction depth in the silicon and the oxide layer thickness before and after diffusion. These quantities were observed as functions of source composition and the time and temperature of diffusion. The quantities calculated from these data were the diffusion constant D_1 in the oxide and an interface coefficient R . The calculations in most instances were based on Eq. (27), page 9. The surface concentration was also calculated on the assumption that the distribution of impurity in the silicon was approximately of the complementary error function type.

As mentioned earlier it is necessary to heat-treat the source material for a few hours at diffusion temperature in order to obtain reproducible diffusion results. A typical bake-out curve is shown in Fig. 5 for a source containing 1.3% phosphorus by weight. Also shown is the relative absence of bake-out effects for a 15% phosphorus source. The points were obtained by diffusing unoxidized samples for 15 minutes each at the times indicated. In general the more concentrated sources come to equilibrium in shorter times.

It will be noted that the surface concentration is quite constant after equilibrium is established. For much longer diffusions the surface concentration obtainable gradually decreases because of source depletion. The equilibrium surface concentration is roughly proportional to the original phosphorus concentration in the source as shown in Fig. 6.

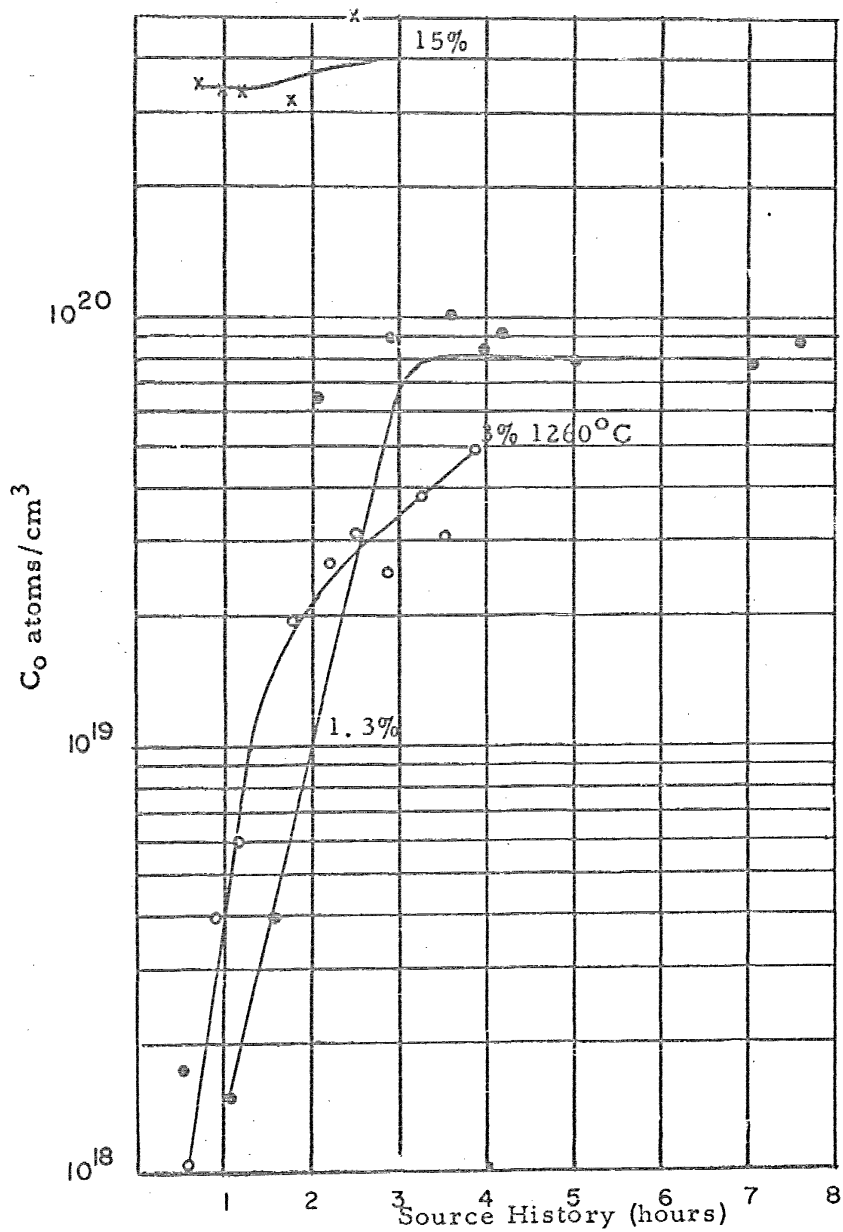


Fig. 5. C_O Versus Source History of 1.3% and 15% for Phosphorus as Diffusant

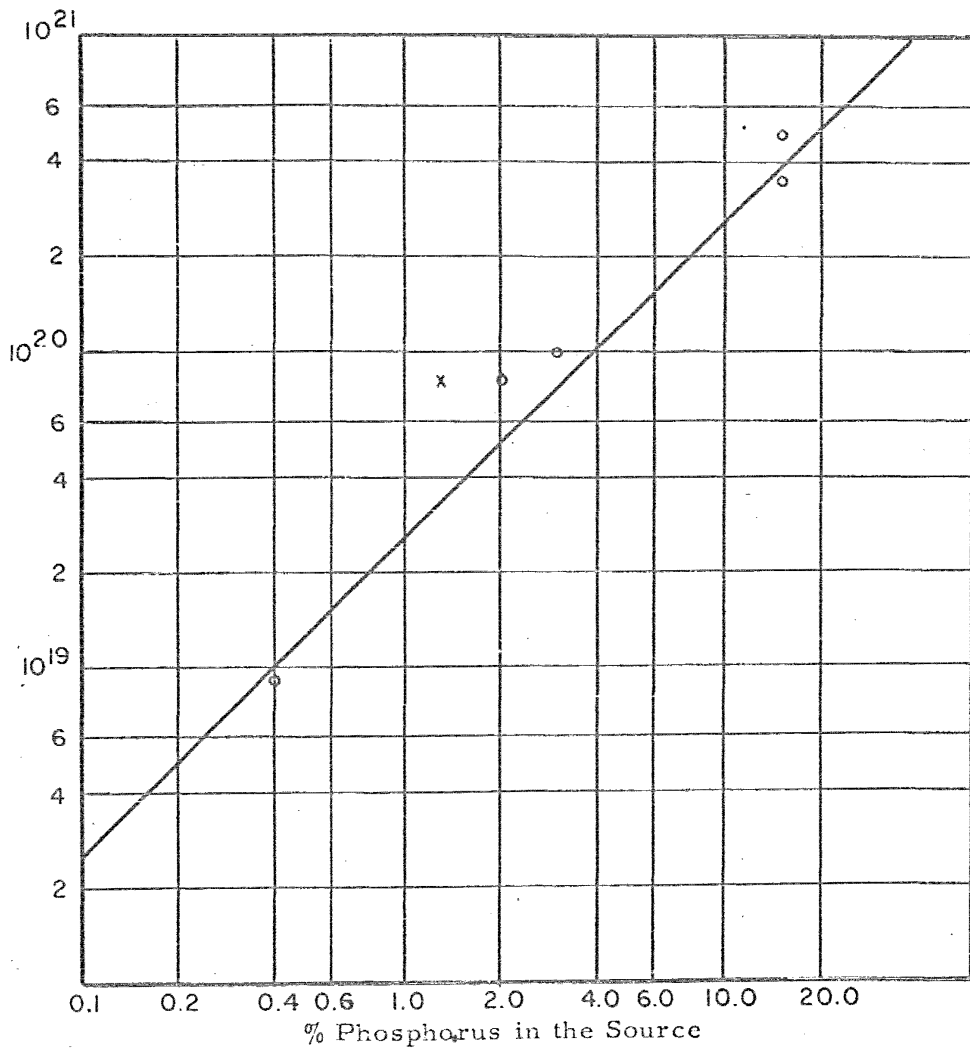


Fig. 6. Surface Concentration Versus Source Strength

The actual concentration of the 2% source was found by chemical analysis to be 1.3%.

When samples that have not been preoxidized are diffused with properly baked out sources it is found that the surface concentration is very nearly independent of diffusion time as shown in Fig. 7. This result would be predicted theoretically regardless of whether the oxidation during diffusion occurs at the silicon-oxide interface or at the oxide surface.

Figure 8 shows the observed temperature dependence of the surface concentration for each of four source strengths, again using samples that were not preoxidized. In general the surface concentration increases with temperature although there is some tendency toward leveling off at the higher temperatures. Experiments using a 0.001% source strength were not successful because the surfaces of the sample were not converted to n-type.

The dependence of the diffusivity in the oxide on temperature is shown in Fig. 9. For high temperatures the curves have approximately the same slopes while for the lower concentrations there is a change in slope at lower temperatures. An empirical expression for D_1 for the 3% source is

$$D_1 = 1.8 \times 10^{-6} e^{-2.36 \frac{q}{kT}} \text{ cm}^2/\text{sec (from 1060 to 1350}^\circ\text{C).}$$

The two curves for 3% sources in Fig. 9 indicate about a 30% scatter in the results from two series of experiments.

In the same figure the values of D_1 obtained by C. T. Sah and his colleagues (Ref. 4) and by A. D. Kurtz and his colleagues (Ref. 5) are shown for comparison. Their D_1 's were obtained from diffusion in an open tube with the source at a lower temperature than the temperature of diffusion. Their values do not agree with the values obtained here. We have not yet attempted measurements under the conditions they used.

Figure 10 shows the oxidation rate versus $1/T$ for different source strengths. The 3% curve was more accurately determined than the others. Although the slopes of the oxidation are not very accurate, the increase in oxidation rate with source strength is marked. An expression for σ^2 for the 3% source is

$$\sigma^2 = 1.95 \times 10^{-5} e^{-2.24 \frac{q}{kT}} \text{ cm}^2/\text{sec.} \quad (52)$$

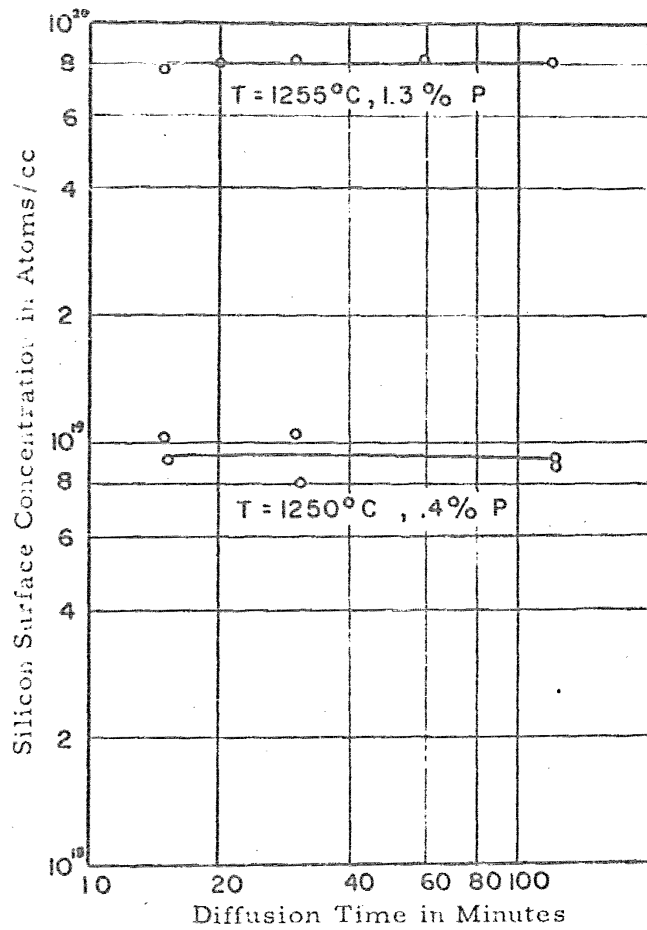


Fig. 7. Surface Concentration at the Silicon Surface as a Function of Diffusion Time

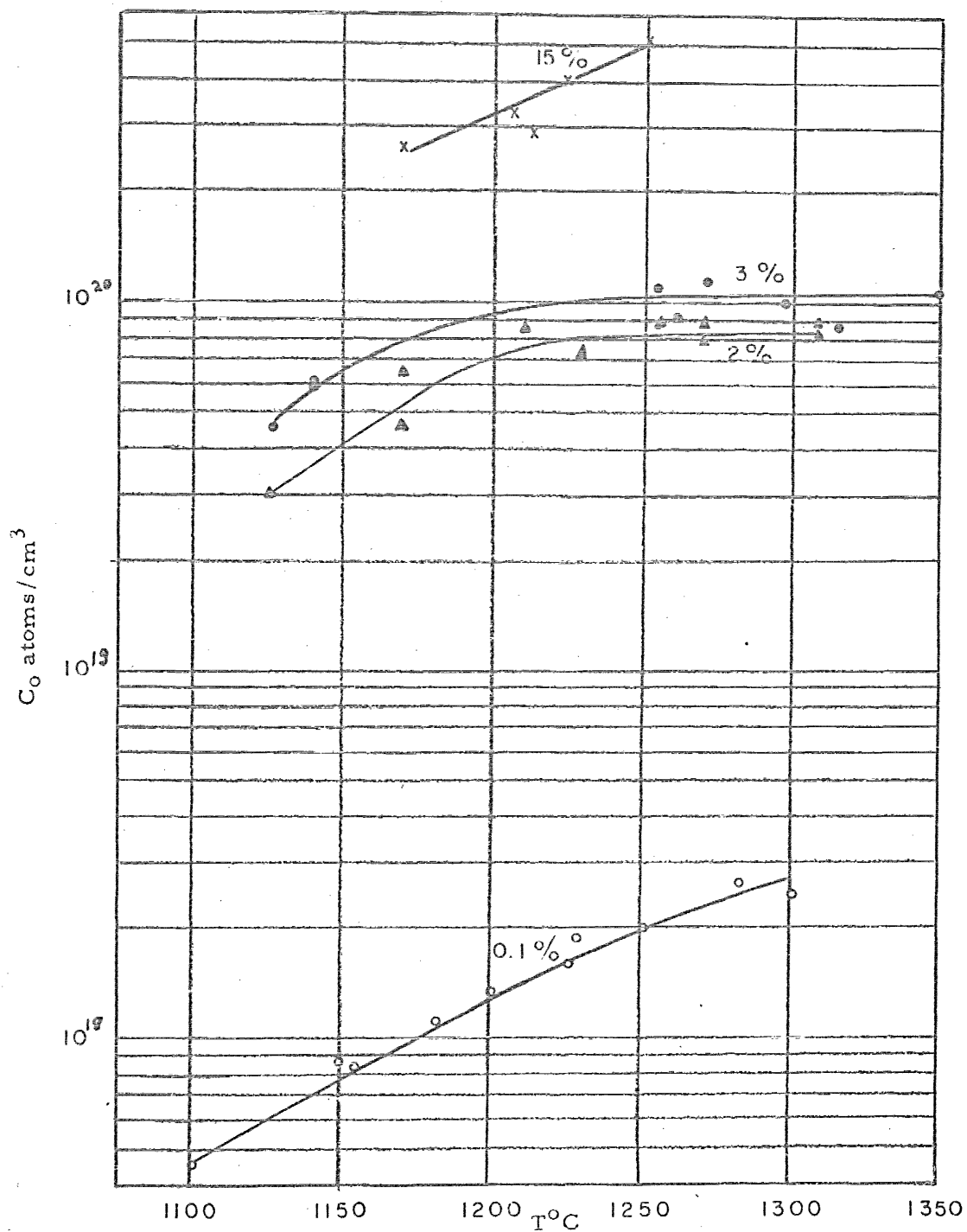
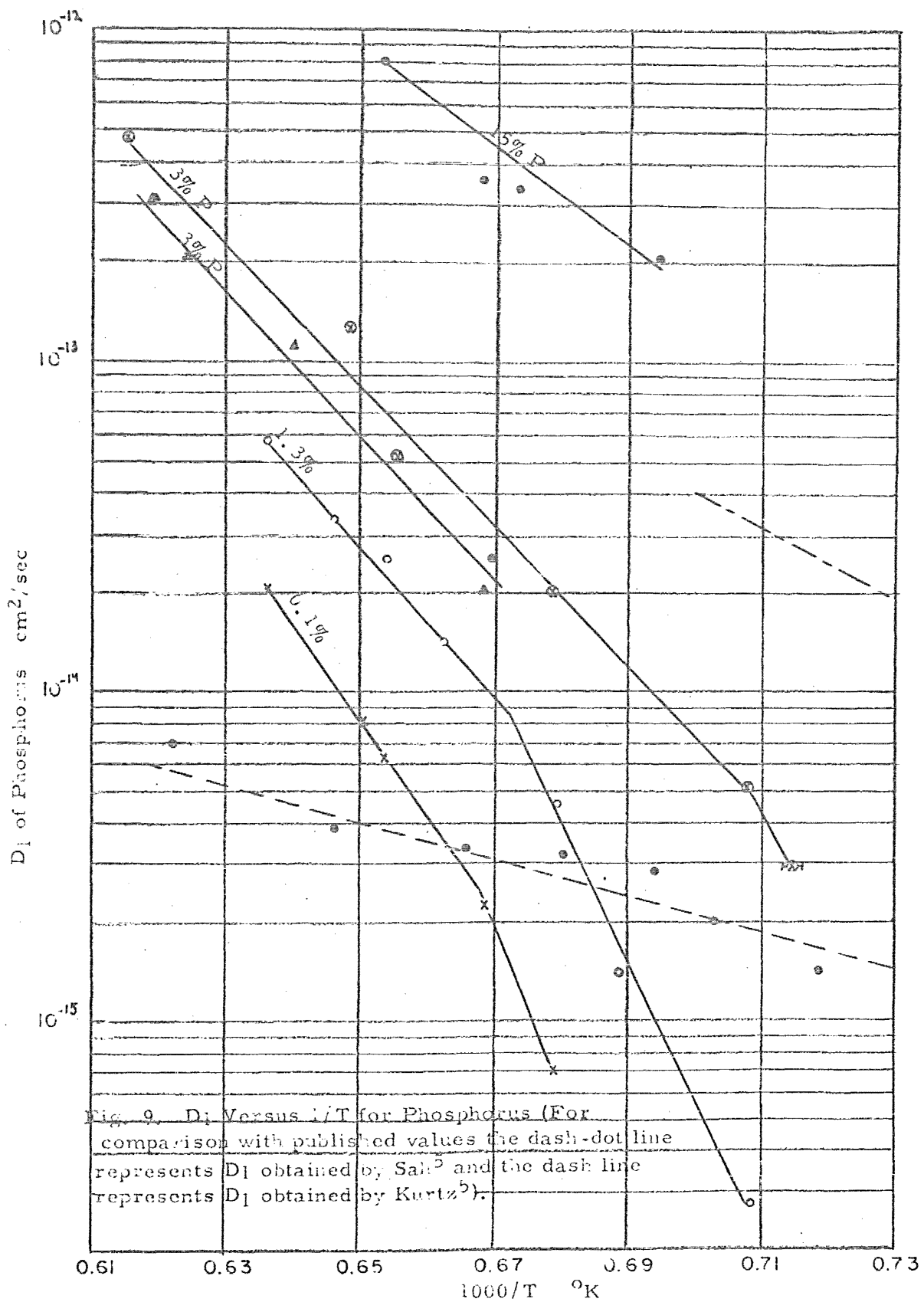


Fig. 8. C_O Versus Temperature for Phosphorus



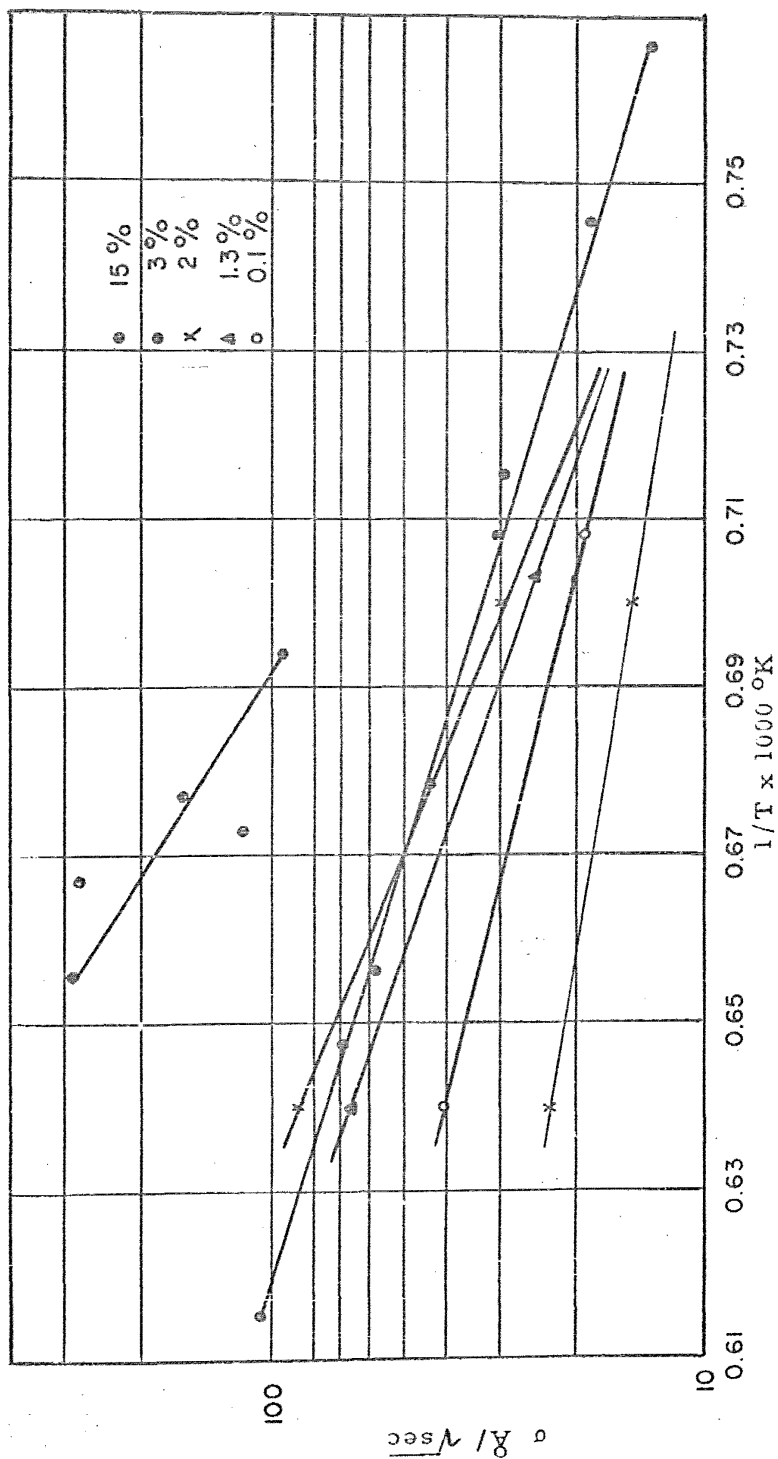


Fig. 10. σ Versus $1/T$ for Phosphorus

Figure 11 shows σ^2 and D_1 versus $1/T$ for the 3% source. This curve is intended to show the relative value of the two physical constants. One is related to the oxidation, the other is related to the diffusion of phosphorus atoms. From this curve it is seen when $T = 1050^\circ\text{C}$ the two differ by an order of magnitude. Thus one cannot get a converted layer unless the diffusion time is very long. If they differ much more than an order of magnitude, there may not be a converted layer, such as the case for boron diffusion at temperatures lower than 1050°C in air. From this result it seems that the diffusion in air in a closed box system is not suitable for temperatures less than 1100°C . Also, values of D_1 determined by using Eq. (27) will not be reliable. In an atmosphere that reduces the rate of oxidation there will be less trouble in diffusion at low temperatures. It is apparent that the highest surface concentration obtainable in an oxidizing atmosphere may be limited by the high oxidation rate, in other words by the difference in magnitudes of σ and D_1 .

Figures 12 and 13 show some values of x_j versus a_0 for the particular diffusion conditions quoted. Figure 14 shows R versus T .

3.42 Experimental Results for Boron Diffusion in Air. The following source strengths of boron have been studied: 0.001, 0.01, and 0.1 per cent. Additional studies of the bake-out time phenomenon were made with source strengths of 0.0003, 0.0006, 0.0013, 0.003, 0.006, 0.5 and 1 per cent. The preparation of the sources is similar to that described for the phosphorus source with P_2O_5 replaced by B_2O_3 . All the diffusions were done in fused quartz capsules which were wrapped with platinum foil (1-mil thick) to make them fairly tight.

The purpose of studying the low source strengths was to relate the source strength to the saturated surface concentration obtainable. This will be discussed later. The other objects were to determine D_1 , the oxide masking effect, the temperature dependence of the surface concentration and the junction depths versus the initial oxide layer. Experimental results are presented in Figs. 15 to 35 and some explanations on these results will be given in the following paragraphs.

Figure 15 gives the surface concentration versus source history. The numerals inside the brackets represent the source concentrations.

First, one will observe that the bake-out time changes with source strength; the higher the source strength the shorter the bake-out time will be. However, for source strengths from 0.006 to 0.5 per cent the variation in bake-out times is very small compared to the variation of source strength by a factor of almost 100. Within these source

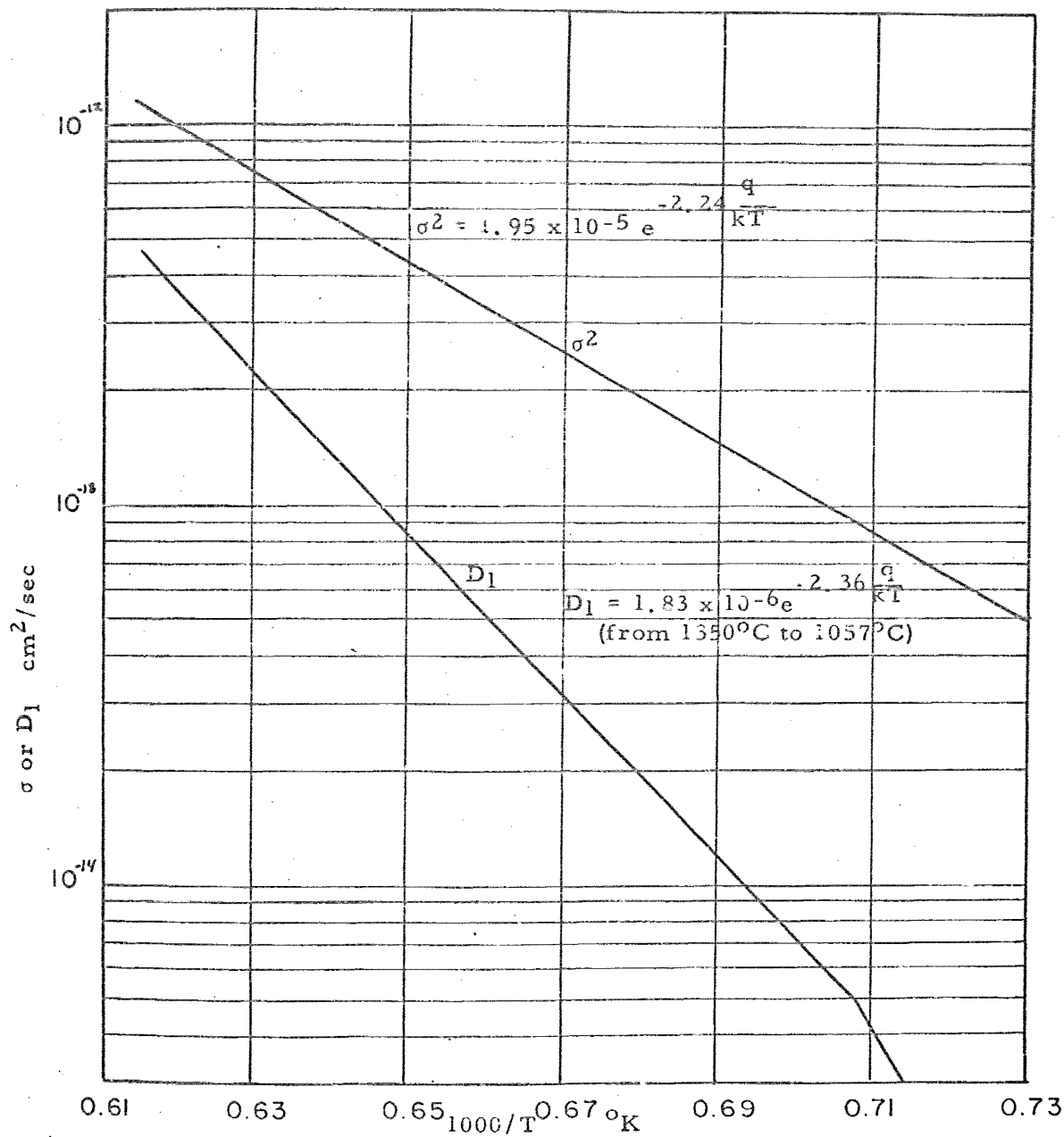


Fig. 11. σ or D_1 Versus $1/T$ for 3% Phosphorus. For the Comparison of the Relative Values of Oxidation Rate and Diffusivity

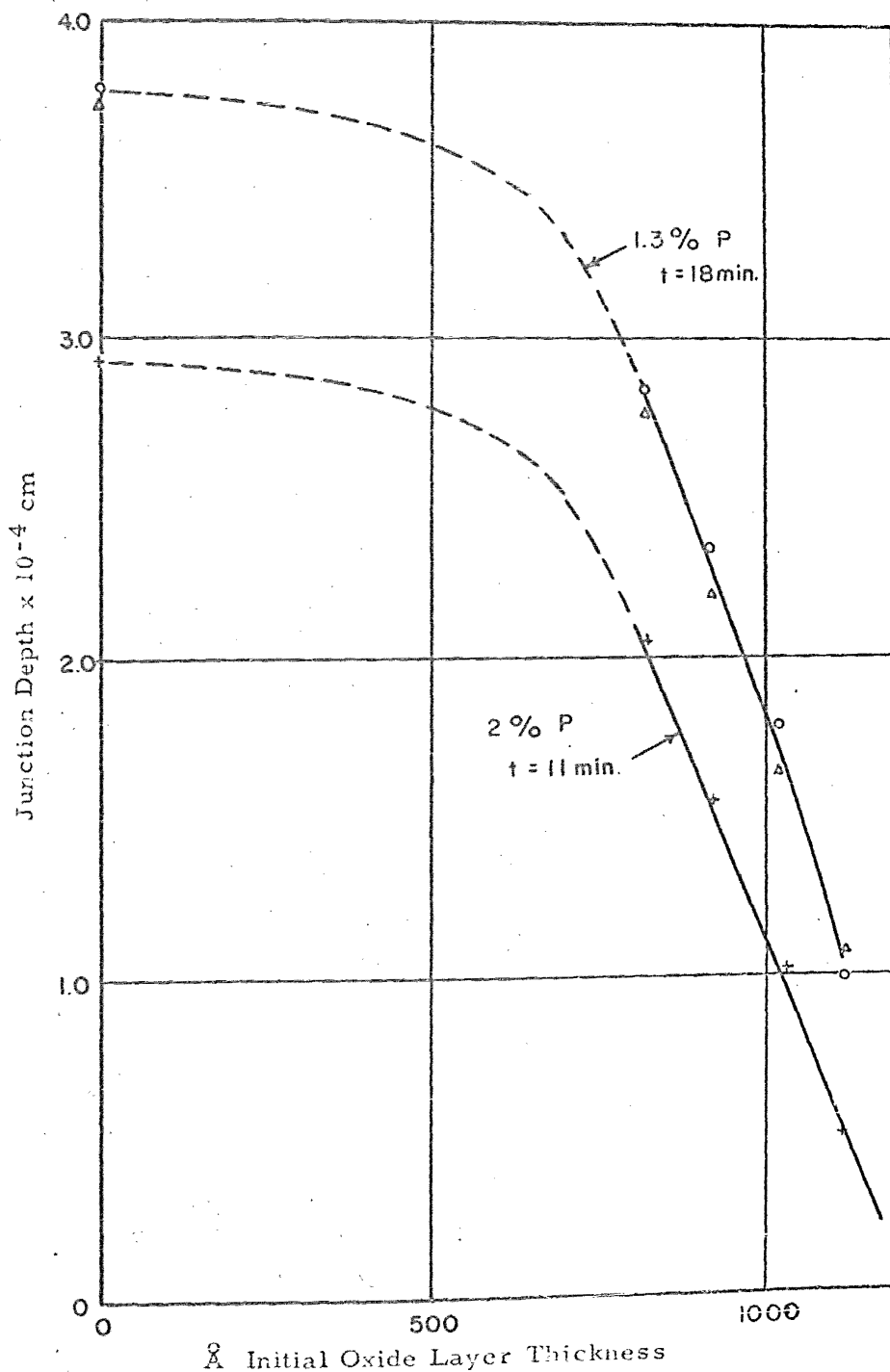


Fig. 12. Junction Depth as a Function of Initial Oxide Layer Thickness

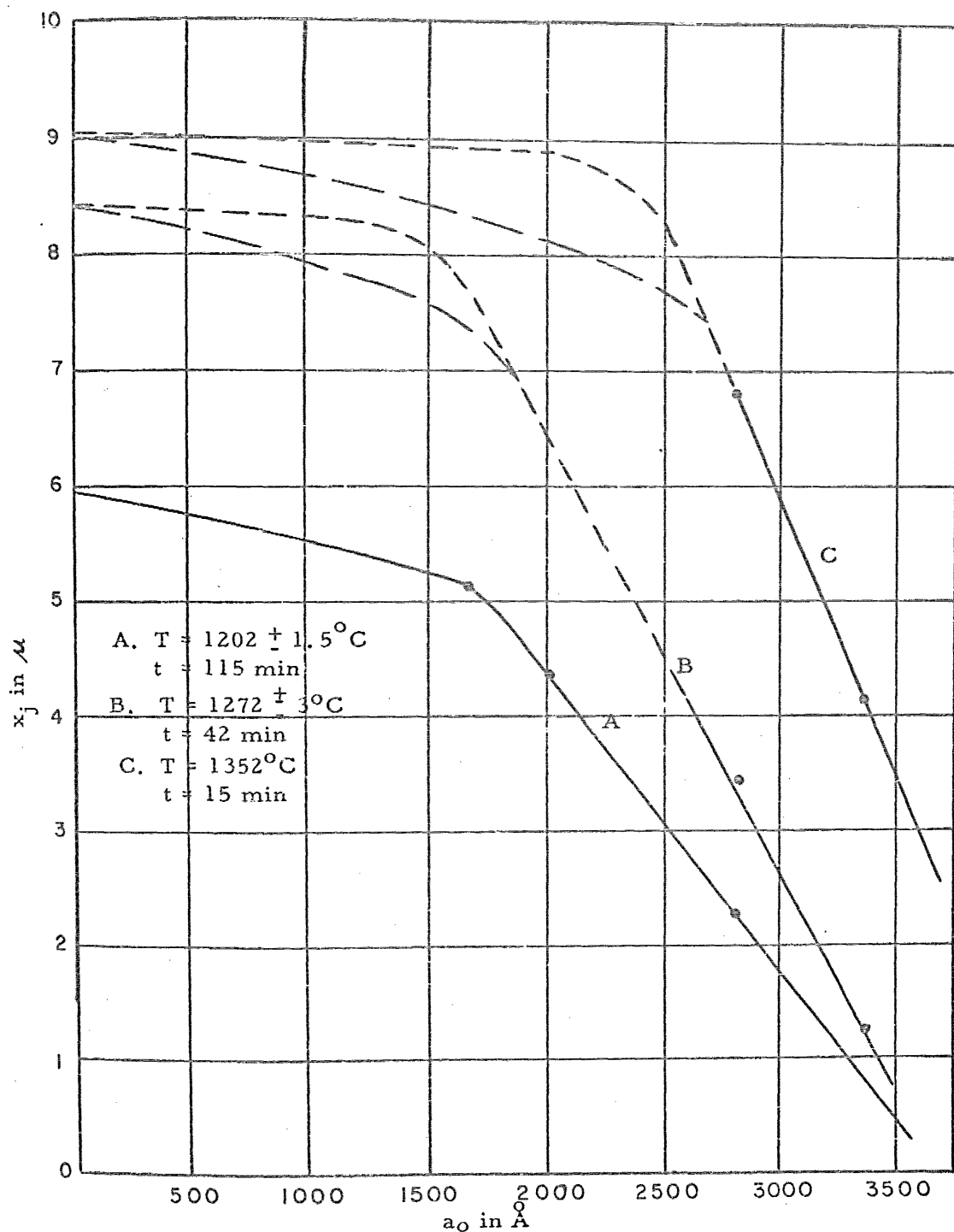


Fig. 13. x_j Versus a_0 for 3% Phosphorus

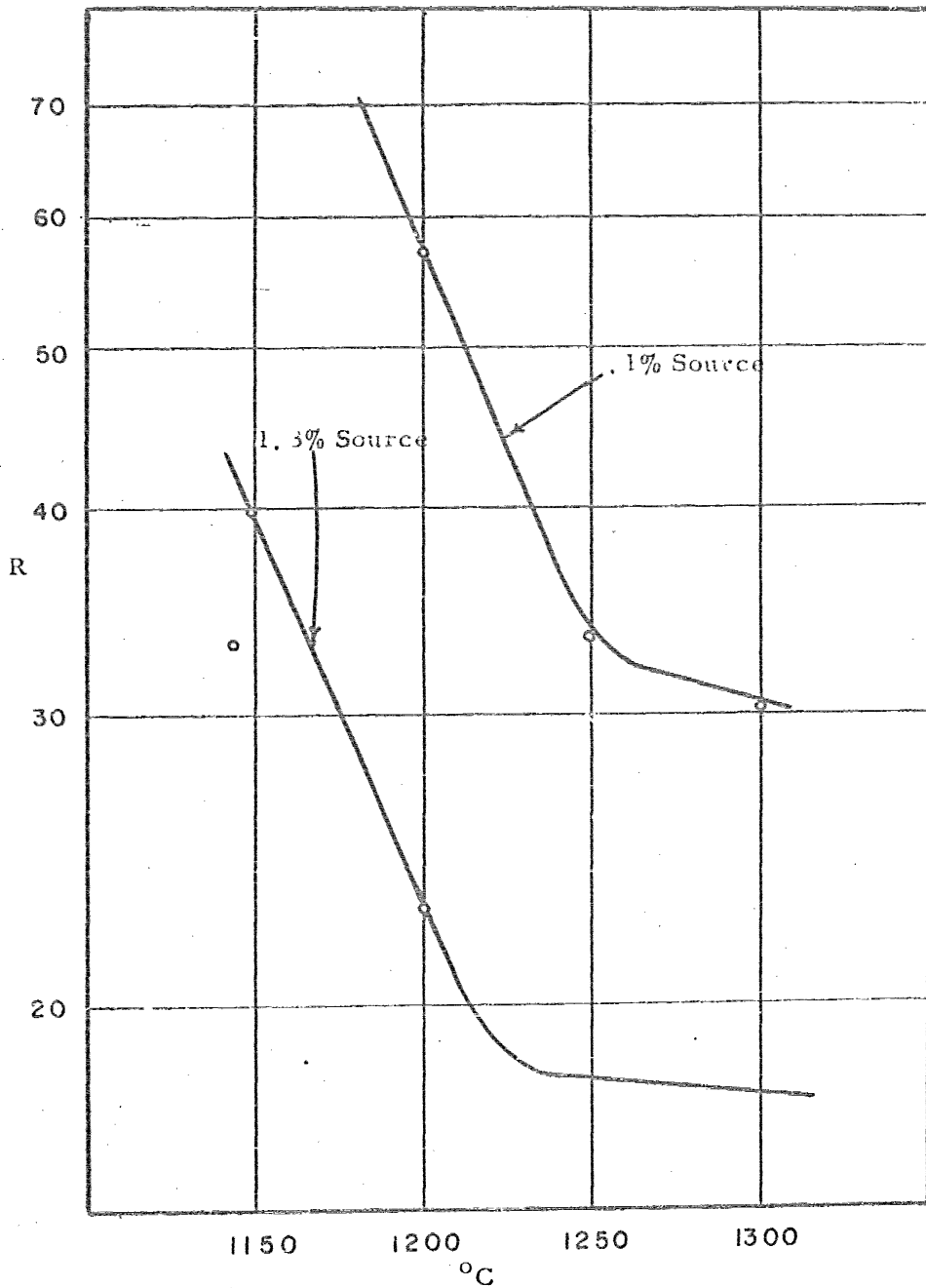


Fig. 14. R Versus T for Phosphorus

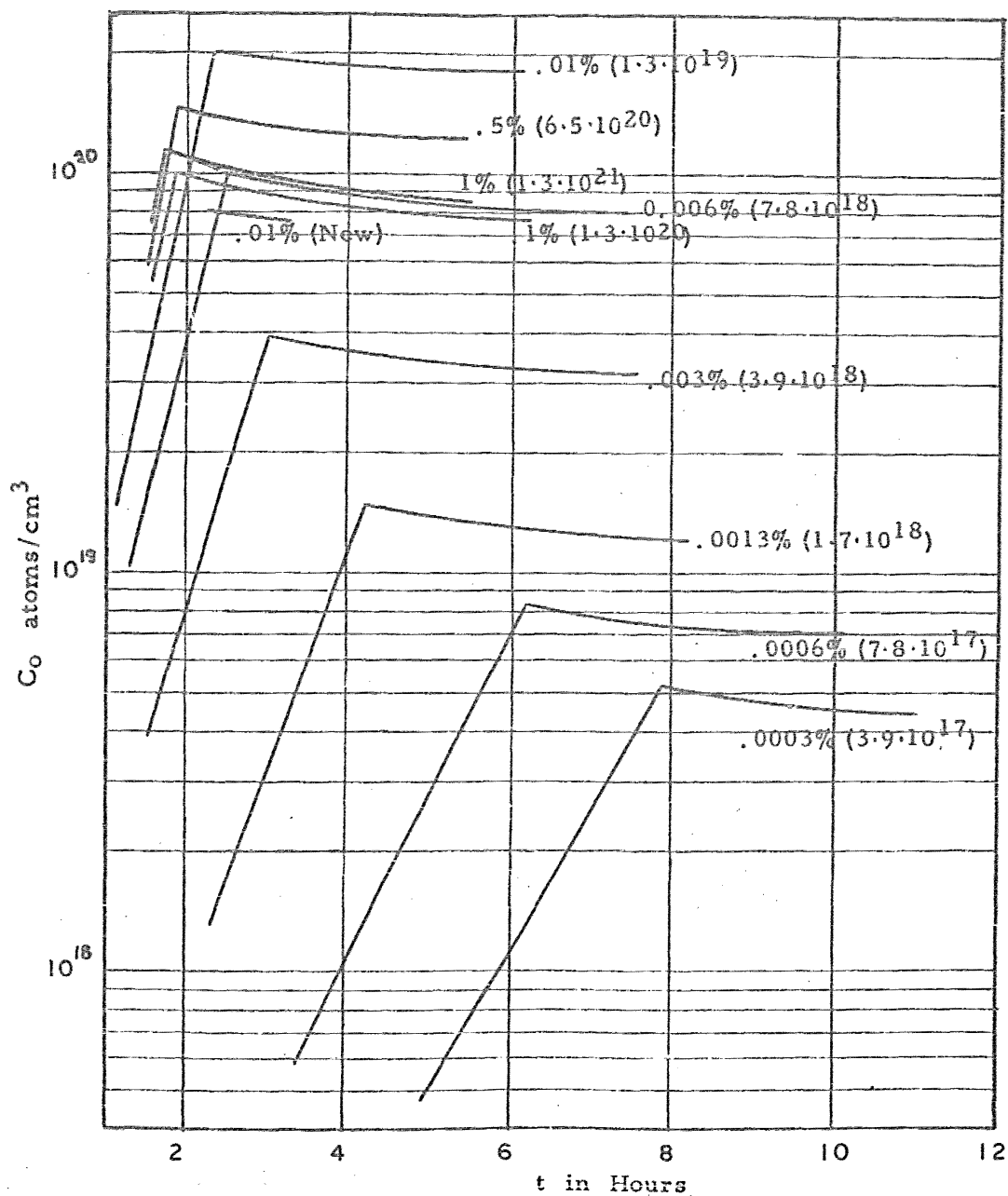


Fig. 15. C_0 Versus Source History for Boron at 1300°C

strengths it seems that the surface concentration obtainable stays within a limited range.

Secondly, two experiments with 0.01% sources were carried out. The second series was done under better controlled temperatures. The variation in temperature in this case was less than $\pm 2^\circ\text{C}$, while the rest of the curves were obtained at a temperature variation of $\pm 9^\circ\text{C}$ when measured with a Pt - Pt+10% Rh thermocouple. The curve labeled with "new" is the second 0.01% source. The surface concentration differs from that obtained with the first by a factor of 2.5. The reason for this difference is not known.

Figure 16 shows the diffusion time dependence of the surface concentration with $a_0 = 0$. It also shows that C_0 is independent of the diffusion time, as was the case with phosphorus.

Figures 17 to 22 show the relation of C_0 versus $1/T$ and the relative effectiveness of oxide masking. Those curves for a_0 different from zero have meaning only when interpreted for the particular diffusion time given. The times of diffusion were arbitrary but were made long enough at each temperature to result in converted surfaces.

Figures 23 to 27 show the relation between σ (the oxidation rate) and $1/T$. Those curves that can be represented by straight lines are given by expressions which contain activation energies. The points for other curves are scattered too much to justify representing them by straight lines. From the curves shown it is seen that at high temperatures the separation of the points for different initial oxide layers is greater than at low temperatures. Also the thicker the initial oxide layer the smaller the value of σ . These differences are beyond the errors in measuring the oxide thickness. In Fig. 25 the curve labeled by letter 'B' was obtained from the old temperature control. By comparison with the other curves shown, which were obtained under a better temperature control, it seems that the variation of the diffusion temperature may not be the major cause of the scattering of the experimental points.

Figure 28 shows the plots of σ versus $1/T$ with different sources for $a_0 = 0$. From these curves it is very hard to find out whether there is some relation between source strengths and the oxidation rates.

Figures 29 to 34 show the relation of x_j versus a_0 . Some of these curves can be approximated by a straight line in the region between 1000 to 3000 Å, but others cannot. The R values obtained from the slopes of these straight lines are presented in Table II. Values in parentheses

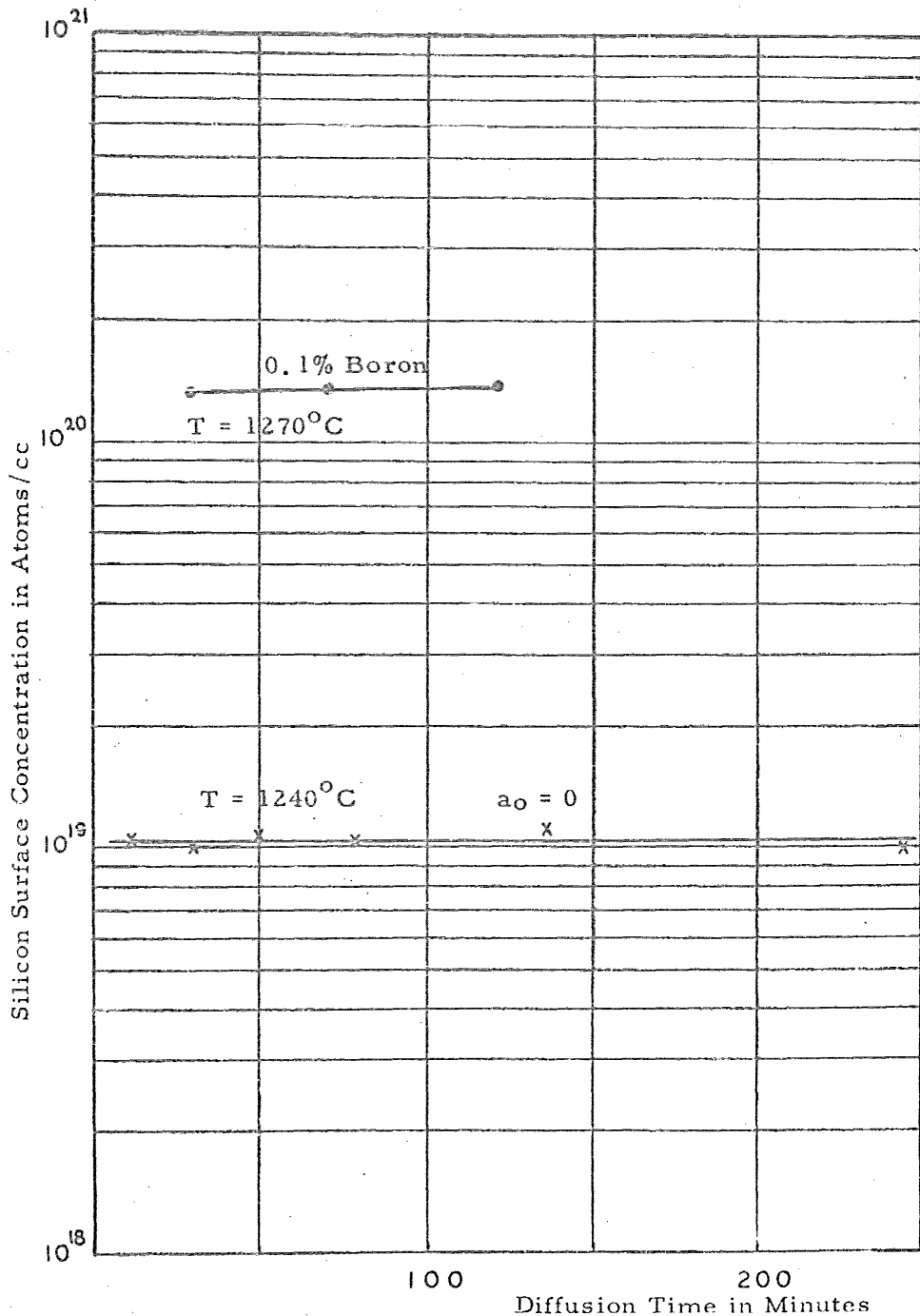


Fig. 16. Silicon Surface Concentration as a Function of Diffusion Time

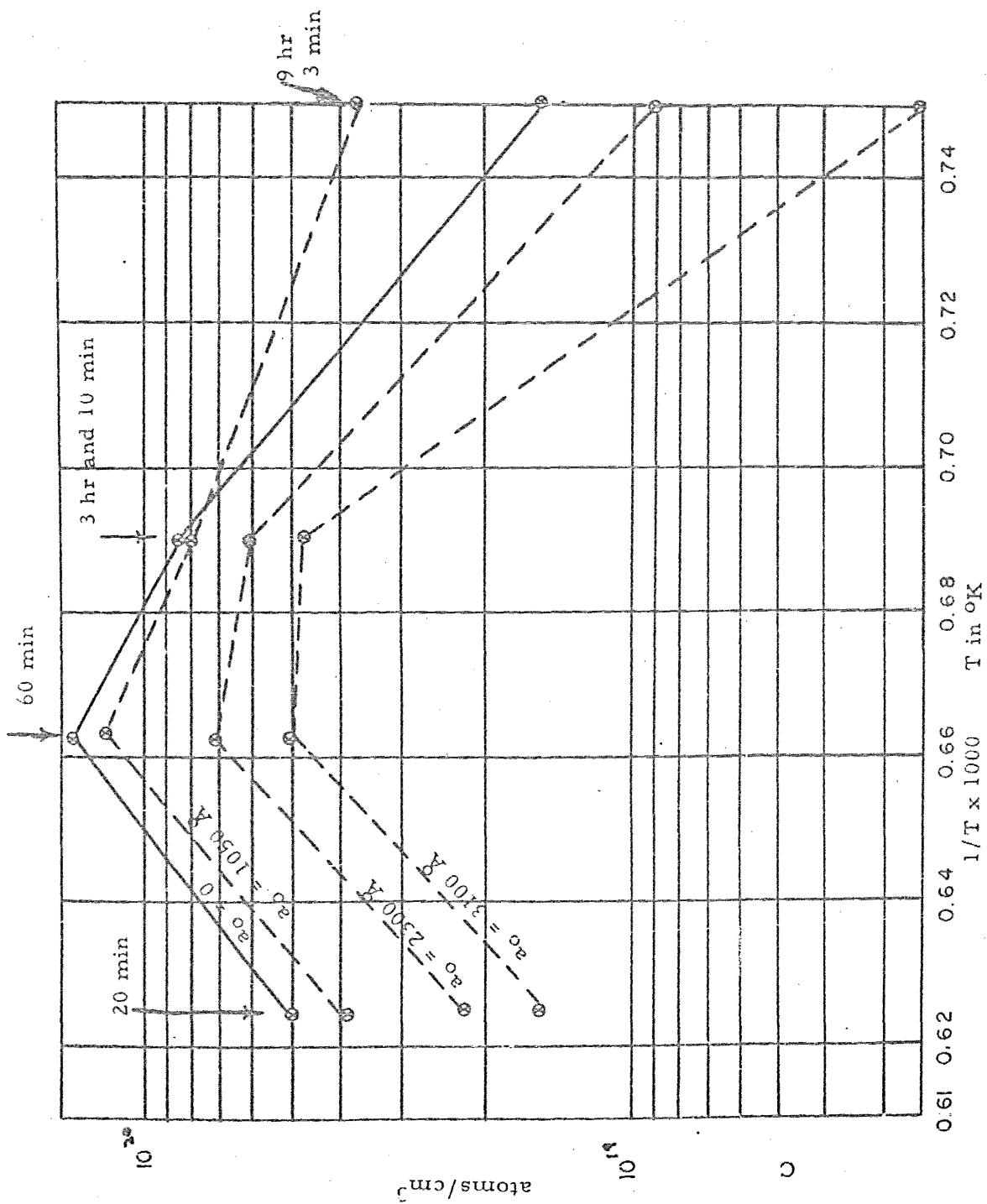


Fig. 17. Co and Cox Versus 1/T for 1% Boron Source

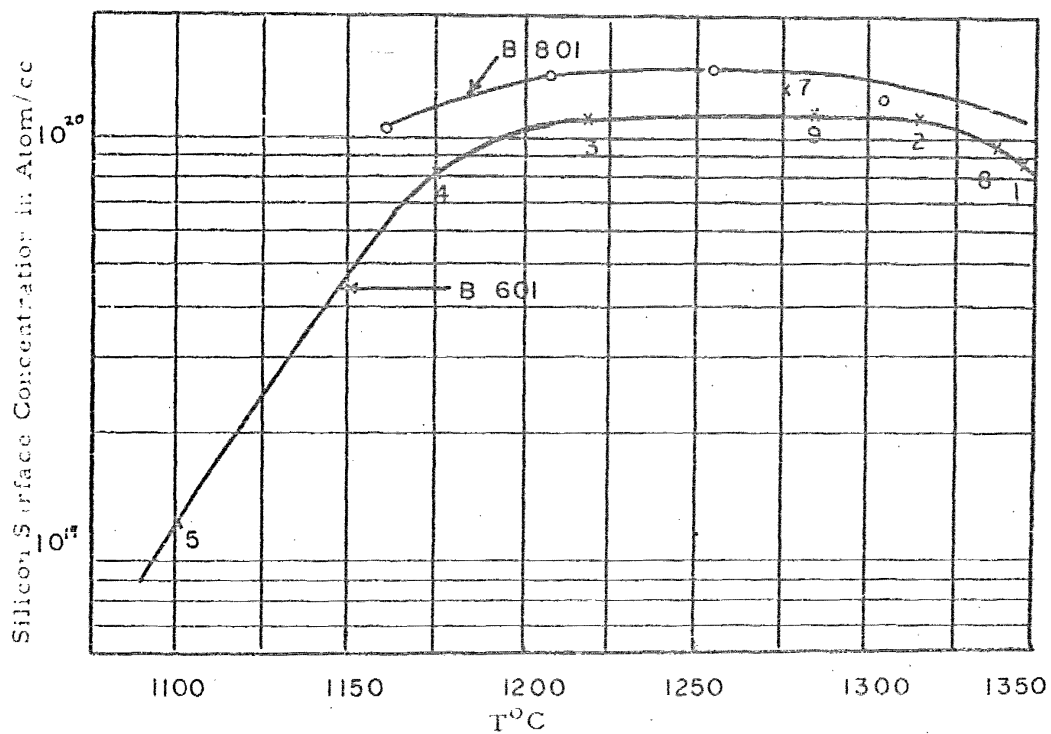


Fig. 13. Surface Concentration at the Silicon Surface as a Function of Temperature, 0.1% Boron

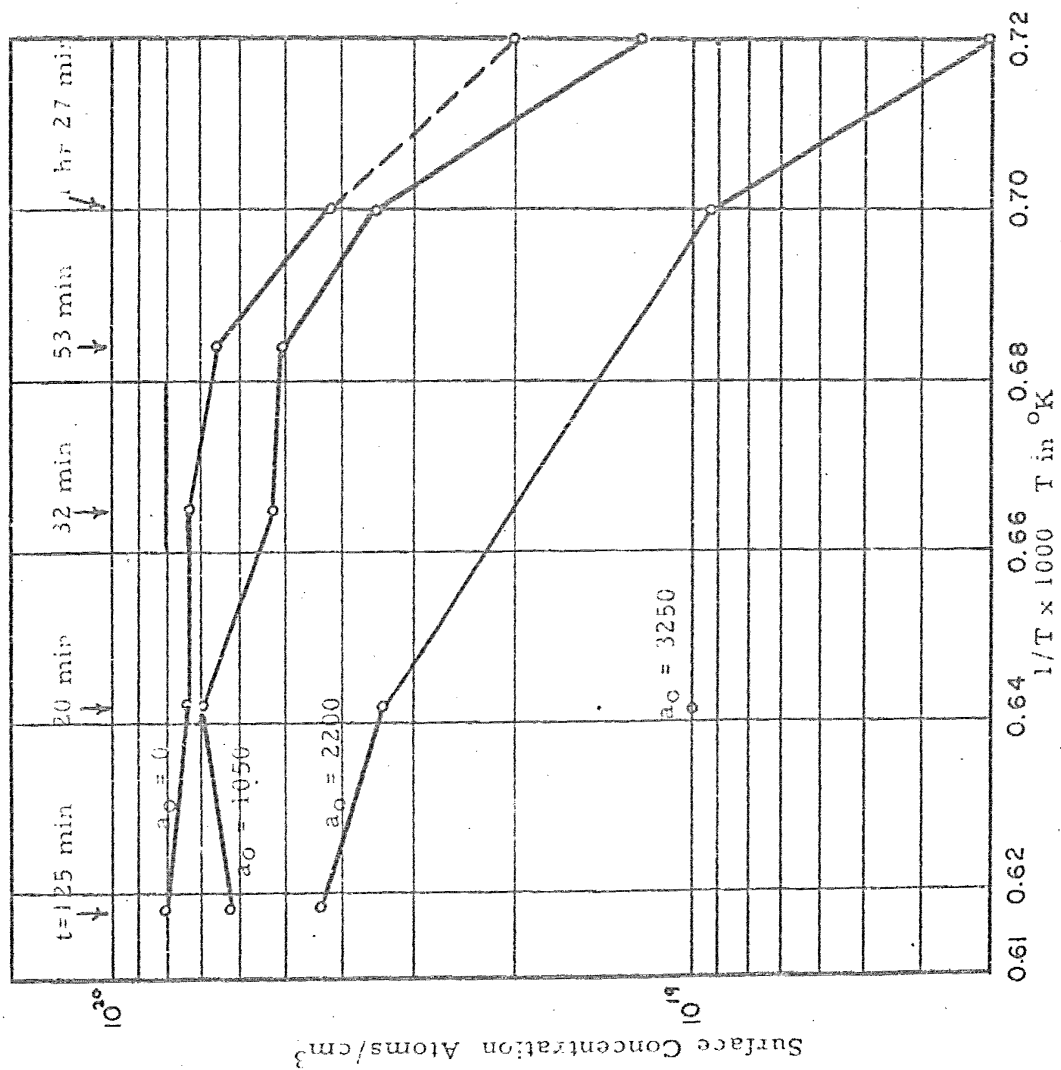


Fig. 19. C_0 and C_{ox} Versus $1/T$ for 0.01% Boron Source Under Better Temperature Control

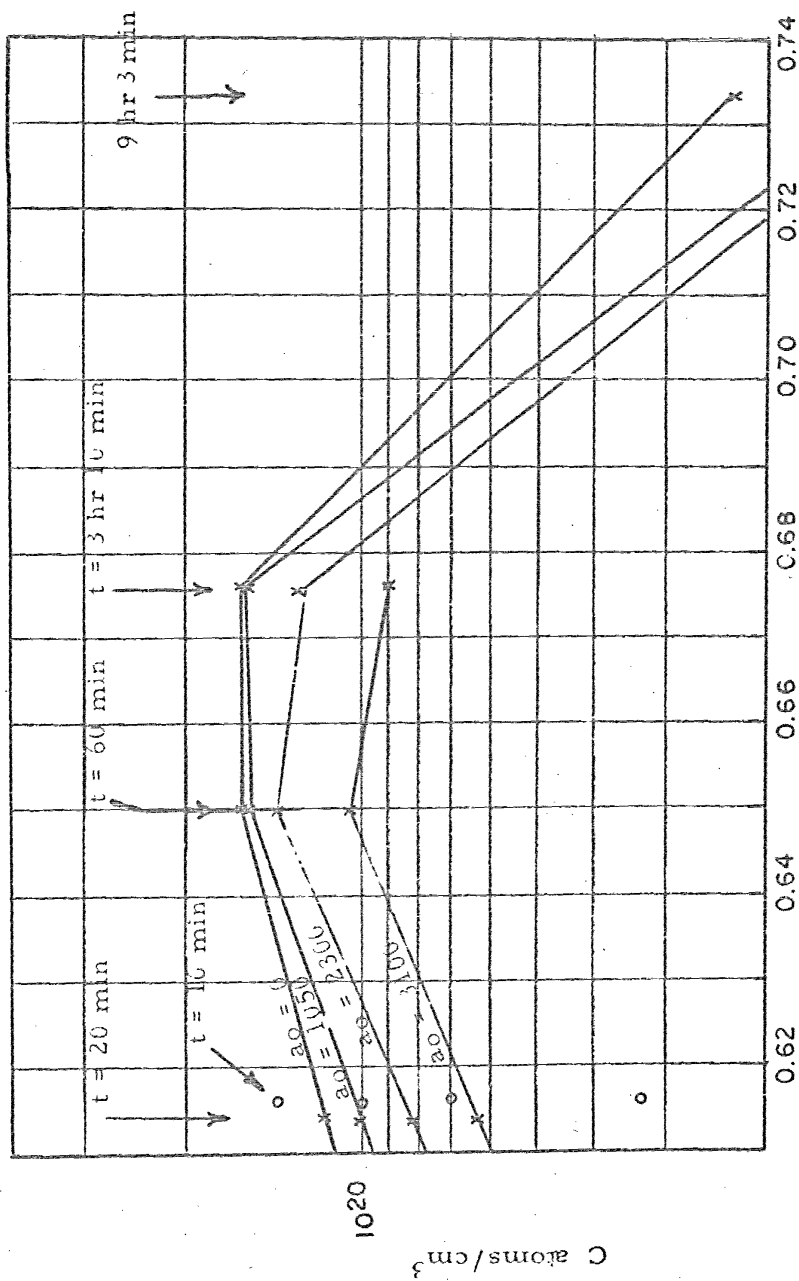


Fig. 20. C_0 and C_{ox} Versus $1/T$ for 0.01% Boron Source

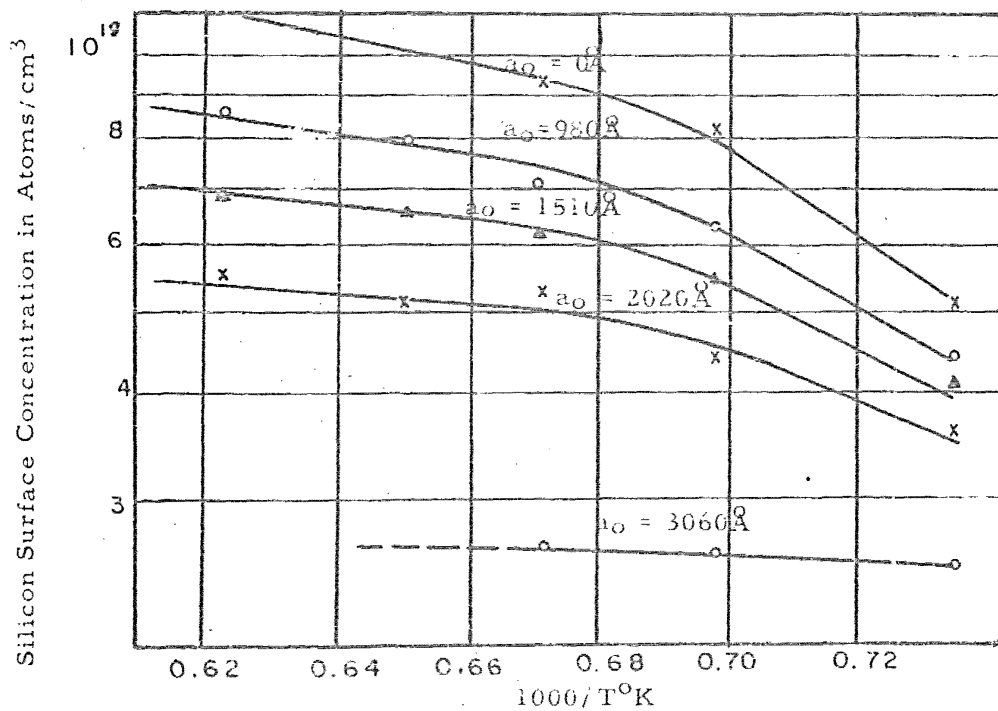


Fig. 21. Silicon Surface Concentration as a Function of Inverse Temperature, 0.001% Boron

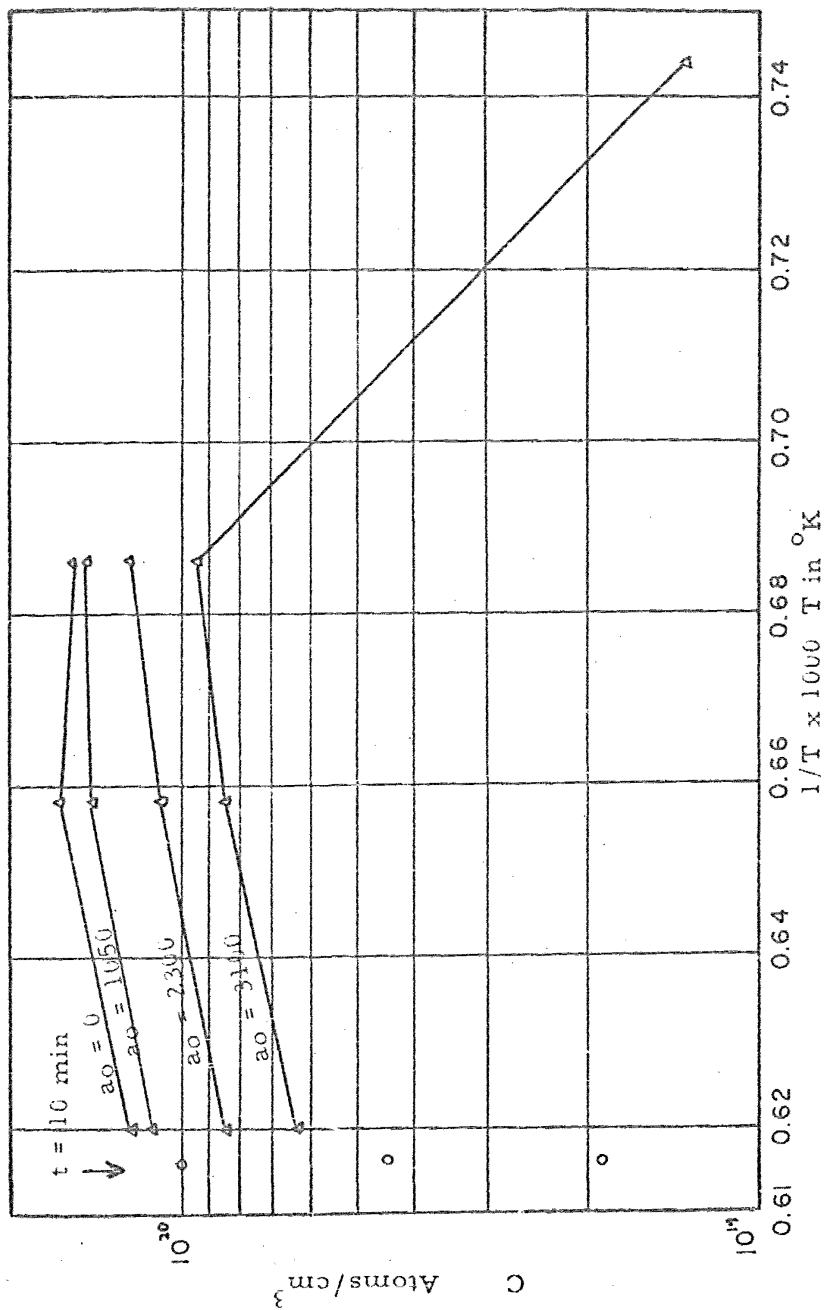


Fig. 22. C_0 and C_{ox} Versus $1/T$ for 0.003% Boron Source

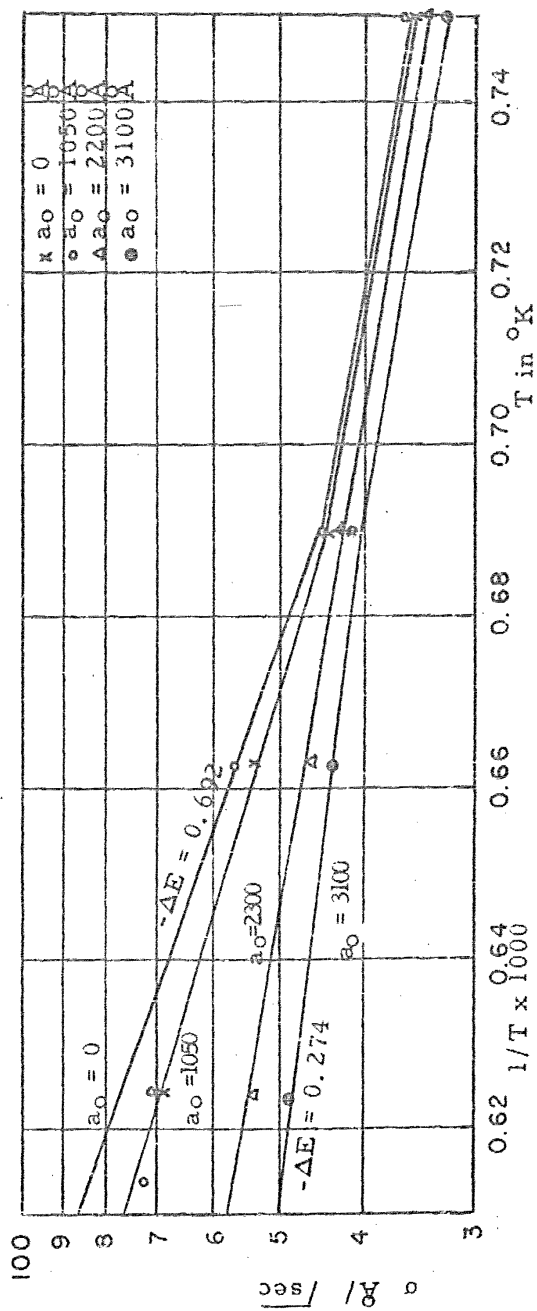


Fig. 23. Oxidation Rate Versus $1/T$, 1% Boron Temperature Variation $\pm 15^{\circ}\text{C}$

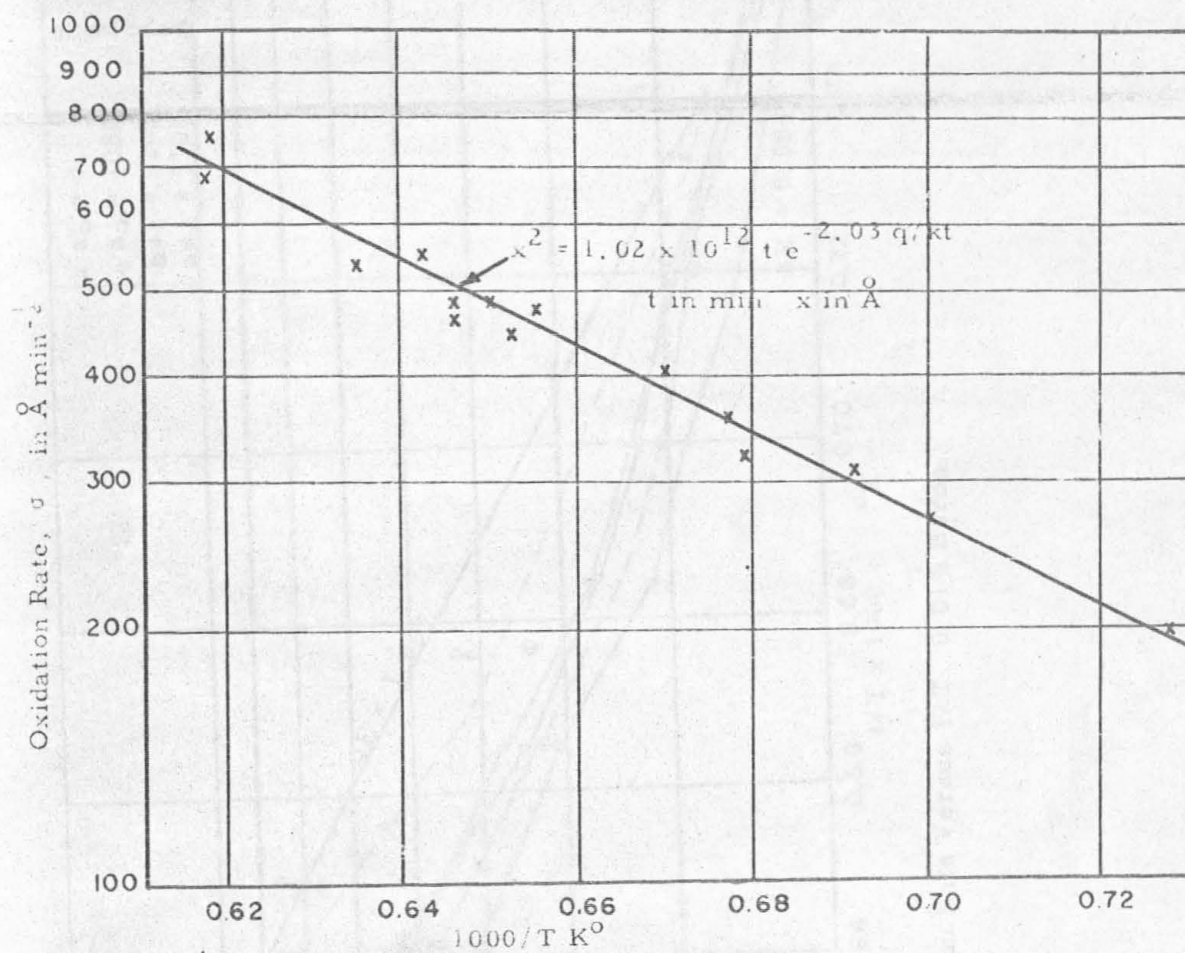


Fig. 24. Oxidation Rate as a Function of Temperature, 0.1% Boron

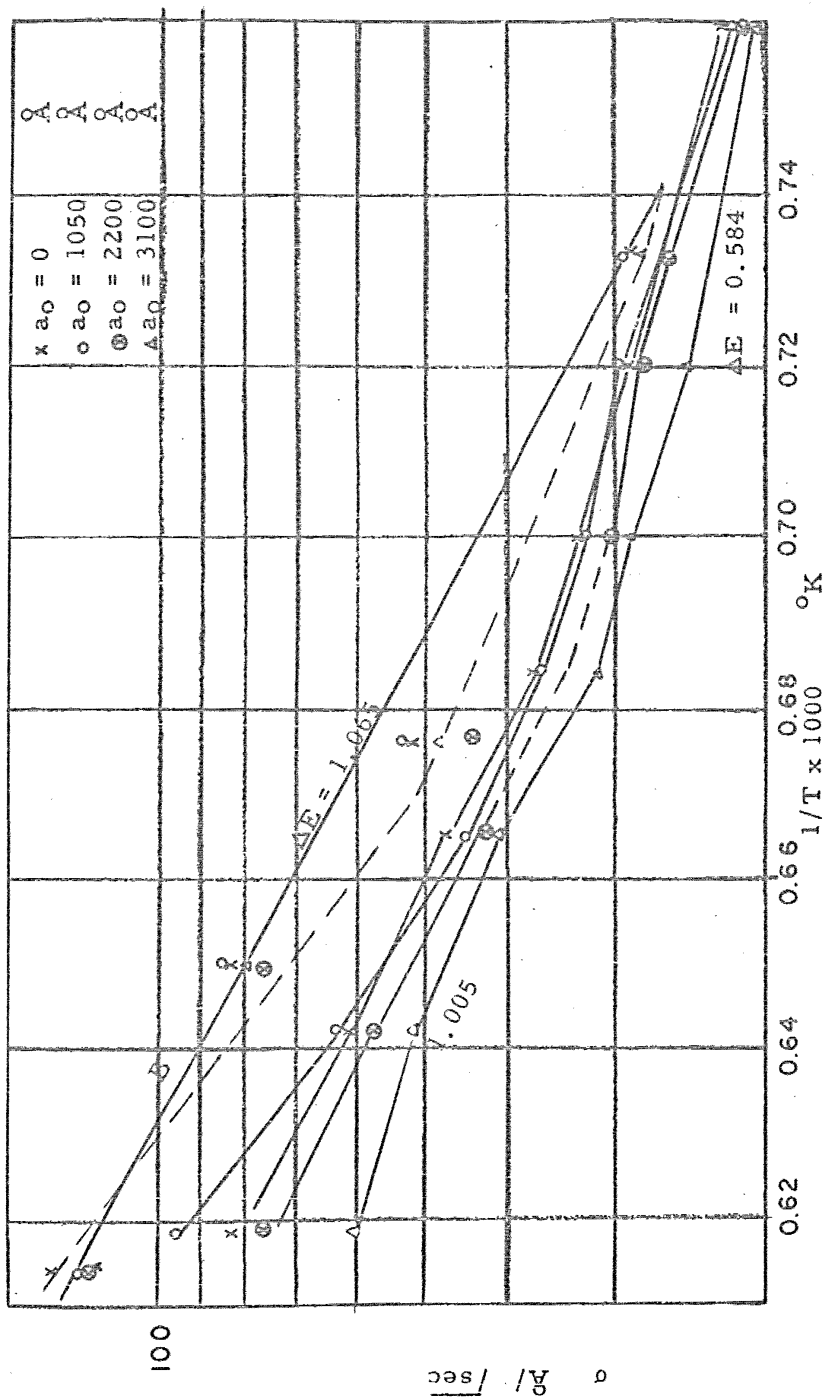


Fig. 25. Oxidation Rate Versus $1/T$ 0.01% Boron

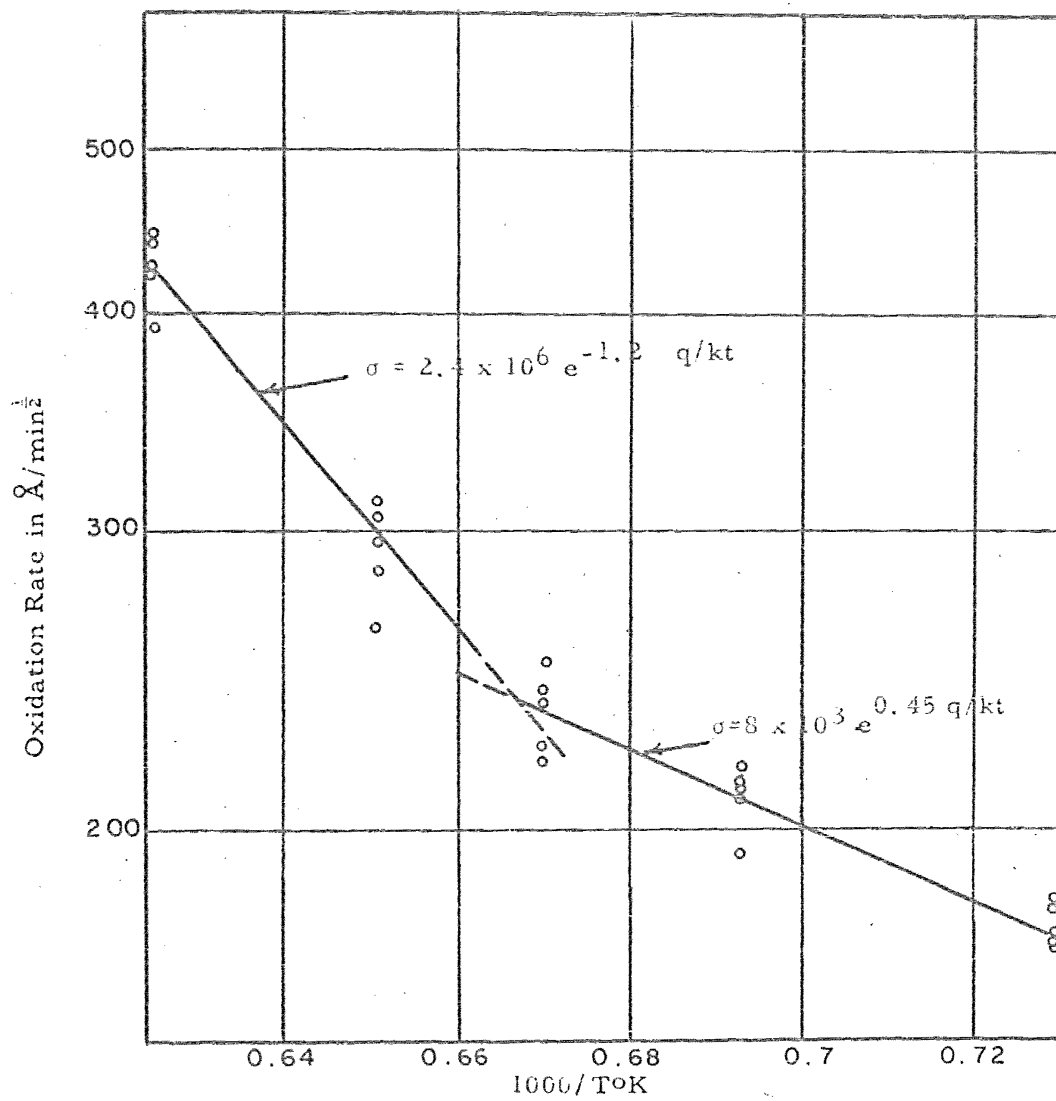


Fig. 26. Oxidation Rate as a Function of Inverse Temperature
0.001% Boron

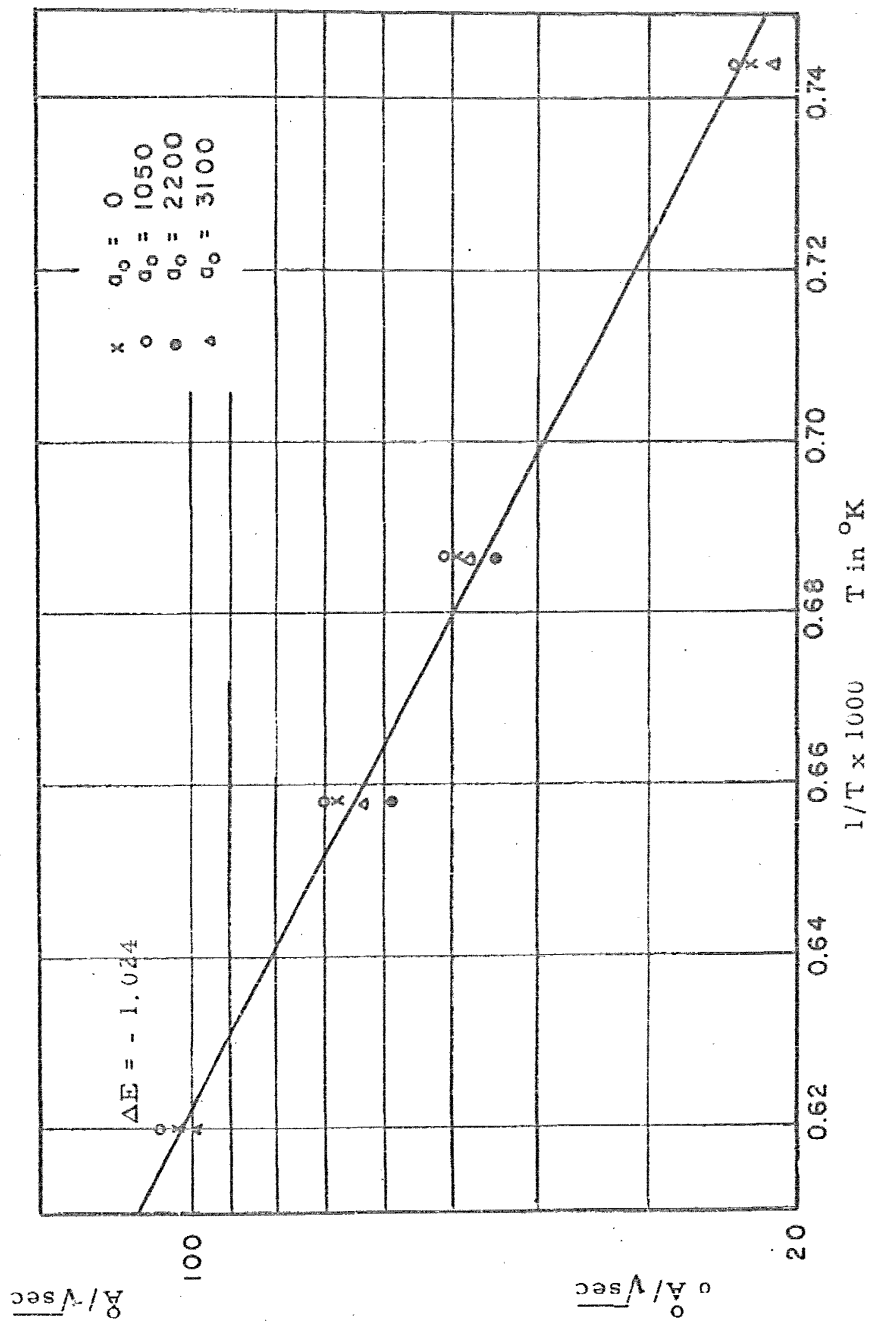
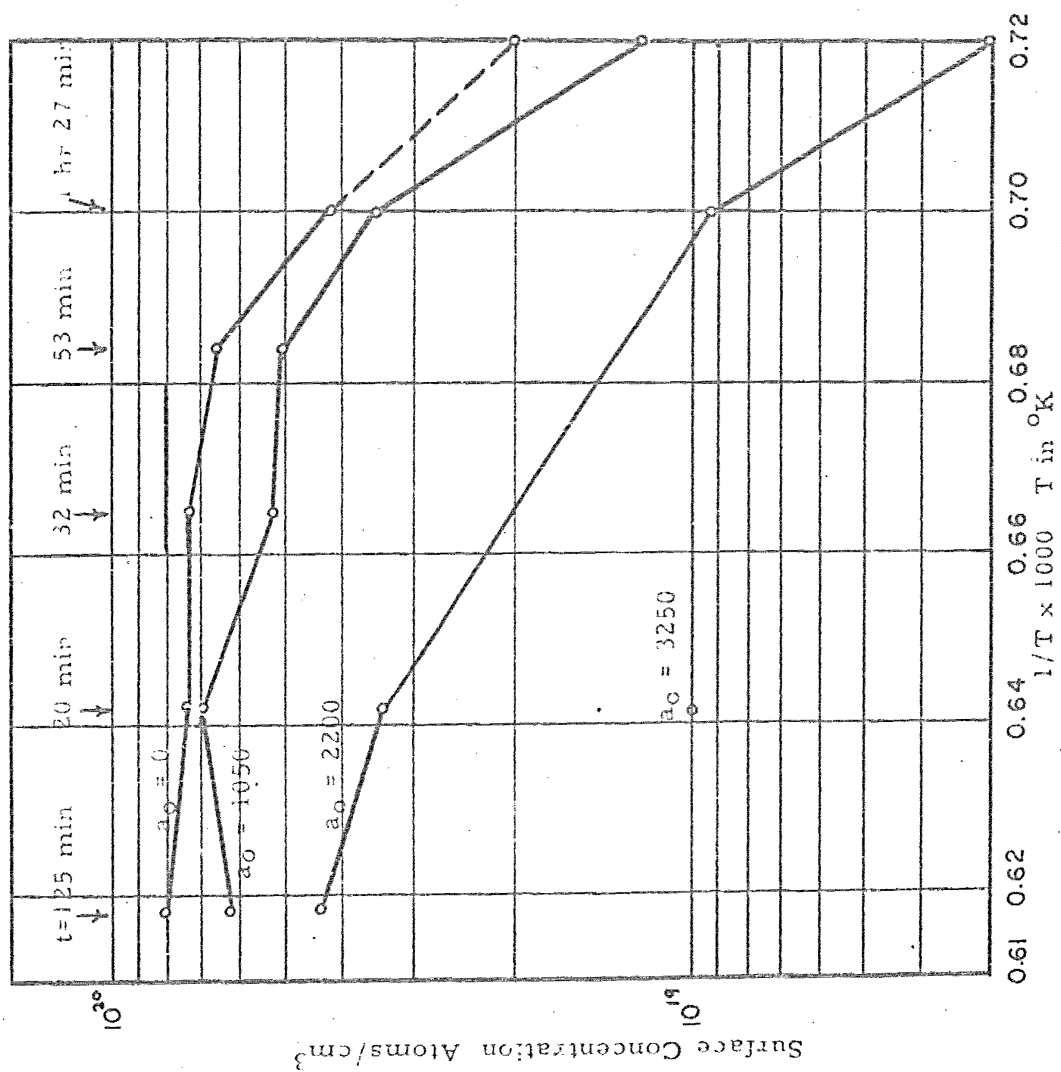


Fig. 27. Oxidation Rate Versus $1/T$ 0.003% Boron; Temperature Variation $\pm 15^{\circ}C$



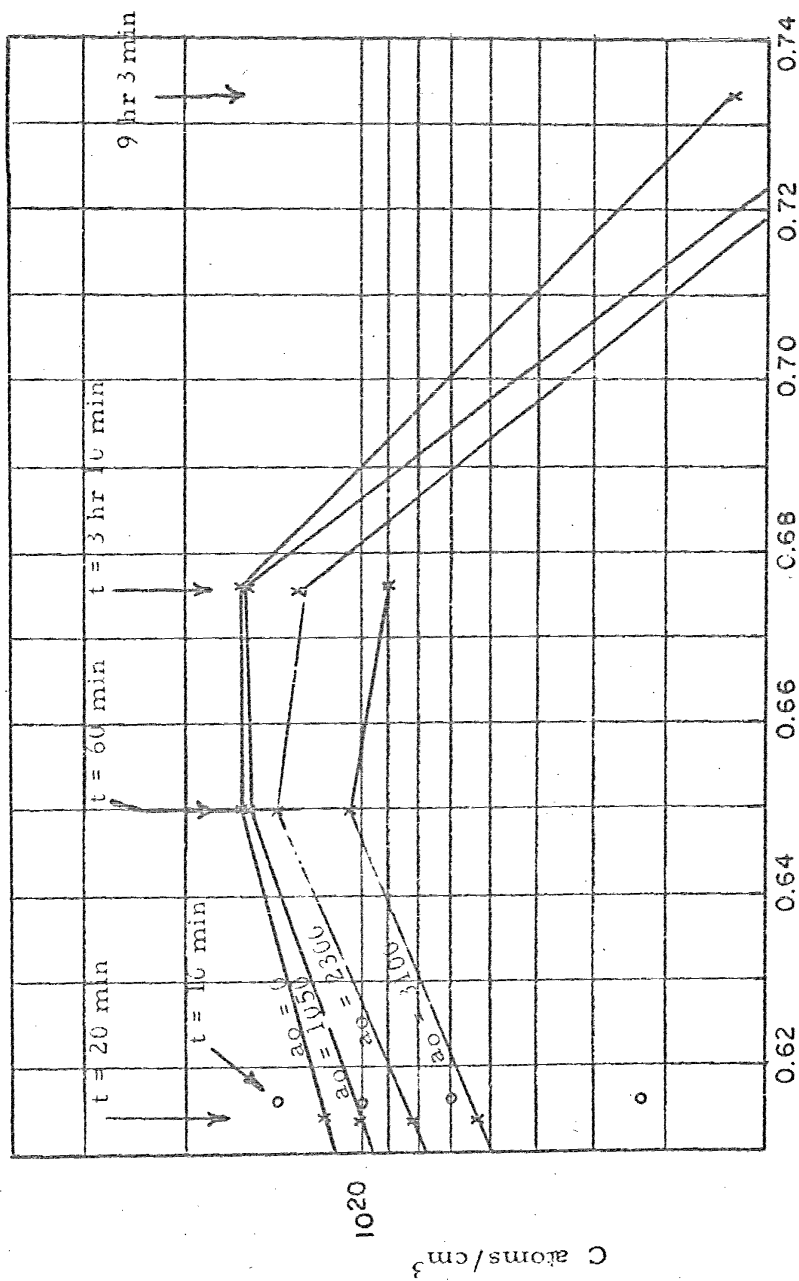


Fig. 20. C_0 and C_{ox} Versus $1/T$ for 0.01% Boron Source

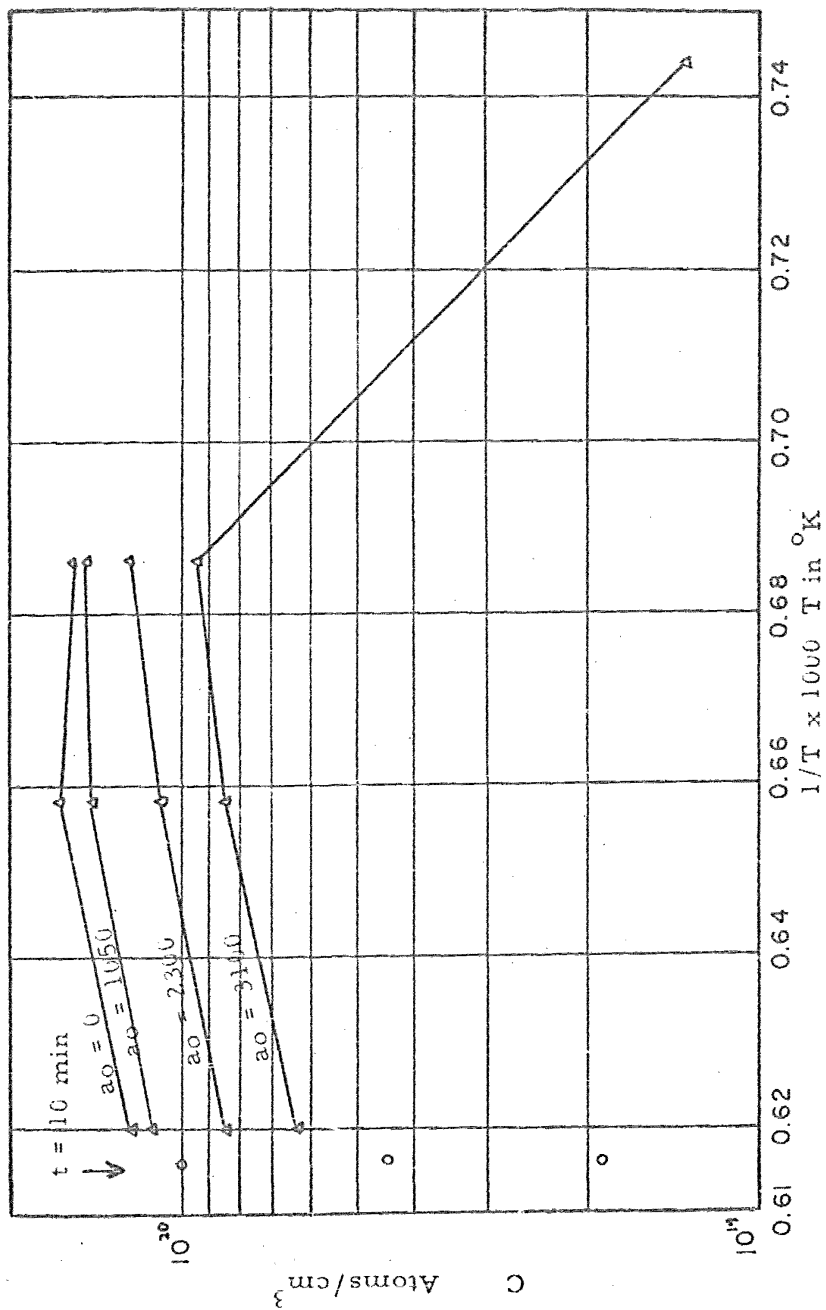


Fig. 22. C_0 and C_{ox} Versus $1/T$ for 0.003% Boron Source

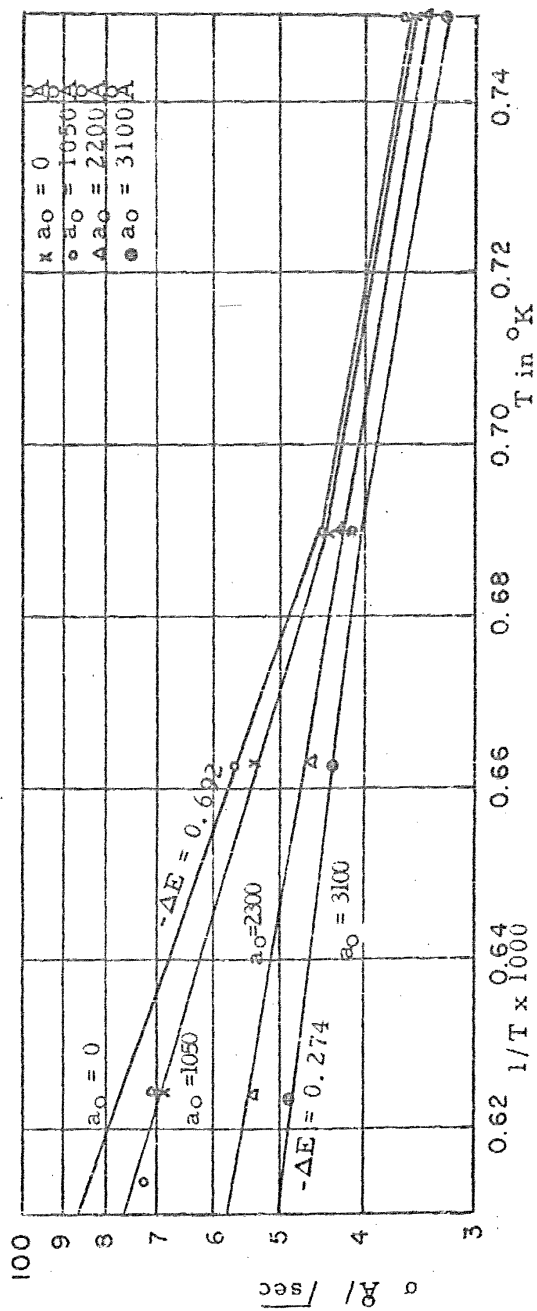


Fig. 23. Oxidation Rate Versus $1/T$, 1% Boron Temperature Variation $\pm 15^{\circ}\text{C}$

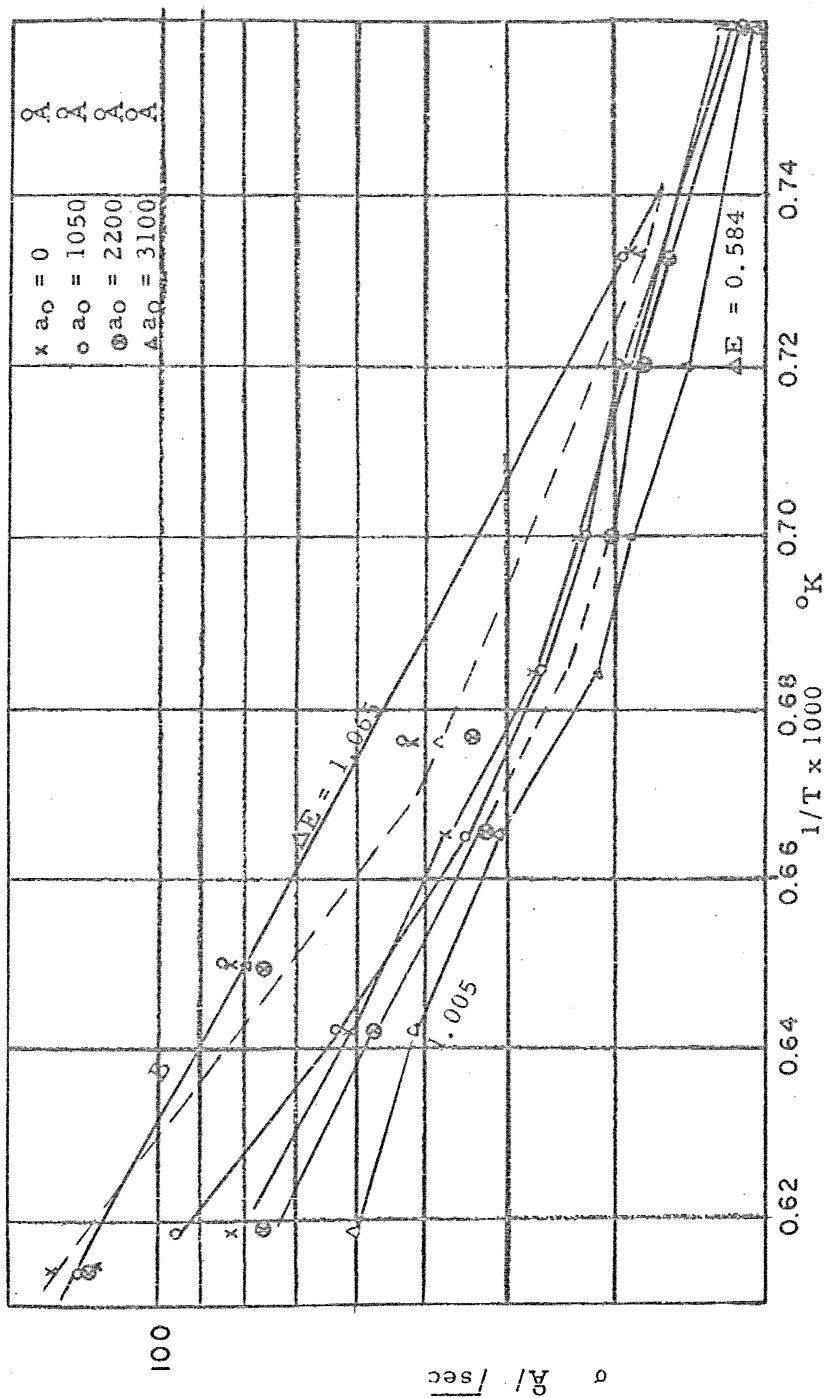


Fig. 25. Oxidation Rate Versus $1/T$ 0.01% Boron

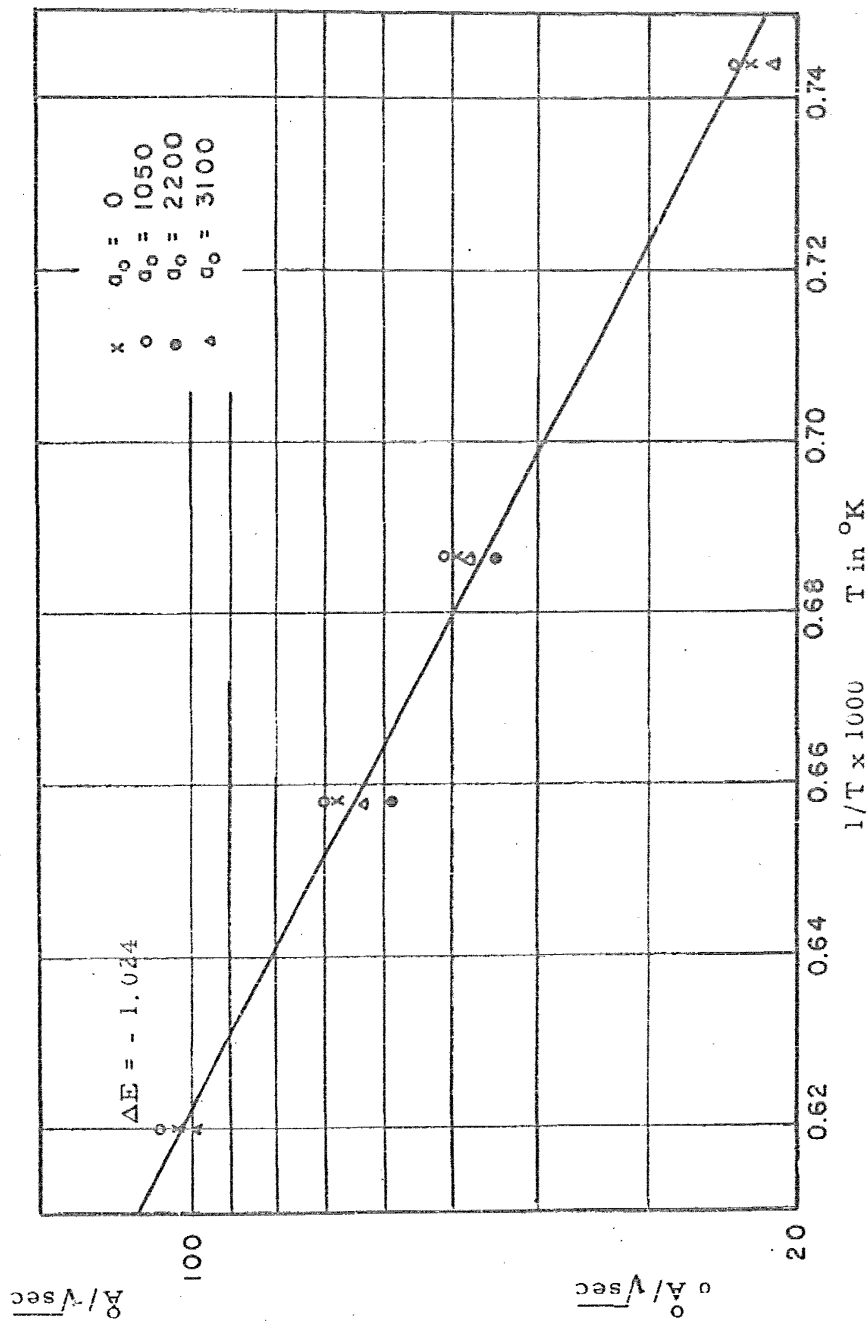


Fig. 27. Oxidation Rate Versus $1/T$ 0.003% Boron; Temperature Variation $\pm 15^{\circ}C$

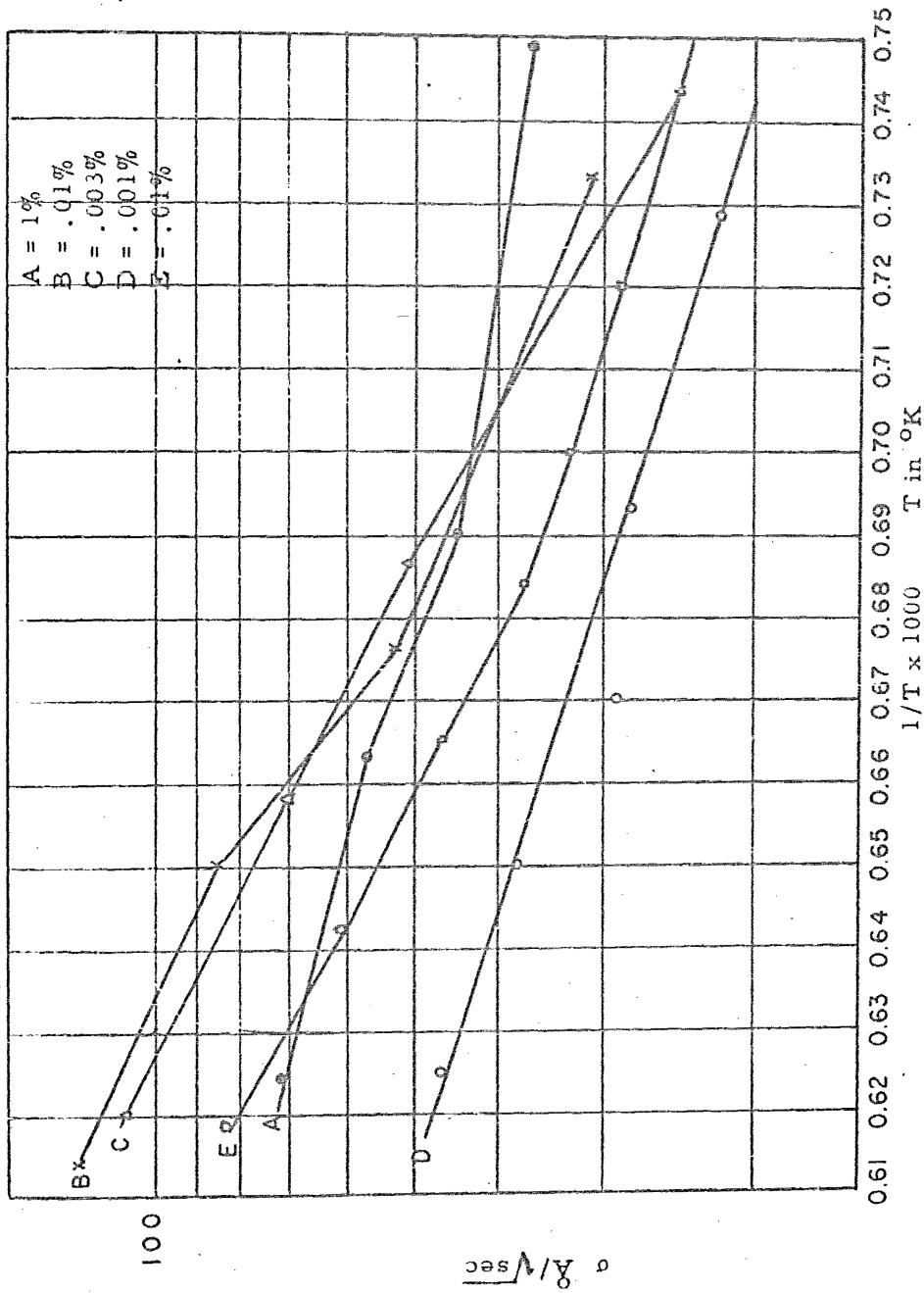


Fig. 28. σ Versus $1/T$ with $a_0 = 0$ for Different Source Strengths

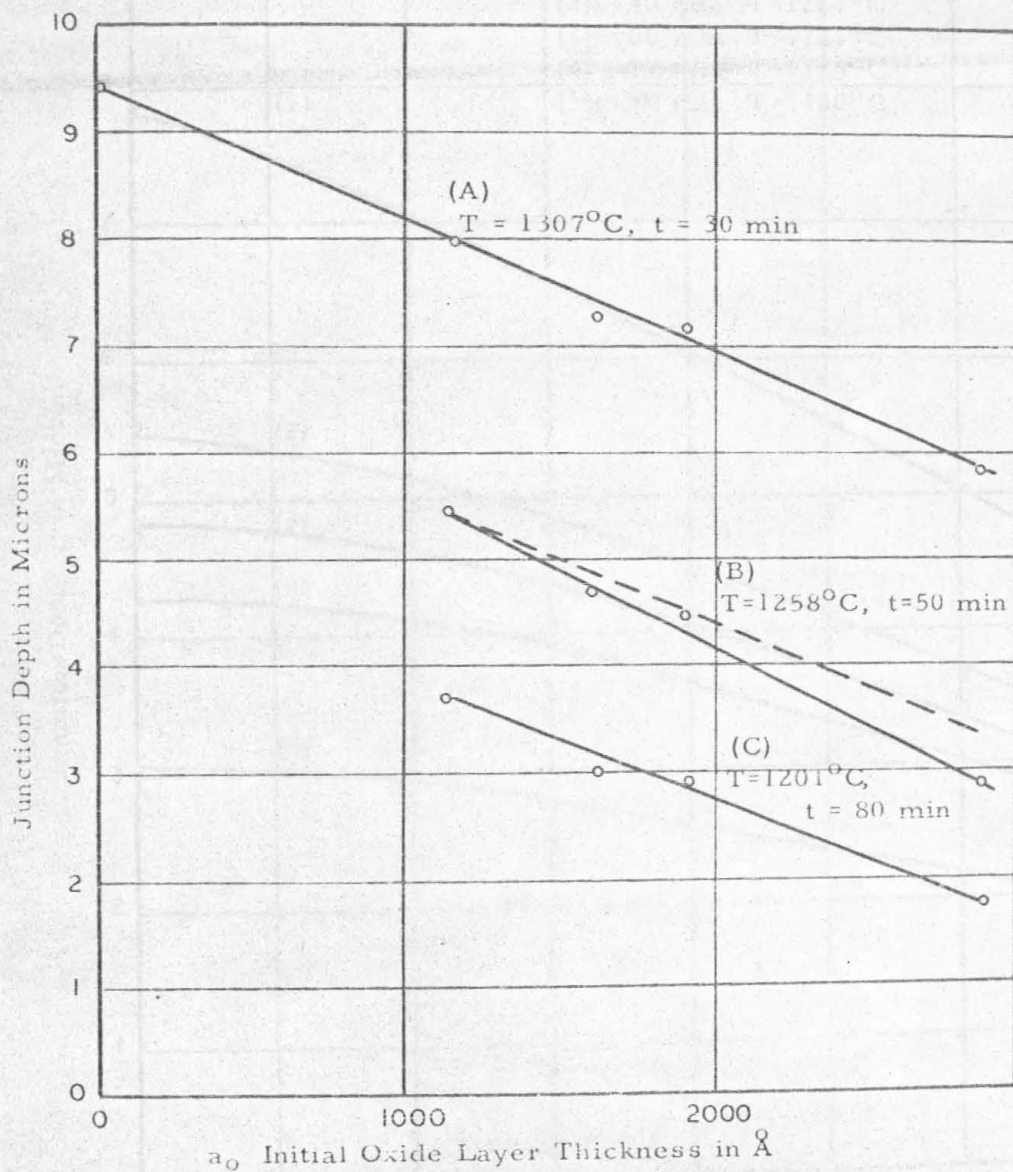


Fig. 29. Junction Depth as a Function of Initial Oxide Layer Thickness, 0.1% Boron

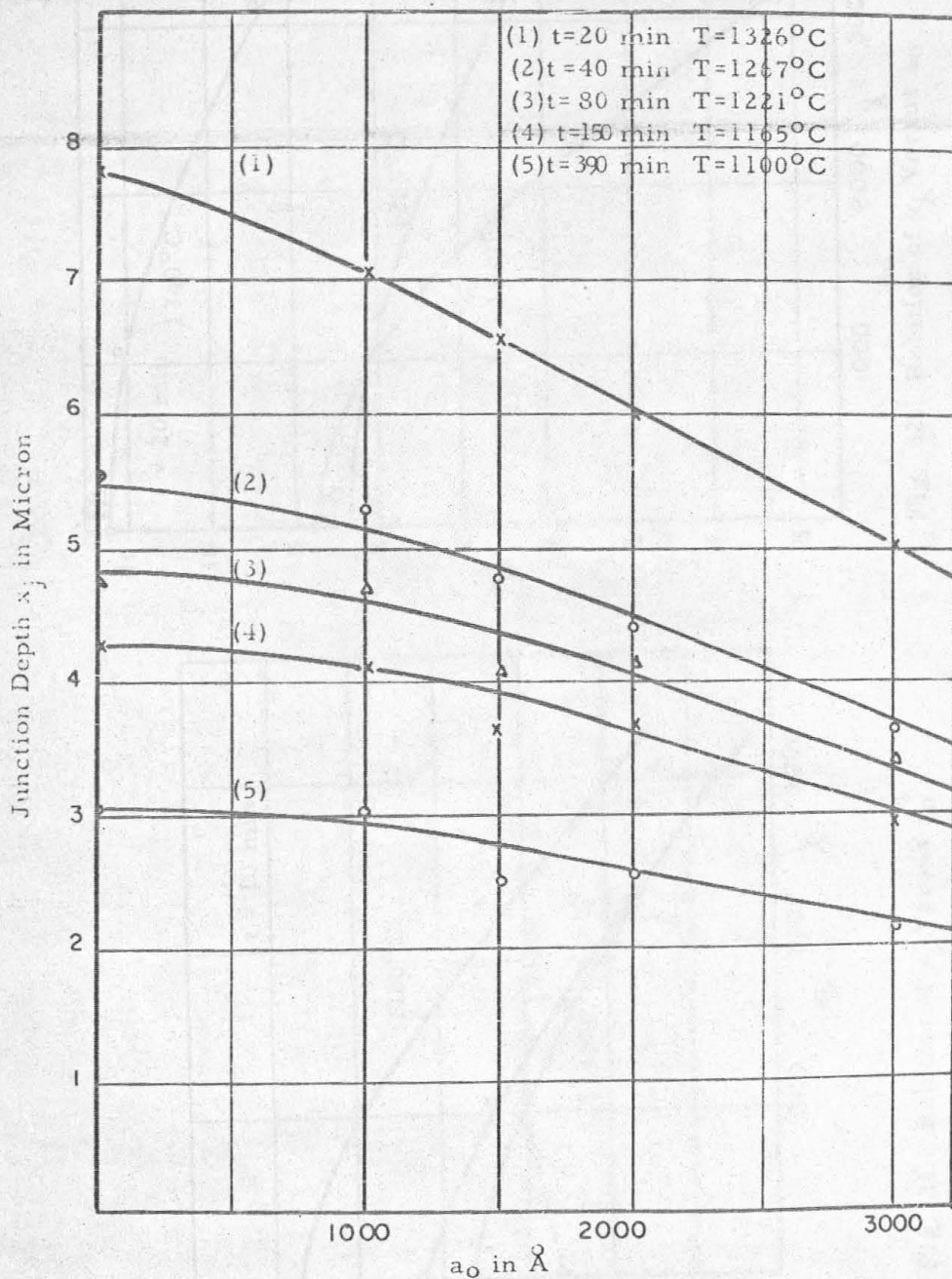


Fig. 30. Junction Depth as a Function of Initial Oxide Layer Thickness
0.001% Boron

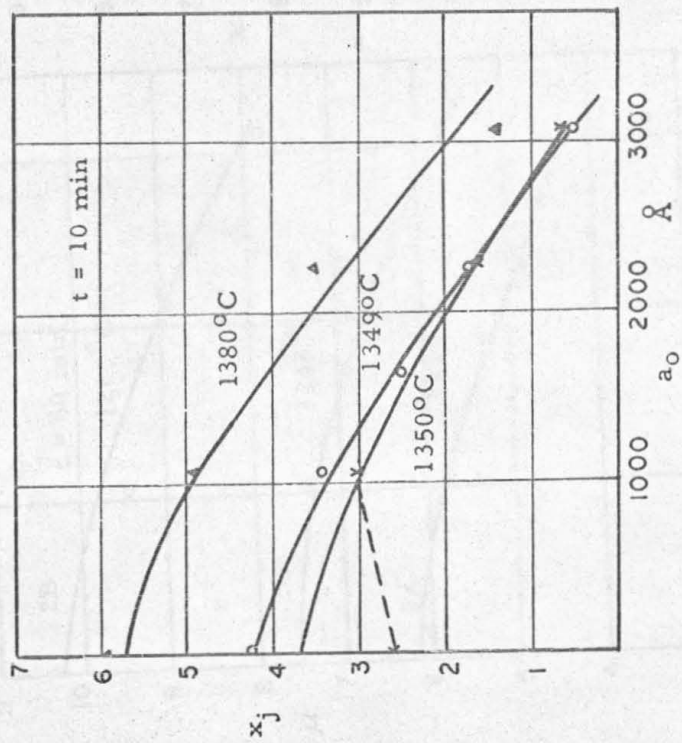


Fig. 31. Relation of x_j Versus a_0

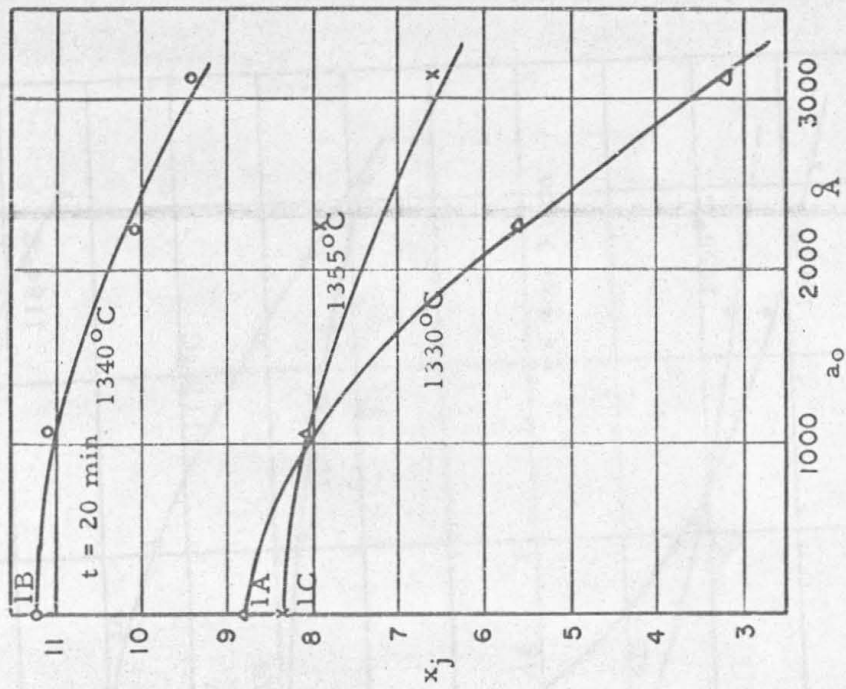


Fig. 32. Relation of x_j Versus a_0

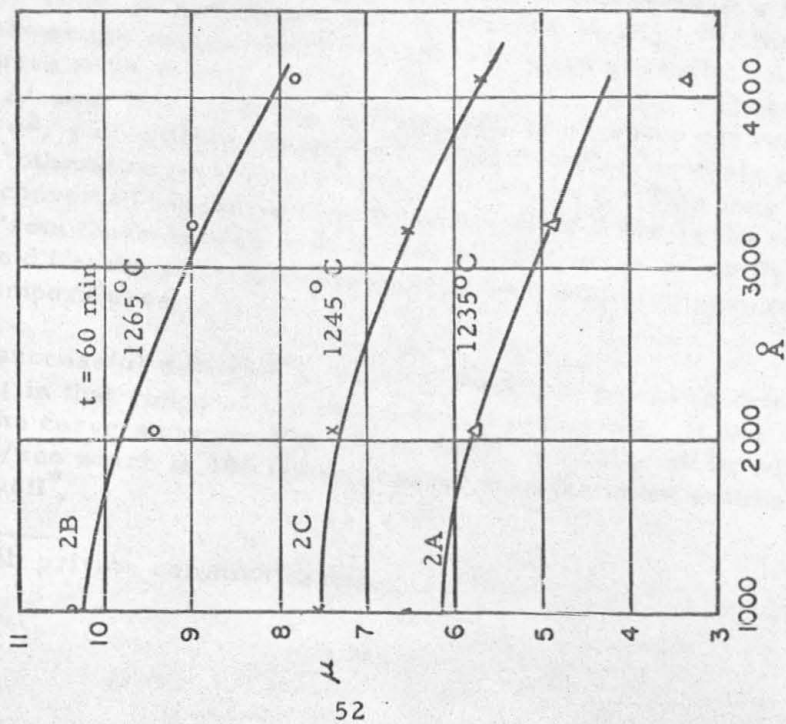


Fig. 33. Relation of x_j Versus a_0

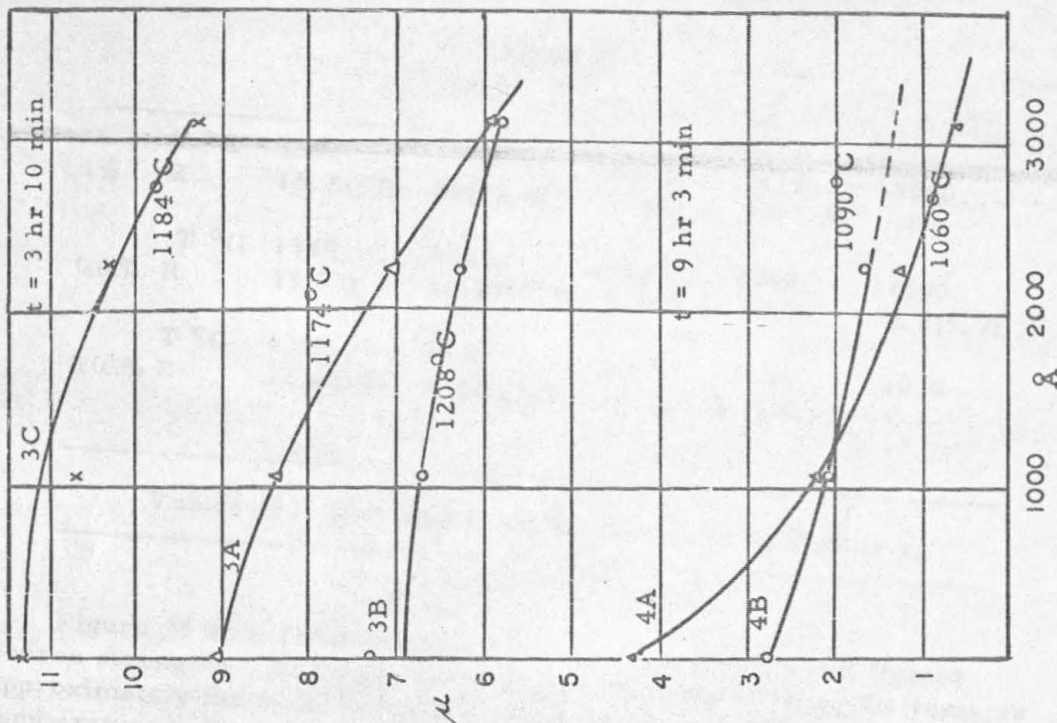


Fig. 34. Relation of x_j Versus a_0

are obtained from the measured D_1 . The R values obtained from these two methods agree moderately well.

TABLE II

	T °C	1380	1330	1235	1174	1060
1%	R	15.2(13)	28(11.5)	10(9)	13(7.5)	5(5)
	T °C	1349	1355	1265	1208	1090
0.01%	R	15(12)	10.2(12.7)	9.6(9.6)	7(8)	3.8(5.7)
	T °C	1350	1340	1245	1184	1070
0.003%	R	12.6(12)	9.2(12.2)	10.2(9.2)	9.8(7.6)	----

Values of R Obtained from the Slopes of x_j Versus a_0

Figure 35 shows the relation between D_1 and $1/T$ for different source strengths. Although there is considerable scatter, D_1 remains approximately the same value for different source strengths at a fixed temperature. Thus, an averaged curve was drawn in Fig. 35, the dotted line, which shows the variations of D_1 with $1/T$ approximately. Also shown is a curve of σ^2 versus $1/T$ for comparison with D_1 . These curves are labeled 'A' and 'B'. It indicates that if D_1 has a value not very much smaller than σ^2 , a converted layer is possible by diffusion in air at that temperature, otherwise no conversion can be obtained. This may explain why no converted layers were obtained at 1000°C for boron even for $a_0 = 0$. From these curves it is suspected that either σ^2 or D_1 or both may have different activation energies at low temperatures from that at high temperatures.

Since no successful diffusion at 1000°C for boron has been obtained, the value of D_1 in that range of temperatures is not known. If one extrapolates the curve shown in Fig. 35 to 950°C the value of D_1 will be 1×10^{-15} cm²/sec which is 10^4 times greater than the value estimated by Frank Keywell*.

*Frank Keywell; private communication.

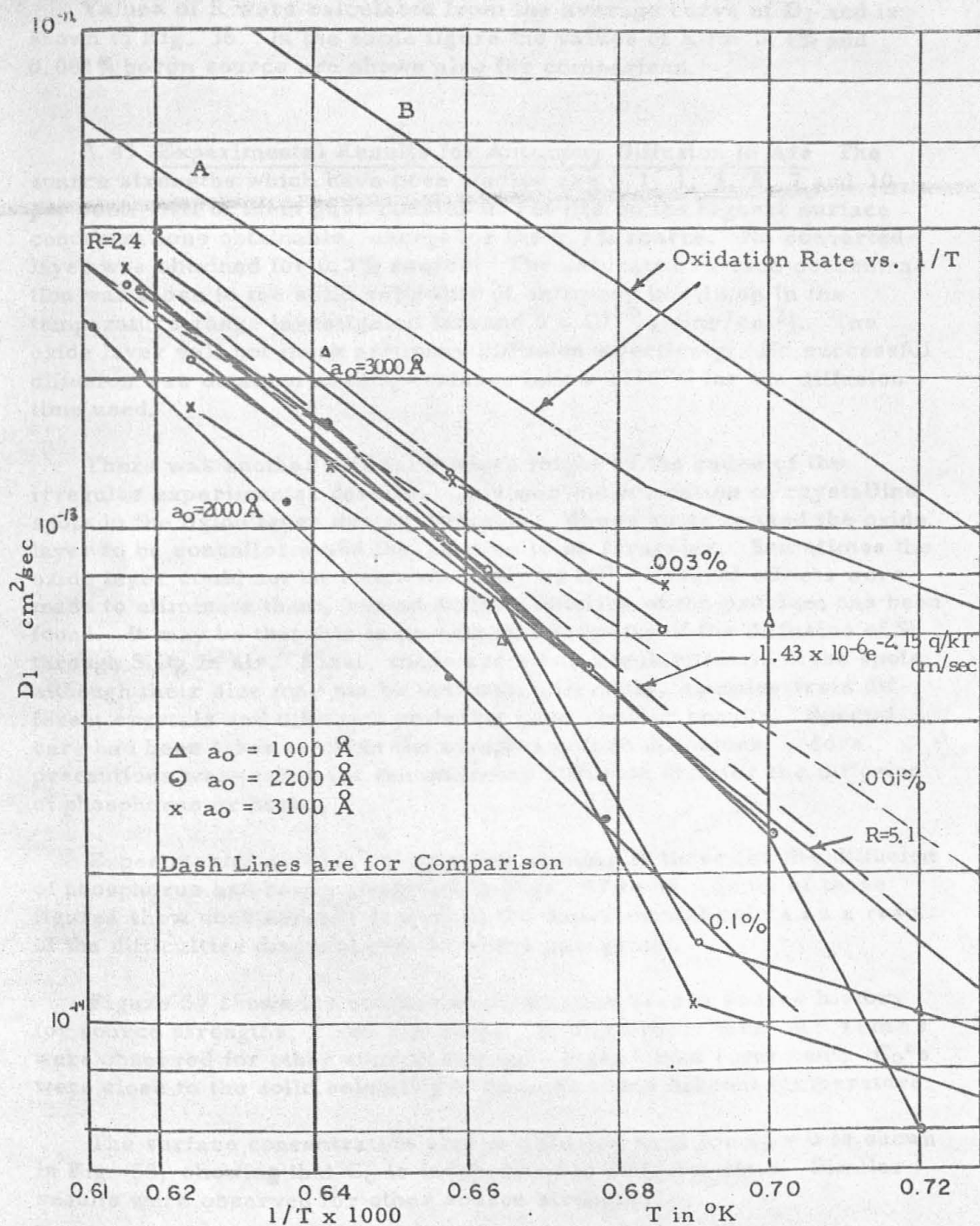


Fig. 35 Relation Between D_1 and $1/T$, Oxidation Rate and $1/T$ for Boron as Diffusant for Different Source Strengths

Values of R were calculated from the average curve of D_1 and is shown in Fig. 36. In the same figure the values of R for 0.1% and 0.001% boron source are shown also for comparison.

3.43 Experimental Results for Antimony Diffusion in Air The source strengths which have been studied are 0.1, 1, 3, 5, 7 and 10 per cent. All of them gave consistent results on the highest surface concentrations obtainable, except for the 0.1% source. No converted layer was obtained for 0.1% source. The saturated surface concentration was close to the solid solubility of antimony in silicon in the temperature range investigated (around 5×10^{19} atoms/cm²). The oxide layer will not mask antimony diffusion effectively. No successful diffusion was obtained at temperatures below 1150°C for the diffusion time used.

There was another difficulty which might be the cause of the irregular experimental results. This was the formation of crystalline spots in the oxide layer during diffusion. These spots caused the oxide layer to be nonuniform and the junction to be irregular. Sometimes the oxide layer could not be removed easily by HF. Several efforts were made to eliminate them, but no definite solution of the problem has been found. It may be that this is an inherent property of the diffusion of Sb through SiO₂ in air. First, there are some regularities in these spots although their size may not be uniform. Secondly, samples from different crystals and different polishing gave similar results. Special care had been taken to clean the samples before diffusions. More precautions were taken for the antimony diffusion than for the diffusion of phosphorus or boron.

Experimental results on antimony similar to those for the diffusion of phosphorus and boron are given in Figs. 37 to 58. Some of these figures show considerable scatter of the experimental points as a result of the difficulties discussed in the above paragraph.

Figure 37 shows the surface concentration versus source history for source strengths, 1 and 5 percent. Similar short bake-out times were observed for other source strengths higher than 1 per cent. C_0 's were close to the solid solubility of Sb in Si at the bakeout temperature.

The surface concentration versus diffusion time for $a_0 = 0$ is shown in Fig. 38, showing that C_0 is independent of diffusion time. Similar results were observed for other source strengths.

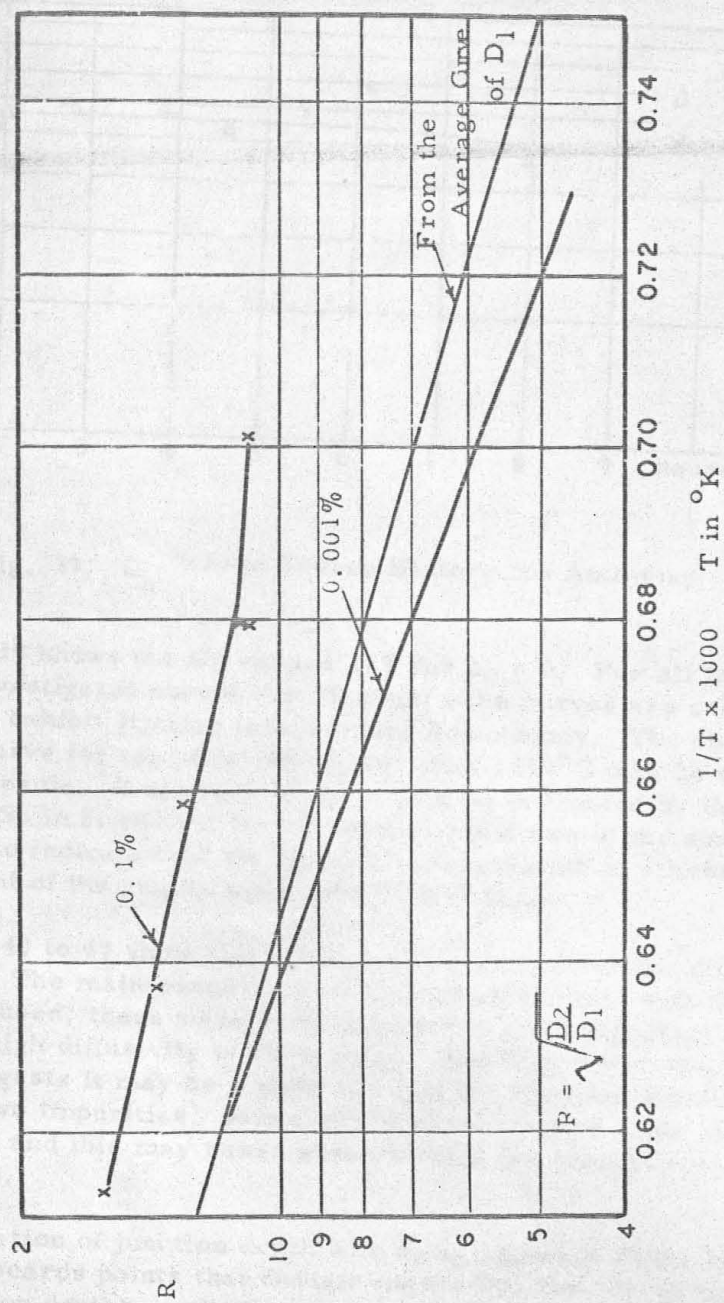


Fig. 36. R Versus $1/T$ for Boron

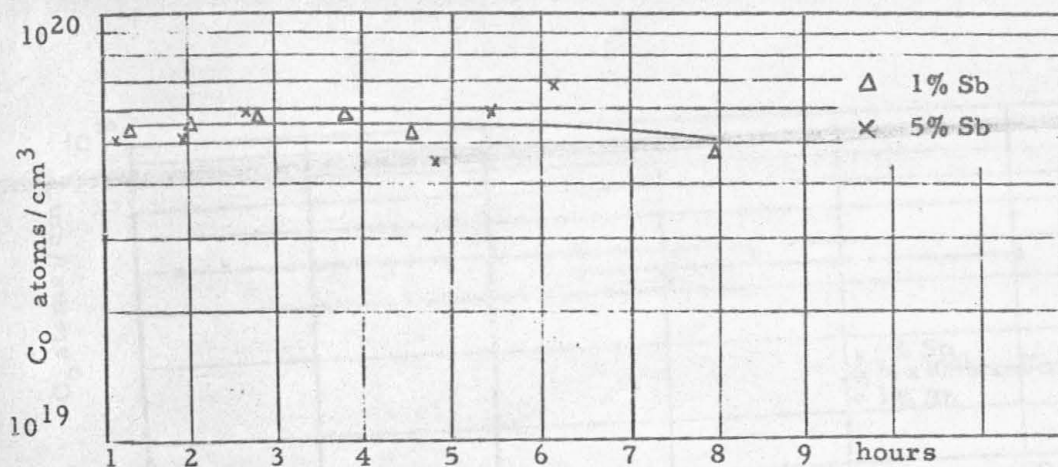


Fig. 37. C_0 Versus Source History for Antimony

Figure 39 shows the C_0 versus $1/T$ for $a_0 = 0$. For all the source strengths investigated except the 3% source the curves are crowded together and exhibit similar temperature dependency. The sharp drop for the 3% curve for temperatures lower than 1230°C may be the result of a loose capsule. It appears obvious that C_0 is limited by the solid solubility of Sb in Si and not by the surface condition of the source. This seems to indicate that the surface concentration at silicon surface is independent of the source strengths in this range.

Figures 40 to 47 show C_{ox} versus a_0 for the particular diffusion time shown. The main conclusion one can draw is that, with the initial oxide layers used, there were very little oxide masking effect on Sb, indicating a high diffusivity of Sb in SiO_2 . The high diffusivity of antimony suggests it may be a good element for studying simultaneous diffusion of two impurities. However, it has a limited value of surface concentration and this may cause some trouble for simultaneous diffusion studies.

The variation of junction depth with a_0 is shown in Figs. 48 to 56. If one discards points that deviate markedly, the curves indicate that the junction depths do not vary substantially for different a_0 's for the diffusion times and temperatures investigated.

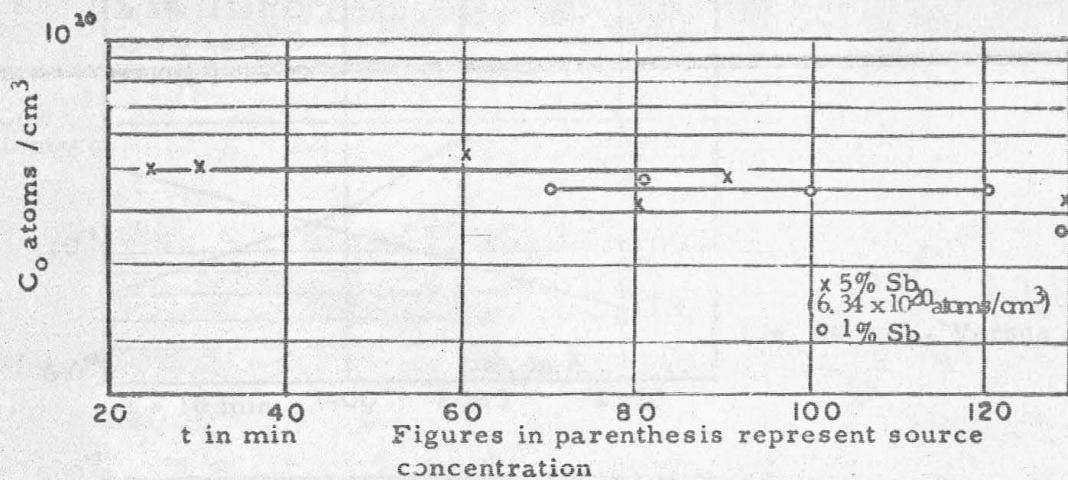


Fig. 38. C_0 Versus Diffusion Time, $a_0 = 0$

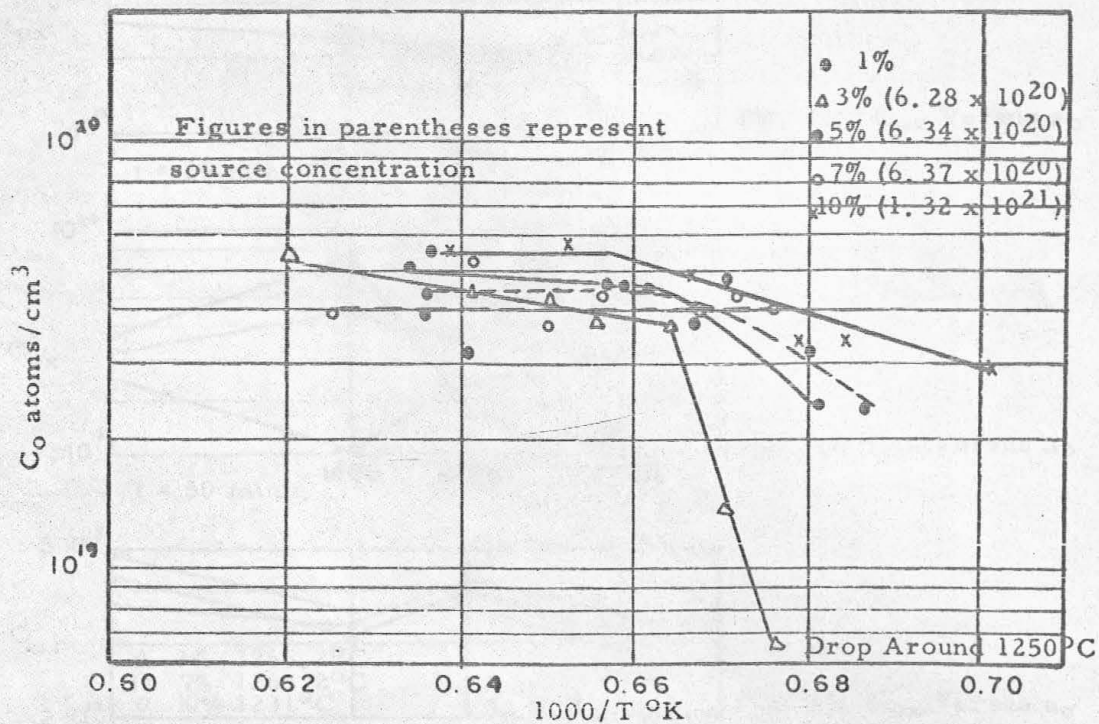


Fig. 39. C_0 Versus $1/T$ for Different Source Strengths

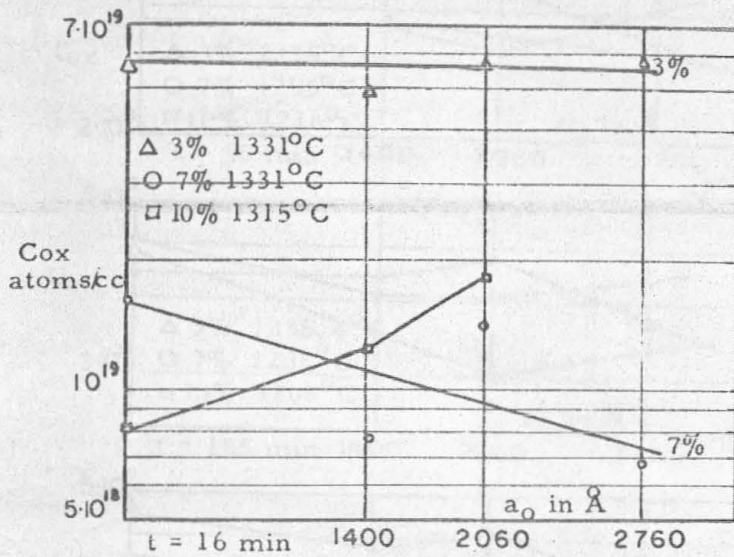


Fig. 40. C_{ox} Versus a_0

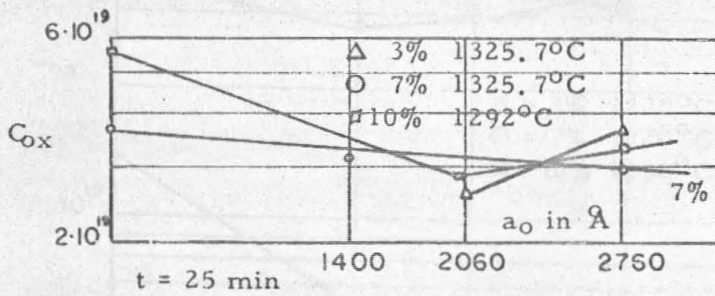


Fig. 41. C_{ox} Versus a_0

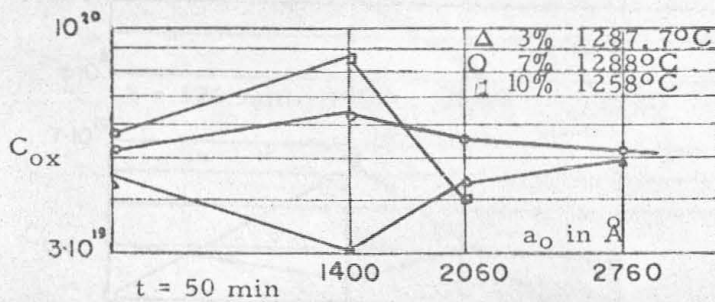


Fig. 42. C_{ox} Versus a_0

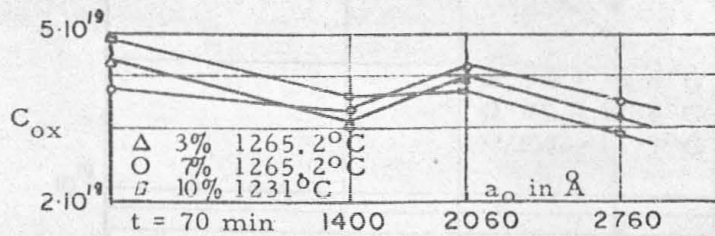


Fig. 43. C_{ox} Versus a_0

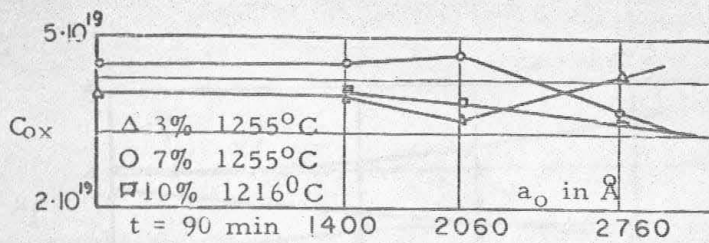


Fig. 44. C_{ox} Versus a_0

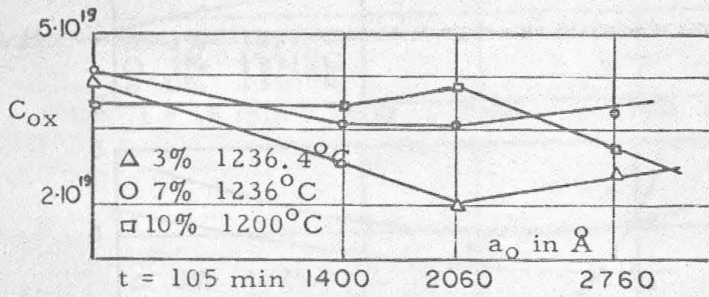


Fig. 45. C_{ox} Versus a_0

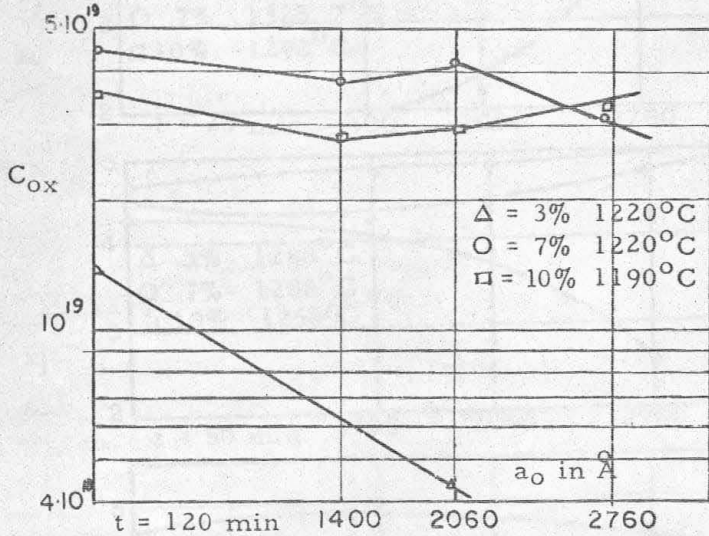


Fig. 46. C_{ox} Versus a_0

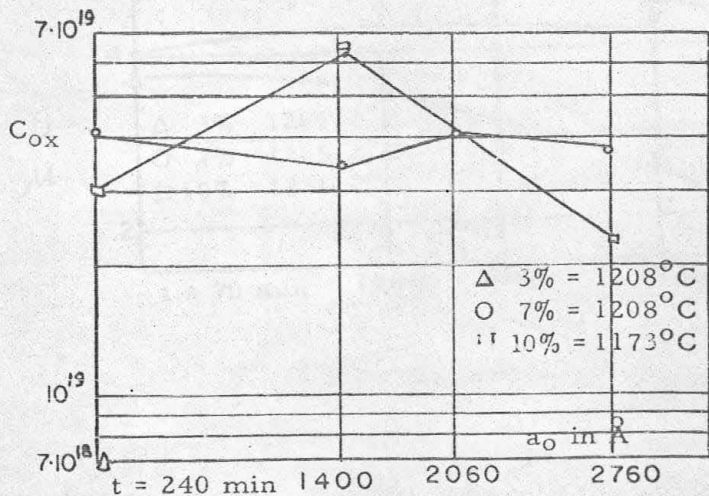


Fig. 47. C_{ox} Versus a_0

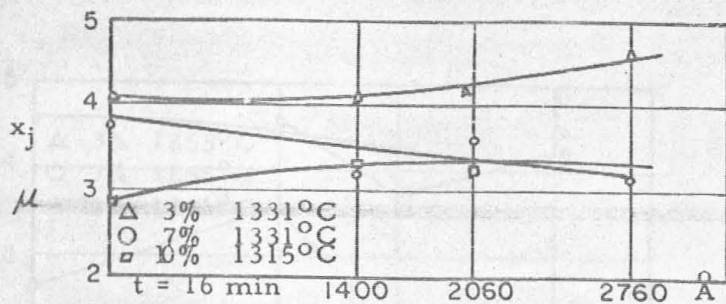


Fig. 48. x_j Versus a_0

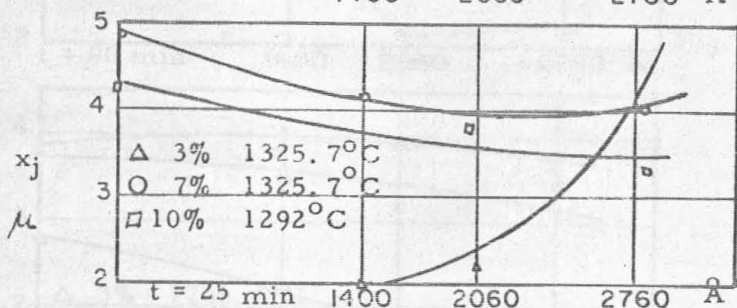


Fig. 49. x_j Versus a_0

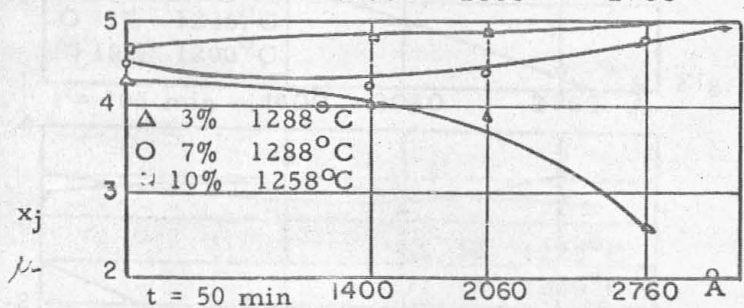


Fig. 50. x_j Versus a_0

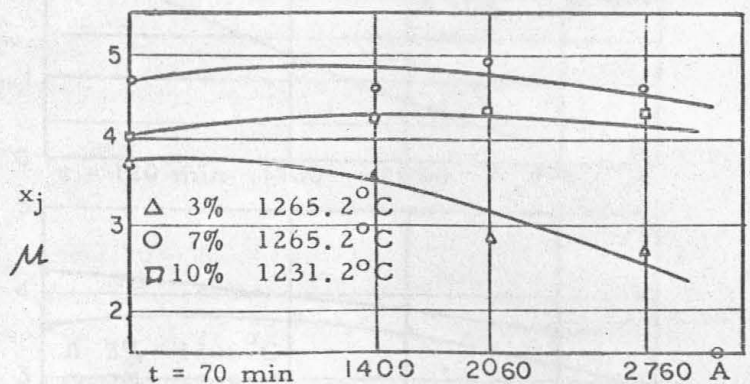


Fig. 51. x_j Versus a_0

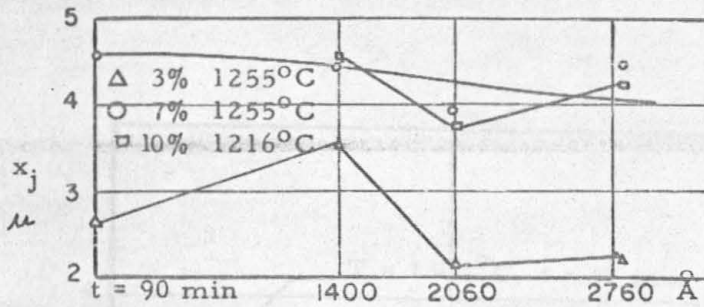


Fig. 52. x_j Versus a_0

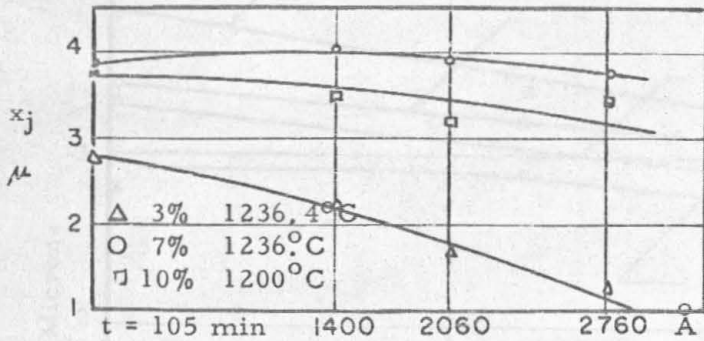


Fig. 53. x_j Versus a_0

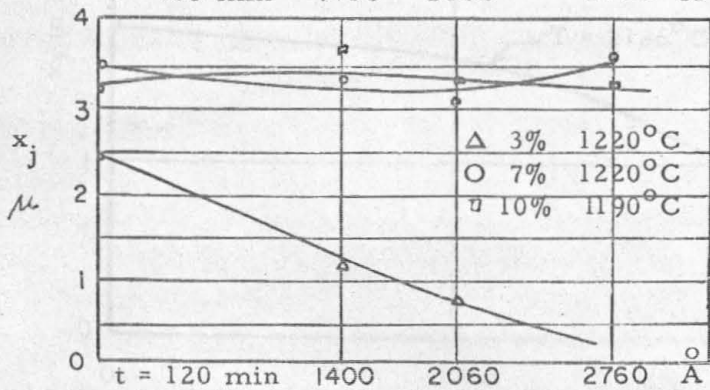


Fig. 54. x_j Versus a_0

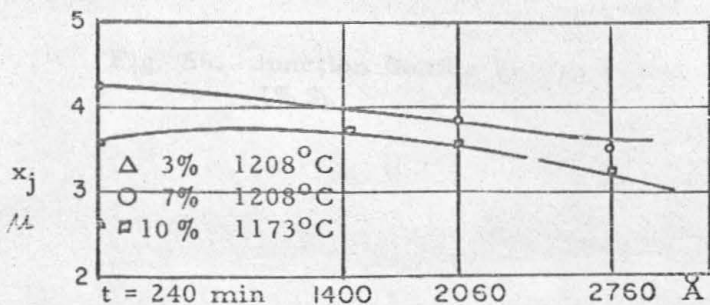


Fig. 55. x_j Versus a_0

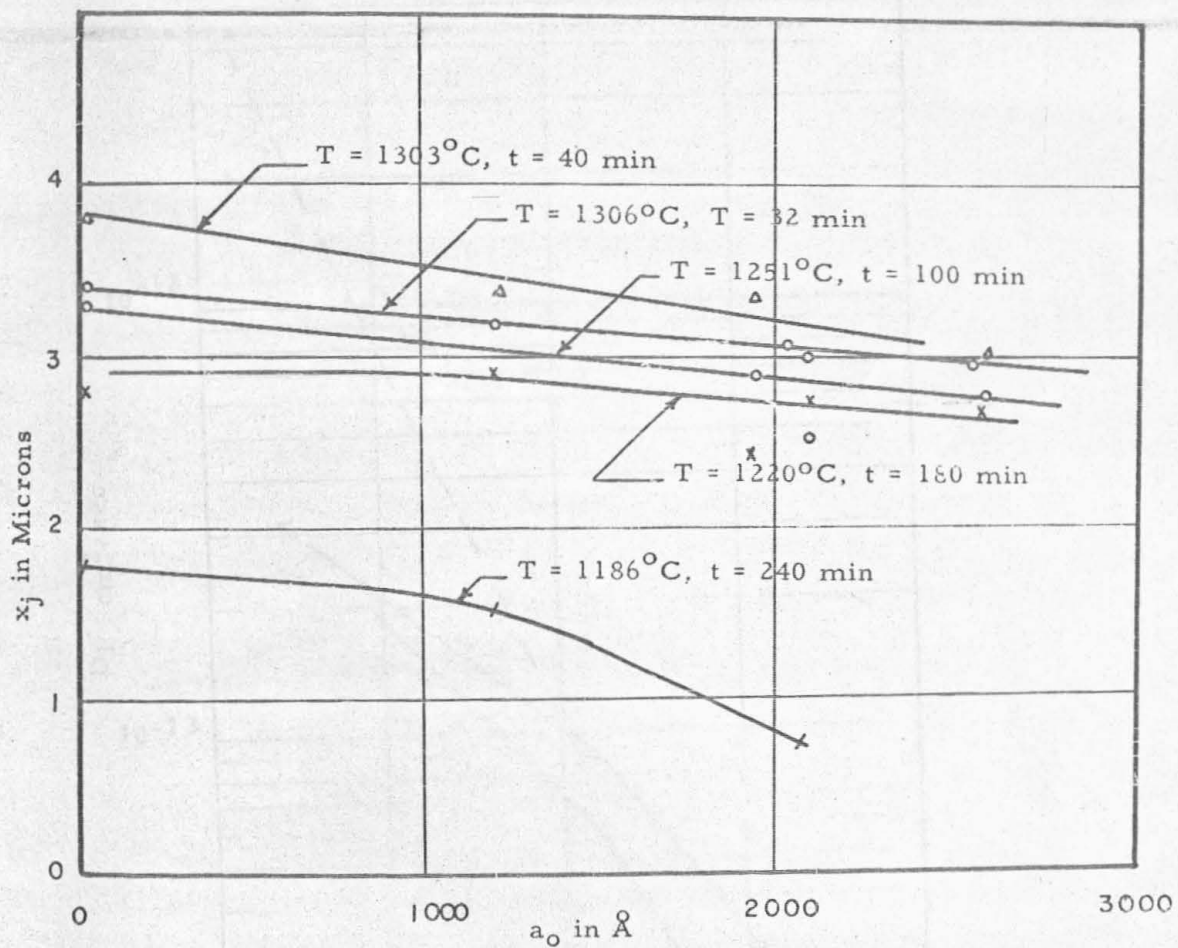


Fig. 56. Junction Depths Versus Initial Oxide Layer Thickness, 1% Sb

As a result of measurement difficulties there were uncertainties in the calculation of D_1 from the experimental results. Only three sets of D_1 seemed to be consistent and they are shown in Fig. 57. If one compares the D_1 's with different source strengths it seems that D_1 for 3% source does not agree with the other two source strengths.

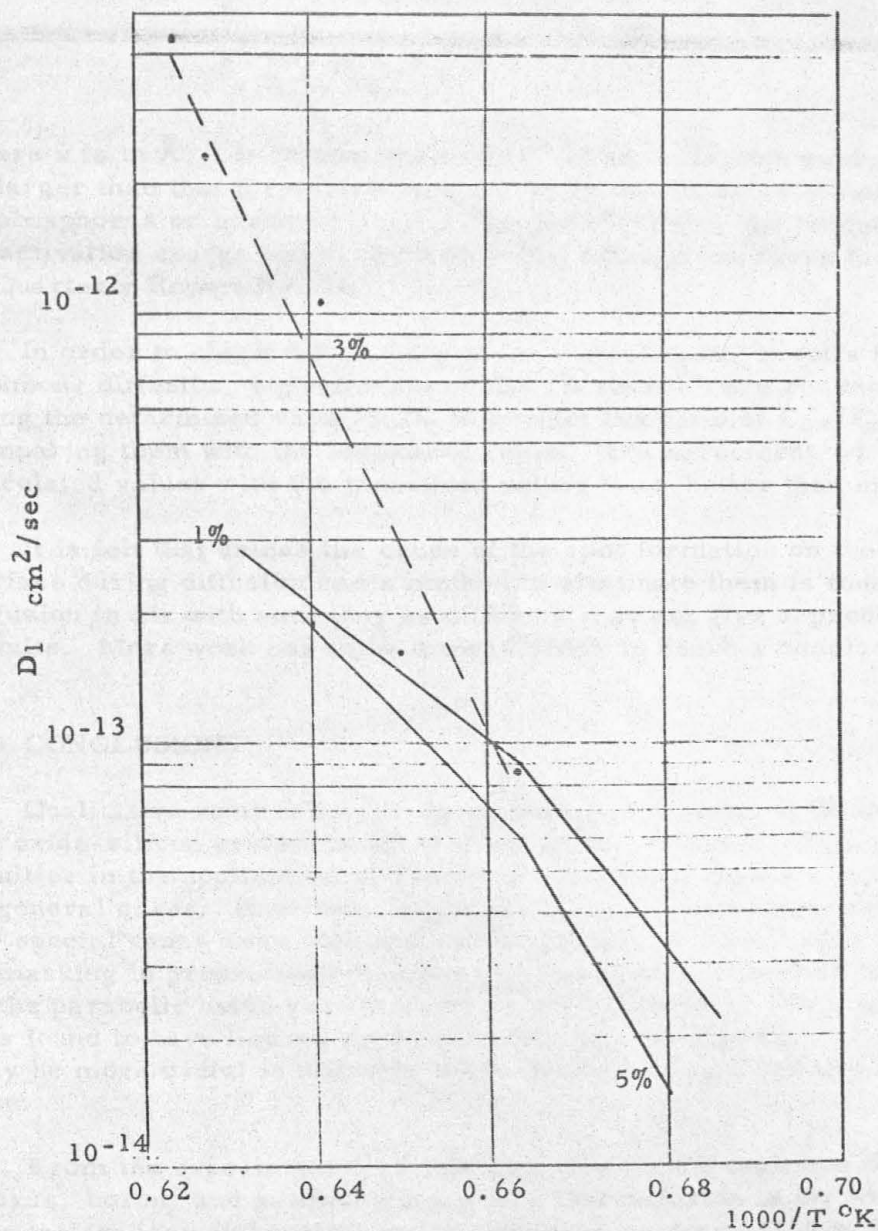


Fig. 57. D_1 Versus $1/T$ for Sb as Diffusant

Figure 58 shows the calculated R from Fig. 57 as a function of $1/T$ for 1 and 5% sources.

An expression of oxide layer thickness as a function of time and temperature under the diffusion condition for the 5% source is

$$x^2 = 1.32 \times 10^{16} t e^{-3.6 \frac{q}{kT}} \quad (53)$$

where x is in Å, t is in minutes. This has an activation energy which is larger than that for oxidation in air or in the diffusion atmosphere of phosphorus or boron sources. For the 1% source the oxidation has an activation energy which is close to the value given above (see Fig. 13 of Quarterly Report No. 5).

In order to check the validity of the experimental results for antimony diffusion, experiments on the 1% source were conducted using the determined value of D_1 to predict the ratio of C_{ox}/C_{no} and comparing them with the measured value. The agreement of the calculated values with the measured values was better than expected.

It is felt that unless the cause of the spot formation on the sample surface during diffusion and a method to eliminate them is found, the diffusion in air with antimony as diffusant may not give reproducible results. More work has to be done in order to reach a conclusion.

4.0 CONCLUSIONS

Qualitative verification of the mathematical model of diffusion in the oxide-silicon system in air was obtained. The mathematical difficulties in the application of Fick's law to this system are very great in general cases. However, relatively simple approximate solutions for special cases were obtained and evaluated. A first-order analysis of masking in preoxidized samples was based on approximating a segment of the parabolic oxide growth curve by a straight line. This approximation was found to have limited application for diffusions in air. However, it may be more useful in diffusion methods permitting a reduced oxidation rate.

From the experimental results obtained for the diffusion of phosphorus, boron, and antimony it appears that diffusion in air with the box system is useful mainly in the temperature range 1150 to 1350°C. For diffusions at temperatures lower than 1150°C a reduction of oxidation rate will be needed.

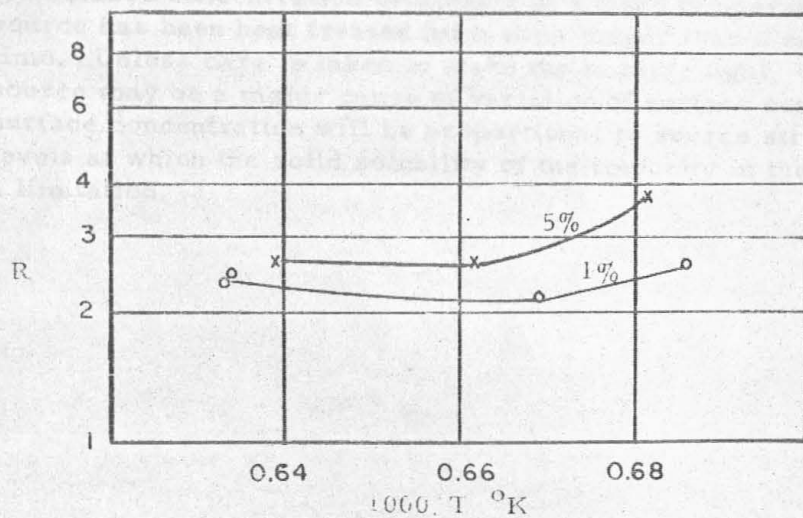


Fig. 5b. R Versus $1/T$ for Sb

Although a conclusive answer to the problems of the oxidation mechanism for silicon in air and the diffusion atmosphere was not obtained, considerable evidence has been accumulated. Some experimental results indicate that the mechanism of oxidation may be different at high and low temperatures. The relative magnitudes of the diffusivity of the diffusant atoms in SiO_2 and the oxidation rate in an oxidation atmosphere governs the diffusion phenomenon. If the square of the oxidation rate has a value larger than D_1 by more than an order of magnitude the diffusion into the silicon will be very much retarded. The "activation energies" for oxidation under diffusion conditions vary with source strength and with the type of diffusant atoms and they differ also from those for oxidation in air and steam.

The source strength of a diffusant may not reproducibly determine the surface concentration obtainable at a fixed temperature unless the source has been heat treated for a time longer than a critical bake-out time. Unless care is taken to make the capsule tight, depletion of the source may be a major cause of variation of surface concentration. The surface concentration will be proportional to source strength up to levels at which the solid solubility of the impurity in the silicon becomes a limitation.

APPENDIX A

THE PREPARATION OF THE STANDARD OXIDE LAYER THICKNESS GUIDE

It is reported that there is a definite relationship between the interference color of the silicon dioxide layer and its thickness (ref. 6). This can be expressed as

$$a = \frac{(2b - 1) \lambda}{4\mu} \quad (\text{A-1})$$

where a = oxide layer thickness in the same units as λ ,
 b = the order of reflection,
 λ = the wavelength of the color which corresponds to the color complementary to that seen by reflection of white light,
 μ = the index of reflection of light waves in SiO_2 . It has a value between 1 and 1.5.

However, this equation cannot be applied readily. A color chart is provided which is shown in Table A-1 (ref. 7). This chart has the drawback of being too subjective. Since the perception of color depends on individuals, deep blue, for example, may represent different thickness to different persons. Moreover, it is very hard to extend this chart to oxide layers thicker than 3000 Å. Thus an easy and objective standard of oxide layers became necessary. It was prepared as follows:

One hundred and fifty samples of silicon were divided into ten groups and oxidized in steam to ten thicknesses from 1000 to 10,000 Å at 1000 Å steps with fifteen samples in each group. The oxidation time was determined by estimation from past experience and the fact that the difference of the time between two groups followed the parabolic relation between thickness and time. Thus, although the thicknesses of the samples of each group might not be exactly 1000 Å, or 2000 Å, etcetera, the thickness differences between successive groups were constant.

One sample from each group was used for thickness measurement by the interference fringe shift method. The sample surfaces were masked and the oxide layers which were unprotected were removed by HF. This produced a step on the sample surface, one side being the oxide surface and the other side the silicon surface. The sharpness of the step was very important for a sharp fringe shift. The sample surfaces were next gold-plated to about 300 Å so that the reflection surfaces were at the same condition for both the silicon side and the oxide side.

TABLE A-1

Color	Brownish White	Clean Brown	Dark Brown	Red Brown	Dark Purple	
λ	685	733	795	850	884	
Color	Dark Violet	Dark Blue	Clearish Blue to Greenish	Still Clear Blue	Pale Blue Green	
λ	925	959	1120	1610	1680	
Color	Pale Green	Clear Yellow Green	Clear Yellow	Golden Yellow	Orange	
λ	1760	1860	1930	2060	2410	
Color	Red	Deep Purple	Violet	Blue	Greenish Blue	Bluish Green
λ	2550	2650	2800	2980	3180	3360

Monochromatic sodium light was used to produce the interference pattern which satisfies the following relationship. (See Fig. A-1).

$$x = \frac{\lambda}{2} \left(\frac{c}{d} \right) \quad (\text{A-2})$$

Thus the oxide layer thickness was determined for each group.

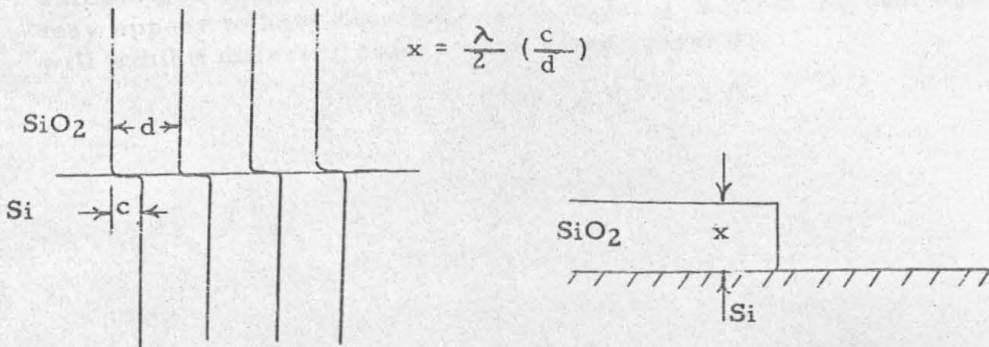


Fig. A-1. The relation between oxide layer thickness and the interference fringe shift produced by a monochromatic light with wavelength λ .

It has been established that the etching rate of a diluted HF solution is constant. Thus if one determines the etching rate experimentally and then removes the oxide layer for a predetermined time, the oxide layer which is removed will be a known quantity. A representative etching curve is shown in Fig. A-2. This was determined by the color chart in Table A-1 and checked with the interference fringe measurements.

Thirteen out of the remaining fourteen samples in each group were etched in the diluted HF solution to steps of $100 \text{ \AA}$, approximately. This was done by regrouping these samples into thirteen, each of which had ten samples with different oxide layer thicknesses. All of them were put into the diluted HF at the same time. The first ten samples were taken out at a time such that approximately $100 \text{ \AA}$ had been removed. $200 \text{ \AA}$ were removed from the second ten samples, etcetera. The interval between two successive groups was constant, which was the time needed to remove $100 \text{ \AA}$. In this way ten overlapping series of oxide layers were obtained. Each series had 14 samples in $100 \text{ \AA}$ steps: thirteen etched samples and one which had not been used. For example, one series had the range from $1000 \text{ \AA}$ to $2500 \text{ \AA}$ and another series had the range from $200 \text{ \AA}$ to $3500 \text{ \AA}$.

These samples were arranged to give a series of standard samples by comparing the colors for the overlapped samples and the thicknesses measured by the interference fringe shift. The series has a range from 500 to $10,000 \text{ \AA}$. When measurements of oxide layer thickness is needed one has only to compare the color of the sample with the standard samples. Since human eyes can distinguish different colors rather accurately, this is a rather objective and fast method. The order of interference color can be determined either by mask etching of part of the sample to be measured and counting the number of color bands under a microscope, or by observing the color change resulting from tilting the sample gradually. Even though two samples of different thicknesses may appear to have the same color under a vertical incident light, they will exhibit different colors when tilted gradually.

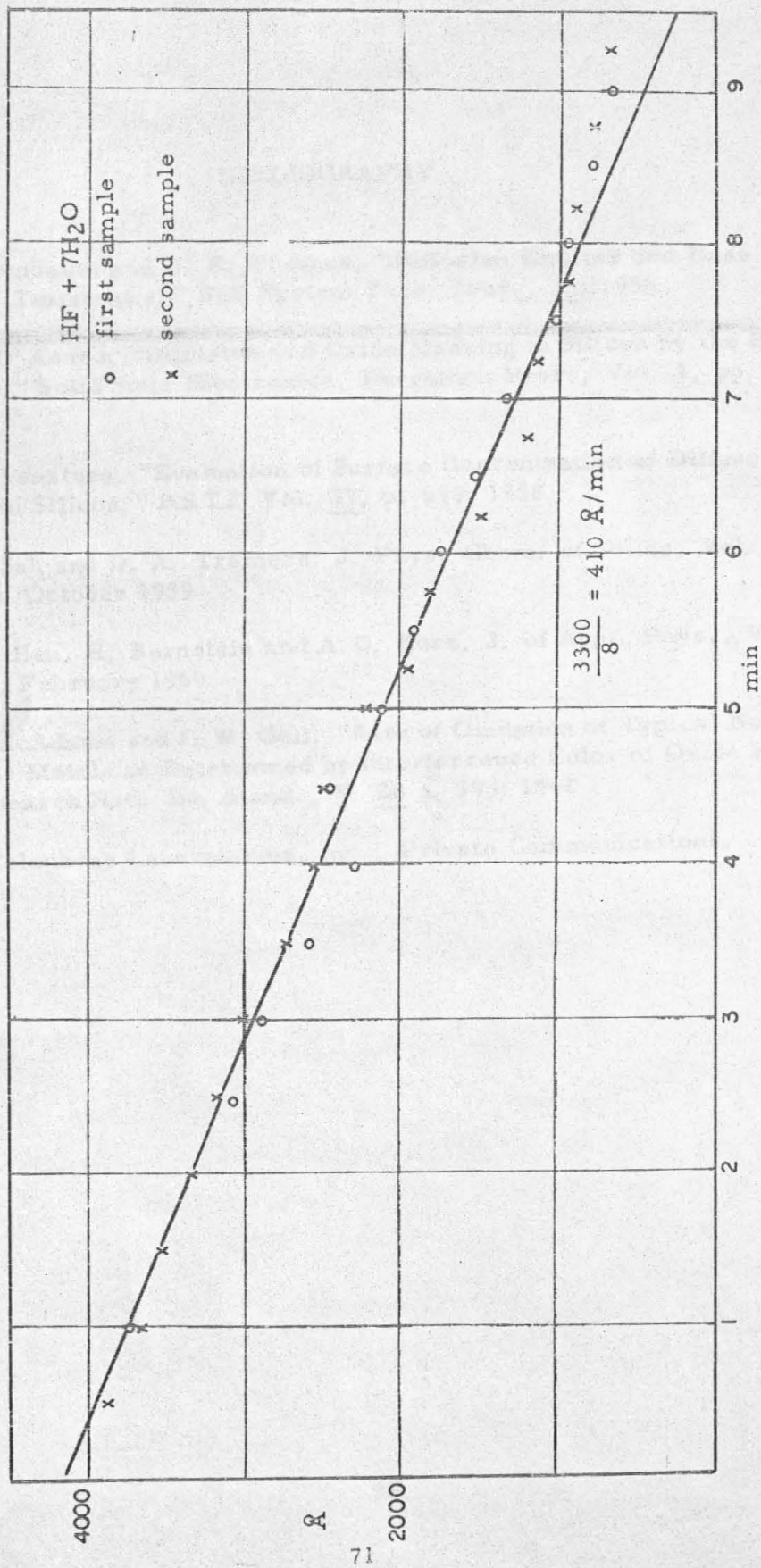


Fig. A-2. Etching Rate of SiO₂ in Diluted HF

BIBLIOGRAPHY

- ¹M. Tanenbaum and D. E. Thomas, "Diffusion Emitter and Base Silicon ~~Transistors~~," Bell System Tech. Jour., 35; 1956
- ²L. A. D'Asaro, "Diffusion and Oxide Masking in Silicon by the Box Method," Solid State Electronics, Pergamon Press, Vol. 1, pp. 3-12; 1960
- ³G. Backenstoss, "Evaluation of Surface Concentration of Diffused Layers in Silicon," B.S.T.J. Vol. 37, p. 699; 1958
- ⁴C. T. Sah and D. A. Tremere, J. Phys. Chem. of Solids, Vol. 11, p. 288; October 1959
- ⁵R. B. Allen, H. Bernstein and A. D. Kurz, J. of Appl. Phys., Vol. 31 p. 334; February 1960
- ⁶D. J. McAdams and G. W. Geil, "Rate of Oxidation of Typical Non-ferrous Metals as Determined by Interference Color of Oxide Films," J. Research Natl. Bu. Stand., V. 28 p. 593; 1942
- ⁷Bell Telephone Laboratories, Inc., Private Communications.

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