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THE EFFECTS OF HIGH TEMPERATURE ANNEALS ON REDUCED OXIDE MOS CAPACITORS

by

Douglas A. Pike, Jr.

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Electrical Engineering

Lehigh University

1974

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

Dec. 9, 1974
(date)

Frank H. Heilscher
Professor in Charge

A K Lunlund
Chairman of Department

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ABSTRACT

Thermally grown silicon dioxide layers on silicon contain an inherent positive charge regardless of growth conditions. This positive charge can be increased by exposure of the oxide to low-oxygen-partial-pressure atmospheres at elevated temperatures. This increase of charge has been attributed to the creation of oxygen vacancies which can be eliminated by reoxidation, allowing the charge to decrease to a normal lower value.

In this study, the reoxidation process and consequential charge decrease have been examined in detail on reduced oxides (oxides exposed to the low-oxygen-partial-pressure atmospheres) and on non-reduced oxides. Reduced oxides have shown a non-growth time lag of 200 minutes during subsequent reoxidation at 925°C, this period coinciding with the time required for the oxide charge to decrease to the values observed in normal (unreduced) oxides. After this time lag the reduced oxides were found to grow at the same rate as unreduced oxides, although the growth rate observed is higher than expected. It has been found that oxides grown at a high temperature and then reoxidized at a lower temperature have a higher growth rate than those grown completely at the lower temperature. During the first several minutes of reoxidation the charge has been observed to increase in initially reduced oxides, followed by a gradual decrease; no such effect has been observed during reanneals in nitrogen. The time required for new oxide growth has been found to be independent of original oxide thickness, but to be strongly dependent on temperature. The oxide charge has been found to be

located near the Si-SiO_2 interface. A qualitative model is proposed to explain the reoxidation process, and suggestions for further experiments are given.

1.0 Introduction

It is well known that the exposure of silicon to an oxiding atmosphere at high temperatures, generally above 900°C, results in the growth of a layer of amorphous silicon dioxide on the silicon surface. This SiO_2 layer is used as an electrical insulator in the fabrication of metal-oxide-semiconductor (MOS) transistors and integrated circuits. This SiO_2 layer is always observed to contain positive charges regardless of the conditions under which it is grown.

This positive charge has been the subject of numerous studies,[1-9] but its origin, despite these efforts, is still obscure. One proposed explanation for the charge is that it originates at positively charged impurity centers, such as Na,[10] which are distributed throughout the oxide. Among others, Revesz and Evans[11] have demonstrated, however, that Na is not likely to be the major cause of the positive charge. An alternate explanation attributes the charge to non-stoichiometry of the SiO_2 layer due to either an excess of silicon or a deficiency of oxygen. Deal et al.[1] and Laverty and Ryan[12] have suggested an excess of unreacted silicon atoms, most likely existing in the SiO_2 layer near the Si-SiO_2 interface, causes the positive charge, while Thomas and Young[2] and Fowkes and Hess[7] suggested charged oxygen vacancies, also near the Si-SiO_2 interface, as the cause.

Fowkes and Hess[7] have purposely altered the stoichiometry of the SiO_2 layer by exposing it to a reducing ambient of CO-CO_2 at an elevated temperature (910°C) which was found to increase the positive oxide charge and the surface state density through the

supposed creation of charged oxygen vacancies. Hess[8] has also studied the effect of refilling these vacancies with oxygen and found that the normal oxide growth was inhibited until a certain time had elapsed and after this time the positive oxide charge had decreased to that of a normal oxide.

The present investigation is concerned with gaining additional insight into the origin and properties of the oxide charge through a detailed examination of the reoxidation kinetics of oxides reduced in a $CO-CO_2$ ambient. The effect of filling these vacancies with oxygen will be monitored by measurement of the oxide charge density versus reoxidation time. Upon reoxidation, the charge of a reduced sample is expected to show a gradual decrease with time, eventually decreasing to the value of an unreduced sample. The surface state charge, which is located within approximately 20Å[13] of the $Si-SiO_2$ interface, would be expected to show a very abrupt decrease because it should not decrease until a new $Si-SiO_2$ interface has been created by oxidation.[9] The reoxidation kinetics will be further monitored by oxide thickness measurements versus reoxidation time for the reduced samples to determine the onset of additional oxide growth and to observe effects on the growth rate. The effects of annealing in a nitrogen ambient will also be studied to determine whether, in fact, the vacancies must be annihilated in order for the charge to decrease.

2.0 Oxide Charge Considerations

The existence of an inherent positive charge in thermally grown silicon dioxide layers on silicon has been noted by many workers,[1-12,14] but its origin is not understood. The oxide charge versus thickness has been measured by some workers by succesively etching the SiO_2 layer in hopes of determining the spatial charge distribution.[1,4,5,8,12] Deal et al.[1] have found that most of the charge lies within 200Å of the Si-SiO_2 interface, independent of the original oxide thickness, by assuming a constant charge density over distance from the interface. A similar number (250Å) has been proposed by Laverty and Ryan,[12] who assumed a distribution linearly decreasing from the interface. Hess[8] has found that the charge lies within 200Å of the interface, assuming a constant charge density, independent of the original oxide charge. Lindmayer's[4,5] experiments showed the location of the oxide charge to be dependent on original oxide thickness if he assumed an exponential charge distribution. His findings, however, appear to be in doubt,[1] due to neglect of several important factors.

The measurement of the charge distribution itself is complicated by difficulties in uniformly etching a large surface area. The shape of the oxide charge distribution, therefore, has in the past been assumed and numerically calculated after the fact for the best fit to the data. The amount of charge has been shown to decrease with increasing temperature of dry oxidation and also to decrease with high temperature (900-1200°) annealing in N_2.[1,6] These effects are currently unexplained.

The study of reduced oxides appears to be particularly promising in the study of oxide charges, since the creation and removal of the charge can be controlled. The kinetics of the reduction process can be fairly well described and reproducible oxide charges can be obtained,[8] therefore a detailed study of the reoxidation kinetics should yield both characteristics and distribution of the oxide charge. Hess had observed that the large positive oxide charge induced by his reduction experiments prohibited further oxide growth for 60 minutes at 910°C in a reduced 1250Å oxide and that thereafter the charge and surface state density were reduced to low values characteristic of an unreduced oxide. This effect will hereafter be referred to as "completely reoxidizing" the oxide. Hess attributed the non-growth of the oxide to oxygen vacancies in the oxide which alter the oxygen flux and hence cause the oxidation rate to go to zero. End[14] has suggested that the reoxidation process is thickness dependent since a 1250Å reduced oxide has been shown to be completely reoxidized in 60 minutes at 910°C while a 1500Å reduced oxide only shows a 30% decrease in oxide charge and no decrease in surface state density during a 60 minute reoxidation at 925°C.

The purpose of this investigation is to determine the reoxidation time at which the reduced oxide is completely reoxidized and to study the reoxidation kinetics by observing the reduction of charge with increasing reoxidation time. Hopefully this time for complete reoxidation can be correlated with the time at which additional oxide growth is observed, as measured by the increase in oxide

thickness. Samples very similar to those used by End[14] (1500Å oxides originally grown in dry O_2 at 1130°C for one hour) and processed similarly (all samples reduced at a partial pressure of oxygen of 7×10^{-18} atm. for five hours at 910°C and reoxidized at 925°C in dry oxygen) are used so that this study can draw upon the results of End's work.

3.0 Experimental Procedure

3.1 Device Fabrication

The devices investigated in this study were fabricated on n-type (phosphorus doped) ⟨100⟩ chem-mechanically polished silicon wafers of 1 to 10 ohm centimeter resistivity. After a normal cleaning procedure (see Appendix A), the samples were oxidized to the desired thickness at 1130°C (and in one case at 925°C) in dry oxygen. All processing was done at a flow rate of 300-500 cm^3/min in a resistance-heated Lindberg three-zone furnace with a mullite-lined silica tube.

The oxidized samples were then reduced in a similar furnace with a CO-CO_2 atmosphere at 910°C for five hours at a total flow rate of 900 cm^3/min. This procedure has been shown[7] to create an equilibrium charge of $N_{ox}=(2.7\pm.1) \times 10^{12}/cm^2$ in a 1250Å oxide when the partial pressure of oxygen is 7×10^{-18} atmospheres. This particular value of charge is obtained by equal partial pressures of CO and CO_2 in the reaction $CO + \frac{1}{2}O_2 \longleftrightarrow CO_2$ and has been chosen as the only partial pressure used in this investigation since it lies midway between the two extremes investigated by Hess.[8] All samples were reduced at the same partial oxygen pressure in hopes of obtaining the same value of oxide charge and similar distributions.

After reduction, the samples were reoxidized at 925°C in dry oxygen in the furnace originally used for the initial oxidation. One sample was processed for each of the different reoxidation times.

Aluminum was then evaporated on the front of each sample in a sputter-ion pumped vacuum system at approximately 10^{-6} torr.

A photolithographic operation was used to define a circular area, or dot, for the metal contact of the MOS capacitors, having a diameter of 20 mils and thus an area of $2.02 \times 10^{-3} cm^2$. This photolithographic technique yields contact areas with an accuracy of better than 1%. The back oxide was then stripped in HF and aluminum evaporated onto the back of each sample.

3.2 Measurement Methods

The high frequency capacitance-voltage (C-V) technique[15] was used to measure the oxide charge and thickness. The equipment consisted of a 1MHz Boonton 71A-R L-C meter and a DC ramp generator with a sweep rate of approximately 1 to 5 volts/second. The shift of the flat band voltage of this C-V curve from the theoretical curve is proportional to the oxide charge[16] as indicated in Fig. 1 and by eq. (1). Eq. (1) shows the effects of ϕms, the work function differance, Q_o, the oxide charge and Q_{ss}, the surface state charge on the flat band voltage:

$$\Delta V_{FB} = \phi_{MS} - \frac{Q_{ss}}{C_{ox}} - \frac{1}{C_{ox}} \int_o^{x_o} \frac{x}{x_o} \rho (x) dx \qquad (1)$$

The last term of eq. (1) is the result of a charge distribution, $\rho(x)$, summed over the entire oxide thickness $(0 < x < x_o)$. This gives the total value of charges, Q_o, distributed in the oxide so that eq. (1) may be rewritten as:

$$\Delta V_{FB} = \phi_{MS} - \frac{Q_{ss}}{C_{ox}} - \frac{Q_o}{C_{ox}} \qquad (1a)$$

The oxide charge, Q_{ox}, will be defined as $Q_{ox} = Q_{ss} + Q_o$ because the

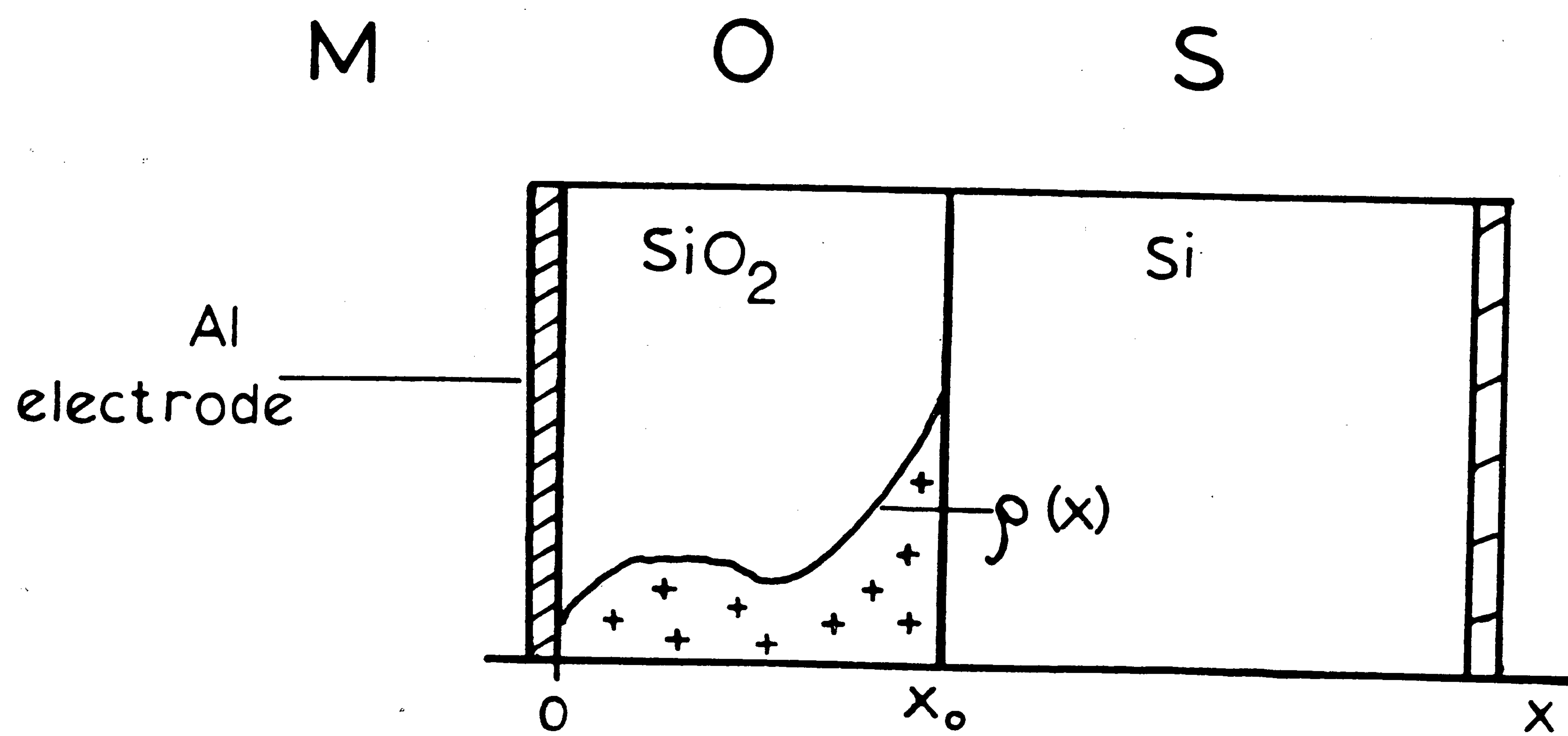


Fig. 1a Arbitrary oxide charge distribution $\rho(x)$ in MOS capacitor.

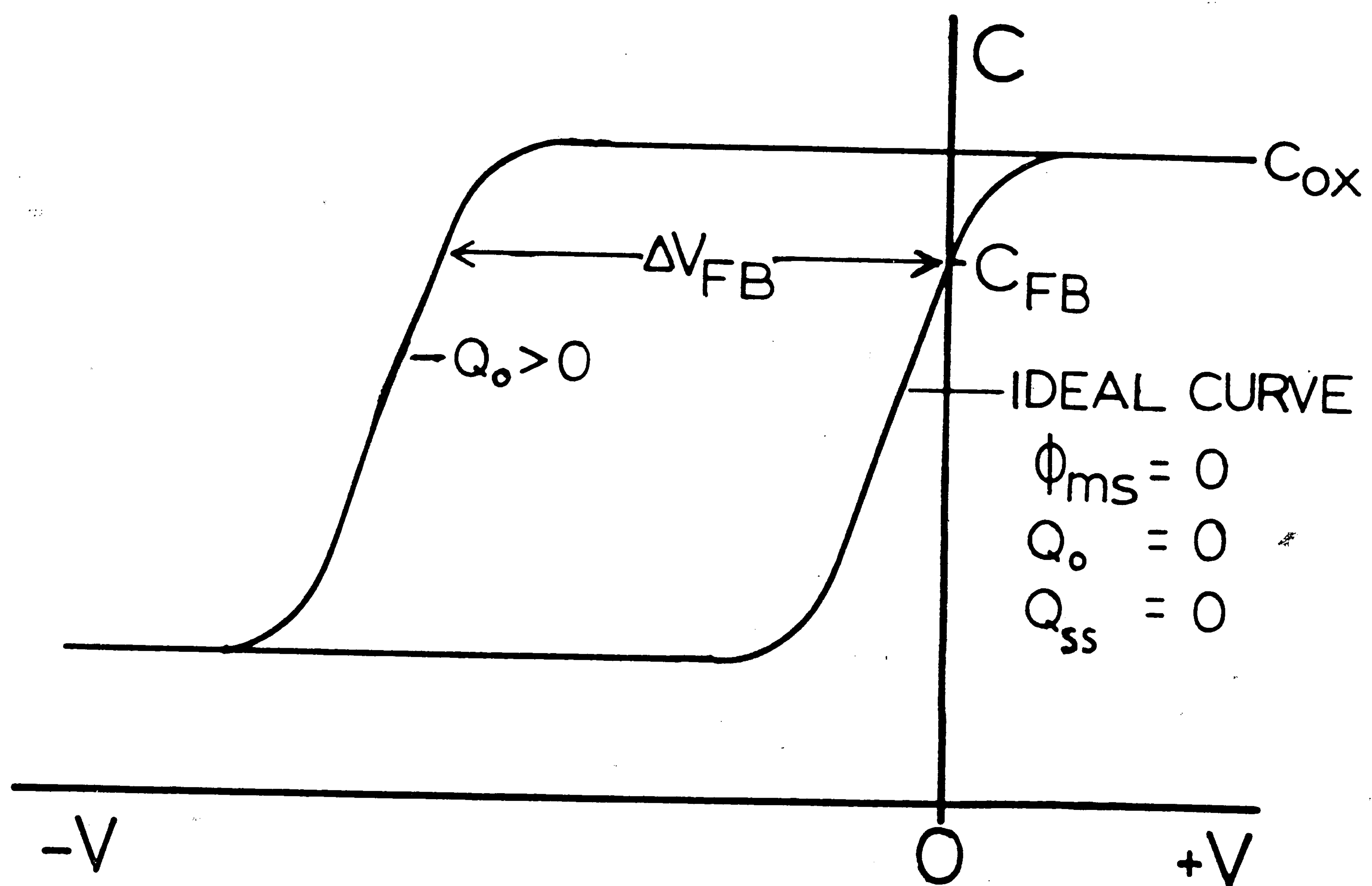


Fig. 1b The effect of fixed oxide charge Q_o on the ideal C-V curve.

two charges, Q_{ss} and Q_o cannot readily be separately determined as shown in a recent study.[17] At flat band, Q_{ss} is considered small with respect to Q_o, so that we have $Q_{ox} \simeq Q_o$ and:

$$Q_{ox} = |\Delta V_{FB} - \phi_{MS}| \cdot C_{ox} \qquad (2)$$

This point will be considered in more detail later.

The effect of Q_{ox} is to shift the entire C-V curve to the left or in the negative voltage direction (see Fig. 1) with no change in shape. This is expected for an n-type substrate, because the larger the positive oxide charge, the more n-type the silicon surface becomes and the larger the negative charge required on the metal electrode to produce the flat band condition.

The samples were placed on an x-y stage and after being contacted by a gold probe were shielded from light while the curves were recorded on an x-y recorder. Typically ten dots were selected on each slice yielding ten different C-V curves from which a distribution of ΔV_{FB} was found (see Fig. 2a). The flat band capacitance was found using the method of Wagner and Berglund[18] and a visual mean recorded along with the error given by the two outside curves. The oxide charge density was found from:

$$N_{ox}\left[cm^{-2}\right] = \frac{C_{ox}}{Aq} \cdot |\Delta V_{FB} - \phi_{MS}| = \frac{Q_{ox}}{Aq} \qquad (3)$$

where A is the area of the dot. The work function difference, ϕ_{MS} (ref. 19), has been taken into account in all measurements because of its large effect on non-reduced and completely reoxidized samples. Typically, ϕ_{MS} ranged between 0.15 to 0.4 volts for most

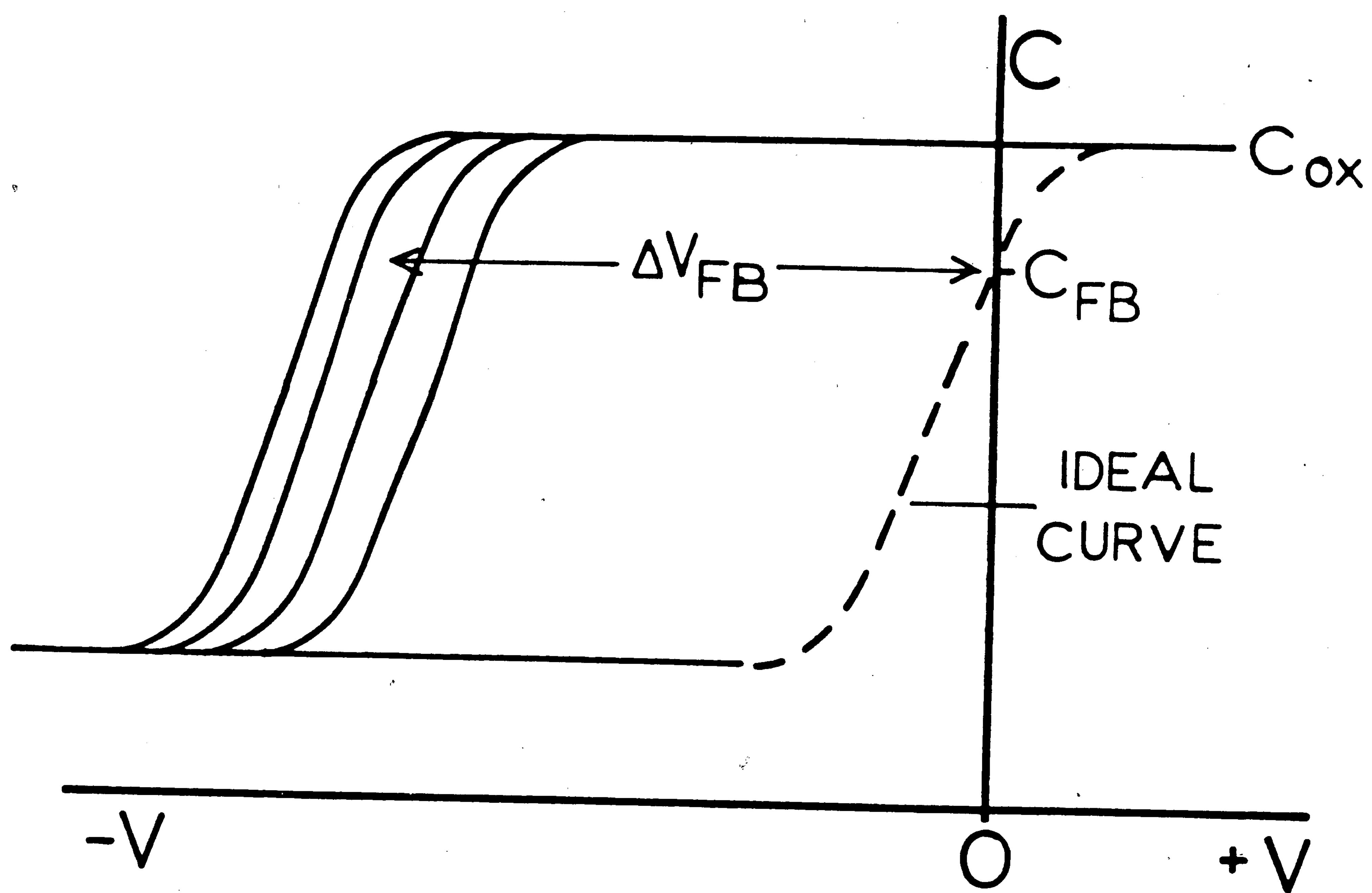


Fig. 2a Variation of ΔV_{FB} for random selection of dots on sample.

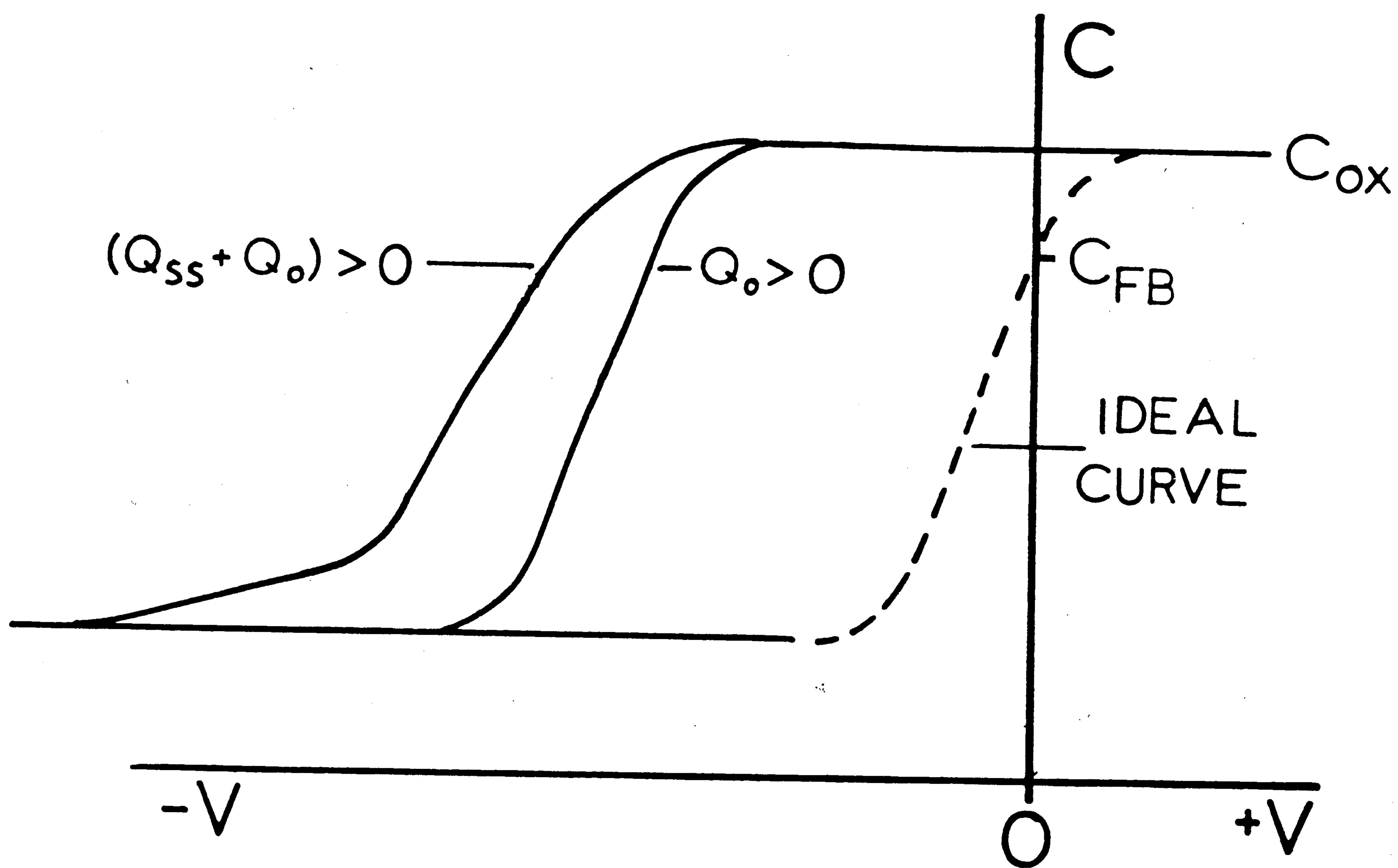


Fig. 2b Effects of oxide charge Q_o and of surface state charge plus oxide charge $Q_{ss}+Q_o$ on ideal C-V curve. (ref. 1)

of the samples.

The oxide capacitance, C_{ox}, measured at a large positive bias to insure that the oxide is not shorted and that the surface is completely in accumulation has been measured on about five dots on each sample and averaged to determine the thickness from $x_o = (K_{SiO_2} \epsilon_o A)/C_{ox}$. The dielectric constant, in this expression is $K_{SiO_2} = 3.9$ for normal oxides, and has been found[8] to be the same for reduced oxides.

The effect of Q_{ss}, the surface state charge, on the C-V curve can be noted qualitatively as in Fig. 2b. An oxide charge, Q_{ox}, has been shown[16] to translate the curve with no shape change while a surface state charge distribution has been shown[1] to decrease the slope in the depletion region of the C-V curve or to "smear" the curve out and also to produce a "tail" before the curve reaches inversion. Quantitatively analyzing these effects on the shape of the high frequency C-V curve has been shown[20] to yield Q_{ss}. Recently McNutt and Sah[17] have reexamined the distortion of the C-V curve from its theoretical shape and have shown that this deviation could also be caused by an inhomogeneous spatial oxide charge distribution.

4.0 Results

4.1 The Oxide Charge

The oxide charge has been measured as a function of reoxidation time at 850°C and 925°C for reduced and for non-reduced oxides of 1000Å, 1440Å and 1740Å original thickness. Fig. 3 shows the oxide charge density versus reoxidation time for 1440Å and a 1000Å reduced oxide, as well as the data (dashed line) for the charge of an unreduced 1440Å oxide. (Oxide charge measurements showed an observed scatter of ±15% for dots randomly located across each slice.) When these curves are extrapolated until intersection with the normal oxide curve, the same reoxidation time (approximately 200 minutes) is found necessary to completely reoxidize the reduced oxides, independent of thickness. Fig. 4 illustrates this same effect for the reoxidation of 1430Å and 1740Å reduced oxides, and again the data (dashed line) of the normal (unreduced) 1440Å oxide. When these curves are extrapolated until they intersect with the dashed curve, a time of approximately 200 minutes is again found for complete reoxidation, independent of thickness. These results disagree with the results of Hess,[8] who found 60 minutes to be sufficient to decrease the charge to the original low value in his reduced 1250Å oxides by reoxidation at 910°C. These results also disagree with End's[14] hypothesis that the longer time necessary for complete reoxidation was due to the thicker oxides of his samples. It is to be noted that End's reoxidation temperature was 925°C (rather than 910°C, which he reported), and was thus 15°C higher than the temperature used in Hess's experiments. The results of this study, as seen in

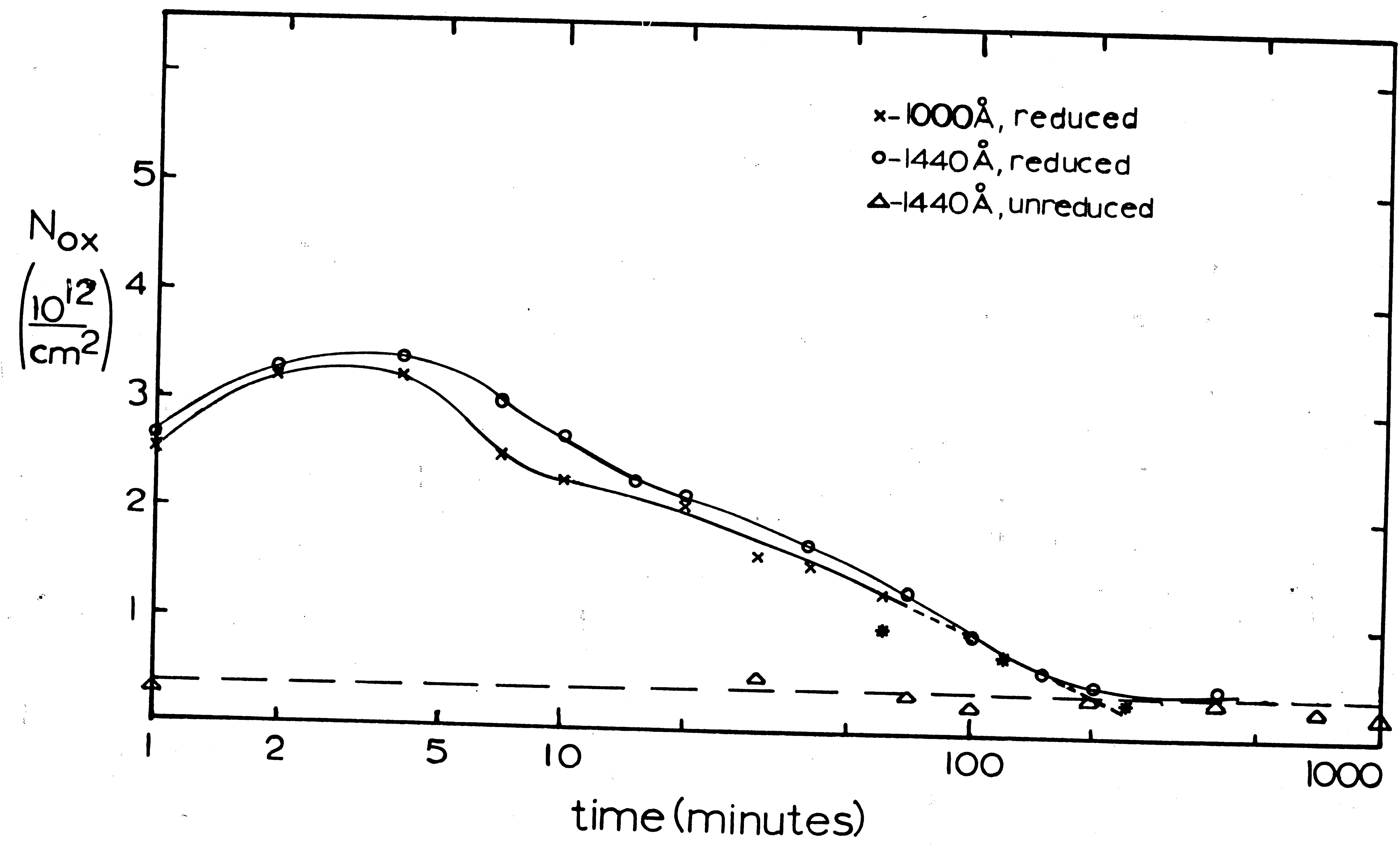


Fig. 3 Oxide charge density N_{OX} as a function of reoxidation time at 925°C.

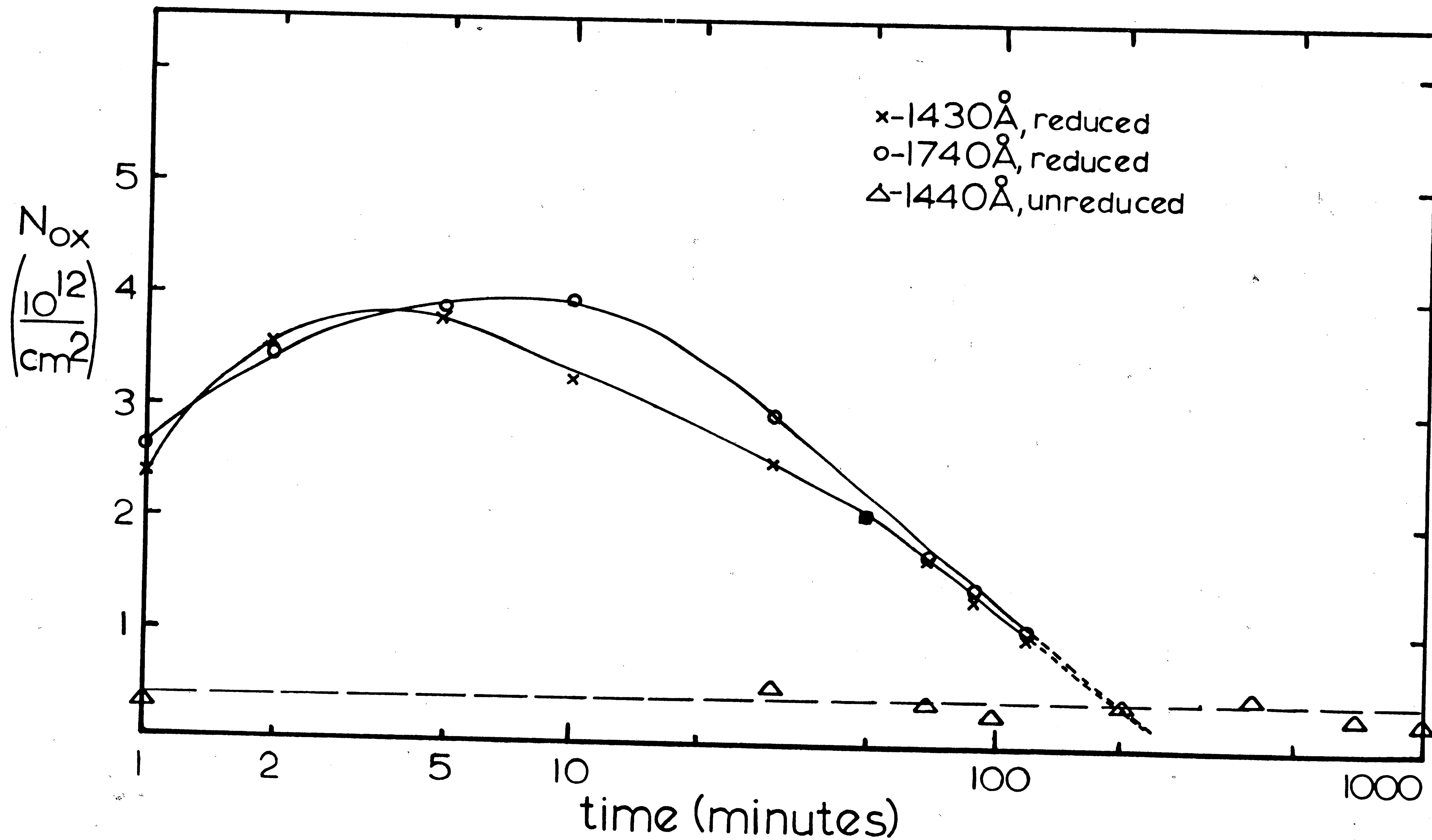


Fig. 4 Oxide charge density N_{OX} as a function of reoxidation time at 925°C.

Fig. 3 do however, agree with End's[14] data for a 60 minute reoxidation of 1440Å reduced oxide at 925°C, which produces a decrease in oxide charge of approximately 30%. The absence of a thickness dependence leads to the conclusion that the reoxidation process is not diffusion controlled, and instead an interfacial reaction must be the controlling mechanism.

Fig. 5 shows the oxide charge density versus reoxidation time at 850°C for a 1440Å reduced oxide. It can be seen by extrapolation that the time for complete reoxidation found by the intersection of the extrapolated line with the dashed normal oxide line is now approximately 1000 min, i. e. five times longer than the time required at 925°C. This indicates that the reoxidation rate controlling process is strongly temperature dependent. If it is assumed that the time required for complete reoxidation as a function of temperature involves a thermally activated process, an activation energy of approximately 2.5 eV is found (see Appendix B). This activation energy compares favorably with those commonly found for interface limited linear oxide growth on silicon.[11]

The shape of the reoxidation curves is of great interest also. It was expected that the charge would show a sharper cutoff with reoxidation time, because it was assumed that the charge was located near the Si-SiO_2 interface; if the rate were diffusion controlled a sharper cutoff would probably have been noted. It is seen above, however, that the rate is not diffusion controlled, so that even if the charge were located near the Si-SiO_2 interface, a sharp cutoff would not necessarily be observed.

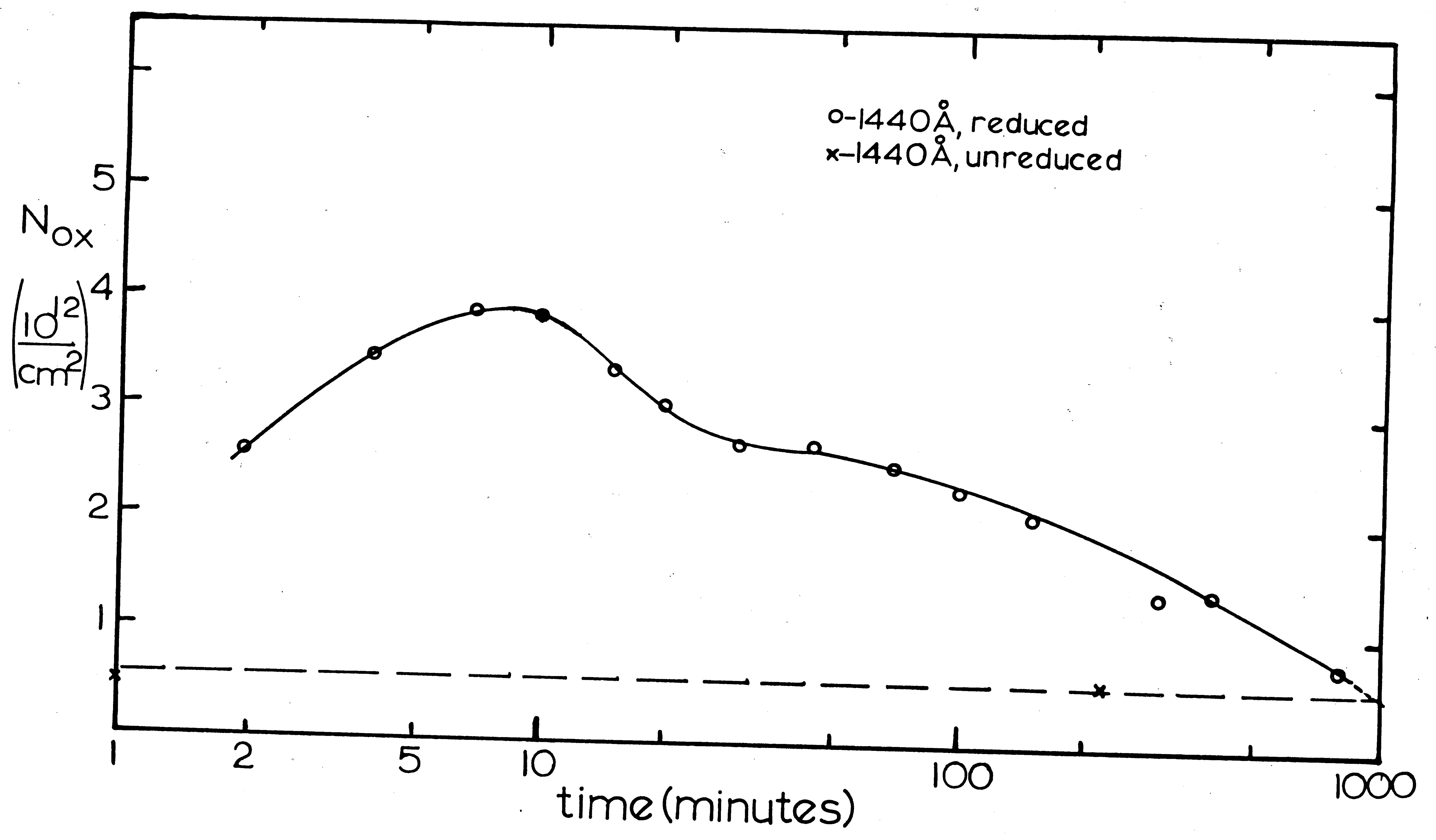


Fig. 5 Oxide charge density as a function of reoxidation time at 850°C.

The increase of charge with reoxidation time for the first few minutes is surprising, since the charge was expected to decrease with the time of reoxidation as the oxygen vacancies are filled.[8] Fig. 6 shows the oxide charge density versus reannealing time in nitrogen for a reduced oxide at 925°C. It can be seen that the neutral ambient, nitrogen, does not affect the oxide charge. Three devices indicated by the star in Fig. 6 (1440Å reduced oxides, annealed in nitrogen for 200 minutes at 925°C) were given subsequent reoxidation treatments at 925°C of 60, 120 and 240 minutes. These samples' data is also plotted in Fig. 3 as stars. It can be seen that the nitrogen anneal had very little effect, if any, on these devices since the data coincides with the curve in which the intermediate high temperature nitrogen anneal was omitted. These experiments indicate that the reduction of charge and also the initial increase of charge depend on the presence of an oxidizing species.

Fig. 7 shows the oxide charge density versus reannealing time at 925°C for 1440Å reduced oxides in oxygen and nitrogen ambients. The samples were fabricated at a time when the deionized water supply was malfunctioning (resistivity, $\rho < 10^6 \Omega$ cm; normally $\rho > 10^7 \Omega$ cm) and further these samples had accumulated dust on their outer surface prior to the final reannealing. (In all other runs, dust effects were minimized by minimizing the time between processing steps.) It is apparent that these factors have affected the initial large increase in positive charge with reoxidation time when Fig. 7 is compared with Fig. 3 and Fig. 6. The charge was not expected to change at all upon reannealing in nitrogen (Fig. 6) (especially not

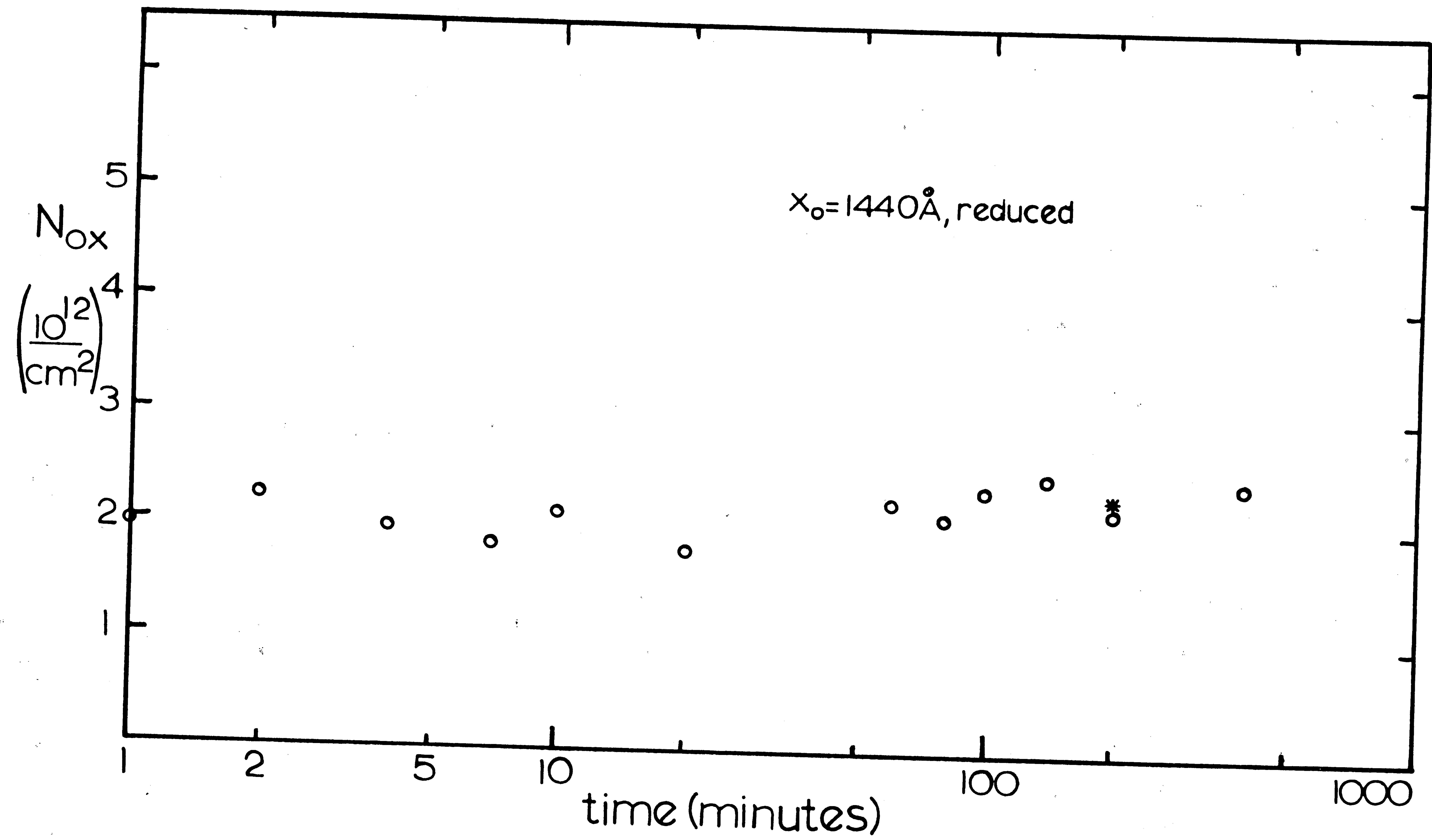


Fig. 6 Effect of N_2 reannealing at 925°C on oxide charge density.

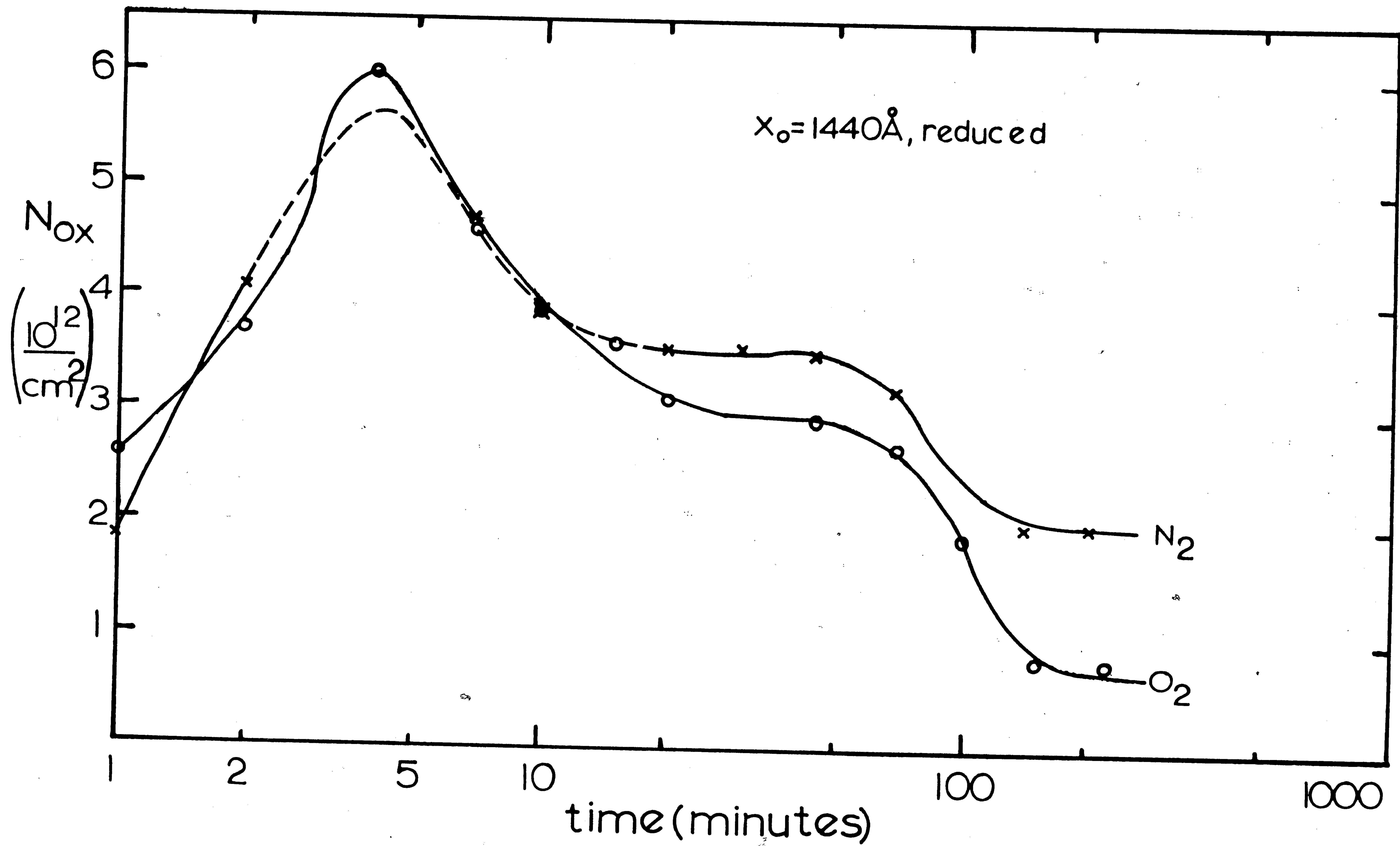


Fig. 7 The effect of N_2 and O_2 reannealing at 925°C on oxide charge density.

to increase) since the samples had already been brought to equilibrium at 910°C in the reduction furnace. It can be concluded that contamination and dust definitely increase the oxide charge when further 925°C reannealing steps for times less than approximately 100 minutes are carried out.

4.2 Surface State Density Considerations

Fig. 8a shows the high frequency (1MHz) C-V curves for different reoxidation times for a 1440Å reduced oxide. The curves can be seen to distort after the first few minutes of reoxidation, and a tail forms in strong inversion which gradually decreases with time, which disappears completely after 200 minutes. A similar distortion of the C-V curves had been observed by Deal et al.[1] on devices in which a negative field was applied across the oxide (metal negative) during anneals at temperatures of 300°- 450°C for periods of two minutes or more. Previous workers[1,20] have suggested that distortion of the C-V curve is due to an increase in the $Si-SiO_2$ interface surface state density, which might be responsible for the increase in oxide charge after the first several minutes of reoxidation of reduced samples. This causes an increase in the apparent oxide charge because any flat band voltage shift causes the calculated oxide charge to increase (Sec. 3.2), as seen in Fig. 8a, which shows a definite increase in the flat band voltage due to the distortion. Fig. 8b shows that nitrogen reannealing at 925°C does not produce this effect. Hence, even if the oxide charge Q_o remained constant, a large increase in the surface state charge Q_{ss} could cause the apparent oxide charge Q_{ss} to increase.

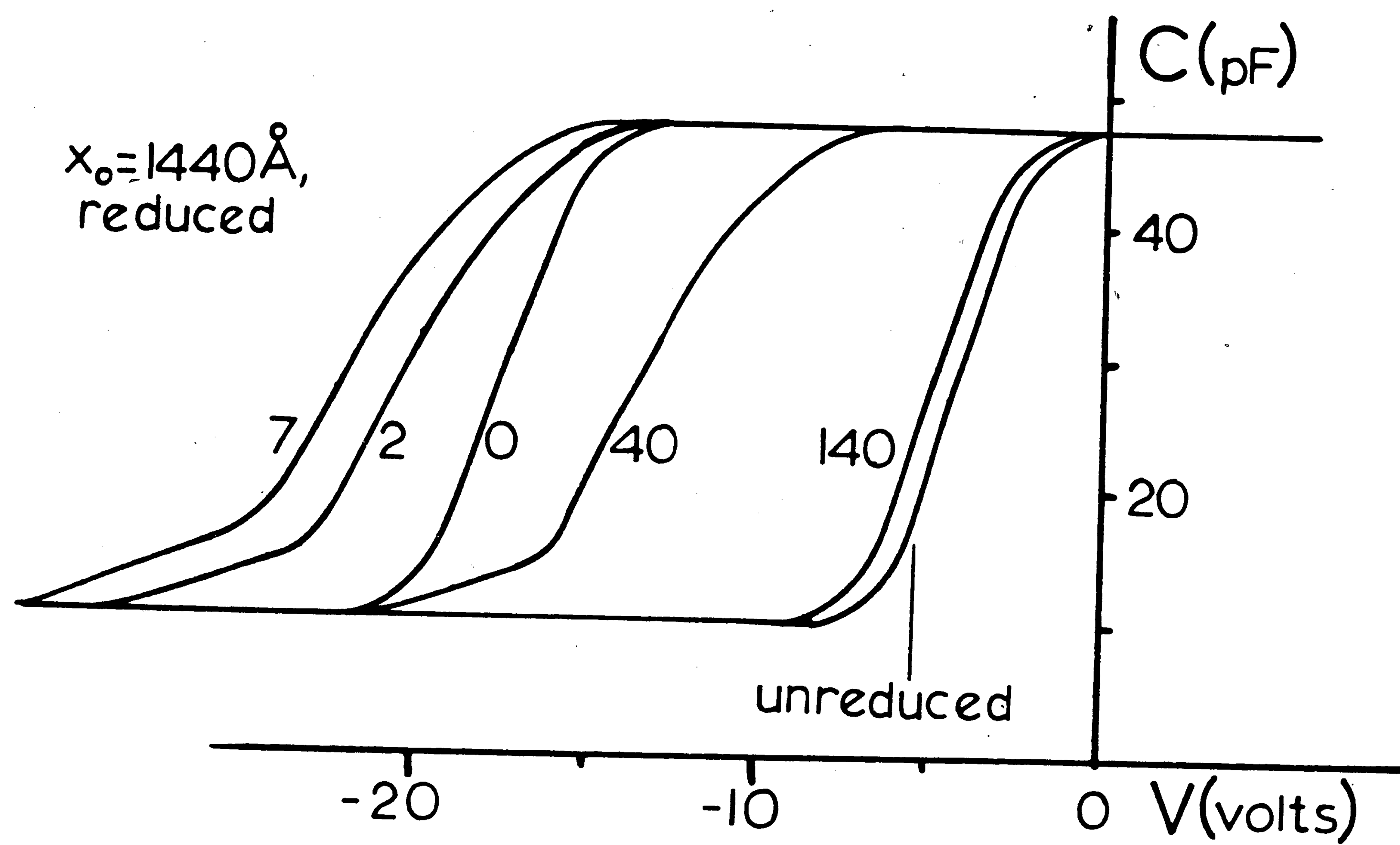


Fig. 8a Distortion of C-V curves as a function of reoxidation time (minutes) at 925°C.

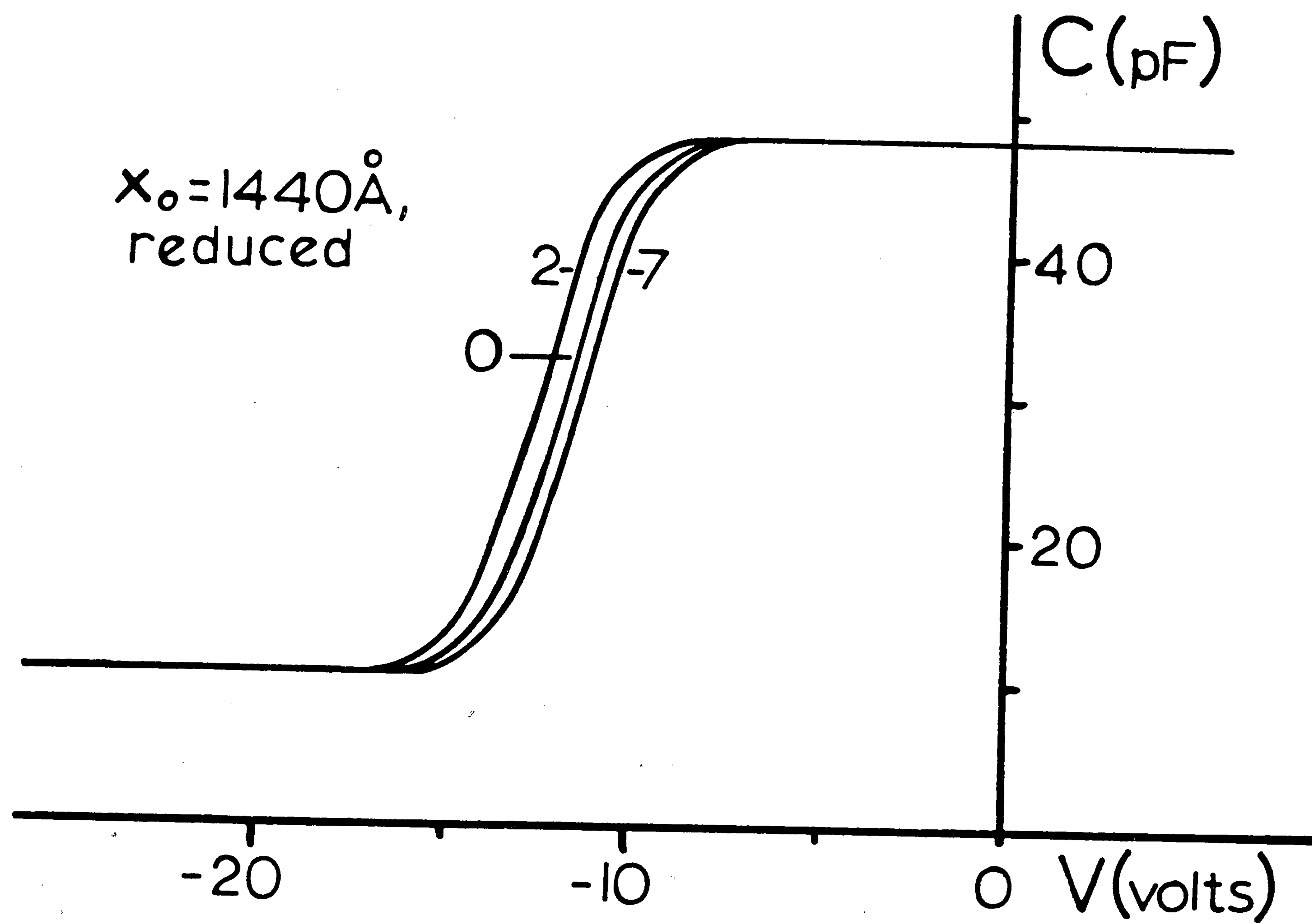


Fig. 8b Effect of N_2 reannealing at 925°C on C-V curves as a function of reanneal time (minutes).

In light of the recent work by McNutt and Sah,[17] the decrease in slope and the distortion of the C-V curve could theoretically be caused by an inhomogeneous oxide charge distribution. A change in the spatial charge distribution could also cause an increase in the apparent oxide charge Q_{ox}, but is is not possible at this time to clearly differentiate between these mechanisms.

4.3 Oxide Thickness

In order to demonstrate that a reduced oxide grows at the same rate as an unreduced (normal) oxide, an oxidation curve was obtained for growth at 925°C in dry oxygen and is plotted in Fig.9. (Oxide thickness measurements showed an observed scatter of ±1.5% for dots randomly located across each slice.) This was done since insufficient data was available on ⟨100⟩ oxides at this low temperature.

Fig. 9 also shows a plot of oxide thickness versus time for samples originally grown at 1130°C to a thickness of 1440Å and then additionally oxidized at 925°C. These samples are observed to grow at a faster rate than samples which have been grown completely at 925°C. This effect has not been noted previously in the literature. Unreduced samples originally grown at 925°C in dry oxygen grow at the same rate when reoxidized at 925°C as expected. Reduced samples of 1440Å originally grown at 1130°C have also been reoxidized at 925°C and after a period of approximately 200 minutes are found to grow at the same rate as unreduced samples which were originally grown at 1130°C (Fig. 9). This effect has been stated, without supporting evidence, in Hess's work.[8] Hence the same conclusion

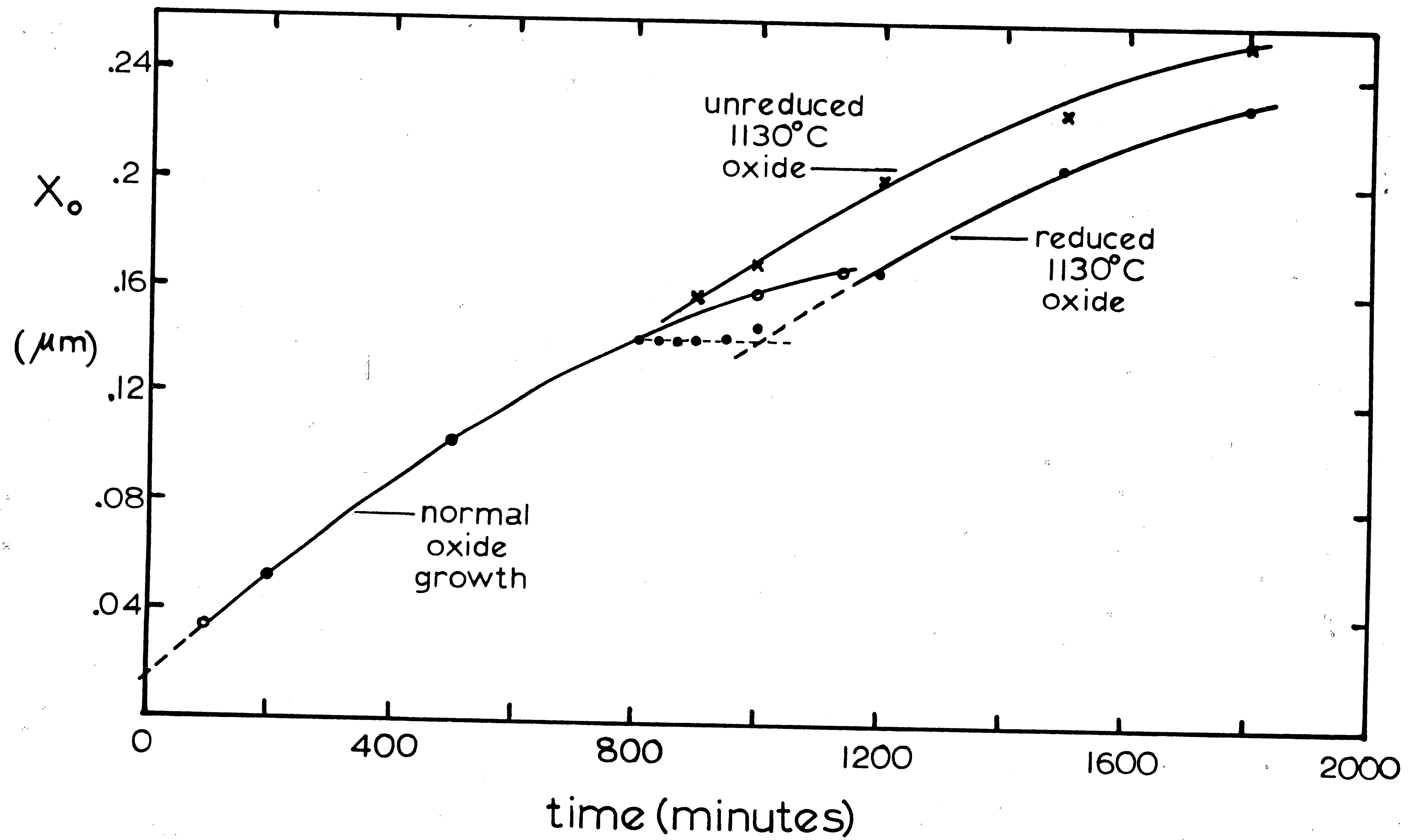


Fig. 9 Oxide thickness as a function of oxidation time at 925°C.

that Hess reached is now substantiated; however great care must be taken in comparing the growth of the two oxides since the data clearly show that reoxidation of a normal oxide at a lower temperature causes a higher growth rate than expected.

The 200 minute time delay before oxide growth coincides with the 200 minute time for the oxide charge to decrease to its normal low value, which shows that the Si-SiO_2 interface is not changed by the oxidizing species until the delay period has elapsed. The 1000Å and 1740Å reduced oxides did not grow during their respective 60 minute and 120 minute reoxidations as expected since their charge had not returned to the normal low value. The 1440Å reduced oxide which was reannealed in a nitrogen ambient also did not grow during its 400 minute treatment.

4.4 Etchback Experiments

In order to determine the location of the oxide charges, etchback experiments were performed on three 1440Å reduced oxides which had been previously reoxidized for 0, 5 and 50 minutes. The oxides were etched in dilute HF ($20H_2O$:1HF) at room temperature yielding an etch rate of approximately 140Å/minute. One sample was processed for each etched thickness. Aluminum contacts were then defined as described earlier.

The etchback data appears in Fig. 10 and shows that most of the charge lies within approximately 300Å of the Si-SiO_2 interface. The results of these measurements agree with similar results obtained on normal oxides[1] and on reduced (but not reoxidized) samples.[8]

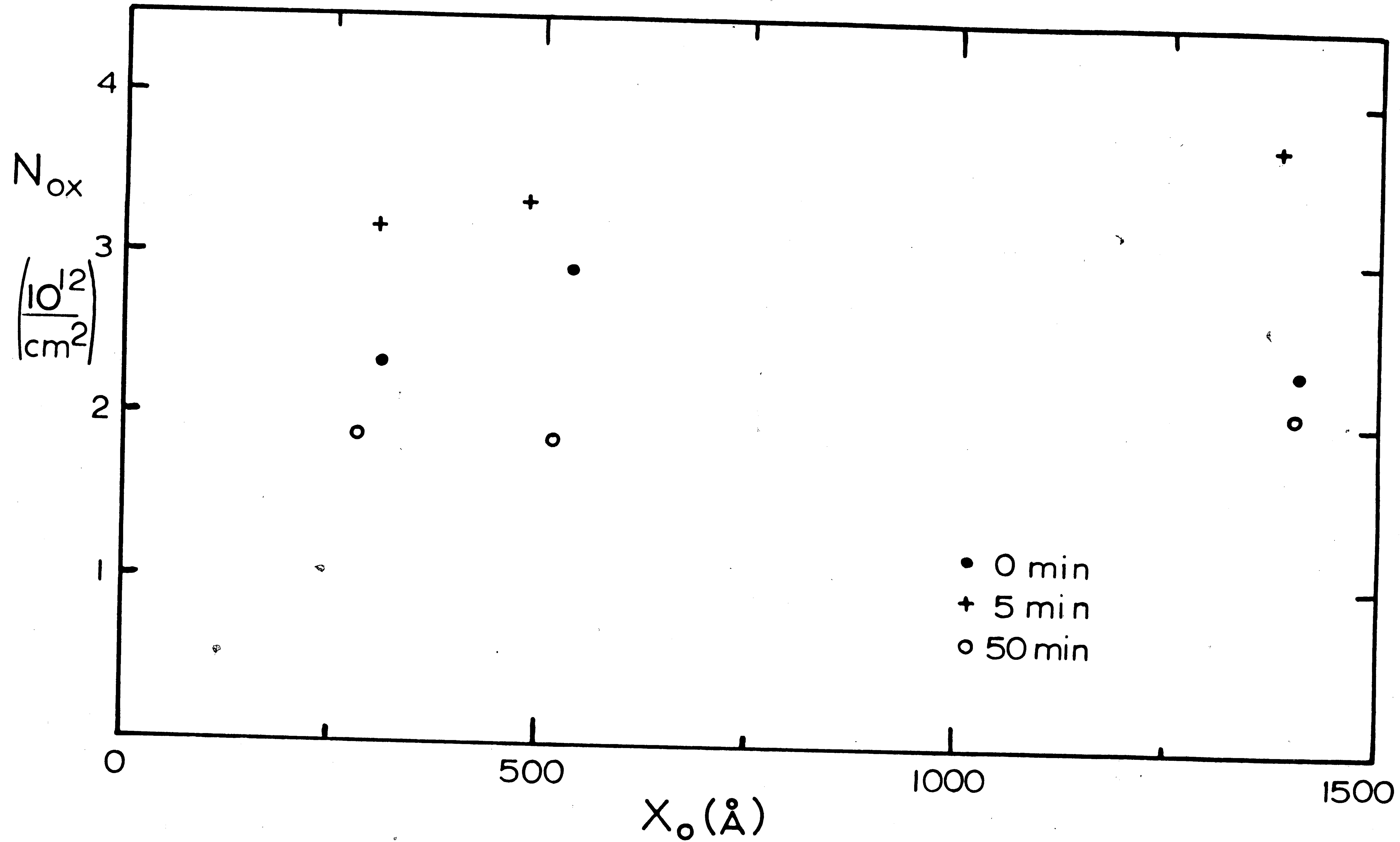


Fig. 10 Oxide charge density versus oxide thickness as a function of reoxidation time at 925°C for reduced oxides.

5.0 Discussion

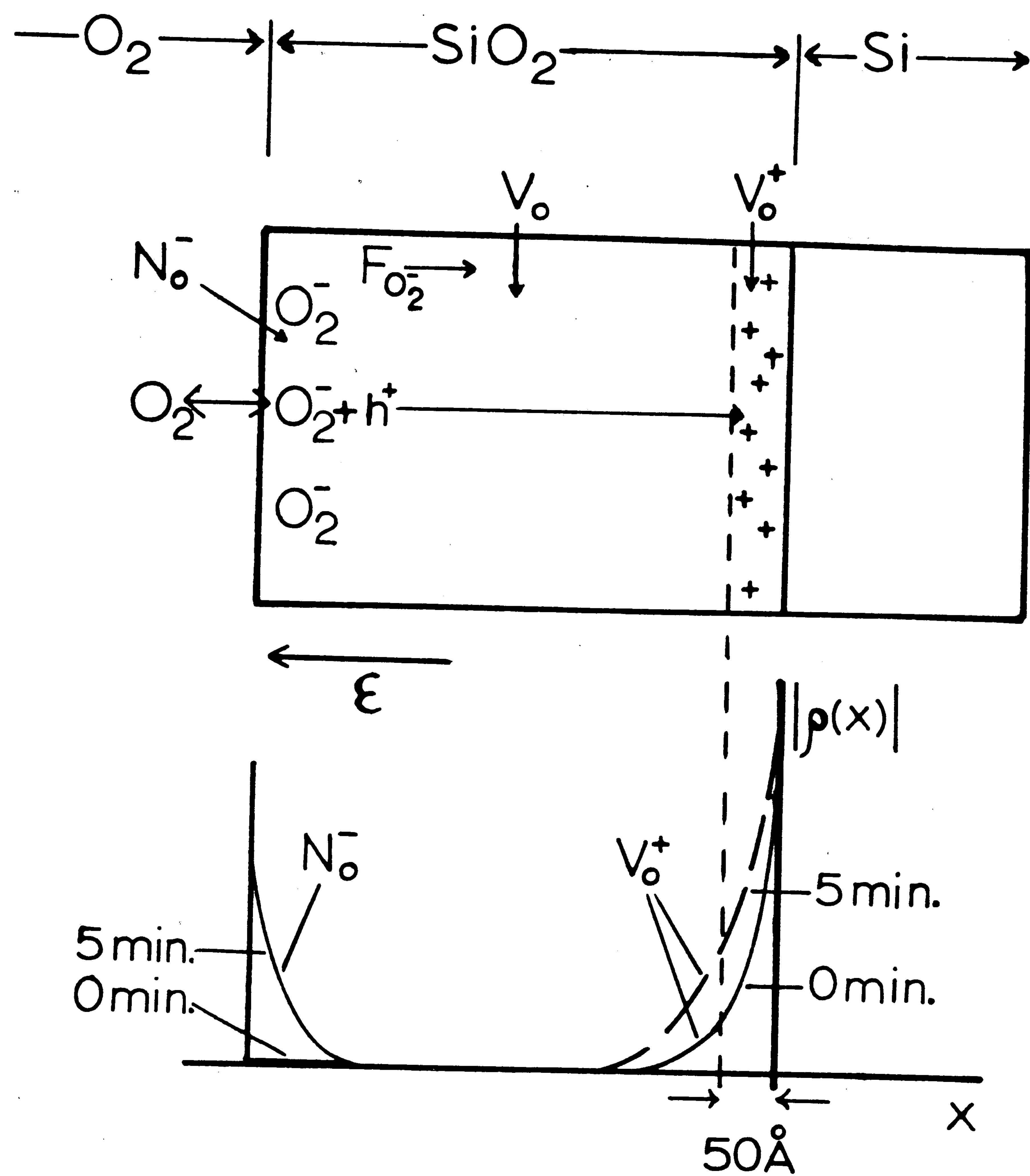
The decrease of the oxide charge with reoxidation time at 925°C of an initially reduced oxide to its normal value has been shown to coincide with the time required for new oxide growth at this temperature. The 200 minute time of complete reoxidation is much longer than the time of 9 minutes which is expected by assuming normal diffusion of oxygen through the film (see Appendix C). This indicates that a mechanism other than diffusion impedes the oxygen transport through the film. After this time lag of 200 minutes of non-growth the reduced oxide is observed to grow at the same rate as an unreduced oxide; however, it is very important to note that this growth rate is very different than would be expected. An oxide originally grown at a high temperature and then reoxidized at a lower temperature grows at a faster rate than one which has been completely grown at the low temperature. This has not been previously noted in the literature. This may suggest that the oxide "remembers" the high temperature treatment (perhaps at the outer surface) and yields a field aided growth or perhaps a higher oxygen solid solubility when reoxidized at a lower temperature. Field retarded growth on normal oxides to produce the lower temperature growth rate could yield a measurement of the expected charge distribution. Variation of the oxygen partial pressure could be used to determine if the oxygen solid solubility is affecting the higher growth rate.[21]

The oxide charge of a reduced oxide was found to increase in the first several minutes of reoxidation and this may be

attributed to an increase in the surface state density which is observed as a distortion of the C-V curves. It has also been observed that an oxidizing species is necessary for this increase and also for the subsequent decrease of oxide charge. Etchback experiments have shown the charge in all of the samples to be near the $Si-SiO_2$ interface.

In light of the above facts and the observed non-thickness dependence of the time required for complete reoxidation, along with the strong temperature dependence ($E_a \simeq 2.5eV$), a qualitative model can be developed to deduce the possible mechanisms involved (see Fig. 11).

Dissociation of an oxygen molecule at the outer surface could produce a singly charged O_2^- ion and a charged hole. This charged hole could rapidly diffuse to the $Si-SiO_2$ interface under the influence of an accelerating field existing near the outer surface. This diffusion of charged holes could produce the increase of charge noted in the first several minutes of reoxidation. The dissociation of oxygen could reach equilibrium in the first several minutes of reoxidation as the solid solubility for oxygen in SiO_2 is attained and the net flux of charged holes across the film would decrease to zero causing no further increase of charge. The field which has accelerated the charged holes would be a retarding field for the oxygen ions and hence the decrease of charge by elimination of vacancies and the growth of additional oxide would be impeded due to field retarded diffusion.[22] As the diffusion flux of oxygen overcomes the retarding field, the oxygen vacancies could start to



V_o = vacancy conc. (see App. C)

N_o^- = O_2^- conc.

$$F_{O_2^-} = qN_o^-\mu_N \mathcal{E} + qD_N \frac{dN_o^-}{dX} \cong 0$$

$$\mu_N = \frac{q}{kT} D_N$$

Fig. 11 Model for reoxidation of reduced oxides.

fill. When most of these are filled, thereby eliminating the charge, the oxide could start to grow again.

This model is qualitative and additional work seems necessary to explain the exact nature of the reoxidation mechanism. Surface state density measurements might be conducted to monitor the change of this charge as a function of reoxidation time to gain further insight into the possibility of charged hole movement. Variation of the partial pressure of oxygen during the reoxidation of reduced oxides could be used to determine whether the measured activation energy is related to the inner interface limited oxide growth, which in earlier studies[21,23] had been shown to be dependent on pressure. Growth in the presence of an external field could be studied to verify the proposed retarding field explanation for non-oxide growth, while at the same time monitoring the effect on the surface state density to reexamine the charged hole explanation. Sucessive etching of the outer surface followed by subsequent reoxidation could also be used to verify the existence of the proposed retarding field near the outer surface.

Although much information has been gained by the reoxidation of reduced and non-reduced oxides, many additional questions have been raised and much more work is required along the lines of the suggestions which have been offered.

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Appendix A

Cleaning Operation for the Silicon Wafers

The samples were degreased by boiling in trichloroethylene, acetone and methanol for about five minutes each. After rinsing in deionized water, the samples were further degreased by boiling in H_2SO_4 buffered with approximately 20% H_2O_2. Next the samples were rinsed in deionized water, etched until hydrophobic in HF, and again rinsed in deionized water. The samples were then preoxidized at 1130°C in wet oxygen for about 50 minutes, yielding a thickness of approximately 6000Å. This oxide was then etched until hydrophobic in HF to remove surface contamination and the samples rinsed in deionized water and oxidized to the desired thickness.

Appendix B

Reoxidation Process Activation Energy

A distribution of the time required for complete reoxidation, Δt, as a function of temperature, $T(^oK)$, for a constant oxide thickness is assumed to be of the form:

$$\Delta t = A \exp(-E_a/kT)$$

E_a = activation energy for complete reoxidation

k = Boltzmann's constant

A = constant

At two different temperatures T_1 and T_2 we have

$$\Delta t_1 = A \exp(-E_a/kT_1)$$

$$\Delta t_2 = A \exp(-E_a/kT_2)$$

$$\Delta t_1/\Delta t_2 = \exp[-E_a/k(1/T_1 - 1/T_2)]$$

$$E_a = -k(1/T_1 - 1/T_2)^{-1} \ln(\Delta t_1/\Delta t_2)$$

For: $T_1 = 925^oC = 1198^oK$; $\Delta t_1 \simeq 200$ minutes (see Fig. 3)

$T_2 = 850^oC = 1123^oK$; $\Delta t_2 \simeq 1000$ minutes (see Fig. 5)

$$E_a = \frac{1.38 \times 10^{-23} \ J/^oK}{(8.9-8.35) \times 10^{-4}/^oK} \ln(1/5)$$

$$E_a \simeq -2.5\text{eV}$$

Appendix C

Expected Oxidation Time to Eliminate Charge

An initially reduced oxide typically has a charge density of $N_{ox} = 2.5 \times 10^{-12}/cm^2$ (Fig. 3). If this charge is assumed to be concentrated within 50Å of the $Si\text{-}SiO_2$ interface, a charged vacancy concentration of

$$V_{ox} = N_{ox} / 50\text{Å} = (2.5 \times 10^{-12}/cm^2)/(5 \times 10^{-7} cm)$$
$$= 5 \times 10^{18}/cm^3$$

is found. Assuming the vacancies (charged or uncharged) to be uniformly distributed across the oxide, the quantity of oxygen required to fill these is:

$$Q(t) = V_{ox} \cdot x_o = (5 \times 10^{18}/cm^3)(1.5 \times 10^{-5} cm)$$
$$= 7.5 \times 10^{13}/cm^2$$

Assuming an infinite source diffusion of oxygen through the film and solving for the diffusion time at 925°C.

$$Q(t) = 2\,(D_{O_2} \cdot t/\pi)^{\frac{1}{2}}\, N_o = 7.5 \times 10^{13}/cm^2$$

D_{O_2} = diffusion constant of dry oxygen in SiO_2

$= 3.2 \times 10^{-9} cm^2/sec$ (ref. 15)

N_o = dry O_2 solid solubility in SiO_2

$= 5 \times 10^{16}/cm^3$ (ref. 15, p. 28)

$$t = (\pi/4)\, Q^2/(D_{O_2} \cdot N_o^{\,2})$$

$$t = \frac{(\pi/4)(7.5 \times 10^{13}/cm^2)^2}{(3.2 \times 10^{-9} cm^2/sec)(5 \times 10^{16}/cm^3)^2}$$

$$t = 550 \text{ seconds} \simeq 9 \text{ minutes}$$

VITA

Douglas Allen Pike, Jr. was born in Harrisburg, Pennsylvania on September 26, 1951 to Mildred R. and Douglas A. Pike, Sr. He graduated from Cedar Cliff High School, Camp Hill, Pennsylvania in June 1969. He entered Lehigh University in September, 1969 and received the degree of Bachelor of Science in Electrical Engineering in May, 1973. Since September, 1973, he has been a teaching assistant in Electrical Engineering at Lehigh University.