

## General Disclaimer

### One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

**FINAL REPORT**

**National Aeronautics and Space Administration  
Electronics Research Center  
Cambridge, Massachusetts**

**Research Grant NGR 36-003-067**

**IMPURITIES AND INTERFACE  
STATES IN THE  $\text{SiO}_2/\text{Si}$   
SYSTEM**

**CASE INSTITUTE OF TECHNOLOGY**

FACILITY FORM 802

**NO7-25945**  
(ACCESSION NUMBER)

**26**  
(PAGES)

**CN 83903**  
(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

Final Report

"Impurities and Interface States in the  $\text{SiO}_2/\text{Si}$  System"

National Aeronautics and Space Administration  
Electronics Research Center  
Cambridge, Massachusetts

Research Grant NGR 36-003-067

Contract Monitor: Frank J. Cocca

Principal Investigator: Alan B. Kuper

March 1, 1967

Abstract

The purpose of this research is: (1) to understand factors contributing to instability in surface properties of silicon planar devices and (2) to provide information which silicon device engineers can use to improve reliability.

Sodium migration in the oxide is being studied because of its importance as a failure mechanism. Combined MOS electrical/radio-chemical analysis, a technique developed under this grant, is the principal experimental method. This gives direct measurement of impurity distribution that underlies electrical instability data. Research includes:

1. Impurity diffusion and drift
2.  $P_2O_5 \cdot SiO_2$  glass stabilization
3. Impurity interaction
4. Theory of impurity distribution

Results are in the form of impurity distribution profiles within  $SiO_2$  compared with electrical Si surface data on the same samples. Results of importance in device processing are:

1. Na is evaporated from within  $SiO_2$  at above  $800^\circ C$  in dry nitrogen.
2. Closely-stacked wafers evaporate Na at an appreciably slower rate.
3.  $P_2O_5$  gettering is partly an interface effect.

Results of importance in evaluation and testing are:

1. Na may remain near the Si interface in hot-bias tests, even though the  $SiO_2$  appears clean electrically.
2. Anion may partly cancel  $Na^+$  after high temperature processing.

Contents

	Page
Introduction	1
Theory of Combined Electrical/Radiochemical (ER) Method	2
Research	
1. Impurity Diffusion and Drift	3
2. $P_2O_5 \cdot SiO_2$ Glass Stabilization	4
3. Impurity Interaction in $SiO_2/Si$	6
4. Theory of Impurity Distribution	9
Discussion of Main Results	16
Experimental Equipment and Techniques	17
Publications	19
Personnel	20
References	22

"Impurities and Interface States in the SiO<sub>2</sub>/Si System"

Purpose: (1) To understand factors contributing to instability in surface properties of silicon planar devices and (2) to provide information which silicon device engineers can use to improve reliability.

Introduction

In order to improve reliability and circumvent certain failure mechanisms, the engineer doing silicon planar circuit design, process, and testing needs to know the facts concerning each mechanism.

Within the last two years it has become clear that impurities, principally Na, are responsible for gross surface instability in SiO<sub>2</sub>/Si planar circuits. Na was shown electrically<sup>(1)</sup> to be capable of causing observed instability and later was shown to be present as a residual impurity in the oxide.<sup>(2, 3)</sup> We then went the next step<sup>(2)</sup> and combined the electrical and radiochemical impurity analysis. This showed directly the correlation between (1) distribution of Na in the oxide and (2) silicon surface potential shifts.

At Case Institute we are continuing to study the effect of impurities under conditions typical of actual process heat treatments, such as diffusion temperatures and times; and under conditions typical of actual device operation and accelerated aging, in particular, "hot-bias" conditions. The present research program includes:

- (1) Impurity diffusion and drift
- (2)  $P_2O_5 \cdot SiO_2$  glass stabilization
- (3) Impurity interaction
- (4) Theory of impurity distribution

Theory of Combined Electrical/Radiochemical (ER) Method

For a conventional MOS (metal-oxide-silicon) capacitor, the flatband voltage ( $V_{fb}$ ) at which the field in the Si is zero may be computed, given oxide thickness and Si impurity concentration. Changes in  $V_{fb}$  for nearly-parallel shifts of MOS capacitance-voltage curve inflections are used to obtain changes in negative charge concentration, ( $\Delta N_s$ ) induced in the Si surface. (4)  $\Delta N_s$  is obtained from

$$\Delta N_s = C_{ox} \Delta V_{fb} / q \quad (1)$$

where  $q =$  |electronic charge|  
 $\Delta V_{fb} =$  initial  $V_{fb}$  - final  $V_{fb}$   
 $C_{ox} = KA/d$   
 $K =$  oxide dielectric constant  
 $A =$  area of the field-plate  
 $d =$  oxide thickness.

$$\Delta N_s / A \Delta V_{fb} = K/qd = 4.0 \times 10^{10} \text{ cm}^{-2} / \text{volt} \quad (2)$$

for  $d = 5400 \text{ \AA}$ .

Also  $\Delta N_s$  equals the change in the weighted integral of charge concentration ( $N(x)$ ) in the oxide, (4)

$$\Delta N_s = A \Delta \left( \frac{1}{d} \int_0^d x N(x) dx \right). \quad (3)$$

Sodium concentration profile in oxide after 10 minutes at 800°C by radiochemical analysis of Na<sup>24</sup> from NaBr. A, covered sample; B, uncovered. R, typical residual Na profile determined by neutron activation.

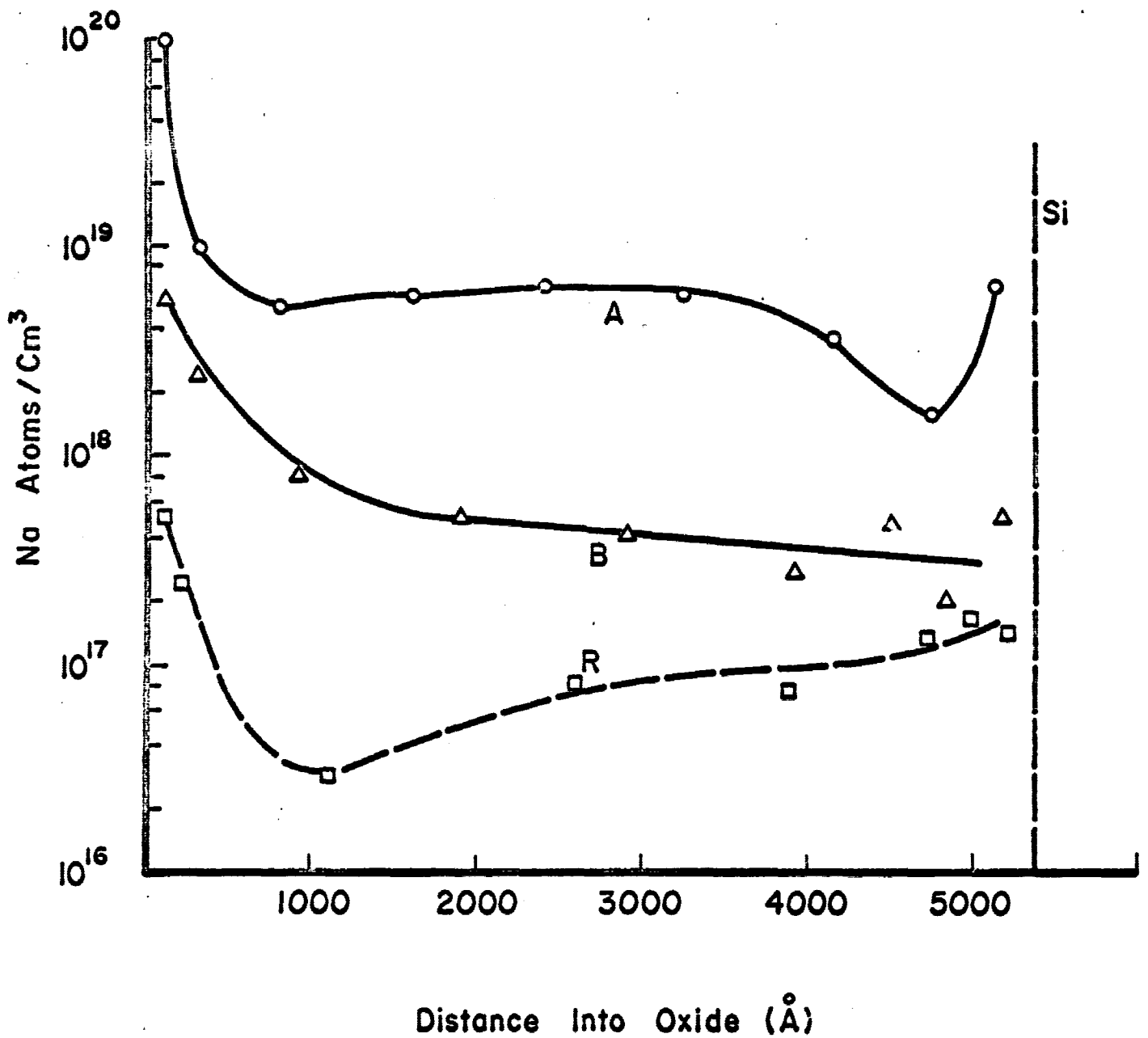


Fig. 1



Change in room temperature MOS flat band voltage vs. time<sup>1/2</sup> at 800° C. A, uncontaminated sample, open surface; B, NaBr contaminated, open; C, NaBr contaminated, covered during diffusion.

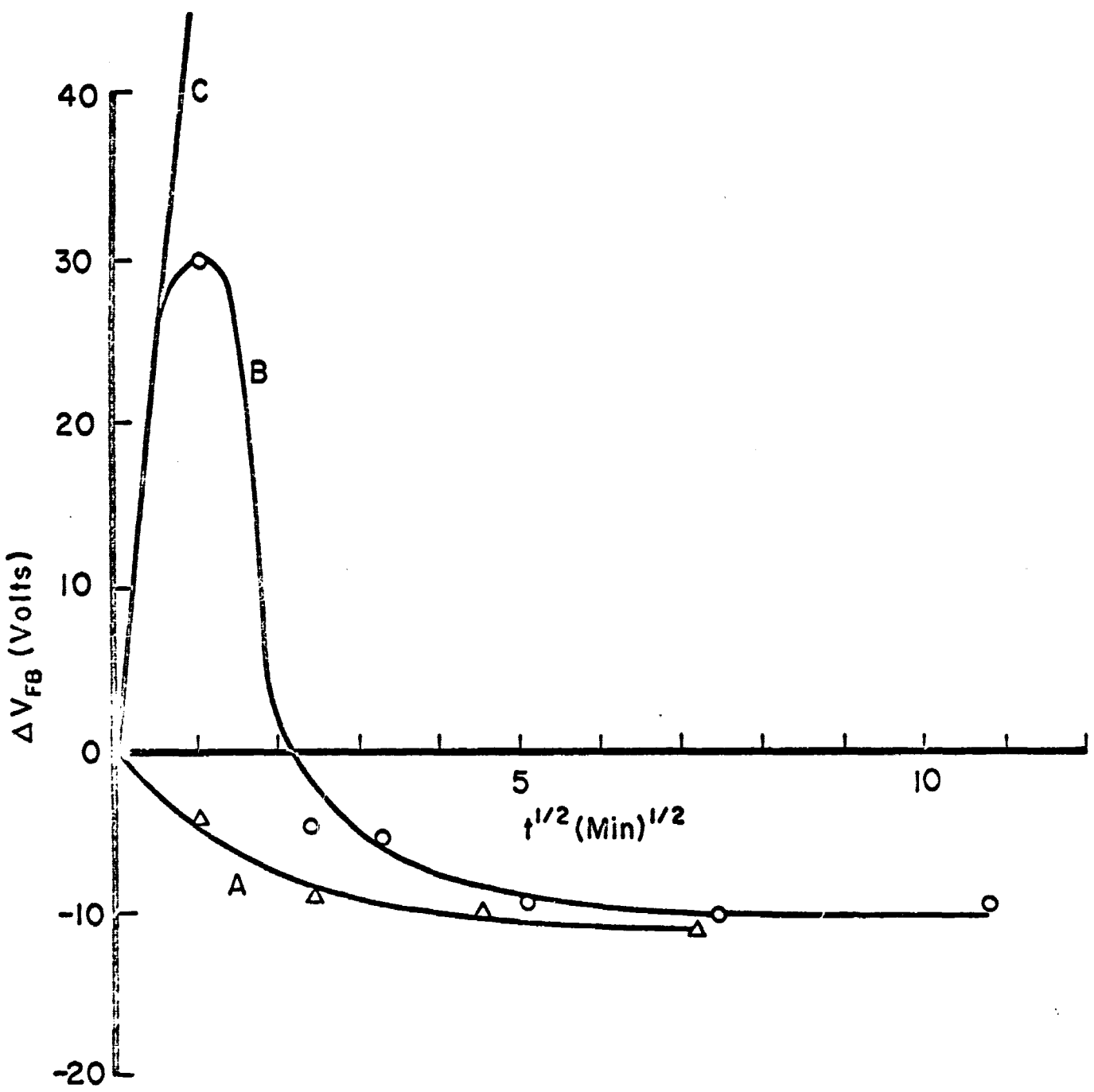


Fig. 2

Change in room temperature MOS flat band voltage vs. time<sup>1/2</sup>  
at temperature for NaBr contaminated covered samples.

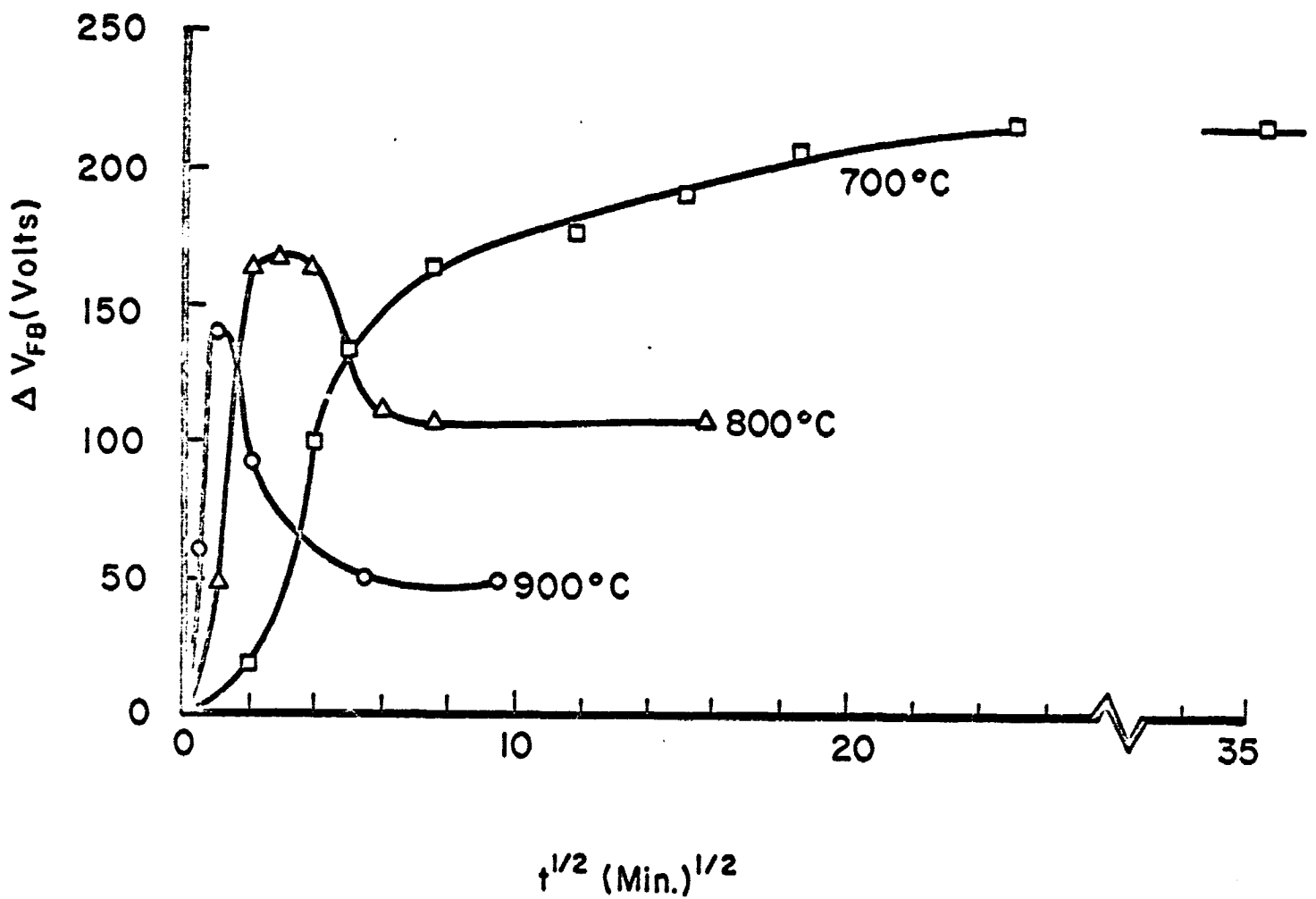


Fig. 3

Na and Br in oxide after 800°C diffusion as in Figure 3. In units of  $10^{12} \text{ cm}^{-2}$ , after 1 min:  $\Delta N = 6.2$ ,  $\Delta N_s = 4.6$ . After 30 min:  $\Delta N = 1.7 \text{ cm}^{-2}$ ,  $\Delta N_s = 0.8$ .

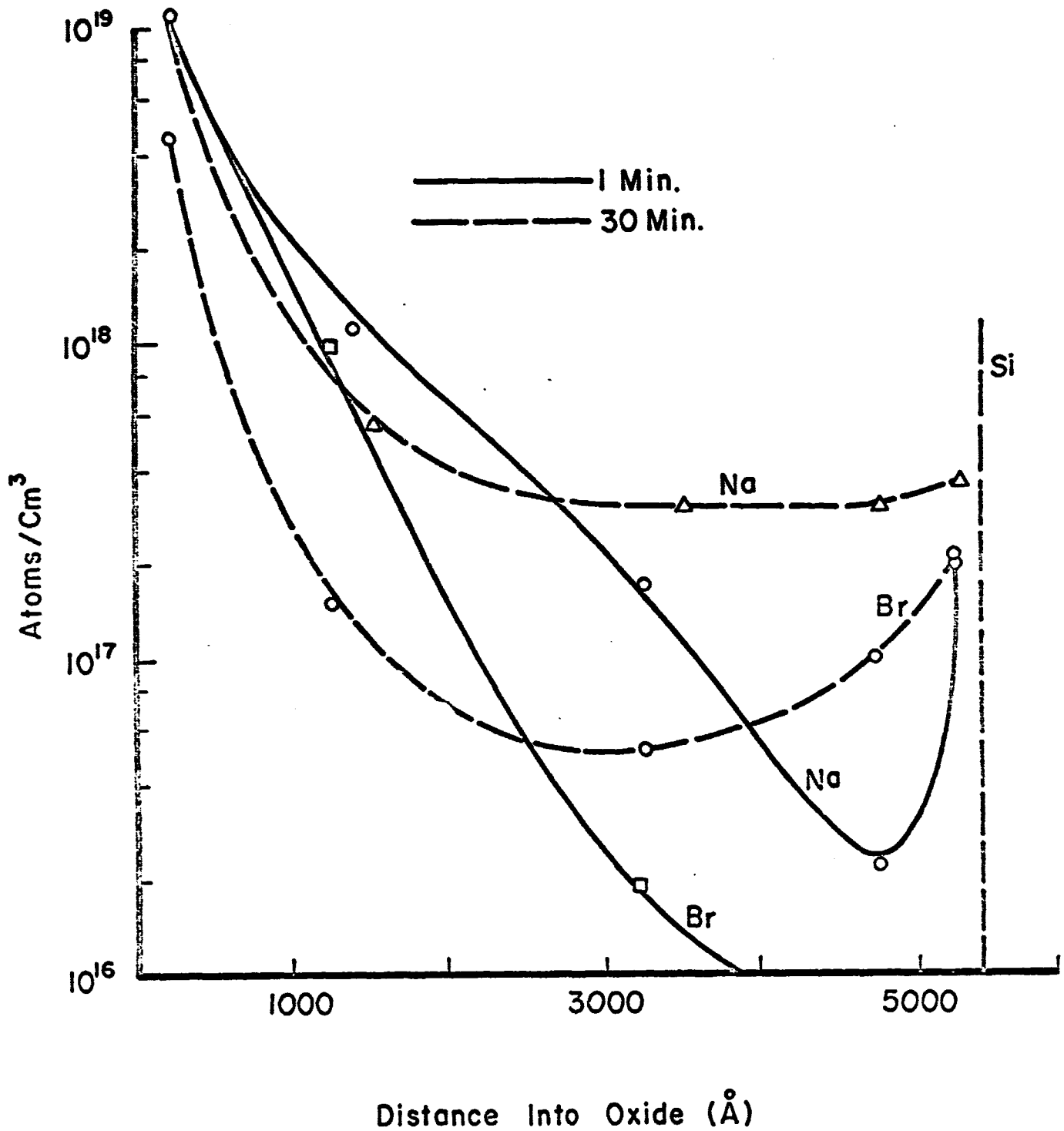


Fig. 4

Third result is that Na dominates NaBr drift results in 200°C "hot-bias" testing. This is shown in Fig. 5 and 6. Br is evidently not sufficiently mobile at 200°C.

Fourth result is that Na alone does not control Si surface potential in the drift experiments. This is shown in Fig. 7. This is of importance in the interpretation of accelerated aging cycles because the electrically "clean" oxide we see in Fig. 6 and 7 still has appreciable Na near the Si.

More detailed discussion of these results and the analysis will be published in the Proc. of the Fifth Annual Symposium on Physics of Failure in Electronics, preprints of which have been submitted to NASA.

Electrical recovery which is not accompanied by complete Na out-drift implies that a fast-diffusing species neutralizes  $\text{Na}^+$  under the out-drift conditions shown in Figs. 6 and 7.

To investigate this we have compared drift of Na at lower electric fields ( $1 \times 10^5$  V/cm) and at lower temperatures in as-grown "wet" oxides versus oxides dried at 800°C for 30 minutes. The results, Fig. 7a, show that electrical drift is faster in dried oxide. Radiochemical analysis of Na distribution in these oxides is being done to try and determine if a water-species is responsible for this result.

(2)  $\text{P}_2\text{O}_5 \cdot \text{SiO}_2$  glass stabilization (W. W. Smith)

It is well-known<sup>(5)</sup> that  $\text{P}_2\text{O}_5 \cdot \text{SiO}_2$  glass layers over  $\text{SiO}_2/\text{Si}$  prevent gross surface instability. We showed<sup>(2)</sup> that the glass acted as a getter for Na and in this way explained stabilization.

Na and Br in contaminated oxide after 200°C forward drift at  $E = 5 \times 10^5$  volt/cm (metal positive). In units of  $10^{12} \text{ cm}^{-2}$ , after 1 min:  $\Delta N = 0.15$ ,  $\Delta N_s = 0.16$ . After 5 min:  $\Delta N = 17.$ ,  $\Delta N_s = 6.4$ . After 15 min:  $\Delta N = 50$ ,  $\Delta N_s = 9.2$ .

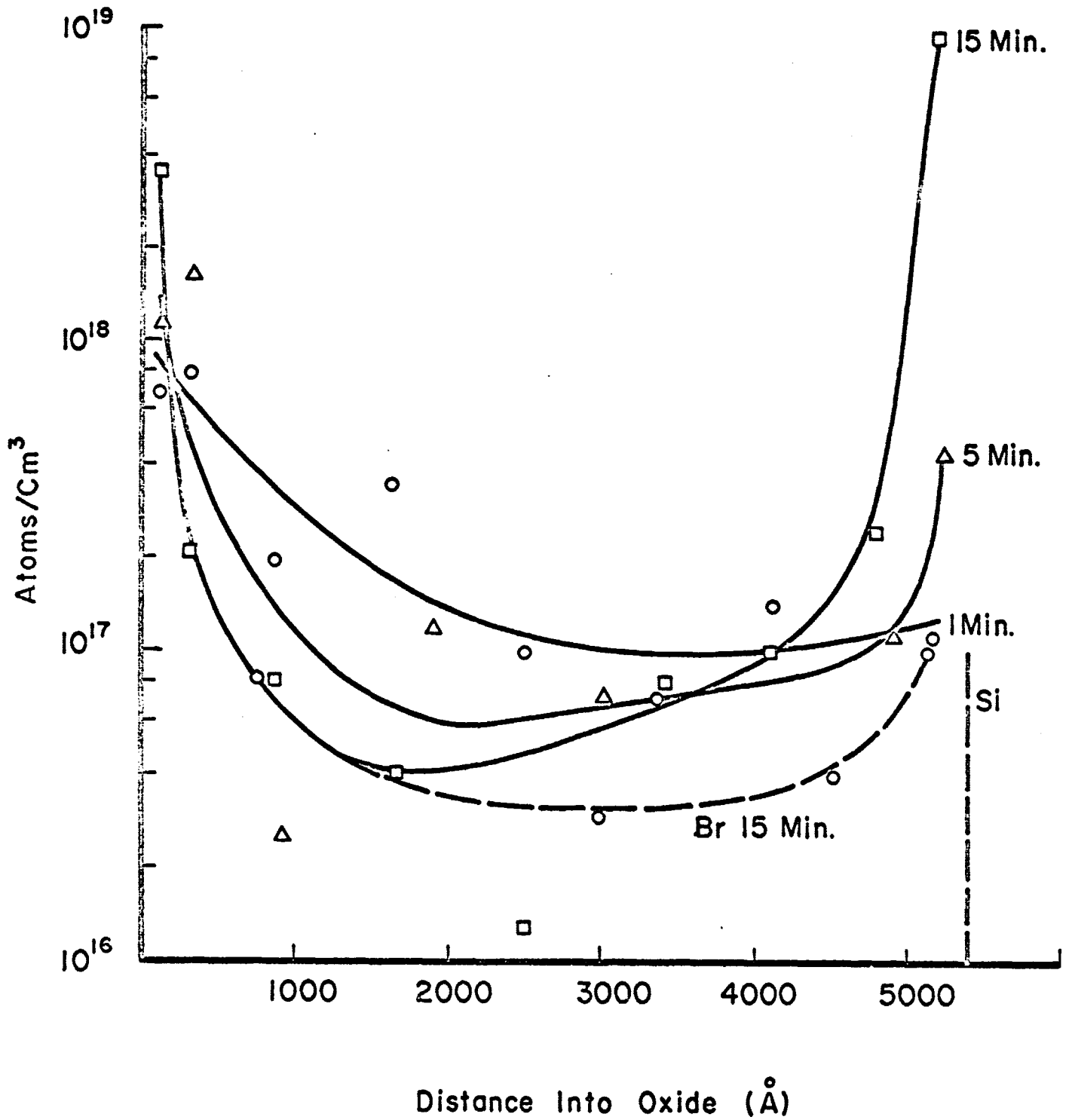


Fig. 5

Na in contaminated oxide. Reverse drift after 15 min. forward drift.  $E = 5 \times 10^5$  v/cm.  $T = 200^\circ\text{C}$ . Br profile, not shown, is like that in Figure 5 and is not significant. In units of  $10^{12} \text{ cm}^{-2}$ , at start of reverse drift (the sample is that of Figure 5);  $\Delta N = 50$ ,  $\Delta N_s = 9.2$ . After 0.5 min:  $\Delta N = 20$ ,  $\Delta N_s = 0.36$ . After 5 min:  $\Delta N^s = 7.5$ ,  $\Delta N_s < 0.04$ . After 15 min:  $\Delta N^s = 0.75$ ,  $\Delta N_s < 0.04$ .

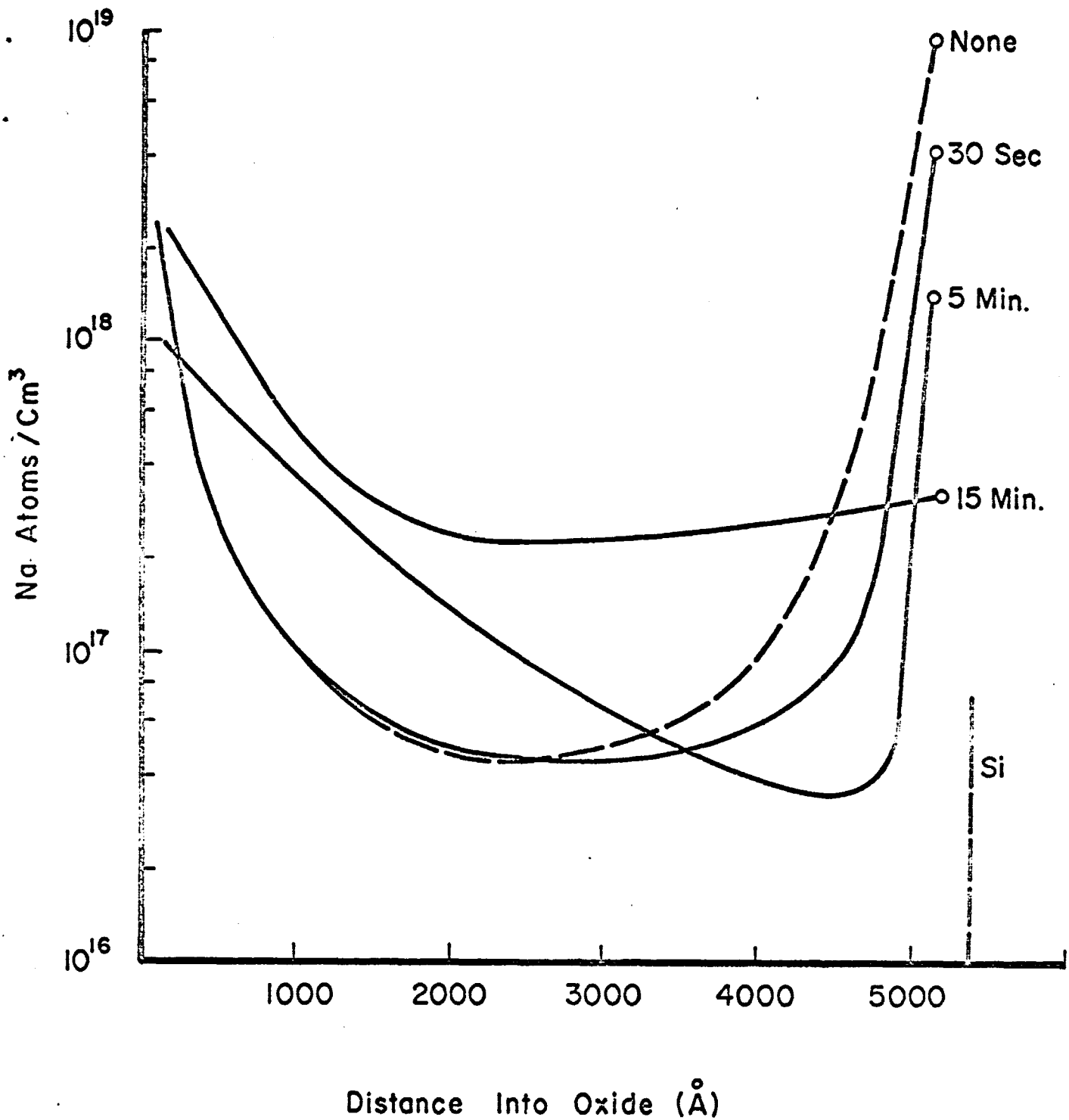


Fig. 6

Comparison of change of charge induced in silicon surface for drift time at 200°C. Na curve is  $\Delta N$  computed by equation (4) from radiochemical data. MOS curve is  $\Delta N_s$  computed by equation (2) from  $\Delta V_{fb}$  electrical data.

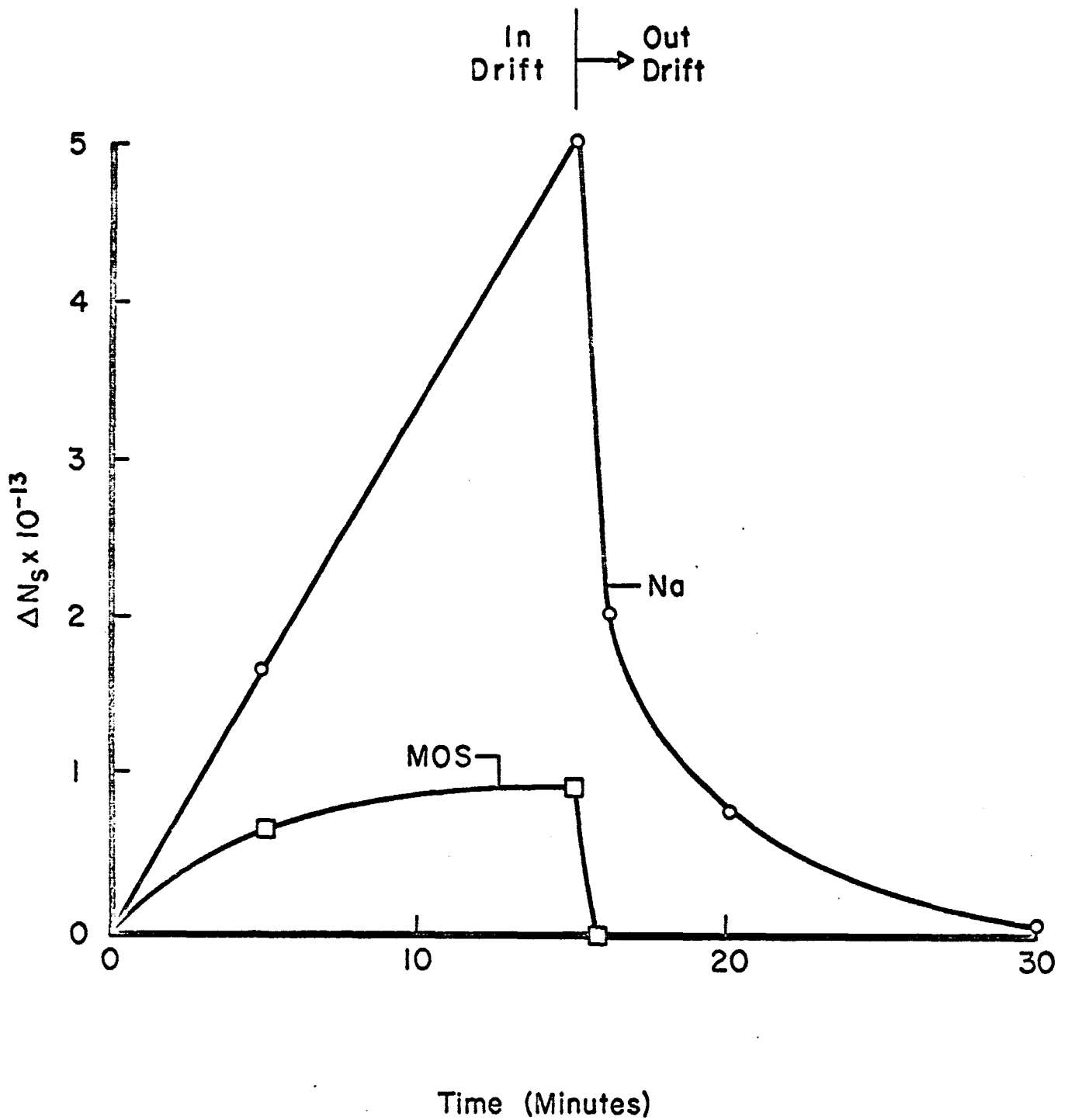


Fig. 7

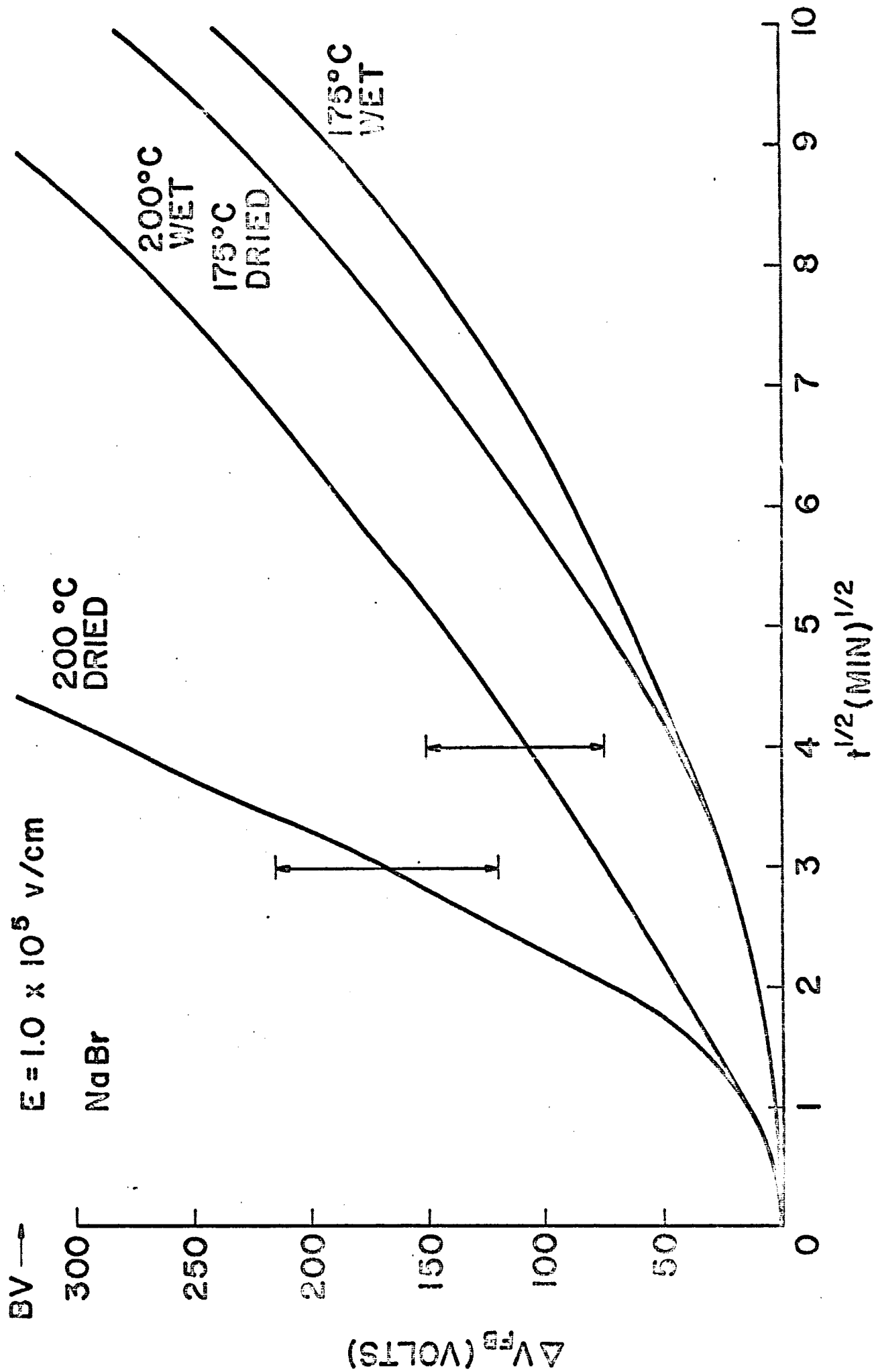


Fig. 7a



To understand the gettering mechanism itself we have been fine-sectioning the glass using very dilute HF: water (1:100), measuring etch-rate by interferometry. By etching, it is possible to locate the glass/SiO<sub>2</sub> interface. ER experiments with radioactive NaBr involving both drift and diffusion have been done. In these experiments the oxide surface is contaminated with Na<sup>24</sup>Br<sup>82</sup> and glassed in P<sub>2</sub>O<sub>5</sub> vapor at 920°C.

Three main results have been obtained.

- (1) Na and Br segregate preferentially not only in the glass but even more in the glass/SiO<sub>2</sub> interface (Fig. 8).
- (2) This interface spike advances as the glass penetrates the oxide during heating (Fig. 9).
- (3) Sodium can be drifted slightly during hot-bias testing; that is, the glass is not an ideal getter (Fig. 10). This result should enable us to separate Na effects from reported polarization<sup>(6)</sup> of the glass, both of which shift Si surface potential.

It is desired to correlate the impurity "gettering" with the actual concentration of phosphorus. For this purpose a beta-counting facility has been set up to count P<sup>32</sup> which can be neutron-activated from P<sup>31</sup>. The counting system utilizes liquid scintillator into which the radioactive solution is dissolved in order to maximize sensitivity. Two photomultiplier tubes are used to count in coincidence which gives low detector noise. Counting results indicate that signal will be more than 10 times background counts for 1% P<sub>2</sub>O<sub>5</sub> glass which is entirely satisfactory. P<sup>32</sup> is a pure

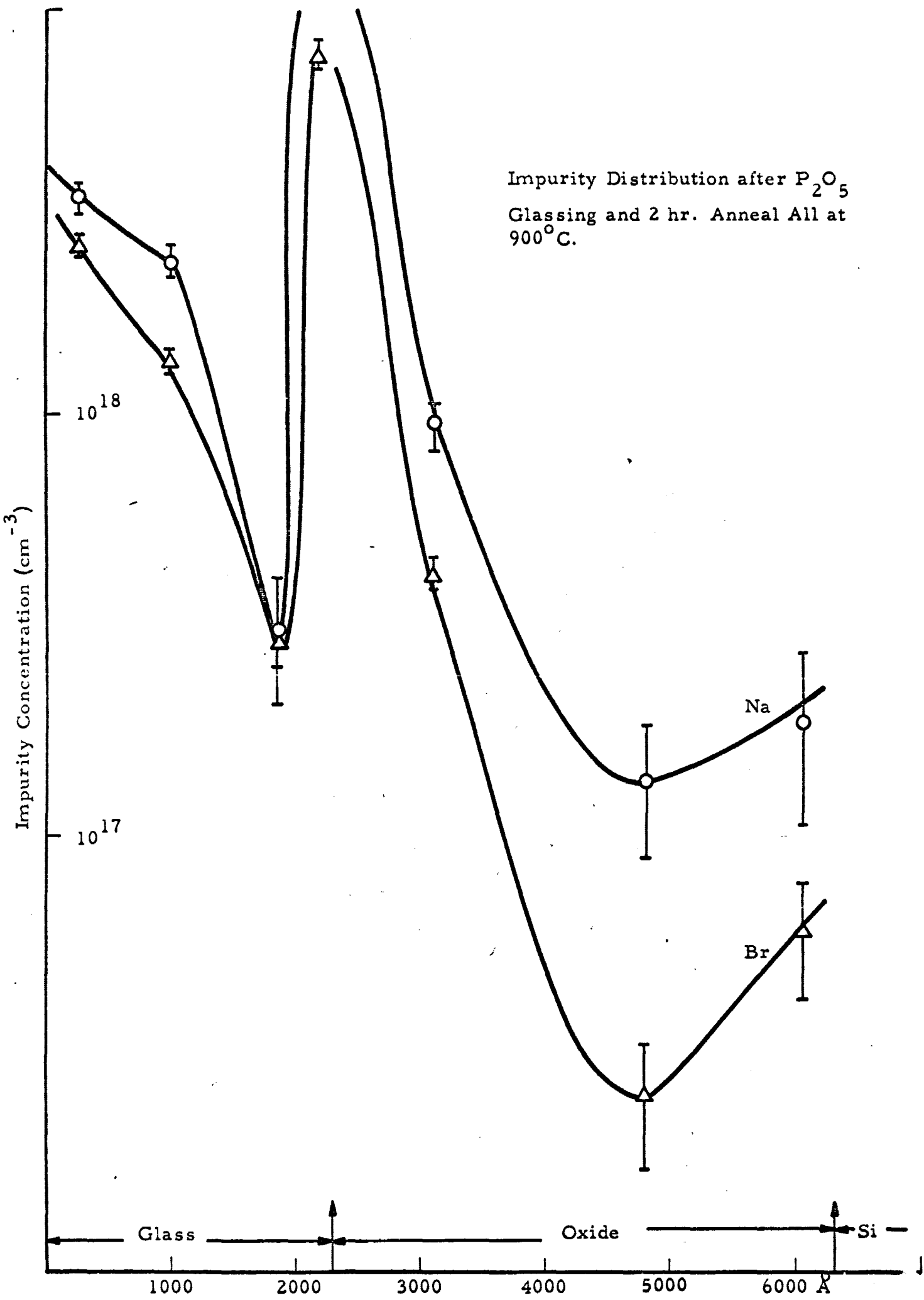


Fig. 8

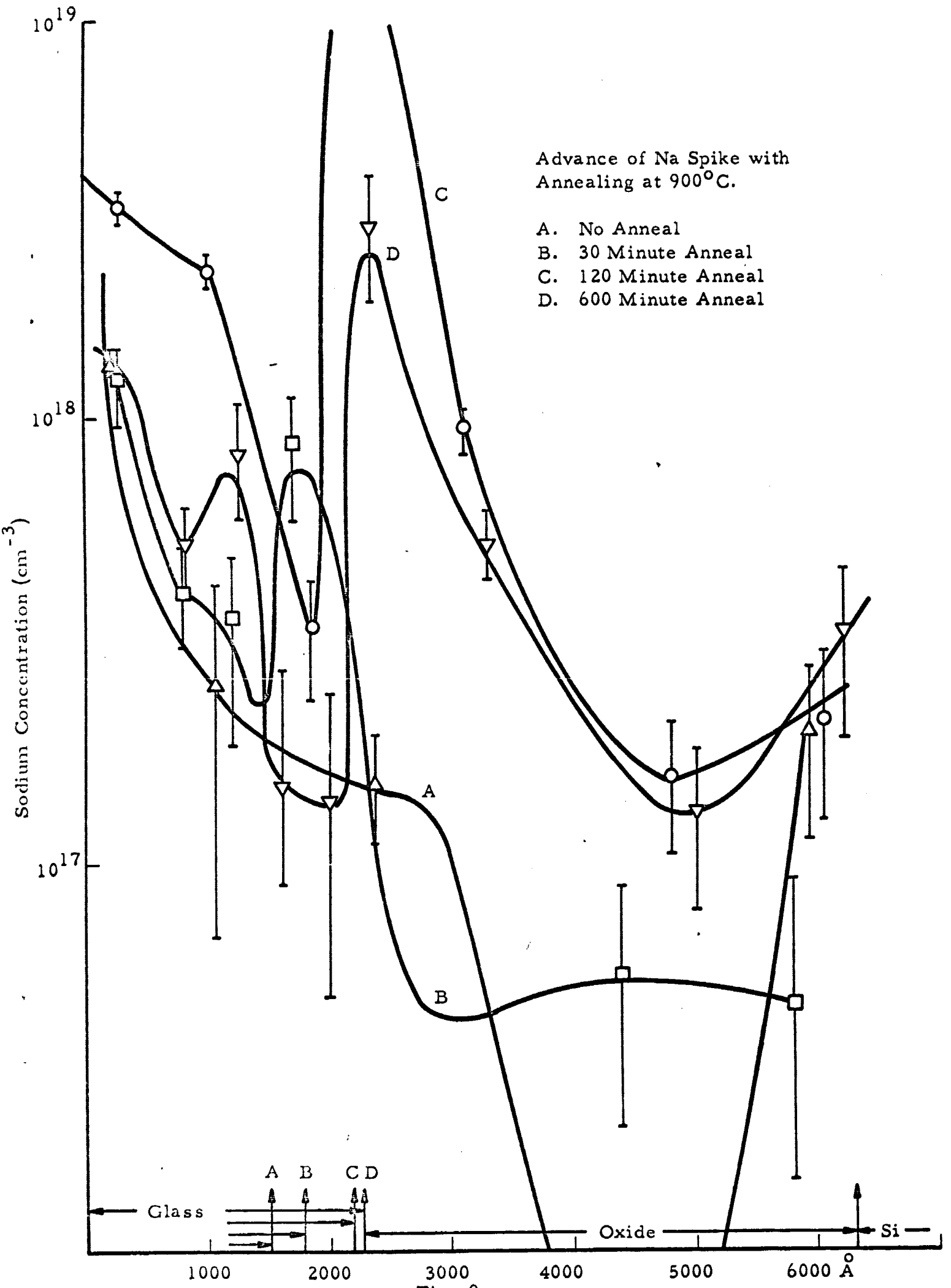


Fig. 9

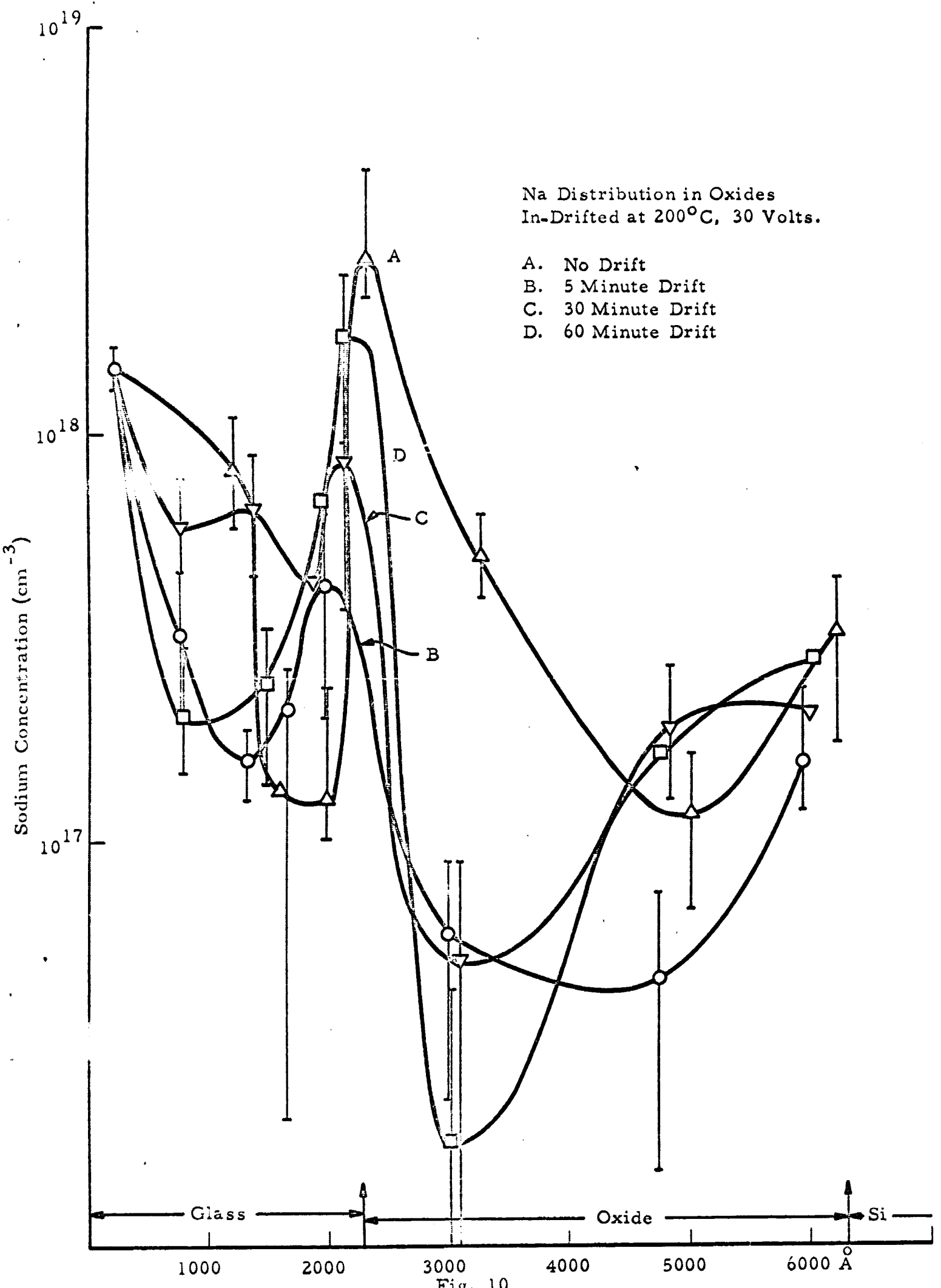


Fig. 10

beta emitter, has a half-life of 14.3 days, and a favorable activation cross-section so no problem is encountered with interference from other isotopes encountered in this experiment: Na, Br, Au, As.

A computer program for analyzing these scintillation data has been written and run.

(3) Impurity Interaction in SiO<sub>2</sub>/Si (G. L. Holmberg)

It is known that not only alkali ions but also water and hydrogen affect Si surface stability in the SiO<sub>2</sub>/Si system. Since these impurities commonly enter in device process and environment, we investigate possible interrelation between these impurities in SiO<sub>2</sub>. For example the field around Na<sup>+</sup> would depend on the presence near it of OH<sup>-</sup>.

A study has been made of methods to determine the interaction of water species and Na. It is concluded that it may be possible to measure hydrogen, oxygen, and Na as well as silicon surface potential on the same sample and correlate the data.

It is planned to measure: Na by neutron activation, hydrogen by tracer, and oxygen by the reaction  $^{18}\text{O} (p, \alpha) \text{N}^{15}$  using a technique described by Choudhury et. al. (7)

The status of new experimental equipment is:

- (1) A cell has been constructed and is in use to permit measurement of MOS C(V) under conditions of controlled temperature and ambient gas pressure (Fig. 11).
- (2) A circulating constant-temperature bath system has been purchased for the cell system (Fig. 11a).

# CONTROLLED-HYDRATION CELL

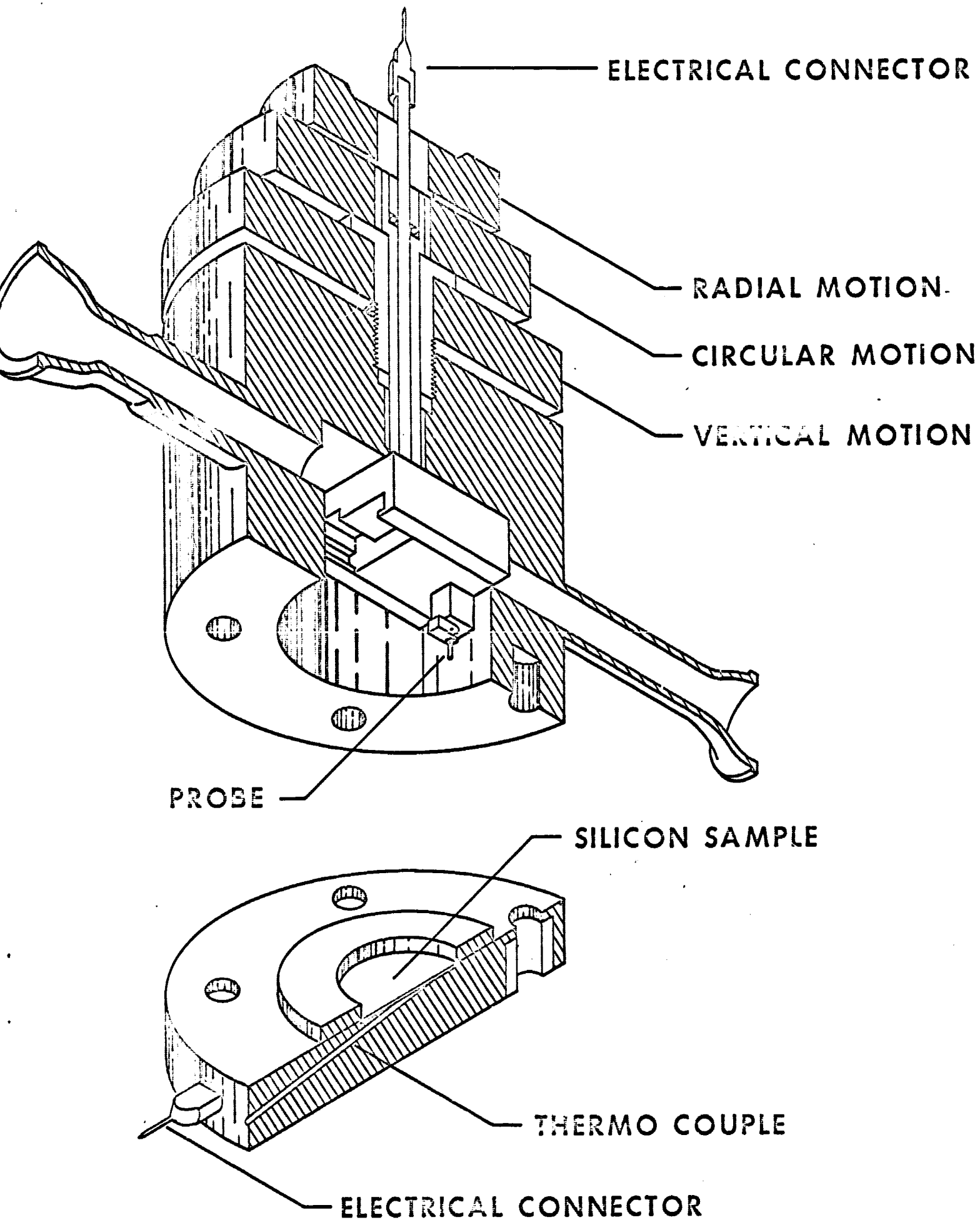
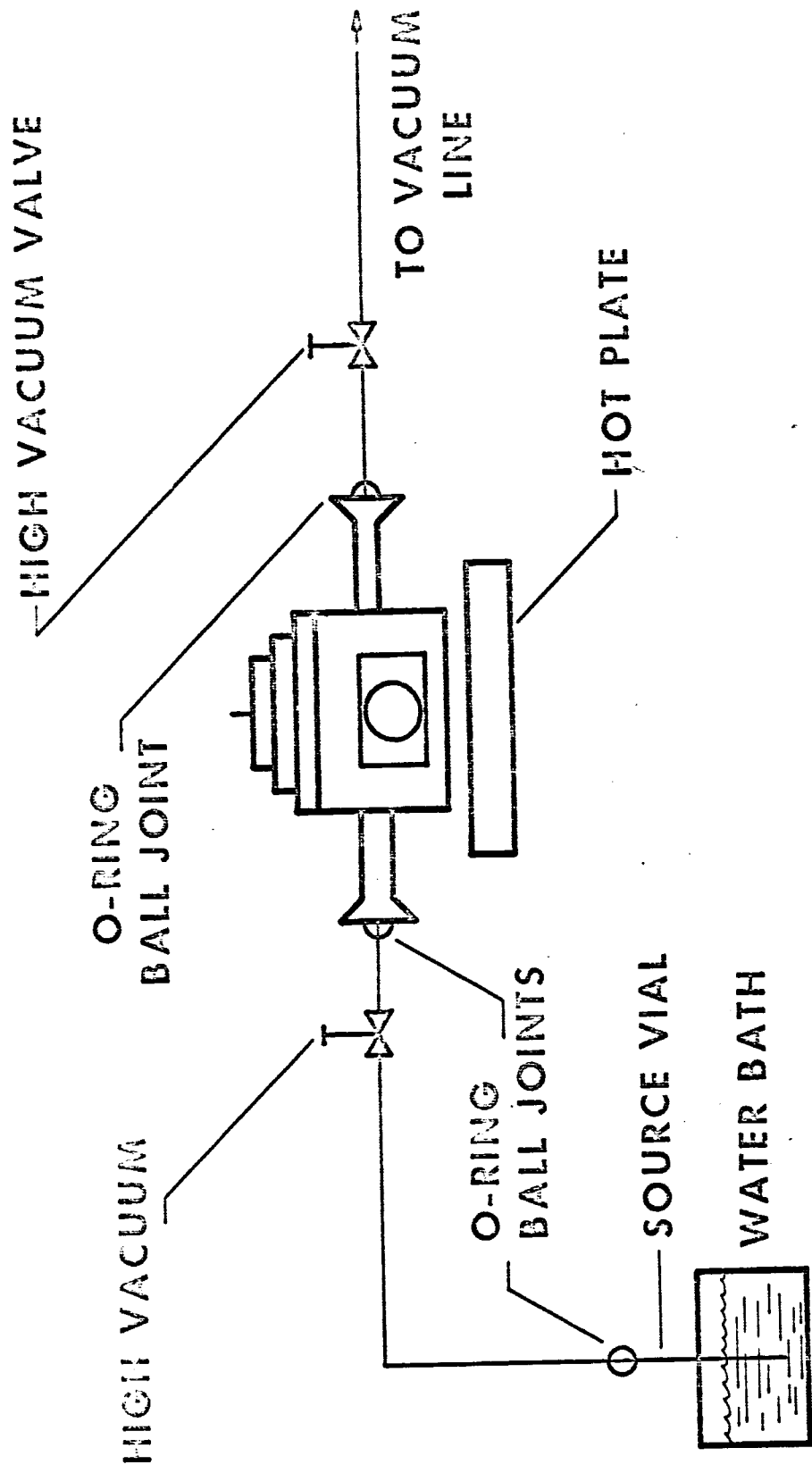


Fig. 11



**CONTROLLED-HYDRATION APPARATUS**

Fig. 11a

(3) A 0.4 MeV Van de Graaf proton accelerator has been made available.

(4) A scattering chamber has been designed.

After a survey of pertinent literature, the following is our first-order model for water in silica:

(1) Water exists in silica as hydroxyl, i. e. Si-OH groups, at least at high temperatures. This is indicated by:

(a) IR absorption studies. The 2.7 micron absorption in silica is present only when water is present in the silica. It is agreed to be the stretching frequency of the Si-OH bond.

(b) The half power dependence of solubility of water on the water vapor pressure indicates that the water breaks up into two species upon entering the glass.

(c) Absorbed water changes all the properties of the silica--viscosity, temperature coefficient of expansion, density--in such a way as to indicate looser three-dimensional bonding in the lattice than in the absence of water.

(2) The solubility of water decreases with temperature, but the diffusion coefficient increases with the temperature in the usual way. The diffusion coefficient is concentration dependent, and the concentration dependence is dependent on the diffusion temperature.

(3) Diffusion of either water or hydrogen into silica produces hydroxyl groups in the silica, as evidenced by the IR absorption produced. If



the sample is heated after the diffusion of either hydrogen or water, both hydrogen and water will be evolved. Since both hydrogen and water produce the same chemical effects in the silica, it is quite possible that they will produce the same electrical effects.

- (4) Two types of hydroxyl seem to exist in the glass, one more mobile than the other. Both, however, exhibit the same IR absorption properties.
- (5) Water molecules do not diffuse as such in glass. This is indicated by the fact that an oxygen tracer in a water molecule diffuses a much shorter distance than the hydrogen of the water in the same diffusion time. A proposed model is the diffusion of associated hydrogen-hydroxyl pairs.
- (6) In a pure oxide, protons do not move in an electric field, as indicated by drift measurements on oxides grown in tritiated steam. Protons do drift, however, if silica is doped with aluminum. Possibly other metal ions will have the same effect as aluminum.
- (7) Water does cause hot-bias instability in electronic devices. Since the instability seems to be caused by positive ion motion, two mechanisms are possible:
  - (a) Protons react with the silica in such a way as to release metal ions, especially sodium, and allow the metal ions to drift.
  - (b) The presence of metal impurities allows the protons of the water to drift.

- (8) Diffusion and solubility of water in a glass are strongly dependent on the thermal processing of the glass prior to the diffusion. Possibly the diffusion of other ions is similarly affected.
- (4) Theory of Impurity Distribution (H. P. Caban-Zeda)

The theoretical treatment of the concentration distribution of Na in a thermally grown film of  $\text{SiO}_2$  depends on the particular model under consideration. Models considered so far are different combinations of the following considerations.

Within the oxide, Na moves by diffusion, and, if ionized, by drift under the action of self-generated and applied fields.

The Na may enter the oxide by any or a combination of the following processes:

- (1) Rate-limited diffusion at the  $\text{SiO}_2$ /air interface.
- (2) Associated with a negative ion (after which there will be generation (dissociation) and recombination).
- (3) Dissociated (ionized) but accompanied by a negative ion.

Theoretical analyses have been done of the following:

- (1) Drift and diffusion of fully ionized positively-charged impurity in a metal-oxide-metal (equivalent to accumulated MOS) short circuited, floating, and with applied bias.
- (2) Generation, recombination, drift and diffusion of ions of Na and negative ions (assumed immobile) through a film of oxide with no applied field. As a first approximation, the distribution of

the negative ion being assumed as a step function near one face of the oxide.

- (3) Different total amounts of ions of Na and a negative ion (assumed dissociated) moving under diffusion and drift (self and applied electric fields) in a metal-oxide-semiconductor system under bias.

Examples of these cases are given in Fig. 11b. Model 1 is included in this report. Results are given in Fig. 12 for calculated distributions of, for example,  $\text{Na}^+$ , across oxide.

We concern ourselves in Model 1 with the steady-state distribution of a positively charged species moving by diffusion and drift under the influence of self and applied fields for a symmetric system consisting of two metal plates separated by a film of homogeneous oxide of thickness  $x_o$ . Across this MOM a constant difference in electric potential is maintained through an external circuit. We assume that the system at all times retains over-all charge neutrality. This problem is similar to  $\text{Na}^+$  in oxide in an MOS with silicon surface accumulated.

Here and elsewhere, since the actual oxide films under consideration are very thin (less than  $10^4 \text{ \AA}$ ) and have an area around  $1 \text{ cm.}^2$ , we will neglect end-effects, effectively assuming infinite cross-sectional area. The problem, then, is a one-dimensional one and will be solved on a per-unit area basis.

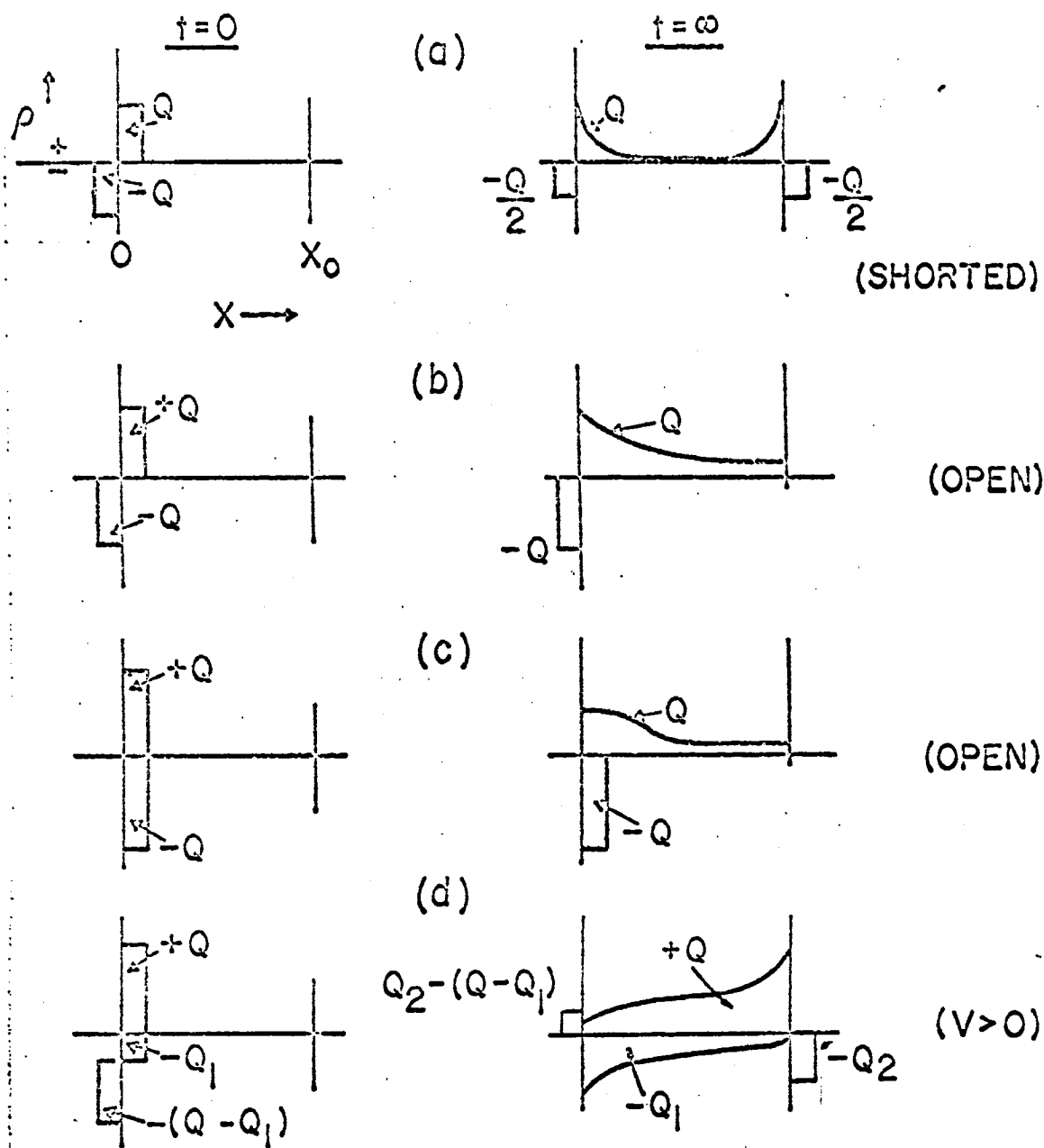


Fig. 11. Approximate Charge Distribution in MOM.

(a) and (b) Model 1. (c) Model 2. (d) Model 3.  
 (In example (d) a larger fraction of cation than anion  
 is shown having entered the oxide.)

For the steady state solution we set the flux of charged particles at any point equal to zero:

$$0 = -D \frac{dN}{dx} + \mu EN \quad (1)$$

where  $N$  = concentration of charged species

$D$  = diffusion coefficient of the charged species

$\mu$  = mobility of the charged species

$E$  = electric field

$x$  = distance into the oxide measured from the left interface of the oxide.

Solving for  $E$  and making use of Einstein's Relation we have:

$$E = \frac{kT}{q} \frac{1}{N} \frac{dN}{dx} \quad (2)$$

where Einstein's Relation is given by

$$\frac{D}{\mu} = \frac{kT}{q} \quad (3)$$

We also have

$$\frac{dE}{dx} = \frac{\rho}{\epsilon} = \frac{q}{\epsilon} N \quad (4)$$

where  $q$  is the charge of the charged particles and  $\epsilon$  is the dielectric constant of the oxide. Differentiating (1) with respect to  $x$  and using (2), (3), and (4)

$$\frac{d^2 N}{dx^2} - \frac{1}{N} \left( \frac{dN}{dx} \right)^2 - \frac{q^2}{kT\epsilon} N^2 = 0 \quad (5)$$

Following the usual procedure for solution, we set

$$P = \frac{dN}{dx} \quad (6)$$

upon which (5) becomes

$$P \frac{dP}{dN} - \frac{P^2}{N} = \frac{q^2}{kT\epsilon} N^2 \quad (7)$$

Upon recognizing that

$$P \frac{dP}{dN} - \frac{P^2}{N} = \frac{N^2}{2} \frac{d}{dN} \left( \frac{P^2}{N^2} \right) \quad (8)$$

(7) becomes

$$d \left( \frac{P^2}{N^2} \right) = \frac{2q^2}{kT\epsilon} dN \quad (9)$$

Due to the movement of the charged species within the oxide film, induced currents will flow through the external circuit and will create an image charge at each metal plate. Since the magnitude of either image charge is smaller than the total charge within the oxide, it is evident from an application of Gauss's Law that at a certain distance,  $x_m$ , within the oxide, there will be zero field and therefore from (1)

$$P(x_m) \equiv P_m = 0 \quad E(x_m) = 0 \quad (10)$$

Letting  $N(x_m) = N_m$  and integrating (9) from  $x_m$  to  $x$  we have

$$\frac{dN}{dx} = \pm N \sqrt{\frac{2q^2}{kT\epsilon} (N - N_m)} \quad (11)$$

where it is evident that the minus sign corresponds to  $0 \leq x \leq x_m$  and the plus sign corresponds to  $x_m \leq x \leq x_o$ . Integrating (11) now, we have

$$N = N_m \sec^2 \left[ \pm \sqrt{\frac{q^2 N_m}{2kT\epsilon} (x - x_m)} \right] \quad \begin{array}{l} (-) \text{ for } 0 \leq x \leq x_m \\ (+) \text{ for } x_m \leq x \leq x_o \end{array} \quad (12)$$

or translating our axes to  $x = x_m$  by letting  $x' = x - x_m$ ,

$$N = N_m \sec^2 \sqrt{\frac{q^2 N_m}{2kT\epsilon} x'} \quad (13)$$

We may now determine  $x_m$  as follows: from (2) we have

$$d\phi = -Edx = -\frac{kT}{q} \frac{dN}{N} \quad (14)$$

And integrating from  $x = 0$  to  $x = x_o$

$$V = \frac{kT}{q} \ln \frac{N(x_o)}{N(0)} \quad (15)$$

where  $V$  is the potential of the left metal plate relative to the right metal plate. Substituting the expressions for  $N(x_o)$  and  $N(0)$  obtained from (12) into (14) we obtain, after some algebra,

$$x_m = \sqrt{\frac{2kT\epsilon}{q^2 N_m}} \tan^{-1} \left[ e^{-\frac{qV}{2kT}} \csc \sqrt{\frac{q^2 N_m}{2kT\epsilon} x_o} - \cot \sqrt{\frac{q^2 N_m}{2kT\epsilon} x_o} \right] \quad (16)$$

From equations (16) and (13) we see that one effect of the externally applied bias is to translate the distribution curve  $N$  vs.  $x$  along the  $x$ -axis in the direction of the more negative metal plate. If we now require that the total amount of the charged species within the oxide be fixed, then, as the curve is displaced horizontally,  $N_m$  must decrease in order to keep the area under the curve constant.

We now proceed to determine this vertical shift of the curve by finding  $N_m$  as a function of the applied bias for a given total amount of the diffusing species within the oxide film,  $N_T$ . From (13)

$$N_T = \int_0^{x_0} N(x) dx = \int_{-x_m}^{x_0 - x_m} N_m \sec^2 \sqrt{\frac{q^2 N_m}{2kT\epsilon}} x' dx' \quad (17)$$

which, after some manipulation, yields

$$N_T = \frac{4kT\epsilon}{q x_0} a \left[ \cosh \left( \frac{qV}{2kT} \right) \csc a - \cot a \right] \quad (18)$$

$$\text{where } a \equiv \sqrt{\frac{q^2 N_m}{2kT\epsilon}} x_0 \quad (19)$$

Equations (18) and (19) determine the vertical displacement of the minimum of the  $N$  vs.  $x$  curve.

The solution to the problem, therefore, is given by equation (12) or (13) together with equations (16), (18), and (19).

It is interesting to note that from our requirement that  $N$  remain finite and equation (13) it follows that  $a < \pi/2$  and thus



$$N_m < \frac{\pi^2 k T \epsilon}{2 q x_o} \quad (20)$$

Finally, for the special case of  $V = 0$  (still retaining the external circuit, however) we have from equation (16)

$$x_m = \frac{x_o}{2} \quad (21)$$

(which was to be expected from symmetry considerations) and from (18)

$$N_T = \frac{4kT\epsilon}{q x_o} a \tan \frac{a}{2} \quad (22)$$

A schematic representation of  $N$  vs.  $x$  is shown in Figure 12.

We may now extend the above solution to the case where the external circuit is removed. Again we assume the system retains over-all charge neutrality. This may be accomplished by depositing the charged species accompanied by an oppositely charged non-diffusing species such that no effective charge is added to the system. We assume that the species are deposited on the left metal-oxide interface where the non-diffusing species will remain.

It is evident that this problem is identical to the previous one, the only difference being in the boundary conditions, which are particularly simple in this case. Since we have assumed over-all charge neutrality, the field at the right metal-oxide interface vanishes and we have

$$x_m = x_o \quad (23)$$

and

$$N_m = N(x_o) \quad (24)$$

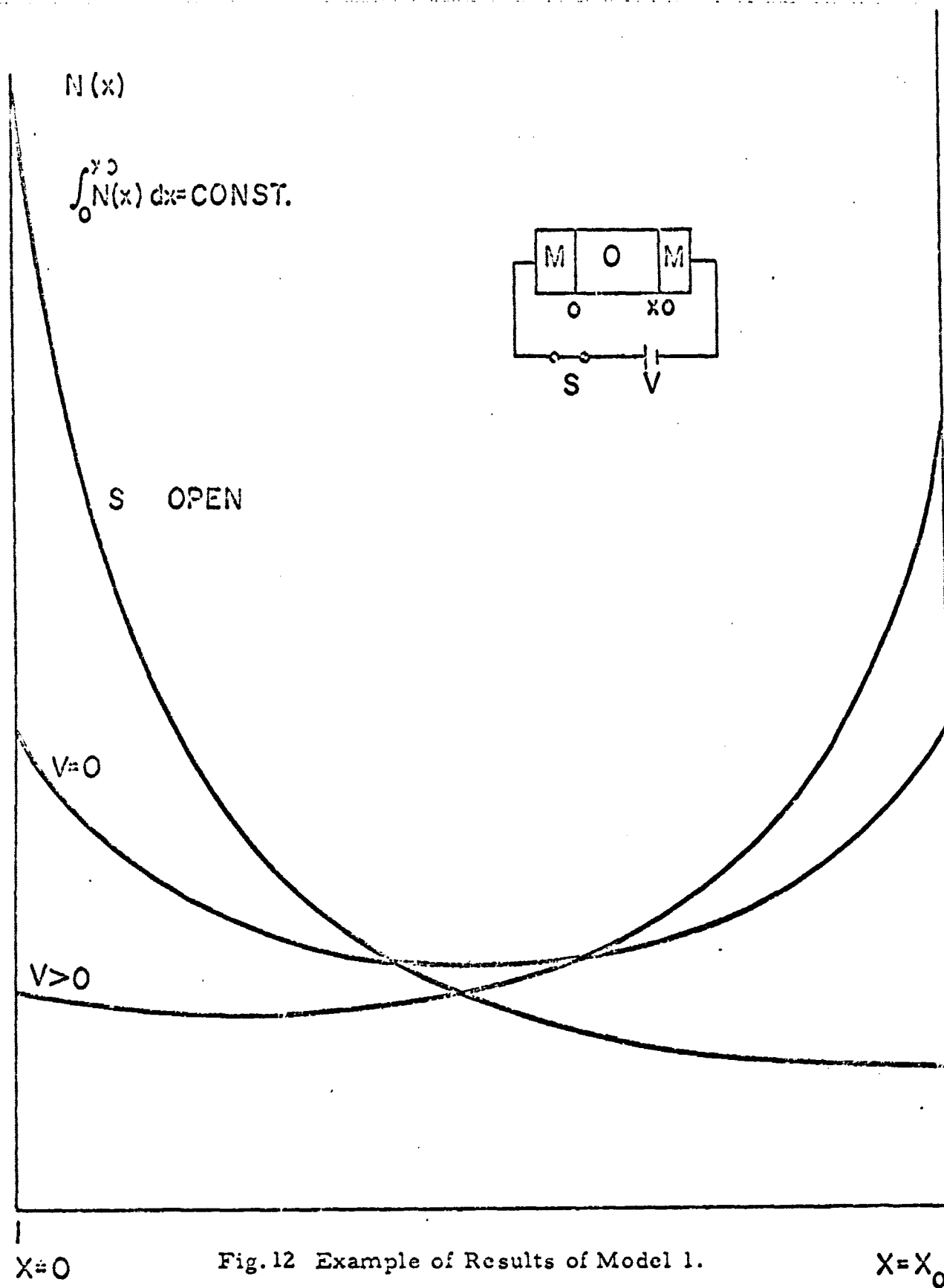


Fig. 12 Example of Results of Model 1.

Thus

$$N = N(x_0) \sec^2 \sqrt{\frac{q^2 N(x_0)}{2kT\epsilon}} (x_0 - x) \quad (25)$$

This case is included with the previous two in Figure 12 where  $N(x)$  is shown for  $V = 0$ ,  $V > 0$ , and  $V$  floating. Total charge is the same for all three cases.

The steady-state MOS case is the same as the MOM except that a fraction of the applied  $V$  appears across the silicon. Although this does not appreciably alter the character of the result, it requires a computer calculation. A program to solve the problem has been written as part of this research.

Three important results are already apparent from the calculation:

- (1) An increase of  $N_a$  at the Si interface, experimentally observed as in Figs. 4, 5, and 6, is explained by the theoretical results in Fig. 12.
- (2) The trend predicted by the theory for the shift of the minimum is in rough agreement with drift experiments shown in Fig. 5.
- (3) This theoretical approach has the advantage that bias may be small, even zero, whereas the previous approach of Collins<sup>(8)</sup> may be used at high  $V$  only.

#### Discussion of Main Results

Results of impurity diffusion in the present research should be of value in determining optimum process for reliability. For example,

making use of our results, a fabrication process which includes a final Na evaporation step with unstacked wafers should make planar circuits less likely to fail due to ion migration. (This assumes, of course, that Na is not introduced in subsequent process.)

Results of our diffusion and drift experiments should be of value in interpreting device failure anomalies. For example, in cyclic hot-bias accelerated aging, the knowledge of Na distribution in oxide which does not appear electrically, can be an aid in interpreting recoverable failure test data.

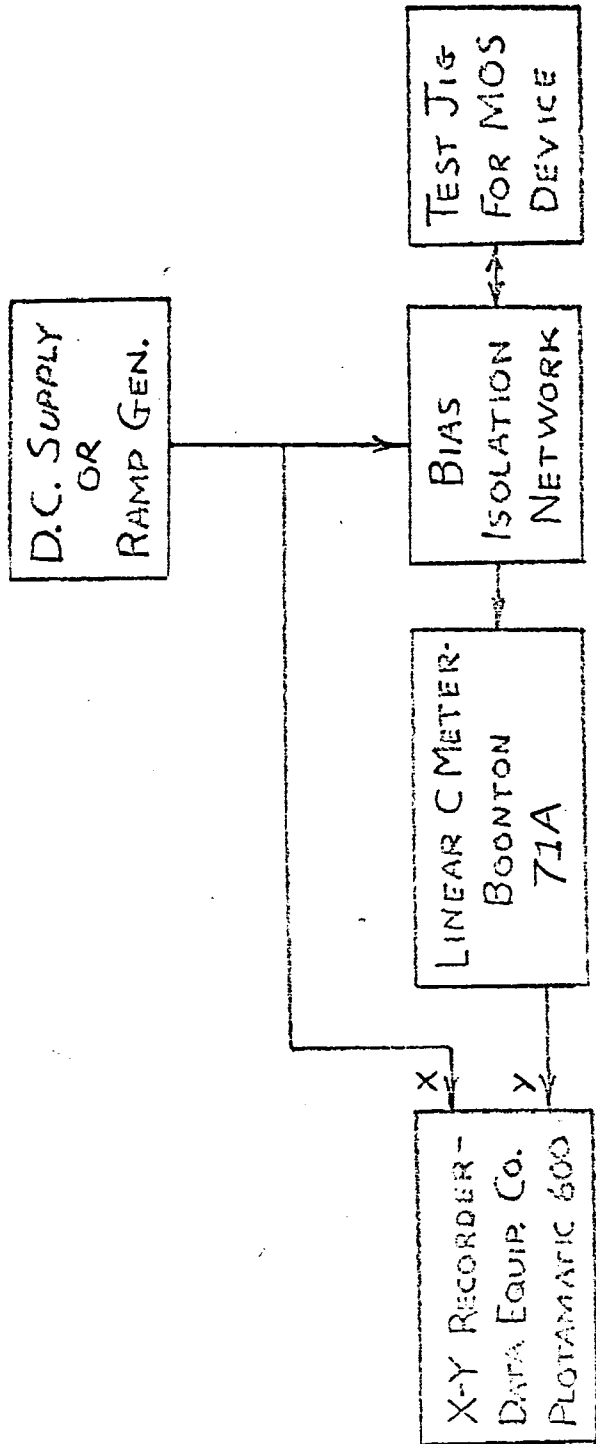
The result of Na segregation at the  $P_2O_5 \cdot SiO_2$  interface in our glass studies may be of value in process for reliability. For example, when removing the glass, it may be important to remove a small amount of oxide as well.

#### Experimental Equipment and Techniques

Principal improvements in experimental technique have been:

- (1) Continuous MOS C(V) plotting system. (Fig. 13) This system makes possible faster and more detailed electrical data-taking than is possible with capacitance bridges nulled at discrete points. It is especially useful for observing transient changes.
- (2) Faster cooling hot-bias jig. (Fig. 13b)

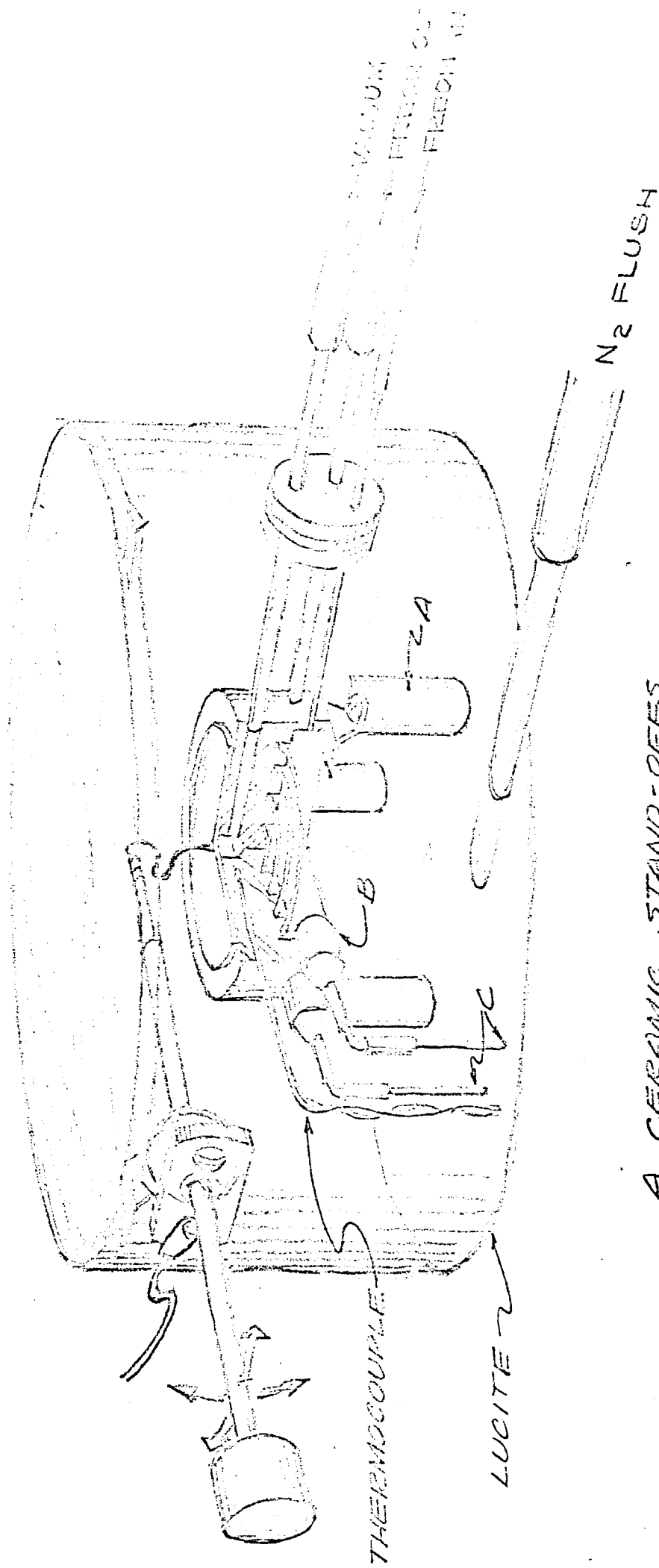
A larger bore Freon line was installed to enable drift samples to be fast-cooled under bias at the conclusion of drift.



BLOCK DIAGRAM OF C-V PLOTTING SYSTEM

Fig. 13

SOLID-STATE ELECTRONICS LABORATORY  
CASE INSTITUTE OF TECH.  
CLEVELAND, O.



- A CERAMIC STAND-OFFS
- B INSULATING BEADS CEMENTED IN
- C HEATER WIRE LEADS

Fig. 136

- (3) Improved quartz sample container for neutron activation.

This container satisfies the reactor water-cooled hole size requirements and is easy to unload with long tongs.

- (4) Computer program for radiochemical data reduction.

A computer program has been written to calculate sodium and bromine concentrations in sections of the oxide from etching and counting data. The computer calculates concentrations of sodium and bromine in each removed section of the oxide and the statistical error associated with the concentration, and prints this along with pertinent information.

The computer first reads in isotope half-lives, analyzer calibrations, etch-rates, and time that the calibration was done. For each wafer, it then reads in a wafer number, wafer description (i. e., the treatment done on the oxide before sectioning), background, and section area. For each of the sections removed from that wafer, it then reads in an identifying number, etching information (either an etching solution concentration plus an etch time or simply a section thickness), the time at which the count was made, length of the count, and the number of counts respectively under the sodium photopeak and under the bromine photopeak.

The computer then takes the sodium and bromine counts and corrects them for decay, background, and interference from

each other. Then, using the known analyzer calibrations and the calculated section volumes, it converts the corrected count information into sodium and bromine concentrations in each section. It then calculates the standard deviation in these concentrations due to the statistical nature of the count information.

Finally, it makes a one-page listing for each wafer. It prints wafer number, wafer description, thickness, concentration, and error information for each section from the wafer; the background, and the date on which the counts were made.

#### Publications

The paper <sup>(2)</sup> published on work done in anticipation of receiving this grant is now the prime reference on identification and distribution of Na in SiO<sub>2</sub> on Si.

A preliminary report of impurity diffusion and drift was presented at the IEEE-Solid-State Device Research Conference, Evanston, Illinois, June 15, 1966.

A paper entitled "Positive and Negative Ion Motion in Thermal Oxide on Silicon by Radiochemical and MOS Analysis," A. B. Kuper, C. J. Slabinski, and E. Yon, will be published in the Proc. of the Fifth Annual Symposium on Physics of Failure in Electronics, Columbus, Ohio, November 14-16, 1966.



A paper on Ion Drift in MOS: Experiment and Theory, was accepted for presentation by A. B. Kuper at the Second Annual IEEE - Silicon Interface Specialists Conference, Las Vegas, Nevada, March 1-3, 1967.

A paper entitled "Combined MOS and Radiochemical Analysis of Impurities in SiO<sub>2</sub> on Si" will be presented by A. B. Kuper at the Semiconductor Device Research Conference, Bad Nauheim, Germany, April 19-22, 1967.

A paper entitled "Theory of Charge Distribution in MOS Oxide" by H. P. Caban-Zeda and A. B. Kuper was accepted for presentation to the Electrochemical Society, Dallas, Texas, May 7-12, 1967.

Theses:

Ph. D. Electrical Engineering, E. T. Yon, Feb. 1966

"Impurity Distribution in Thermal Oxide on Silicon"

M.S. -EE, C. J. Slabinski, Feb. 1967

"Drift and Diffusion of Positive and Negative Ions in Silicon Dioxide Passivating Films on Silicon"

Personnel

Principal Investigator: Alan B. Kuper; B. S., Physics, 1949, University of Chicago  
Ph. D., Physics, 1955, University of Illinois  
Research Associate, 1955-57, Princeton University  
Member Technical Staff, Bell Telephone Laboratories, 1957-1964  
Assoc. Prof. Engineering, Case Institute of Tech., 1964 -

Faculty Associate: Wen H. Ko, Ph. D. Electrical Engineering, 1959,  
Case Inst. of Tech., Assoc. Prof. Eng., Case  
Inst. of Tech.

Eugene T. Yon, Ph. D. Electrical Engineering, 1966,  
Case Inst. of Tech., Assistant Prof. Eng., Case  
Inst. of Tech.

Floro P. Miraldi, D. Sc., Nuclear Engineering, 1959,  
Mass. Inst. of Tech., Assoc. Prof. Eng., Case  
Inst. of Tech.

Graduate Students: Chester J. Slabinski, M. S. E. E., Case, 1966

Gary L. Holmberg, M. S., Nuclear Eng., Case, 1965

Hector P. Caban-Zeda, B. S. E. E., Univ. of  
Puerto Rico, 1961

Winthrop W. Smith, B. S., Engineering Science,  
Johns Hopkins, 1965

References

1. E. H. Snow, A. S. Grove, B. E. Deal, and C. T. Sah, "Ion Transport Phenomena in Insulating Films", J. Appl. Phys., Vol 36, pp 1664-1673 (May, 1965).
2. E. Yon, W. H. Ko, and A. B. Kuper, "Sodium Distribution in Thermal Oxide on Silicon by Radiochemical and MOS Analysis", IEEE Trans., Vol ED-13, pp 276-280 (February, 1966).
3. H. G. Carlson, G. A. Brown, C. R. Fuller, and J. Osborne, "The Effect of Phosphorus Diffusion in Thermal Oxides on the Elevated Temperature Stability of MOS Structures", Proc. Fourth Symp. Physics of Failure in Electronics, Batelle, Columbus, Ohio (November, 1965).
4. A. S. Grove, B. E. Deal, E. H. Snow, and C. T. Sah, "Investigation of Thermally Oxidized Silicon Surfaces using MOS Structures", Solid State Electr., Vol 8, pp 145-163 (February, 1965).
5. Surface Effects issue, IBM J. Res. and Devel., Vol 8 (September, 1964).
6. E. H. Snow and B. E. Deal, "Polarization Phenomena and Other Properties of Phosphosilicate Glass Films on Silicon", J. Electrochem. Soc., Vol 113, pp 236-269 (March, 1966).
7. A. Choudhury, et. al., "Study of Oxygen Diffusion in Quartz by  $O^{18}$  (p,  $\alpha$ )  $N^{15}$ ", Solid-State Commun. 3, 119 (1965).
8. F. C. Collins, "Electrochemical Behavior of Grown Oxide Films on Silicon", J. Electrochem. Soc. 112, 786 (1965).