POSITIVE AND NEGATIVE ION MOTION IN THERMAL OXIDE ON SILICON BY RADIOCHEMICAL AND MOS ANALYSIS

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ABSTRACT

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Failure of conventional Si planar devices by surface potential shift due to oxide impurities has been studied by combined MOS and radiochemical analysis. Radioactive NaBr contaminant was used to study both anion and cation distributions and kinetics.

Experimental evidence is presented that Na in the oxide near the Si interface acts to accumulate electrons at the surface of n-type Si.

Less well-known is the role of the anion in determining failure in this mode. At temperatures above 800°C, Br is found to diffuse into the oxide more slowly than Na and partly to neutralize Na^+.

Conventional hot-bias drift experiments at 200°C have been extended to include impurity distribution as a function of time within the oxide. The kinetics of Na flow in the oxide to and away from the Si interface compared to Si surface potential shifts suggest the presence of a rapidly-equilibrating negative species which can neutralize Na^+ but not deplete an n-type Si surface.

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INTRODUCTION

Failure of silicon (Si) planar circuit elements often results from uncontrolled shift of Si surface potential.[1] The shift is in such a direction as to indicate the presence of positive charge within the oxide especially near the Si interface.[1,2,3] Experiments indicate that the charges are sodium (Na) ions because (1) sufficient residual Na has been found in conventional oxides to account for the shifts[4,5] and (2) deliberate contamination with NaCl results in shift kinetics similar to those observed in failure tests.[3] Na diffusion rate has been found to depend on the anion of the contaminating compound,[4] the rate increasing in the order NaBr, NaCl, NaOH. To study the effect of the anion in the Na contamination failure mode was the purpose of this investigation.

THEORY

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 were used in the present study to obtain changes in negative charge concentration ($-\Delta N_s$) induced in the Si surface.[6] ΔN_s is obtained from

$$\Delta N_s = C_{ox} \Delta V_{fb} / q \tag{1}$$

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

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

for $d = 5400$ Å.
Also ΔN_s equals the change in the weighted integral of charge concentration ($N(x)$) in the oxide,[6]

$$\Delta N_s = \Delta \, (1/d \int_0^d xN(x)\, dx\,). \tag{3}$$

Net impurity concentration measured in the present work by sectioning and radiochemical concentration profiling was used to compute a similar weighted average (ΔN).

$$\Delta N = \sum_i (x_i/d)\, N\,(x_i)\, \Delta x_i \tag{4}$$

where x_i = x coordinate of the center of the i^{th} section of width Δx_i
$N(x_i)$ = Na minus Br concentration in the section.
Then $\Delta N_s / \Delta N$ = fraction of net charged oxide impurities corresponding to a given ΔV_{fb}.

EXPERIMENT

Two types of experiments were done. (1) Deliberately contaminated samples were heated to 700 - 900°C to diffuse radioactive NaBr surface contamination into the oxide, or (2), ions were drifted in the oxide by an electric field while the sample was at 200°C. In both cases ΔN_s was obtained from the shift of the MOS characteristic, and the profile of the contaminating atoms was measured directly in the same samples by etch-sectioning and gamma-ray spectrometry.[4] Electrical and radiochemical data were then compared.

Oxide was grown on one inch diameter electromechanically polished Si wafers, 10 mils thick with an n-type resistivity of 10 ohm-cm and (111) crystallographic orientation. The Si samples were cleaned in electronic grade trichloroethylene, acetone, methanol, and water, followed by a soak in 80°C nitric acid[7] and rinse in 3 megohm-cm water. Samples were oxidized in an all-quartz system at 1200°C in wet oxygen to an oxide thickness of about 5400 Å.

Electrical capacitance versus voltage measurements of uncontaminated samples yielded a voltage shift from the theoretical curve of 17 volts of which approximately 1 volt is due to work function difference. This shift, from Equation (2), corresponds to an equivalent interface charge density of 7×10^{11} charges/cm.^{2} After heating in dry nitrogen (Figure 2) a density of 3×10^{11} cm^{-2} was obtained which is comparable to reported[3] minimum values of 2×10^{11} charges/cm.^{2} for (111) crystal orientation. This is believed to be interface charge characteristic of the SiO_2/Si transition structure.[8]

After oxidation, the samples were deliberately contaminated by dipping in a solution of radioactive $Na^{24}Br^{82}$ in methanol. Methanol was used for better wetting and more uniform drying in preference to water solution.

Sodium bromide was used for contamination because both sodium and bromine could be traced by gamma-ray spectroscopy. Some electrical experiments were done using NaCl and NaOH. Results using these compounds were qualitatively the same as in the NaBr experiments, indicating that the NaBr results would yield typical anion behavior.

Samples for electrical drifting experiments had a large gold plate, vacuum-evaporated on the oxide over the contamination, and a gold contact evaporated on the back of the silicon for good electrical contact. For hot bias drifting, the sample was placed on a metal contact block heated by an internal resistance element. The block made good electrical contact to the gold on the back of the sample and a probe made contact to the gold field plate. Drifting was done at a temperature of 200°C in dry nitrogen with an applied field of 5×10^5 volts/cm in the oxide, which is an order of magnitude lower than oxide dielectric breakdown. Capacitance-voltage data was measured with a Wayne-Kerr radio frequency bridge

type B601 at 1 mH. No drift was observed during measurement at room temperature.

Samples used for diffusion experiments done at 700, 800, and 900°C in dry nitrogen did not have evaporated gold contacts because of undesirable gold diffusion during the high temperature treatments. Clean, polished, bare silicon wafers were used as covers to keep NaBr from evaporating at the diffusion temperature.

For electrical measurements a 20 mil diameter gold tipped probe was pressed against the oxide surface to act as the field plate. Capacitances of about 3 pf obtained with the 20 mil probe were measured at 1 mH with a Boonton 75A-S8 capacitance bridge.

Following drift or diffusion and electrical measurements, part of the oxide on the sample was removed to eliminate edge effects leaving a flat area of 1-2 cm^2 in the center. This oxide was then removed in planar sections using dilute hydrofluoric acid. The characteristic gamma energy spectrum of Na^{24} and Br^{82} from each etch section was counted with a NaI (Tl) scintillation detector and 256 channel pulse-height analyzer. Since a known volume of the oxide was in each etch section, the measured activity, when compared to a $Na^{24}Br^{82}$ standard, yielded the actual sodium and bromine concentration in the section.

RESULTS AND DISCUSSION

Diffusion

Polished silicon wafers had to be used to keep the NaBr from evaporating from the samples as mentioned. That the NaBr indeed evaporates is shown in Figure 1 where sodium profile in covered and non-covered wafers has been determined radiochemically. Sodium in the bulk of the oxide for the uncovered sample is an order of magnitude lower than the covered case though greater, for this time and temperature, than residual concentrations. Evaporation of sodium can be observed in electrical measurements also. Figure 2 illustrates the observed electrical shift as a function of $time^{1/2}$ for an 800°C diffusion. The shift for a covered sample, curve A in Figure 2, goes off the scale of the graph within 5 minutes and does not return to zero even under an extended diffusion time (Figure 3), indicating that sodium diffuses into the oxide and stays in. Curve B, for an open sample, initially rises as sodium ions diffuse into the oxide but then returns to zero as sodium evaporates. The curve then goes negative which may be explained by the evaporation of positive ions such as residual sodium, water species; or by annealing of the oxide-silicon interface. This improvement in the samples heated with open surfaces suggests that such a heat treatment may be a good method for removing unwanted sodium contamination in device processing. Curve C, for an uncontaminated sample, also exhibits the cleaning effect seen for the open contaminated sample.

F1 →

F2 →

Electrical results of the diffusion experiments for covered contaminated samples is shown in Figure 3. The 700°C curve rises

F3 →

to a saturation value at ΔV_{fb} = 215 volts. This behavior can be explained by in-diffusion of the positively charged sodium ions to an equilibrium distribution. Radiotracer results, Figure 4, verify this model, since the distributions from two different samples, one diffused 1 hour and the other diffused 4.5 hours, are essentially identical, indicating that equilibrium has been reached in 1 hour. Bromine concentrations in the bulk of the oxide shown in Figure 4 are very near the limits of detectability for bromine and may be artifact. It is evident that bromine does not appreciably diffuse into the oxide at this temperature.

F4 ——>

The curves for 800°C and 900°C in Figure 3 show a different behavior than the 700°C case. The electrical shift peaks and then saturates at a lower value. This saturation indicates that appreciable evaporation is not occurring. These electrical data may be explained by ion cancellation. Sodium diffuses into the oxide to a quasi-equilibrium distribution. Slower-moving bromine diffuses into the oxide and partly cancels the electrical shift caused by positively charged sodium ions. This is verified by the radiotracer results shown in Figure 5. After 30 minutes the bromine concentration in the oxide, especially near the oxide-silicon interface, is within a factor of two of the sodium concentration. Roughly similar behavior is observed for the 900°C case.

F5 ——>

Br distribution, like that of Na, is roughly U-shaped as seen especially in Figure 5. The high concentration at the oxide surface is assumed to be characteristic surface-to-bulk segregation for the oxide. The raised concentration near the silicon may be due to segregation of impurity to the interface "phase." In addition, the spikes may be due to electrostatic binding, Na^+ being bound by image force to the silicon and Br^- tending to pair with Na^+. In this case the approach of an anion would tend to release a Na^+ ion from the vicinity of the silicon.

In Figures 4 and 5, the calculated value of ΔN from Equation (4) is tabulated and compared with the electrically measured value of ΔN_s determined from Equation (2). ΔN is consistently higher than ΔN_s by a factor of 1.5 to 4. This implies that only part of the Na induces charge in the Si because some Na is neutral or is paired with anions other than Br^-.

Drift

The purpose of the drift experiments was to study the motion of the sodium and bromide ions under the influence of an electric field. The radiochemical results of a hot-bias experiment with the metal field plate positive is shown in Figure 6. Sodium moved through the oxide as a positive ion and progressively piled up with time at the oxide-silicon interface. Measured bromine concentration is less than 10^{17} atoms/cm^3, close to the limit of detectibility for the bromine. Negative bromide ions would not be expected to drift toward the oxide-silicon interface with the positive applied field.

F6 ——>

Figure 7 shows the results of reversing the direction of the field (reverse drift) after forward drifting for 15 minutes. Bromine distribution was like that in Figure 6 indicating that it

F7 ——>

did not drift or contribute significantly at 200°C.

Kinetics of sodium concentration at the oxide silicon interface for the forward and reverse drifted cases are seen to be roughly symmetric. However, kinetics of the measured voltage shift were not symmetric. ΔV_{fb} reverse drift electrical "recovery" was much faster than forward drift. ΔV_{fb} returned to zero after only 30 seconds of reverse drift, while the time to remove the sodium from the interface was at least 15 minutes. This is shown more clearly in Figure 8 where calculated and measured values of the induced charge in the Si are compared.

F8 →

SUMMARY AND DISCUSSION

To summarize:

1. NaBr contamination can be readily evaporated from SiO_2 on Si by heating, for example to 800°C in dry nitrogen.

2. This contamination will be retained within the oxide if a close-fitting "cover" is used.

3. Diffusion of NaBr contamination at above 800°C results in silicon surface potential shifts which are not simply monotonic.

4. Radiochemical impurity distribution measurements suggest that these shifts are due to diffusion of both Na and Br across the oxide; the slower Br anion partly cancelling the charged Na near the silicon.

5. Hot-bias drift of NaBr contamination, studied by combined MOS and radiochemical analysis, shows that silicon surface potential shifts are correlated with spikes of Na concentration in the oxide at the silicon interface. However when drift polarity is reversed, Na flows out with a time constant similar to that for in-flow while the surface potential recovery is faster.

This slower Na impurity recovery underlying assymmetric electrical recovery may be used to explain results observed by Hofstein.[9] He monitored surface potential shift at 200°C, during sequences of alternation of drift voltage polarity on oxides believed to be relatively Na-free and found:

1. Initial in-drift (field plate positive) was relatively slow; recovery fast.

2. Subsequent in-and out-drift was fast and symmetric.

3. If out-drift bias (field-plate negative) were maintained for a time comparable to initial in-drift time, next in-drift was again slow.

These results are readily explained in terms of Na by the data in

Figures 6, 7, and 8. That is, if out-drift is terminated when electrical recovery is complete, a Na spike will still remain in the oxide at the Si, and subsequent electrical in-drift will be fast. Slow in-drift as in the initial in-drift will only occur if out-drift is continued for a time long enough to return the Na distribution back to the initial state, i.e. with the spike removed from the Si interface.

The question remains: what is causing the compensation of Na at the Si interface during fast in- and out-drift cycles? Br is not found in sufficient concentration at 200°C (Figure 6) to be responsible. A fast-diffusing accidental anion species may be responsible. In these as-grown "wet" oxides the likeliest species is OH, a faster diffusor than Br. Gold is another possibility since neutron activation analysis has shown it to be present in our oxides at ppm concentrations.

Reverse drift in these experiments returns ΔV_{fb} to zero but not to negative values. Thus the rapidly-equilibrating species must be able to neutralize Na^+ but not be normally negatively-charged at the Si interface. For example this might be OH which is on the average neutral but tends to be OH^- in the neighborhood of Na^+ at the Si interface.

CONCLUSION

Anions as well as Na^+ appear to play a part in determining failure due to surface potential shift in planar Si devices.

Detailed study of oxide impurity distributions and kinetics by combined electrical/radiochemical technique has led to clearer understanding of process steps which decrease the likelihood of this mode of failure.

ACKNOWLEDGEMENTS

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Figure 1. Sodium concentration profile in oxide after 10 minutes at 800°C by radiochemical analysis of Na^{24} from NaBr. A, covered sample; B, uncovered. R, typical residual Na profile determined by neutron activation.

Figure 2. Change in room temperature MOS flat band voltage vs. time $^{1/2}$ at 800°C. A, uncontaminated sample, open surface; B, NaBr contaminated, open; C, NaBr contaminated, covered during diffusion.

Figure 3. Change in room temperature MOS flat band voltage vs. time $^{1/2}$ at temperature for NaBr contaminated covered samples.

Figure 4. Na and Br in oxide after 700°C diffusion as in Figure 3. In units of 10^{12} cm^{-2}, after 1 hour: $\Delta N = 27.$, $\Delta N_s = 6.7$. After 4.5 hours: $\Delta N = 27.$, $\Delta N_s = 6.4$.

Figure 5. Na and Br in oxide after 800°C diffusion as in Figure 3. In units of 10^{12} cm^{-2}, after 1 min: $\Delta N = 6.2$, $\Delta N_s = 4.6$. After 30 min: $\Delta N = 1.7$ cm^{-2}, $\Delta N_s = 0.8$.

Figure 6. 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} 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: $\Delta N = 50$, $\Delta N_s = 9.2$.

Figure 7. Na in contaminated oxide. Reverse drift after 15 min. forward drift. $E = 5 \times 10^5$ v/cm. T = 200°C. Br profile, not shown, is like that in Figure 6 and is not significant. In units of 10^{12} cm^{-2}, at start of reverse drift (the sample is that of Figure 6); $\Delta N = 50$, $\Delta N_s = 9.2$. After 0.5 min: $\Delta N = 20$, $\Delta N_s = 0.36$. After 5 min: $\Delta N = 7.5$, $\Delta N_s < 0.04$. After 15 min: $\Delta N = 0.75$, $\Delta N_s < 0.04$.

Figure 8. Comparison of change of charge induced in silicon surface for drift time at 200°C. Na curve is ΔN computed by equation(4) from radiochemical data. MOS curve is ΔN_s computed by equation(2) from ΔV_{fb} electrical data.

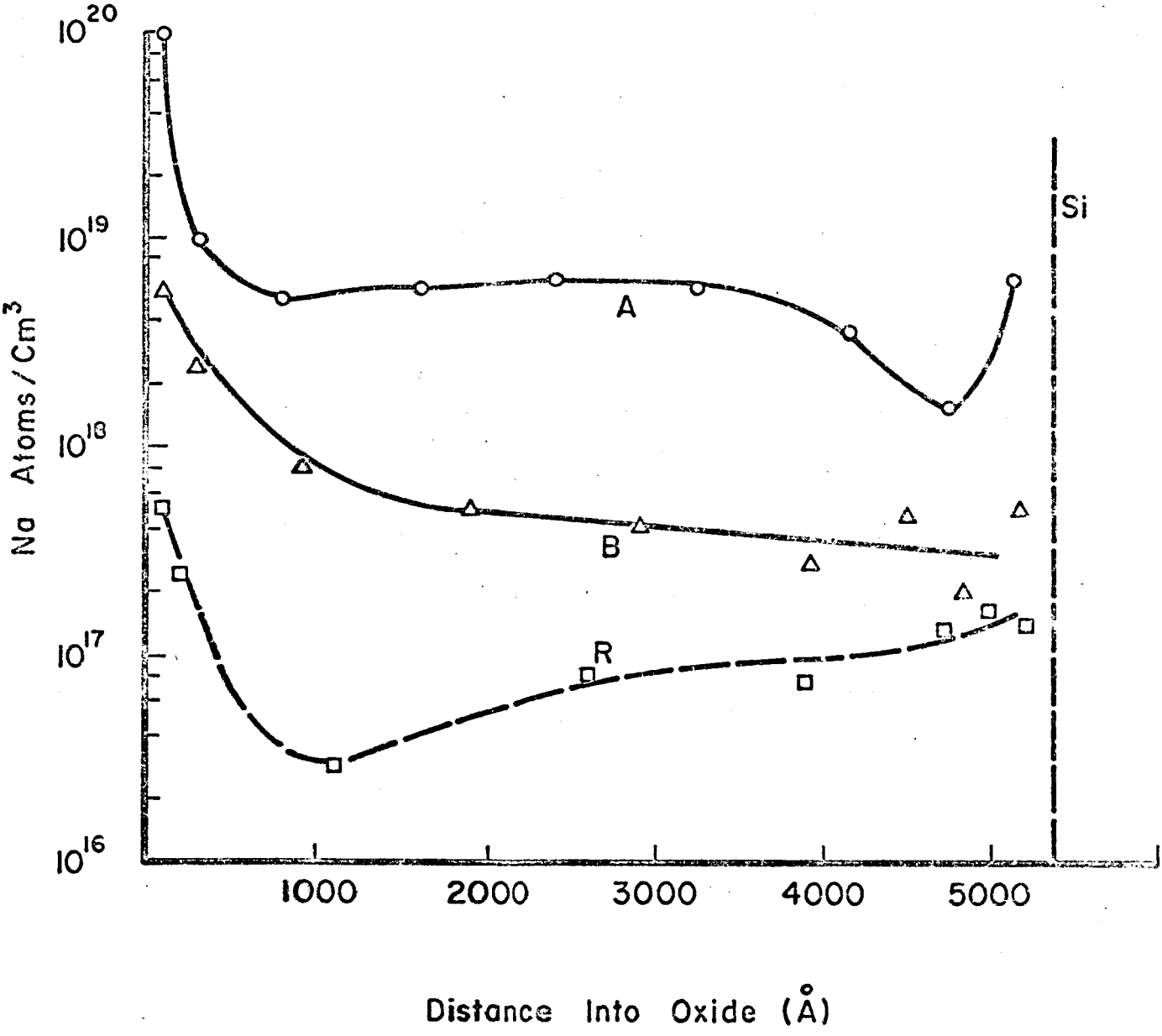
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
Na Atoms / Cm^3
Si
A
B
R
1000
2000
3000
4000
5000
Distance Into Oxide (Å)

Fig 1

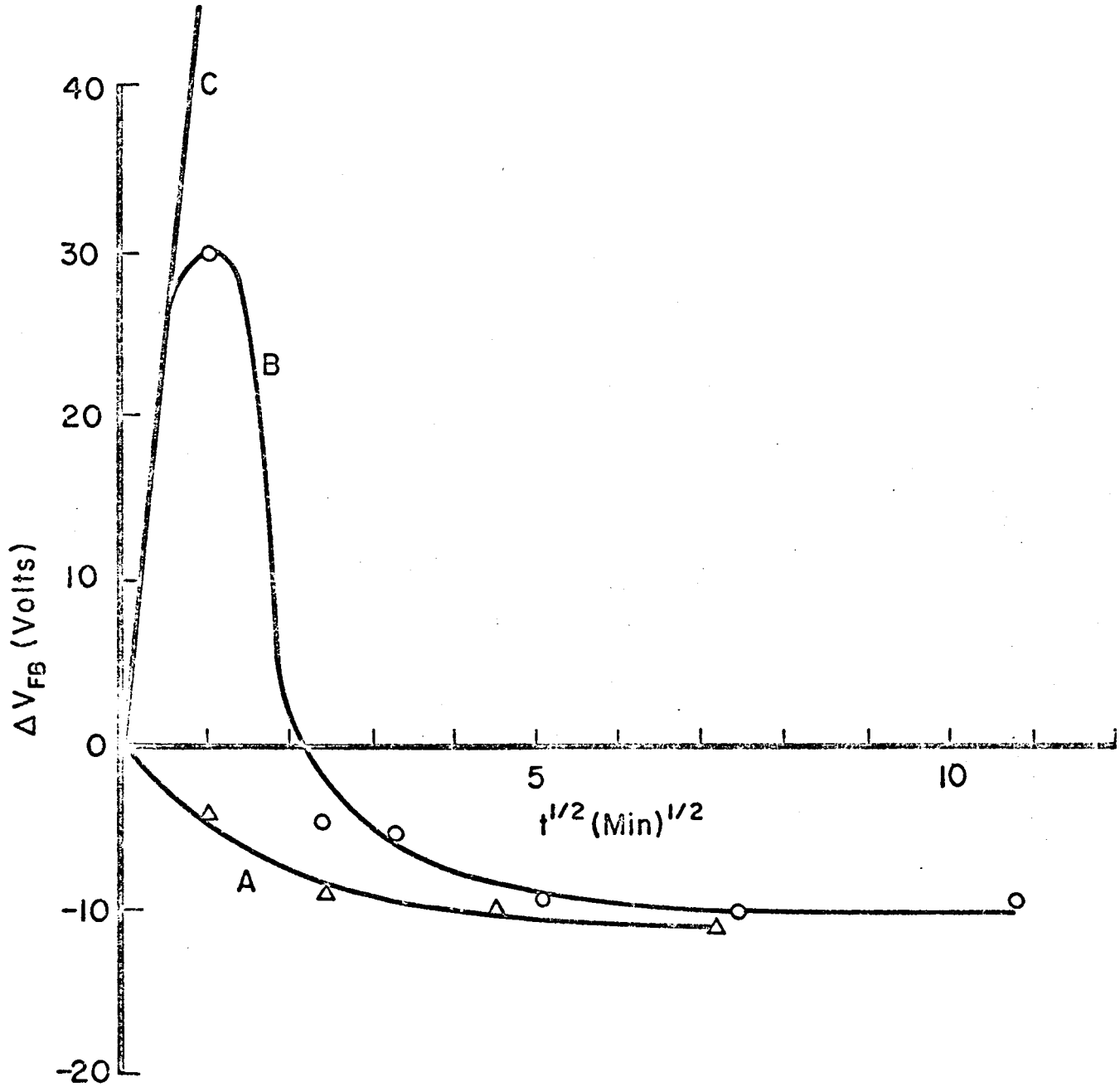

Fig. 2

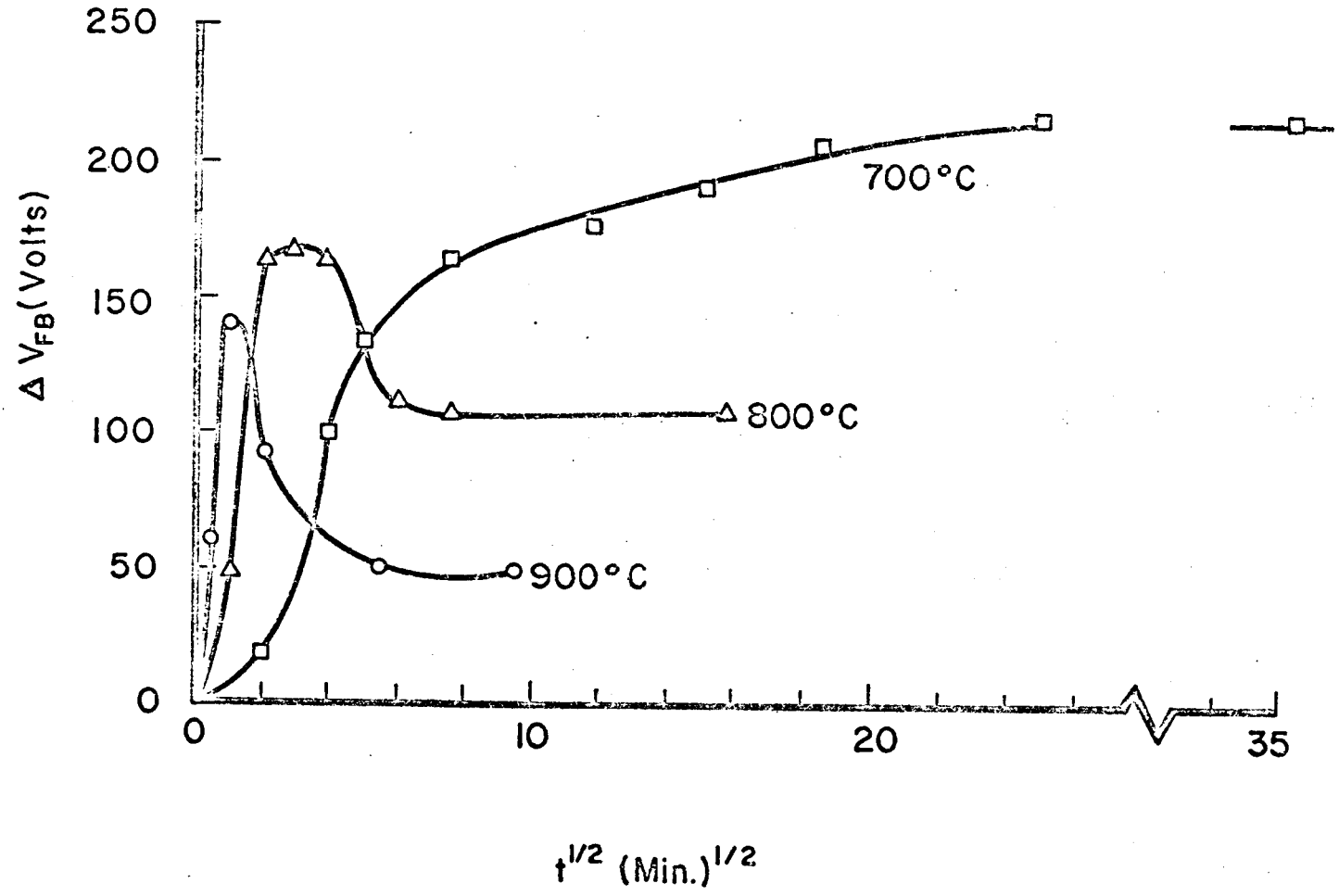
250
200
150
100
50
0
0
10
20
35
Δ V_FB (Volts)
t^1/2 (Min.)^1/2
700°C
800°C
900°C

Fig. 3

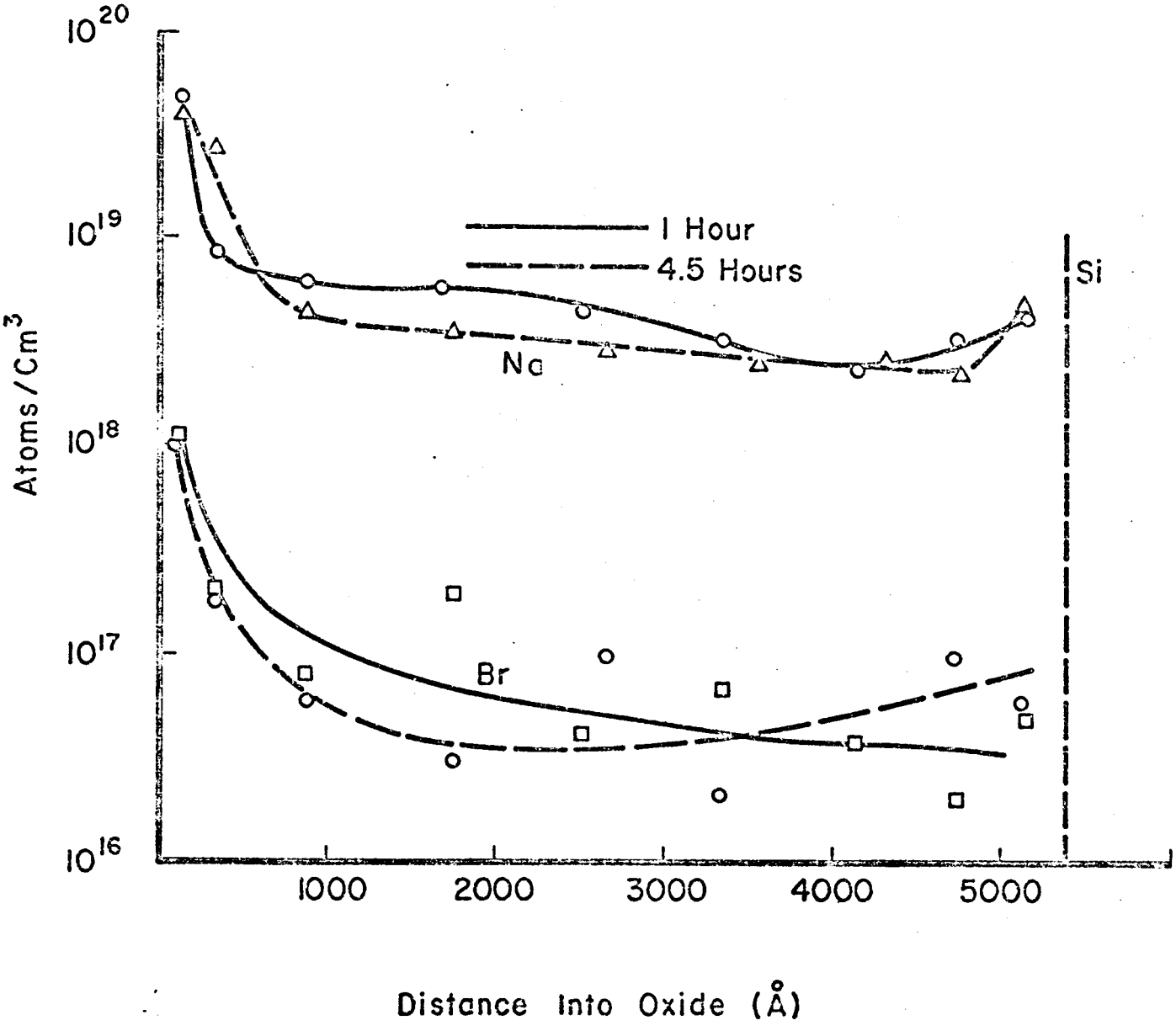
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
Atoms/Cm^3
1 Hour
4.5 Hours
Si
Na
Br
1000
2000
3000
4000
5000
Distance Into Oxide (Å)

Fig. 4

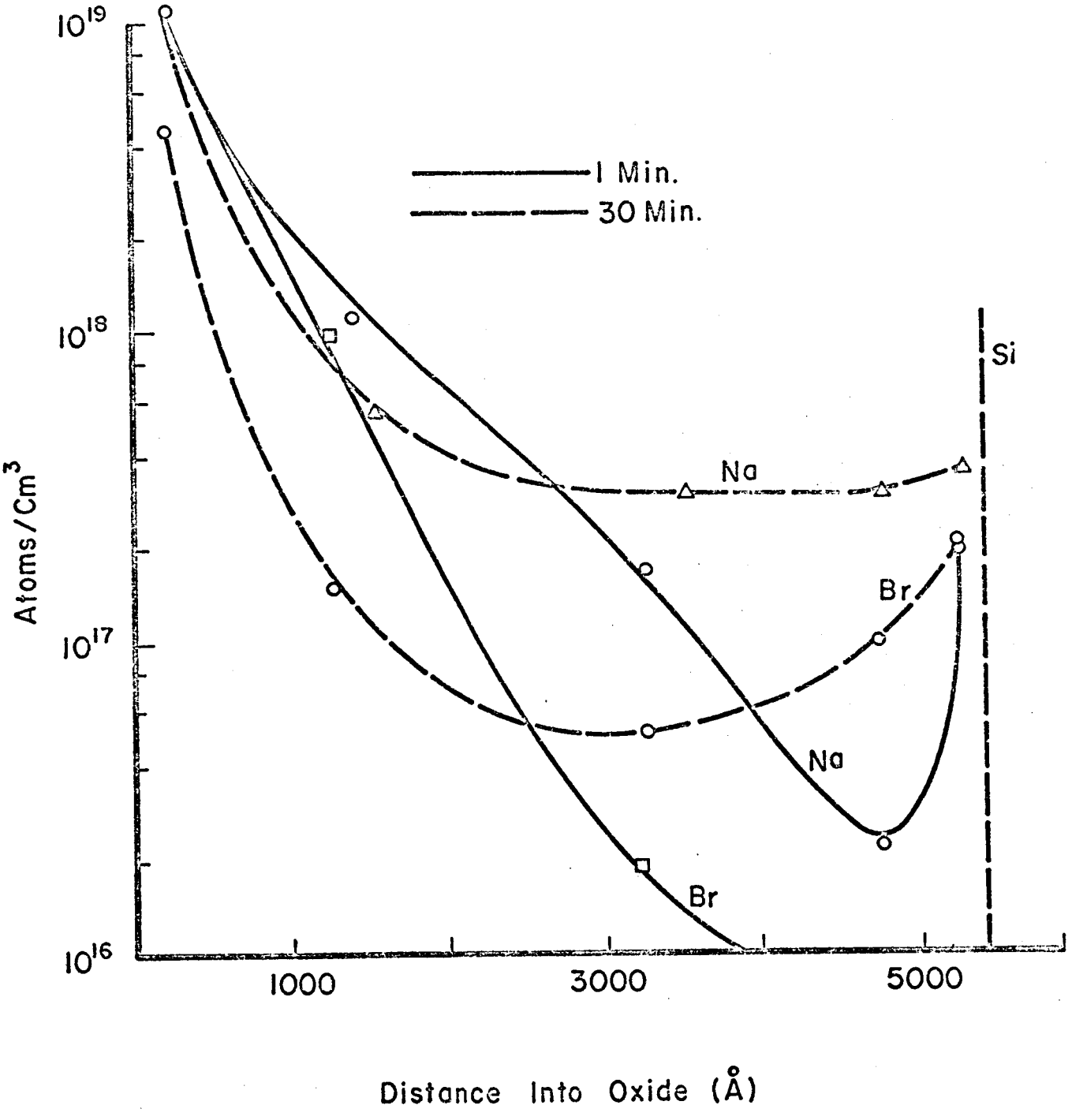
1 Min.
30 Min.
Na
Br
Na
Br
Si
10^{19}
10^{18}
10^{17}
10^{16}
Atoms/Cm^3
1000
3000
5000
Distance Into Oxide (Å)

Fig. 5

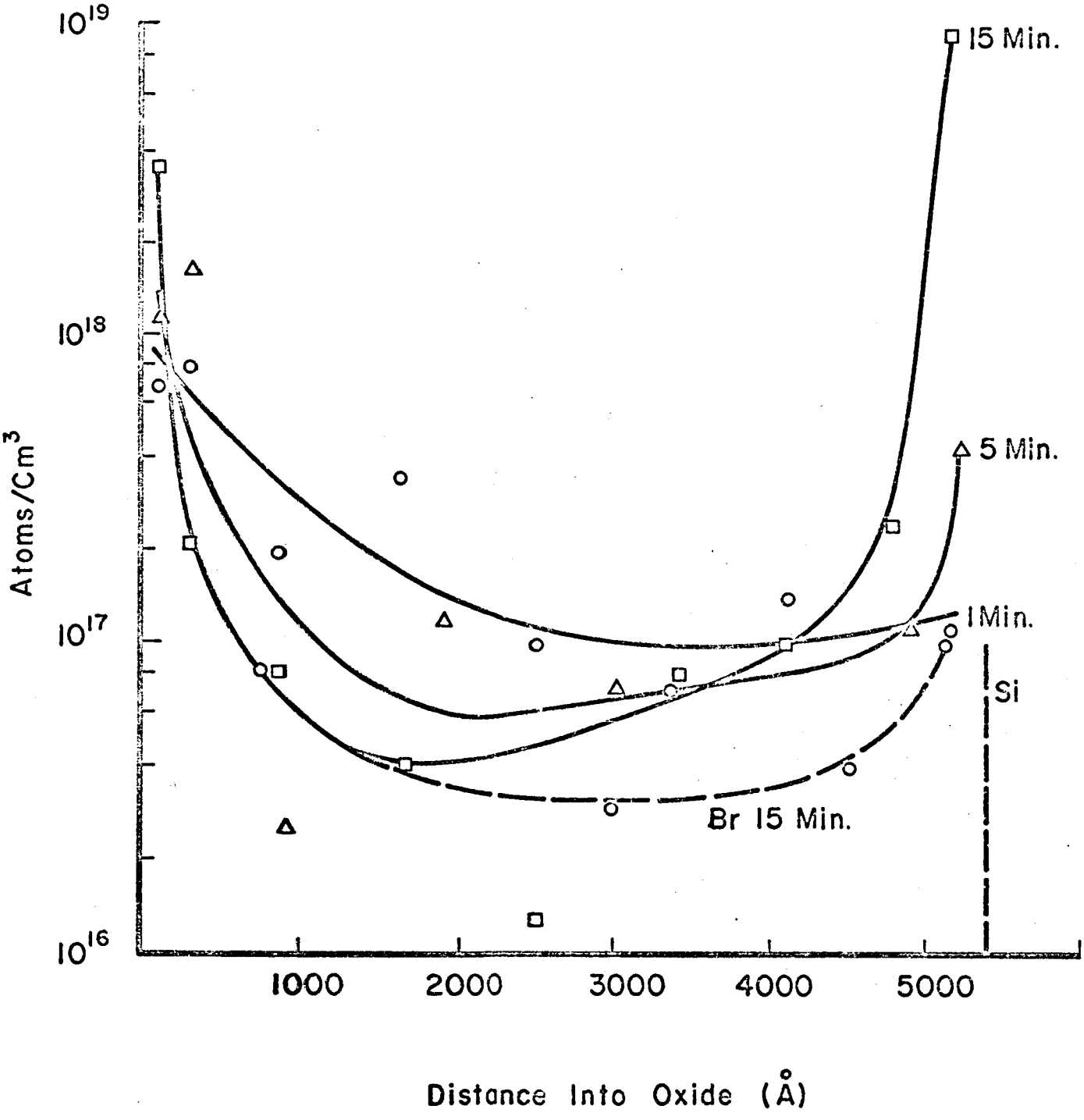
10^{19}
10^{18}
10^{17}
10^{16}
Atoms/Cm^3
15 Min.
5 Min.
1 Min.
Si
Br 15 Min.
1000
2000
3000
4000
5000
Distance Into Oxide (Å)

Fig. 6

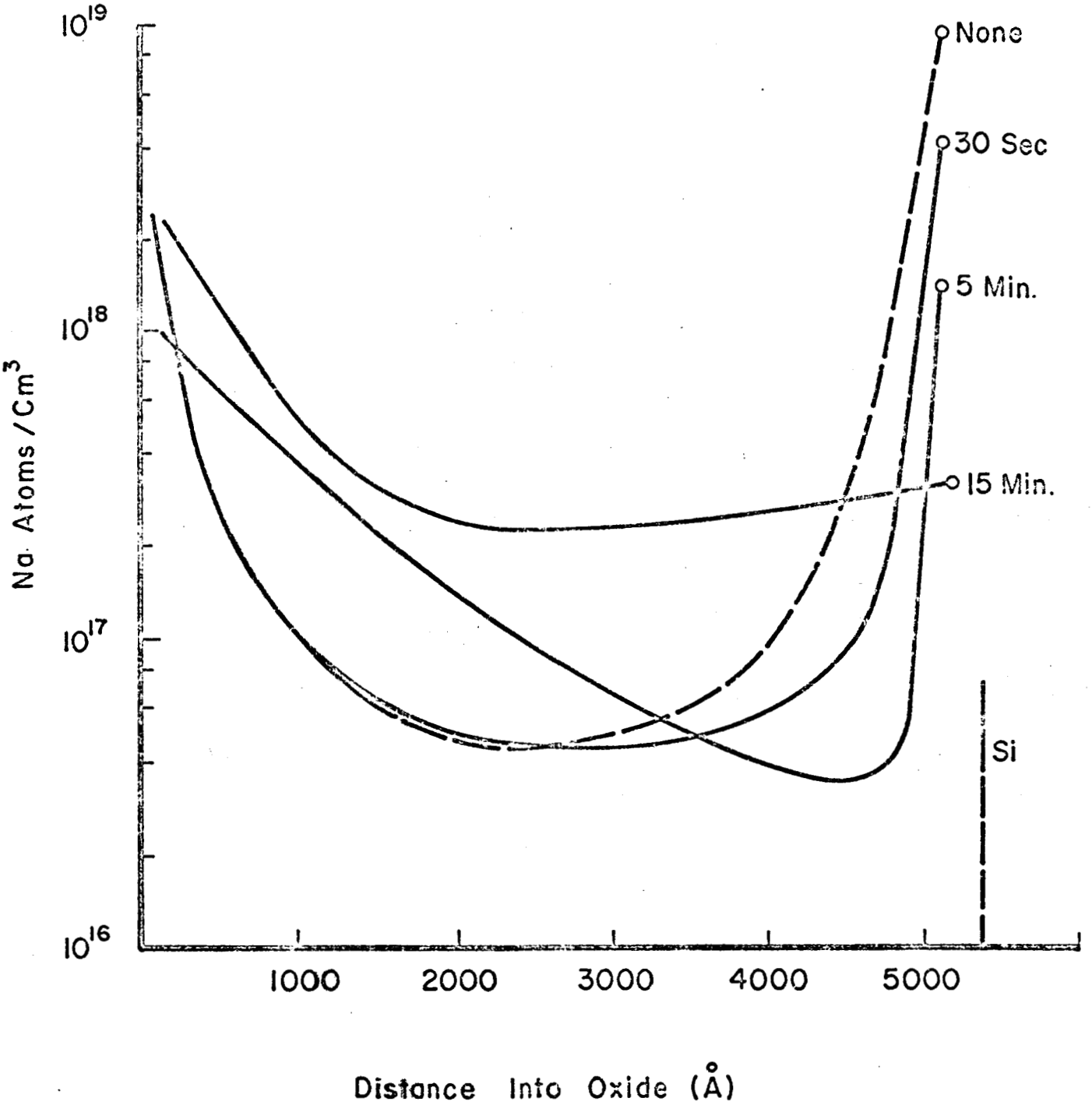
10^{19}
10^{18}
10^{17}
10^{16}
Na. Atoms / Cm^3
None
30 Sec
5 Min.
15 Min.
Si
1000
2000
3000
4000
5000
Distance Into Oxide (Å)

Fig. 7

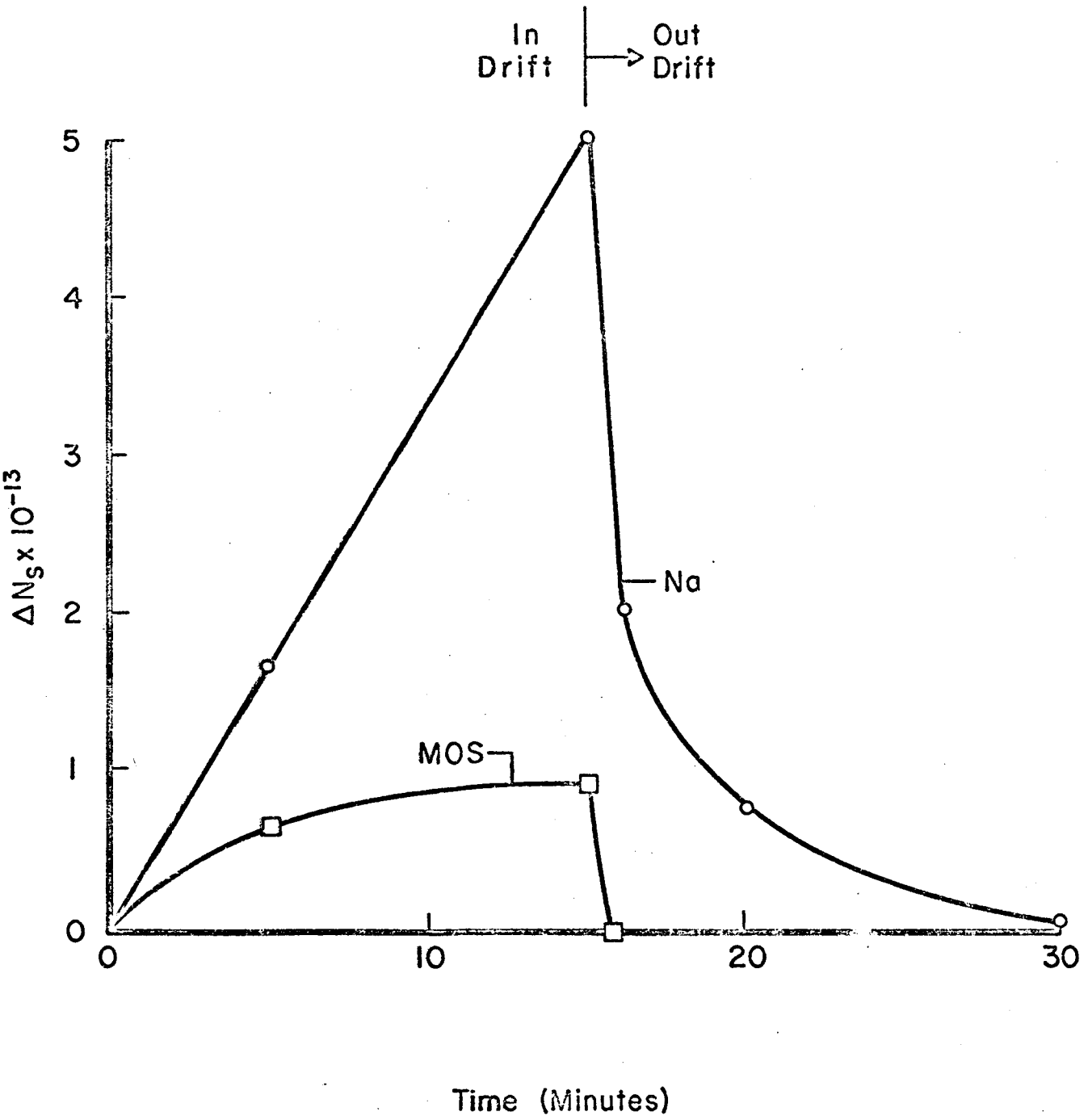
In Drift
Out Drift
5
4
3
2
1
0
$\Delta N_s \times 10^{-13}$
Na
MOS
0
10
20
30
Time (Minutes)

Fig. 8