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COMMUNICATIONS RESEARCH CENTRE  
Ottawa, Ontario

Research Contract on Thin Dielectric Films  
File Number 01GR36001-1-0520  
Serial Number 0GR1-0218

From September 30, 1972 to May 1, 1973

Prepared by  
R.A. Clarke, M.A. Hopper and L. Young

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DEPARTMENT OF ELECTRICAL ENGINEERING  
FACULTY OF APPLIED SCIENCE  
THE UNIVERSITY OF BRITISH COLUMBIA

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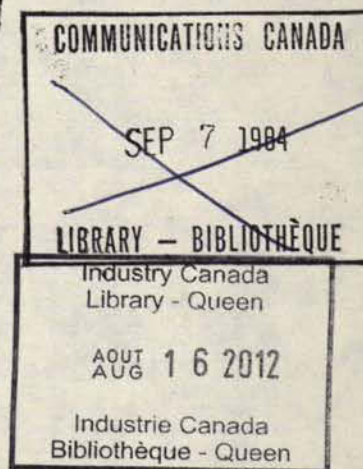
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## Introduction

As stated in previous reports<sup>1</sup> one aim of this project is to study the growth kinetics of a thin oxide on silicon by means of in-situ ellipsometry. In addition to this research, a correlation is being sought between the optical, electrical and physical properties of these oxides. Work in the past 6 months towards these goals has been of two types: the placing of the oxidation apparatus into an operational mode, and the initiation of actual experiments. The results of the former work are outlined in the next section where modifications and additions to the previously described system<sup>1</sup> are detailed. Upon completion of the construction phase, experimental studies of the oxide-semiconductor system under growth conditions progressed rapidly and initial results are reported in Section 3. Conclusions based on these results and an outline of future research is given in Section 4.

Having now begun actual experiments it is felt that a more detailed review of recent literature on the subject is warranted. Such a review is given below.

The oxidation rate of silicon has been found to depend in various ways on a number of factors. These factors include substrate orientation, preparation and temperature, oxidation atmosphere, partial pressure of the oxidizing species and the presence of external stimuli such as ultraviolet radiation and electric fields. The high temperature ( $900^{\circ} - 1200^{\circ}\text{C}$ ) oxidation of silicon to large oxide thicknesses,  $d_{\text{ox}}$ , has been studied most extensively.<sup>2-21</sup> A summary of the details of several of these and other oxidation experiments is given in Table 1 for quick reference. Under the above conditions the general consensus is that oxidation proceeds by the diffusion of an oxygen species (anion or molecular) to the Si - SiO<sub>2</sub> interface where it subsequently reacts with a silicon atom to form SiO<sub>2</sub>.<sup>8,9,11,13</sup>

Two growth characteristics have been recognized experimentally in this region: a linear characteristic (reaction rate limited growth) and a parabolic characteristic (diffusion limited growth). In the former case, which is most pronounced for thinner oxide thicknesses, the oxidizing species is considered to diffuse quite readily through the existing oxide. The reaction rate at the Si - SiO<sub>2</sub> interface being relatively slow, this process then controls the growth rate. The latter case is approached for thicker oxides where a large concentration gradient of oxidizing species is set up across the oxide, while the interface reaction proceeds toward equilibrium.

In general, therefore, a mixed linear-parabolic expression of the form

$$\frac{d_{ox}^2}{k_p} + \frac{d_{ox}}{k_l} = t + \tau \quad (1)$$

has been found to fit experimental kinetic data where  $d_{ox}$  is the oxide thickness at time  $t$ ,  $k_l$  and  $k_p$  are the linear and parabolic rate constants, and  $\tau$  is an initial time corresponding to the thickness of oxide found at  $t = 0$  by extrapolation of the linear portion of the curve. In the case of dry oxidation, for example, Deal and Grove found (perhaps somewhat arbitrarily) the extrapolated thickness to be  $d_{ox} = 230 \pm 30 \text{ \AA}$  for all oxidations carried out between 700° - 1200°C. Deal and Grove have also shown both the linear and parabolic rate constants to be temperature dependent in the following way

$$k_p = k_{op} \exp (-Q_p / kT) \quad (2)$$

$$k_l = k_{ol} \exp (-Q_l / kT) \quad (3)$$

The constant  $k_{op}$  and  $k_{ol}$  and the activation energies  $Q_p$  and  $Q_l$  are usually obtained from Arrhenius plots of  $\log k_p$  vs.  $1/T$  and  $\log k_l$  vs.  $1/T$  respectively.

Recent work extending the study of oxidation kinetics to thinner films

( $10\text{\AA} < d_{\text{ox}} < 500\text{\AA}$ ) has been published by a number of groups.<sup>22-26</sup> Two additional growth regions must now be considered: a logarithmic (or inverse logarithmic) growth ( $5\text{\AA} < d_{\text{ox}} < ?$ )<sup>26,27</sup> and an initial faster growth due to chemisorption ( $d_{\text{ox}} < 5\text{\AA}$ ).<sup>28-31</sup> This latter region will not be considered at present since it is only studied in conjunction with surfaces that are atomically clean initially.

In the region  $15\text{\AA} < d_{\text{ox}} < 60\text{\AA}$  Goodman and Breece<sup>22</sup> found that, at  $T = 600^{\circ}\text{C}$  for both "wet" and "dry" oxidations, an initial rapid growth (until  $d_{\text{ox}} \sim 20\text{\AA}$ ) was followed by a linear growth region. Similar findings were obtained by Aboaf<sup>23</sup> in NO and  $\text{H}_2$  mixtures at higher temperatures. Van der Meulen<sup>24</sup> on the other hand, found that by extending his observations to films of  $d_{\text{ox}} \leq 300\text{\AA}$ , the second region of oxide growth could better be described by the more usual linear-parabolic expression. He then calculated his linear rate constants having first assumed values of  $k_p$  obtained from the data of Deal and Grove.<sup>14</sup> It is interesting to note that by extending the use of Eqn. 1 into this region of film thickness Van der Meulen's linear rate constants differ by a factor of 2, for a given substrate orientation and oxidation temperature, from those found by Deal and Grove, the latter essentially ignoring data for  $d_{\text{ox}} < 200\text{\AA}$ .

A much wider range of oxide thicknesses ( $10\text{\AA} < d_{\text{ox}} < 1400\text{\AA}$ ) was considered by Smith and Carlan.<sup>26</sup> Their kinetic data, however, is in considerable disagreement with the data of Van der Meulen in equivalent growth regions. A logarithmic characteristic extending as far as  $d_{\text{ox}} = 80\text{\AA}$  was observed (at  $T = 890^{\circ}\text{C}$ ). This region was followed by a period of rapid growth, tending finally towards a parabolic growth rate for  $d_{\text{ox}} < 600\text{\AA}$ . No simple explanation is immediately obvious for the large difference observed between the data of these latter two groups.

The growth kinetics of very thin films (grown at  $T = 400^{\circ}\text{C}$ ) were considered by Fehlner.<sup>27</sup> It was demonstrated that his data could be fit by both direct and inverse logarithmic growth laws. He also replotted the data of Goodman and

Breece and found it also could be fit by logarithmic laws. But, since with a direct logarithmic law realistic values of the physical constants of the system were unobtainable, it was concluded that only an inverse logarithmic law of the form

$$\frac{1}{d_{\text{ox}}} = A - B \ln t \quad (4)$$

was applicable. Such a law has been developed from the Cabrera and Mott oxidation theory for the case of cation ( $\text{Si}^+$ ) migration under constant voltage, high field conditions.<sup>28,27</sup> This development has been questioned recently, though, by Ghez<sup>34</sup> who shows that a better asymptotic form of the Cabrera and Mott growth law would be

$$\frac{1}{d_{\text{ox}}} = A' - B' \ln\left(\frac{t + \tau}{d_{\text{ox}}^2}\right) \quad (5)$$

The orientation dependence of growth rates has been considered by several authors.<sup>10,15,17,23,24,27</sup> Where effects were observed, oxidation rates increased on going from (100) to (111)-oriented substrates. This effect is generally attributed to the difference in the number of accessible bonds per unit area on each surface. Only the linear rate constant has been found to be affected, a fact consistent with the reaction-rate limited nature of the process responsible for this type of growth. It is interesting to note that neither Aboaf nor Fehlner observed an orientation dependence of the growth rates of ultra thin oxides with  $d_{\text{ox}} \leq 30\text{\AA}$ .

It has often been observed that kinetic data alone cannot provide sufficient information to determine unambiguously the oxidation mechanisms occurring. For this reason the dependence of  $k_l$  and  $k_p$  on oxidant partial pressure is often studied. The pressure dependence of  $k_p$  has been shown theoretically by Wagner<sup>34,20</sup> to depend on the diffusing species. If an ionic form of oxygen is diffusing through the oxide, charge neutrality conditions require an accompanying free

electron or hole current. If these carriers are extrinsic, (i.e., produced by the ionization of oxygen) then the diffusant can be identified by the following pressure dependences of the parabolic rate constant.

$$k_p \propto p^{1/6} \rightarrow O^{--}$$

$$p^{1/4} \rightarrow O^-$$

$$p^{1/3} \rightarrow O_2^{--}$$

$$p^{1/2} \rightarrow O_2^-$$

However if the electronic carrier density is intrinsic to the oxide

$$k_p \propto p^{1/2} \rightarrow O^- \text{ or } O^{--}$$

$$p \rightarrow O_2^- \text{ or } O_2^{--}$$

For a neutral molecular diffusant such as  $O_2$  the pressure dependence would be linear, i.e.

$$k_p \propto p \rightarrow O_2$$

Deal and Grove<sup>14</sup>, on the basis of a linear dependence of both the linear and parabolic rate constants on oxygen partial pressure, concluded that molecular oxygen was the dominant diffusing species at high temperatures. Further work by Van der Meulen<sup>24</sup> indicated that the pressure dependence of  $k_l$  tends towards a  $p^{1/2}$  behavior at lower temperatures. Ghez<sup>25</sup> presents a more general model than Deal and Grove<sup>1</sup>, explaining this behaviour in terms of two competing processes at the Si-SiO<sub>2</sub> interface. Molecular oxygen, upon diffusing to this interface, is thought either to react directly with a Si-Si bond to form SiO<sub>2</sub> or dissociate first to atomic oxygen prior to reaction with Si. The former process appears to be dominant at high temperatures and the latter at lower temperatures. As a result of this dual process, Ghez proposes that the linear



rate constant will vary between  $k_l \propto p$  and  $p^{1/2}$  for decreasing temperatures.

This variation is in qualitative agreement with experiment.

The one serious argument against the above analysis is that for the lower pressures Van der Meulen and Ghez are basing their calculations of linear rate constant on data from a thickness region not even considered at higher pressures. Thus they may be extracting numbers from a growth characteristic that should not be described by a linear - parabolic equation.

In addition to studying the pressure dependence of the rate constants external stimuli have been applied to the silicon substrate in attempts to determine further the nature of the oxidation mechanism.<sup>18-21</sup> Jorgensen<sup>18</sup> (and Laverty and Ryan<sup>20</sup>) has found that growth could be either slowed or enhanced by the application of fields across the oxide depending on the polarity of applied voltage. He interpreted this result as indicating that ionic migration through the oxide was responsible for oxidation. This interpretation was questioned by Raleigh<sup>19</sup> who proposed that no field effect would be felt by the diffusing species whether ionic or molecular and that retardation of growth simply implied an electrolytic decomposition reaction was being set up (where, as in this case, ohmic contacts had been made to the oxide). At the appropriate thickness, the parabolic growth rate would become equal to the decomposition rate and growth would halt, a feature which was observed experimentally by Jorgensen. These proposals were put into more rigorous form by Collins and Nakayama and shown to be at least consistent with the Wagner electrochemical model of oxide growth.<sup>16</sup>

The effect of ultraviolet light on silicon oxidation kinetics has been studied principally by Oren and Ghandhi.<sup>21</sup> Their findings indicated that the primary effects of U.V. irradiation are felt in the early reaction rate limited stages. This was attributed to the effect of a large generation of electrons at the Si-SiO<sub>2</sub> interface on the rate limiting process occurring there. This might be expected since the oxidation of silicon requires that it be elevated to a

higher charge state by the liberation of electrons into the oxide.<sup>21</sup> Interesting corroboration of their hypothesis was obtained from measurements of the C-V characteristics of each structure. Assuming surface charges are related to the presence of a silicon-rich transition region at the Si-SiO<sub>2</sub> interface, a reduction of surface charge (and hence M.O.S. C-V curve offset) would be expected if the interface reaction rate could be speeded up and the density of dangling bonds lowered. Such a reduction was observed for U.V. irradiated samples.

## 2. Experimental Apparatus

Several modifications have been made in the experimental system described in a previous report.<sup>1</sup> Several views of the system as it now stands including a picture of the present sample holder are shown in Fig. 1. A schematic of the system is also given (Fig. 1 (e)).

The most fundamental change made was in the method of sample heating. Temperatures between R.T. and the melting point of silicon can now be reached by employing direct resistance heating. The copper leads of a high current U.H.V. feed-through have been extended by means of tantalum rods and the silicon substrates are held, by tantalum supports, between these rods. Good contact between silicon and tantalum is obtained by first platinizing the rods and then carrying out a sintering process at high temperatures in vacuum. Substrate temperatures are monitored by optical pyrometry and, as shall be seen later, by the ellipsometer itself. Alignment of the sample for optical measurements has been somewhat simplified by the introduction of the sample holder into the chamber vertically from the top rather than horizontally from the back as previously attempted.

In addition to sample holder modifications, a titanium sublimation chamber has been added (c.f. Fig. 1 (c)) to provide faster pump-down times and lower ultimate pressures. The system can now operate in the  $10^{-9}$  torr range and it is hoped

that with further baking the  $10^{-10}$  torr range will be reached.

The overall capabilities of the system now include in-situ pre-oxidation cleaning by Ar ion-bombardment or  $H_2$  annealing, oxidation in ultra pure oxygen (or suitable gas mixtures) at any temperature between R.T. and  $1200^\circ\text{C}$  and over a range of partial pressures, and post-oxidation annealing in any desired ambient. The sample is monitored continuously during these treatments by means of a computer-controlled ellipsometer at an incident angle of  $68^\circ \leq \phi \leq 72^\circ$  and wavelength of incident light (He-Ne laser) of  $\lambda = 6328 \text{ \AA}$ . Extra ports on the chamber are available for in-situ probing of the sample to permit I-V and C-V measurements to be made.

### 3. Experimental Results and Discussion

Ellipsometric data for "as received" silicon substrates as a function of temperature in vacuum are shown in Fig. 2(a) (curves A-B-C). Such heating and cooling experiments before and after each oxidation provide much useful information. First, the true value of initial oxide thickness is obtained. Since at a given temperature changes in  $\Delta$  are inversely proportional to thickness changes, (i.e.  $\delta\Delta = +0.1^\circ \rightarrow \delta d_{\text{ox}} \sim -0.5 \text{ \AA}$ ) it is obvious that the apparent room temperature film thicknesses on the substrate (as determined at points A and C) are considerably different before and after heating. The temperatures reached were insufficient to sublime  $\text{SiO}_2$  thus it would seem that a physisorbed material (possibly  $\text{H}_2\text{O}$ ) has been outgassed from the sample. Any measurements made before heating would therefore have put  $d_{\text{ox}}$  in error by  $\sim 30 \text{ \AA}$ . While this result is somewhat of an extreme case, qualitatively similar findings were obtained with all samples.

Also obtained from the curve A-B-C are values of the optical constants of the substrate at elevated temperatures. Such information is vital for the calculation of oxide thicknesses during actual oxide growth. After outgassing

of the sample, the curve B-C is fairly reproducible and the changes in  $\psi$  and  $\Delta$  can be directly related to increased values of  $n_s$  and  $k_s$  respectively where the latter quantities are defined as the real and imaginary parts of the substrate complex refractive index. For convenience this index will be written  $N = n_s (1 - i K_s)$  where  $k_s = n_s K_s$ . Theoretical calculations employing the computer program of McCrackin<sup>38</sup> are seen in Fig. 2(a) as the almost vertical solid lines. Each line of given  $n_s$  and  $K_s$  represents a locus of points of increasing oxide thickness (hatchmarks indicate 5Å intervals beginning at  $d_{ox} = 5\text{Å}$  and  $K_s$  is taken as 0.006 for all theoretical points of this figure). Although not demonstrated, increasing  $k_s$  (and decreasing  $\Delta$ ) could be misinterpreted as increasing oxide thickness for this range of  $d_{ox}$ . To simplify theoretical calculations it is necessary, therefore, to determine  $k_s$  at the appropriate temperature prior to commencing oxidation. The optical constants are then assumed constant, independent of oxide thickness, for a given temperature (i.e. power input).

It is interesting to note that at a particular oxide thickness the values of  $\psi$  and  $\Delta$  are related to a unique temperature. Thus if a suitable means of calibration is found, the ellipsometric data provide a fairly sensitive gauge of the substrate surface temperature. This fact has been noted by Ibrahim and Bashara<sup>39</sup> who have empirically determined an expression for  $\psi$  as a function of  $T$ . Our preliminary data from curves such as shown in Fig. 2(a) calibrated against an optical pyrometer suggest they have overestimated the surface temperature at high temperatures. This is probably due to their use of a thermocouple for calibration purposes that was not directly in contact with the surface.

Another factor to be considered in the accurate determination of oxide thicknesses is the surface roughness<sup>40,41,38</sup>. The chemically-mechanically polished surfaces of our wafers (supplied by Monsanto) are taken to provide data for which the true bulk values of substrate optical constants can be

assumed<sup>36</sup>. This is not the case if the heating cycle is carried to extreme temperatures in high vacuums. This is indicated by curve D-E and point F in Fig. 2(a). At a temperature of 860°C and a vacuum of  $2 \times 10^{-7}$  torr these decreasing values of  $\Delta$  and  $\psi$  were obtained over a period of ~ 15 minutes. Under the low pressures employed no appreciable oxide growth was possible. Despite this, upon cooling to room temperature, the point F was obtained corresponding to a large effective oxide growth. That these changes were due to surface roughness produced by silicon sublimation was confirmed by scanning electron microscope (SEM) examination, as seen in Fig. 2(b)).

Data obtained during actual sample oxidation at 1 atm of ultrapure oxygen and  $T = 900^\circ\text{C}$  is shown in Fig's. 3(a) and (b). In Fig. 3(a) the measured  $\Delta$  and  $\psi$  data (circles) are compared with theoretical curves (solid curve calculated with the refractive index of the film  $n_f = 1.48$ ). The substrate optical constants assumed were  $N = 4.27 (1 - 0.038 i)$ . The excellent fit of theory to experiment for a single set of parameters demonstrates that meaningful information is available from data obtained from a substrate at high temperatures. The value of  $n_f = 1.48$  suggested by Fig. 3(a) for the oxide refractive index is higher than normally reported, though, for room temperature oxides (i.e.  $n_f = 1.46^{42,26}$ ). This could be due to a dependence of  $n_f$  on either temperature, wavelength of light employed or method of oxide growth. The change is in the wrong direction one would expect from simple thermal expansion effects at high temperatures and no difference in oxide quality is expected for our particular experimental arrangement. Unfortunately no published data is available on the value of  $n_f$  expected for  $\text{SiO}_2$  at  $\lambda = 6328\text{\AA}$  but the use of the longer wavelength light is likely to be the reason for the differences.

Similar plots of  $\psi$  vs.  $\Delta$  for increasing  $d_{\text{ox}}$  were employed by Smith and Carlan to determine the optical constants of their silicon substrates<sup>26</sup>. They concluded that the value of  $n_s$  decreased for  $d_{\text{ox}} > 300 \text{\AA}$  from 4.08 to 4.05



(at R.T. and  $\lambda = 5461\text{\AA}$ ). Such changes are not observed in our data and could well be consistent, within their larger experimental error, with a value of  $n_f$  larger than the one they assumed ( $n_f = 1.46$ ).

Having corrected for temperature and cell window effects on  $\psi$  and  $\Delta$  the calculated value of  $d_{ox}$  for  $\text{SiO}_2$  are plotted versus time in Fig. 3(b). A smoothly varying curve from  $10\text{\AA}$  to  $1600\text{\AA}$  is apparent. No particularly linear region of growth is evident and certainly no justification for extrapolation to  $230\text{\AA}$  at  $t = 0$ , as was found to be the case by Deal and Grove<sup>14</sup>, is apparent. A log-log plot of this data will be discussed later in connection with other data.

In Fig. 4(a), a  $\psi$  vs.  $\Delta$  plot is shown for a sample oxidized in 1 atm of  $\text{O}_2$  at  $740^\circ\text{C}$ . Only the first  $150\text{\AA}$  of growth was followed. The experimental data (circles) follow closely the shape of the theoretically calculated curves (solid lines) for which  $n_f = 1.46$  was assumed. The slight departure from theory for thicker oxides reflects the fact that a better estimate of the film index would be  $n_f = 1.48$  as shown in Fig. 3(a). From these results it can also be seen that an initial estimate of  $n_s = 4.18$  at  $T = 740^\circ\text{C}$  is consistent for all the data (a value of  $K_s = 0.034$  was determined before oxidation).

A plot of the calculated  $d_{ox}$  vs. oxidation time for this and other samples at other oxidation temperatures is shown in Fig. 4(b). In all cases smooth curves monotonically increasing in time can be observed. Computer calculations are being carried out to determine whether a simple functional relationship, that can be explained in the context of present theories of oxidation kinetics, is applicable. Information such as the values and temperature dependence of the linear and parabolic rate constants should also be obtainable from data such as this.

One interesting point to note is the difference between the curves labelled

740°C (a) and (b). Oxidation conditions, identical in all respects except oxygen flow rate (the flow for (a) being higher by a factor of  $\sim 2$ ), were employed during these two runs. Temperatures during each run, as determined from the ellipsometric data were estimated to be within  $\pm 5^\circ\text{C}$  of each other, a variation insufficient to produce the observed differences in growth rates. No flow rate dependence of growth rate was found by Deal and Grove in their oxidations at higher temperatures<sup>14</sup> despite a 50 fold flow change. It was concluded that the gas-phase transport process had relatively little importance in the control of the overall oxidation rates. This may not be true however for lower temperature oxidations or for our particular oxidation set-up (i.e. cold wall chamber). These points are being investigated further.

To obtain a preliminary interpretation of the data both  $\log d_{\text{ox}}$  vs.  $\log t$  and  $d_{\text{ox}}$  vs.  $\log t$  plots were made, of which Fig. 4 (c) is one example. For the sample oxidized at 900°C (see also Fig. 3(a) and (b)) a straight line log-log plot was obtained of slope  $\frac{1}{n} = 2/3$  over the range  $100\text{\AA} < d_{\text{ox}} < 1600\text{\AA}$ . One could therefore write an empirical growth law of the form

$$x^n = At \quad (1)$$

with  $n=1.5$ . This particular power law is not unusual in itself<sup>24</sup> as it could be represented by a combination of parabolic and linear growth terms. Only the extensive region over which this single value of  $n$  appears to hold is somewhat unusual. It seems unlikely that a single unique set of thickness independent rate constants could be found for this entire curve.

In the case of the sample (b) oxidized at 740°C, also plotted in Fig. 4 (c), no linear region is obvious for the unadjusted data (circles). Taking into account the existence of  $10\text{\AA}$  of oxide at  $t = 0$ , the dashed curve can be obtained (for which  $n \sim 1.0$ ). At these lower temperatures and small oxide thicknesses a linear growth rate is therefore approximated. The latter data plotted on

semi-log paper shows no evidence of logarithmic behaviour when either corrected or uncorrected and only a suggestion of inverse logarithmic behaviour over the limited region of  $15\text{\AA} < d_{\text{ox}} < 25\text{\AA}$ . It is apparent that if logarithmic contributions to the growth rate exist they are small in relation to the linear and parabolic contributions and limited at best to our initial growth region with  $d_{\text{ox}} \leq 40\text{\AA}$ . This is directly in contrast to the findings of Smith and Carlan<sup>26</sup> who as stated earlier found a logarithmic rate of growth dominant for  $d_{\text{ox}} \leq 80\text{\AA}$ .

In Fig. 5 an example of our oxidation data is shown in comparison with available oxidation data at  $920^{\circ}\text{C}$  of Deal and Grove<sup>14</sup>, Smith and Carlan<sup>26</sup> at  $890^{\circ}\text{C}$  and Van der Meulen<sup>24</sup> at  $850^{\circ}\text{C}$ . It can be seen in this figure that the amount of previously existing data in the thin film region is rather limited for the purposes of making judgements concerning oxidation mechanisms. Of these data that of Van der Meulen would appear to agree the most closely with ours in terms of curve shape.

#### 4. Conclusions and Future Research Planned

The value of in-situ ellipsometry for providing abundant, accurate data both on the kinetics of silicon oxide growth as well as on several fundamental features of the silicon surface itself has been demonstrated. Heating of a silicon substrate in vacuum after a period of exposure to the room ambient has shown that large changes occur in the effective film thickness. These changes have been attributed to the outgassing of a physisorbed layer on the silicon dioxide surface. Any previous measurements made therefore with samples open to the atmosphere are subject to suspicion. Continued heating to higher temperatures was seen to produce the opposite effect or an apparent film growth. This was attributed to thermal etching and the corresponding effects of surface roughness on the ellipometer measurements. Silicon optical constants were seen to be sensitive to changes in substrate temperatures. With suitable

calibration this temperature dependence was found to provide an excellent sensor of the substrate surface temperature. The oxidation kinetics of several samples at different temperatures were followed and correlation with one of the two previous workers who have studied this particular oxide thickness range was found.

In future work it is hoped that advantage can be taken of the large amount of data which is generated by the in-situ ellipsometry technique (as contrasted with the amount obtained by the periodic removal of the specimen from the oxidation system) to allow a study of oxidation kinetics with a precision not permitted previously. Experiments concerned with the effects on the growth rate constants on oxygen partial pressure, U.V. radiation, and application of field are planned. In the latter case, by the application of thin platinum electrodes, it is hoped that not only the growth kinetic variations can be followed but also the I-V and C-V characteristics of the Si-SiO<sub>2</sub> structure. Internal photo-emission experiments will also be permitted by such electrodes.

# REFERENCES

1. Research Contract Reports (1) A. Shousha and L. Young, and (2) R. Clarke, M. A. Hopper and L. Young, File #01GR36001-1-0520 Serial # OGR1-0218.
2. D. J. McAdam and G. W. Geil, J. Res. N.B.S. 28 593 (1942).
3. M. B. Bodsky and D. Cubicciotti, J. Am. Chem. Soc. 73, 3497 (1951).
4. J. T. Law, J. Phys. Chem. 61, 1200 (1957).
5. J. W. Evans and S. K. Chatterji, J. Phys. Chem. 62, 1064 (1958).
6. C. T. Sah, H. Sello and D. A. Traymore, J. Phys. Chem. Solid 11, 288 (1959).
7. J. R. Ligenza, J. Phys. Chem. 64, 1017 (1960).
8. J. R. Ligenza and W. G. Spitzer, J. Phys. Chem. Solids 14, 131 (1960).
9. W. G. Spitzer and J. R. Ligenza, J. Phys. Chem. Solids 17, 196 (1961).
10. J. R. Ligenza, J. Phys. Chem. 65, 2011 (1961).
11. N. Karube, K. Yamamoto and M. Kamiyama, Jap. J. Appl. Phys. 2, 11 (1963).
12. B. E. Deal, J. Elec. Soc. 110, 527 (1963).
13. W. A. Pliskin and R. P. Gna11, J. Elec. Soc. 111, 872 (1964).
14. B. E. Deal and A. S. Grove, J. Appl. Phys. 36, 3770 (1965).
15. W. A. Pliskin, I.B.M. J. Res. Develop. 10, 198 (1966).
16. T. Nakayama and F. C. Collins, J. Elec. Soc. 113, 706 (1966).  
F. C. Collins, T. Nakayama, J. Elec. Soc. 114, 167 (1967).
17. A. G. Revesz and R. J. Evans, J. Phys. Chem. Sol. 30, 551 (1969).
18. P. J. Jorgensen, J. Chem. Phys. 37, 874 (1962).  
J. Elec. Soc. 110, 461 (1963).  
"Oxidation of Metal and Alloys" Paper given at  
Amer. Soc. of Metals meeting Oct., 1970.  
J. Chem. Phys. 49, 1594 (1968).  
J. Elec. Soc. 114, 820 (1967).
19. D. O. Raleigh, J. Elec. Soc. 113, 782 (1966).
20. S. J. Laverty and W. D. Ryan, Int. J. Electronics 26, 519 (1969).
21. R. Oren and S. K. Ghandhi, J. Appl. Phys. 42, 752 (1971).
22. A. M. Goodman and J. M. Breece, J. Elec. Soc. 117, 982 (1970).
23. J. A. Aboaf, J. Elec. Soc. 118, 1370 (1971).
24. Y. J. Van der Meulen, J. Elec. Soc. 119, 530 (1972).



## REFERENCES (continued)

25. R. Ghez and Y. J. Van der Meulen, J. Elec. Soc. 119, 1101 (1972).
26. T. Smith and A. J. Carlan, J. Appl. Phys. 43, 2455 (1972).
27. F. P. Fehlner, J. Elec. Soc. 119, 1723 (1972).  
F. P. Fehlner and N. F. Mott, "Oxidations of Metals and Alloys" Chapter 3.
28. N. Cabrera and N. F. Mott, Report Prog. Phys. 12, 163 (1948-49).
29. R. J. Archer and G. W. Gobeli, Phys. Chem. Solids 26, 221 (1969).
30. F. Meyer and G. A. Bootsma, Surf. Science 16, 221 (1969).
31. C. A. Carosella and J. Comas, Surf. Sc. 15, 303 (1969).
32. B. A. Joyce and J. H. Neaves Surf. Sc. 27, 499 (1971).
33. R. Ghez, J. Chem. Phys. 58, 1838 (1973).
34. C. Wagner, Z Physik Chem. B21, 25 (1933).
35. F. Meyer, E. E. de Kluizenaar and G. A. Bootsma, Surface Sc. 27, 88 (1971).
36. K. Vedam and S.S. So, Surface Sc. 29, 379 (1972).
37. M. M. Ibrahim and N. M. Bashara, Surface Sc. 30, 632 and 680 (1972).
38. F. L. McCrackin, Tech. Note 479 National Bureau of Standards (1969).  
J. Res. N.B.S. 67A, 363 (1963).
39. M. M. Ibrahim and N. M. Bashara, J. Vac. Sc. Tech. 9, 1259 (1972).
40. I. Ohlidal and F. Lukes, Optica Acta 19, 817 (1972).
41. R. M. A. Azzam and N. M. Bashara, Phys. Rev. B. 5, 4721 (1972).
42. R. J. Archer, J. Opt. Soc. Am. 52, 970 (1962).

## FIGURE CAPTIONS

### Figure

1. (a) Overall view of oxidation chamber and computer operated automatic balancing ellipsometer.  
 (b) Frontal view of oxidation chamber and ellipsometer.  
 (c) Top view of oxidation chamber and vacuum pumping equipment.  
 (d) Sample holder.  
 (e) Schematic of sample chamber and vacuum equipment.
2. (a) Experimental  $\Delta, \psi$  data from silicon sample, for  $P_{O_2} = 5 \times 10^{-8}$  torr, as a function of temperature during heating and cooling (curve A-C) between room temperature and  $\sim 750^\circ\text{C}$ . Also the effect of thermal etching at constant temperature ( $T \sim 860^\circ\text{C}$ ) is shown (squares of curve D-E) and the subsequent difference in room temperature  $\Delta$  and  $\psi$  (point F). Theoretical (solid vertical) curves of  $\Delta$  vs.  $\psi$  were calculated for  $3.9 < n_s < 4.2$  and  $K_s = 0.006$  as a function of  $d_{ox}$  (hash marks are at  $5\text{\AA}$  intervals).  
 (b) S.E.M. micrograph (2000X) of a thermally etched silicon substrate.
3. (a) Experimental  $\psi, \Delta$  data (circles) for increasing thickness are plotted for comparison with theory (solid curve,  $n_f = 1.48$ ). The effect of small changes in  $n_f$  on curve shape is also seen (dashed curves).  
 (b) Values of  $d_{ox}$  determined from  $\psi, \Delta$  data are plotted versus oxidation time for (111)-oriented Si sample at  $T \sim 900^\circ\text{C}$  in 1 atm.  $O_2$ .
4. (a) Experimental data (circles) taken at  $T = 740^\circ\text{C}$  of  $\Delta$  and  $\psi$  as a function of increasing oxide thickness. Data are compared with theory (solid curves) on expanded scale.

FIGURE CAPTIONS (continued)

Figure (continued)

4. (b) Typical oxidation kinetics data (circles) in the thin film region. Oxide thickness vs. time is plotted for a number of samples at different temperatures.  
  
(c) Plot of  $\log d_{ox}$  vs.  $\log t$  for two samples. For sample at  $900^{\circ}\text{C}$ ,  $n = 1.5$  for  $100\text{\AA} < d_{ox} < 1600\text{\AA}$  while for the  $740^{\circ}\text{C}$  sample after subtraction of  $10\text{\AA}$  from each thickness (dashed line),  $n \sim 1$  for  $20\text{\AA} < d_{ox} < 100\text{\AA}$ .
5. Comparison of oxidation kinetics data from Deal and Grove<sup>14</sup> (x -  $920^{\circ}\text{C}$ ), Smith and Carlan<sup>26</sup> (□ -  $890^{\circ}\text{C}$ ), Van der Meulen<sup>24</sup> (⊙ -  $850^{\circ}\text{C}$ ) and present results (—  $900^{\circ}\text{C}$ ).

AUTHORS	OXIDATION APPARATUS	SAMPLE AND CLEANING PROC.	OXIDATION ATMOSPHERE	TEMPERATURE RANGE	THICKNESS RANGE	METHOD OF MEAS. $d_{ox}$	CONCLUSIONS
J. T. Law <sup>4</sup>	Vac. Chamber Si. filament	High resis. Si, Chem. (HF)	$10^{-3} - 5 \times 10^{-3}$ mm $O_2$	700 - 1000°C	?	$O_2$ pressure	Parabolic growth rate, linear dep. on $P_{O_2}$ for $p > 2 \times 10^{-2}$ mm, Si evap. rate reduced by presence of $SiO_2$ .
J. R. Ligenza and W. G. Spitzer <sup>8</sup>	-Press. Chamber -Res. heated tube furnace	100 $\Omega$ -cm Si, Chem. ( $HNO_3$ )	120 atm. of steam and 1 atm. $O_2$ (used $O_{16}$ & $O_{18}$ )	650°C 950°C	?	weight meas. on microbal. & IR spect.	In steam, rate strongly orientation dep. but average 75Å/min. (i.e. linear growth). Exchange of $O_{18}$ for $O_{16}$ in steam indicates $H_2O$ diffusing. $O_2$ oxid. independent of orientation.
P. J. Jorgensen <sup>18</sup>	-	mech. pol. Si	-	850°C	~ 1000-6000Å	Ellipsometry and mult. beam interferom.	Pt. electrodes allowed field effect on oxidation rate to be shown, indicating ionic oxygen the diffusing species.
N. Karube et al <sup>11</sup>	tube furnace	(111) 2000 $\Omega$ -cm p-Si, CP-4 etch.	1 atm. $O_2$	1250°C	3000Å +		Used $^{32}P$ tracer & chem. back etching to show oxygen species diffusing.
B. F. Deal & A. S. Grove <sup>14</sup>	tube furnace	(111) 1.3 $\Omega$ -cm p-Si, chem.	1 atm. $O_2$ & steam	700°-1200°C	200-10000Å	mult. beam interferom.	Linear growth rate at low thicknesses tending to parabolic for thicker oxides. $k_p$ and $k_l \propto P_{O_2}$ .
A. G. Revesz & R. J. Evans <sup>17</sup>	tube furnace & R.-F. heated furnace	(111) 10 $\Omega$ -cm p-Si, chem. and H etch at 1200°C	1 atm. dry and wet $O_2$	900°-1300°C	50-8000Å	Ellipsometry and mult. beam interferom.	Linear and parabolic rate constants depend on $H_2O$ in oxidizing atmosphere and Na contam. of oxide.
R. Oren & S. K. Ghandhi <sup>21</sup>	R.-F. heated furnace	(111) 10 $\Omega$ -cm n-Si, Chem. (HF), Etched in HCl gas at 1100°C	1 atm. dry $O_2$	950°-1200°C	150-3000Å	mult. beam interferom.	U.V. radiation increases initial (linear) growth rate. Also reduces surface charge density.
A. M. Goodman <sup>22</sup> & J. M. Breese	tube furnace	(100) 10 $\Omega$ -cm p-Si, Chem. (HF)	1 atm. dry and wet $O_2$	600°C	15-60Å	Ellipsometry	Rapid initial growth ( $d_{ox} \rightarrow 20Å$ ) followed by linear growth rate. (logarithmic?)
J. A. Aboaf <sup>23</sup>	R.-F. heated furnace	(100) 10 $\Omega$ -cm p-Si, Chem. (HF)	$O_2$ - $N_2$	950°-1140°C	20-25Å	-	Rapid initial then linear growth rate. No orientation dependence.
Y. J. Van der Meulen <sup>24</sup>	tube furnace	(100) & (111) 2 $\Omega$ -cm p-Si, Pre-oxidation and Chem. (HF)	0.1-1 atm. $O_2$	700°-1000°C	20-300Å	Ellipsometer at 70°/5461Å	Rapid then linear-parabolic growth $k_l \propto$ to between $p^{1/2}$ and $p^1$ - suggests two competing surface reactions occurring. Large orientation dependence.
T. Smith & A. J. Carlan <sup>26</sup>	R.-F. heated furnace	(111) 10 $\Omega$ -cm n-Si, Mech. pol. Chem. (HF)	0.1-1 atm. $O_2$ in $N_2$	890°-1000°C	10-1400Å	Ellipsometer at 70°, 80°/5461Å	No pure linear growth. Initial logarithmic region ( $d_{ox} < 100Å$ ) then $\rightarrow$ parabolic growth. Finds $d_{ox} \propto p^{1/2}$ . Also suggests substrate optical constants depend on $d_{ox}$ .

Table I: Summary of some of the presently available literature on oxidation of silicon.



Fig. 1 a) Overall view of oxidation chamber and computer operated automatic balancing ellipsometer

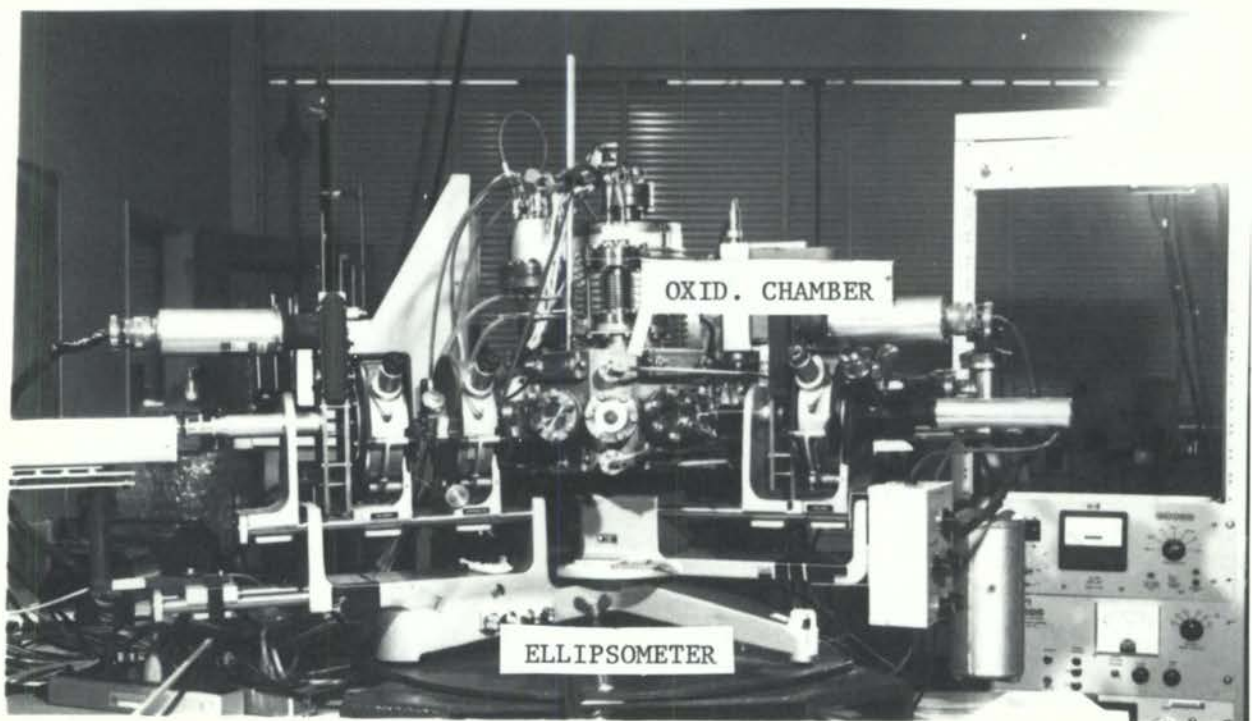


Fig. 1 b) Frontal view of oxidation chamber and ellipsometer



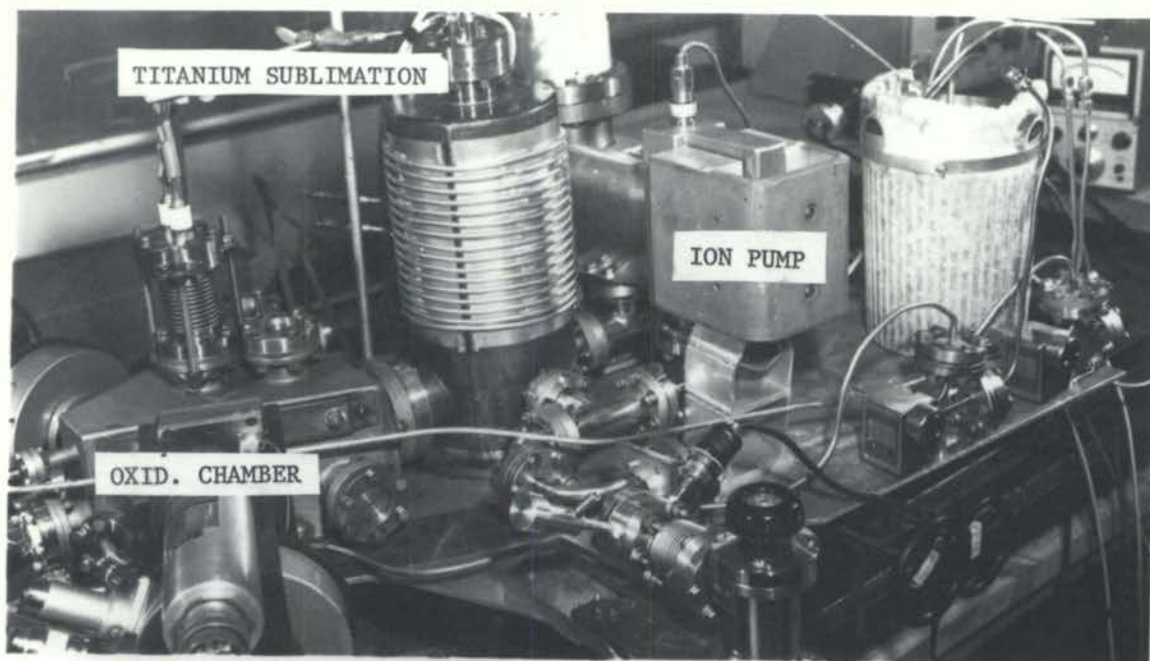


Fig. 1 c) Top view of oxidation chamber and vacuum pumping equipment

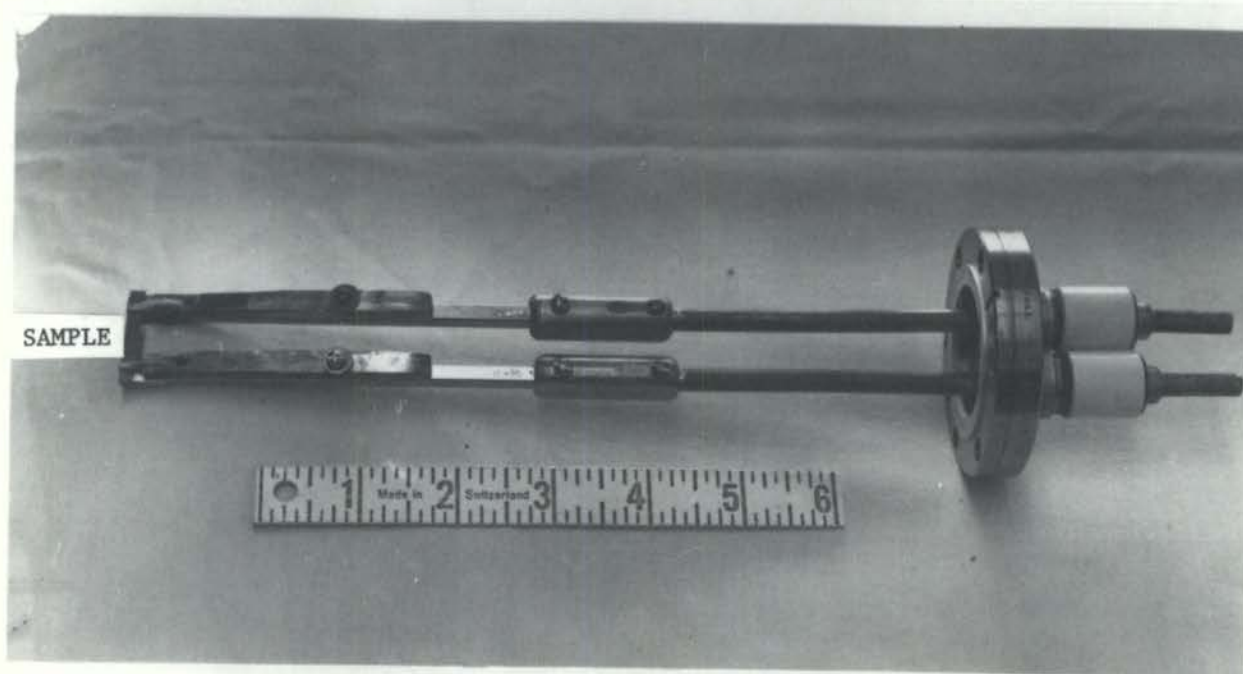


Fig. 1 d) Sample holder

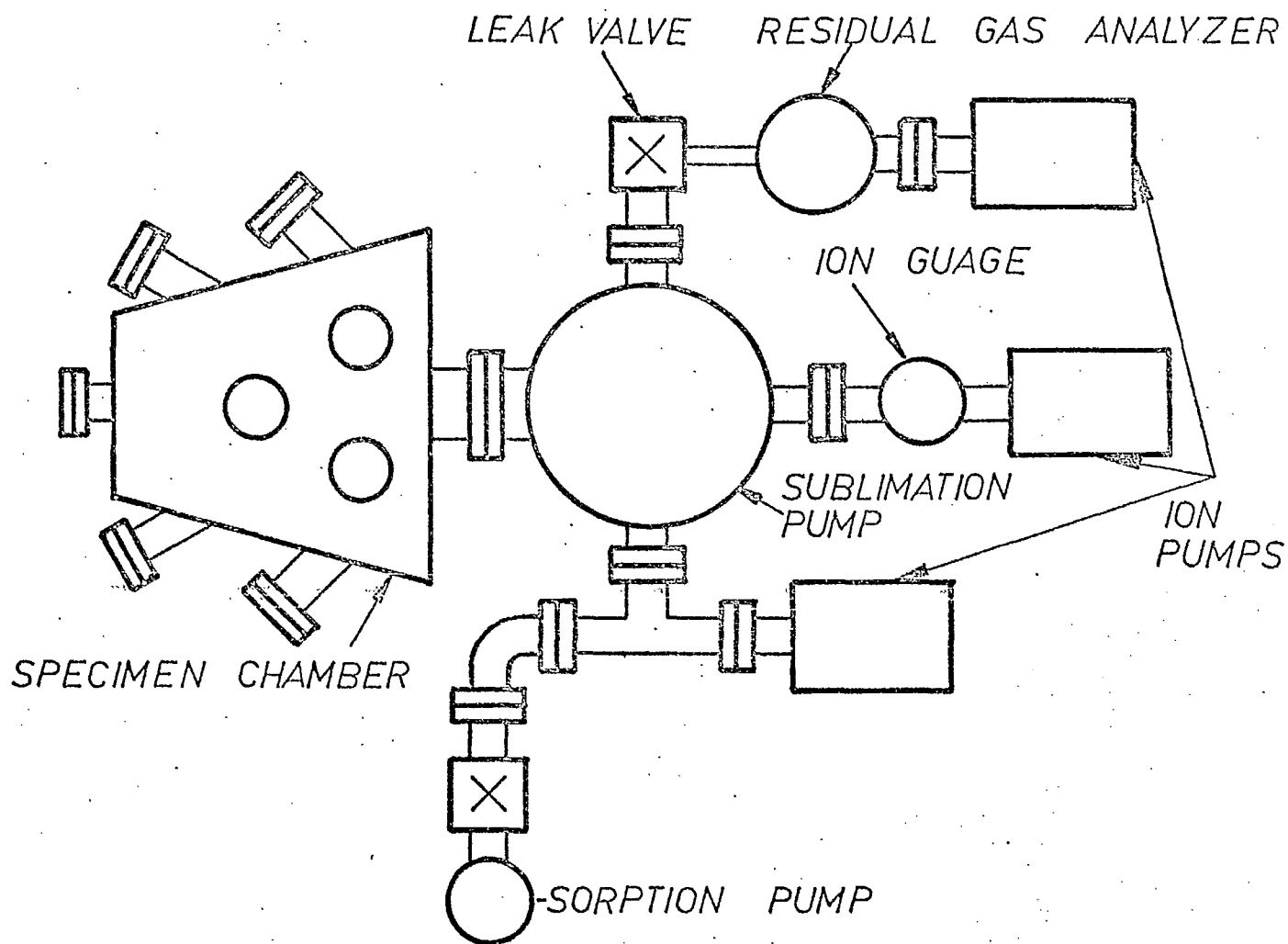


Fig. 1 e) Schematic of sample chamber and vacuum equipment

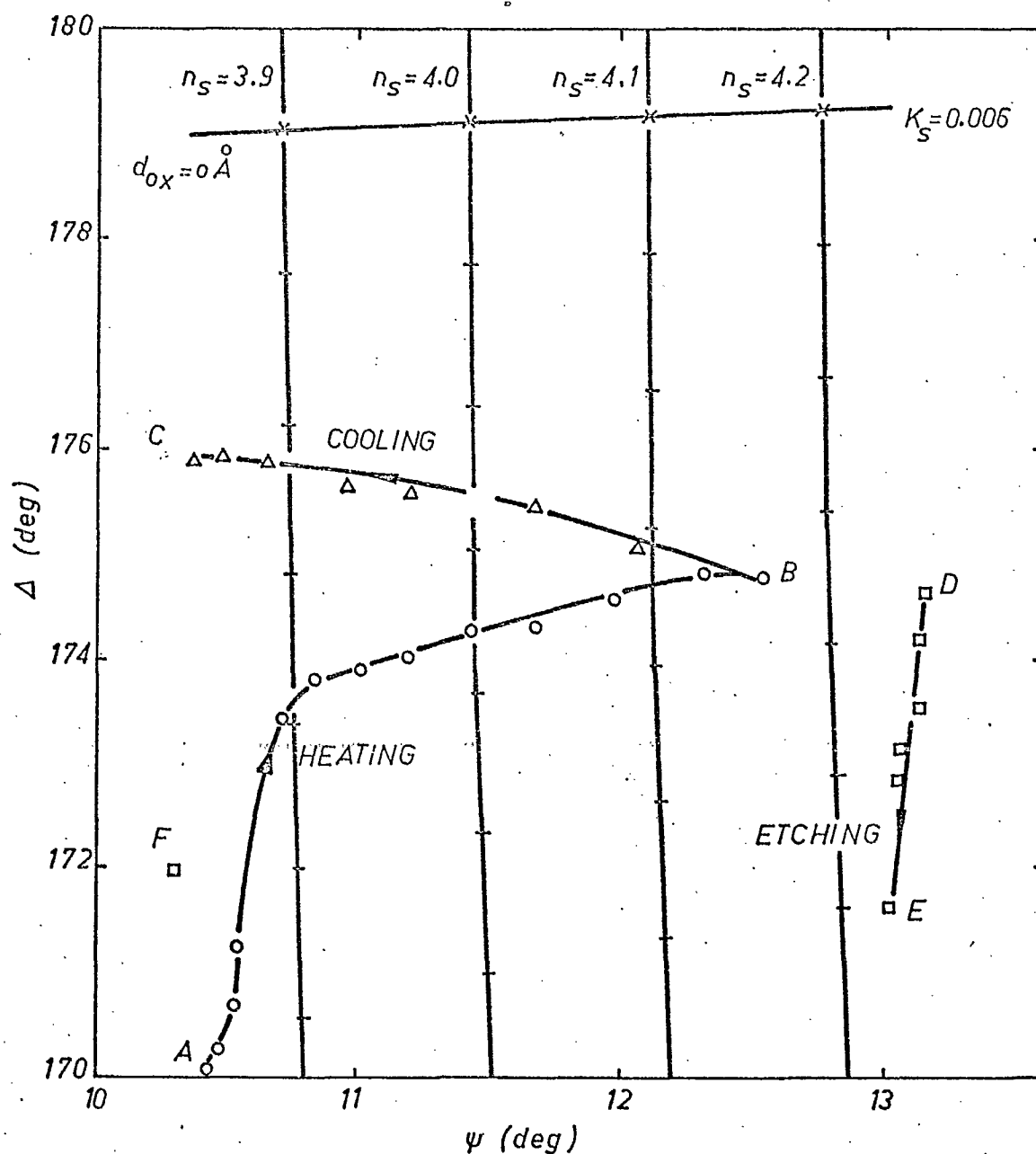


Fig. 2 a) Experimental  $\Delta, \psi$  data from silicon sample, for  $P_{O_2} = 5 \times 10^{-8}$  torr, as a function of temperature during heating<sup>2</sup> and cooling (curve A-C) between room temperature and  $\sim 750^\circ\text{C}$ . Also the effect of thermal etching at constant temperature ( $T \sim 860^\circ\text{C}$ ) is shown (squares of curve D-E) and the subsequent difference in room temperature  $\Delta$  and  $\psi$  (point F). Theoretical (solid vertical) curves of  $\Delta$  vs.  $\psi$  were calculated for  $3.9 < n_s < 4.2$  and  $K_s = 0.006$  as a function of  $d_{ox}$  (hash marks are at  $5 \text{ \AA}$  intervals).



Fig. 2 b) S.E.M. micrograph (2000X) of a thermally etched silicon substrate.

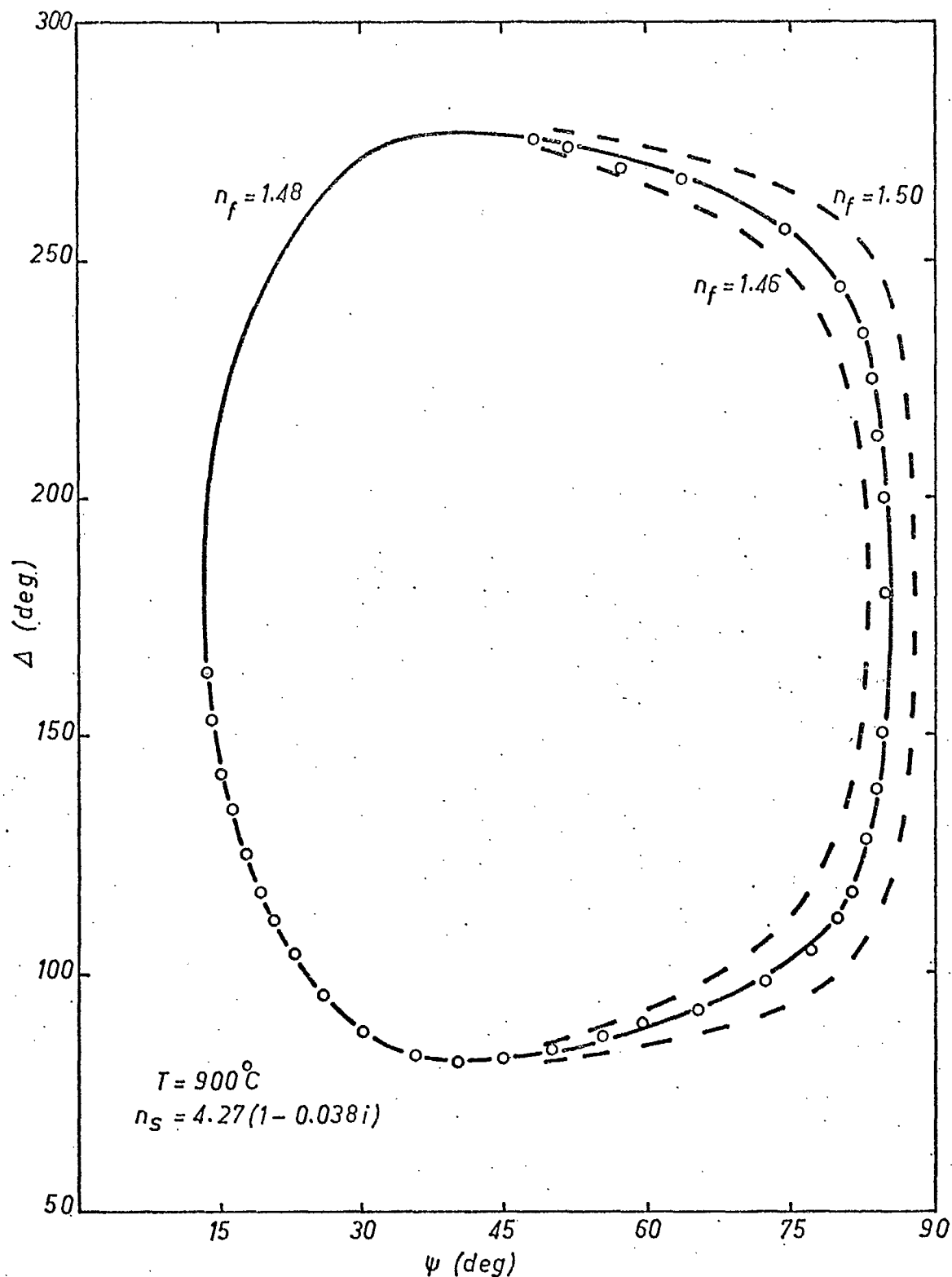


Fig. 3 a) Experimental  $\psi, \Delta$  data (circles) for increasing thickness are plotted for comparison with theory (solid curve,  $n_f = 1.48$ ). The effect of small changes in  $n_f$  on curve shape is also seen (dashed curves).



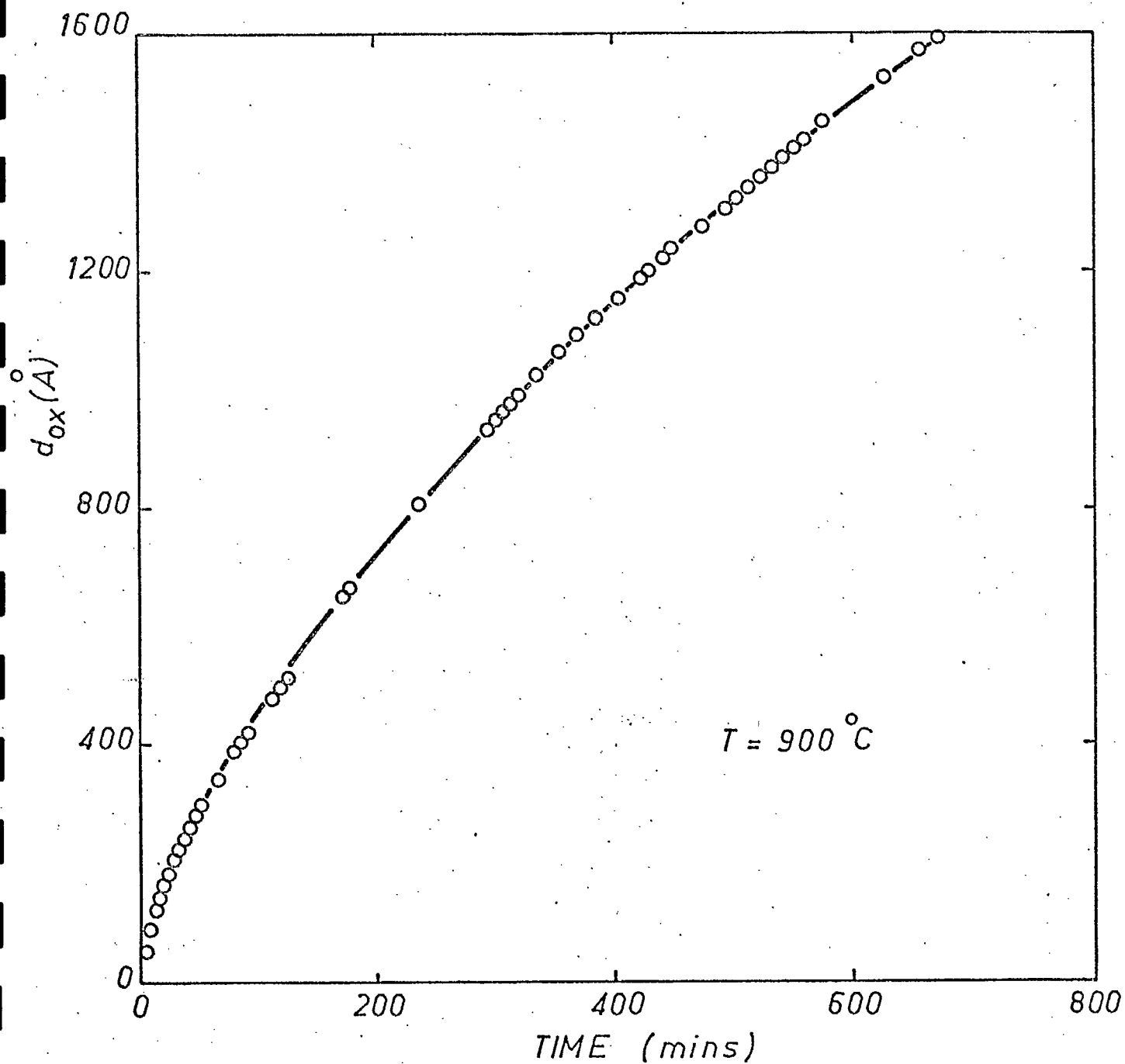


Fig. 3 b) Values of  $d_{ox}$  determined from  $\psi, \Delta$  data are plotted versus oxidation time for (111)-oriented Si sample at  $T \sim 900^{\circ}C$  in 1 atm.  $O_2$ .

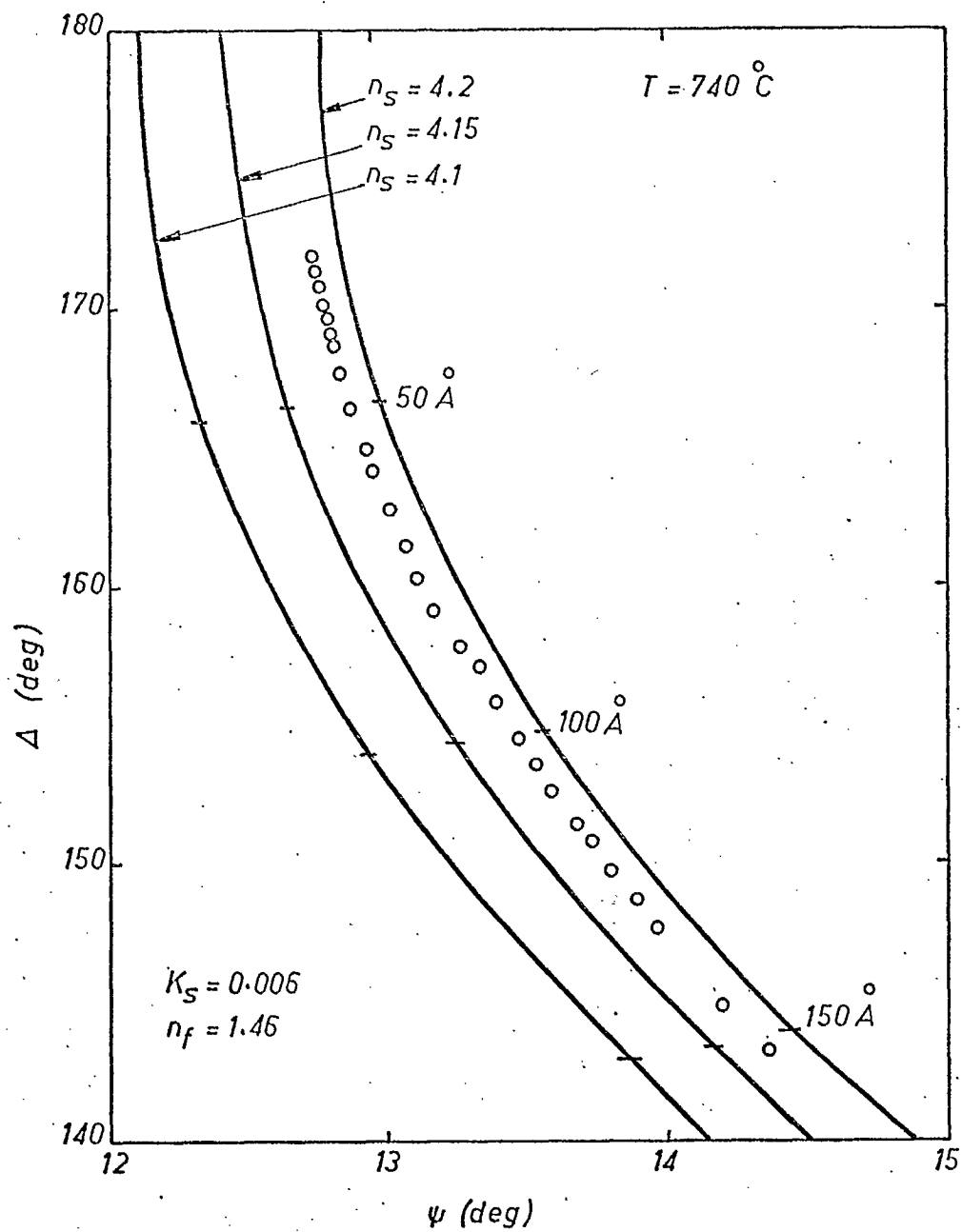


Fig. 4 a) Experimental data (circles) taken at  $T = 740^{\circ}\text{C}$  of  $\Delta$  and  $\psi$  as a function of increasing oxide thickness. Data are compared with theory (solid curves) on expanded scale.

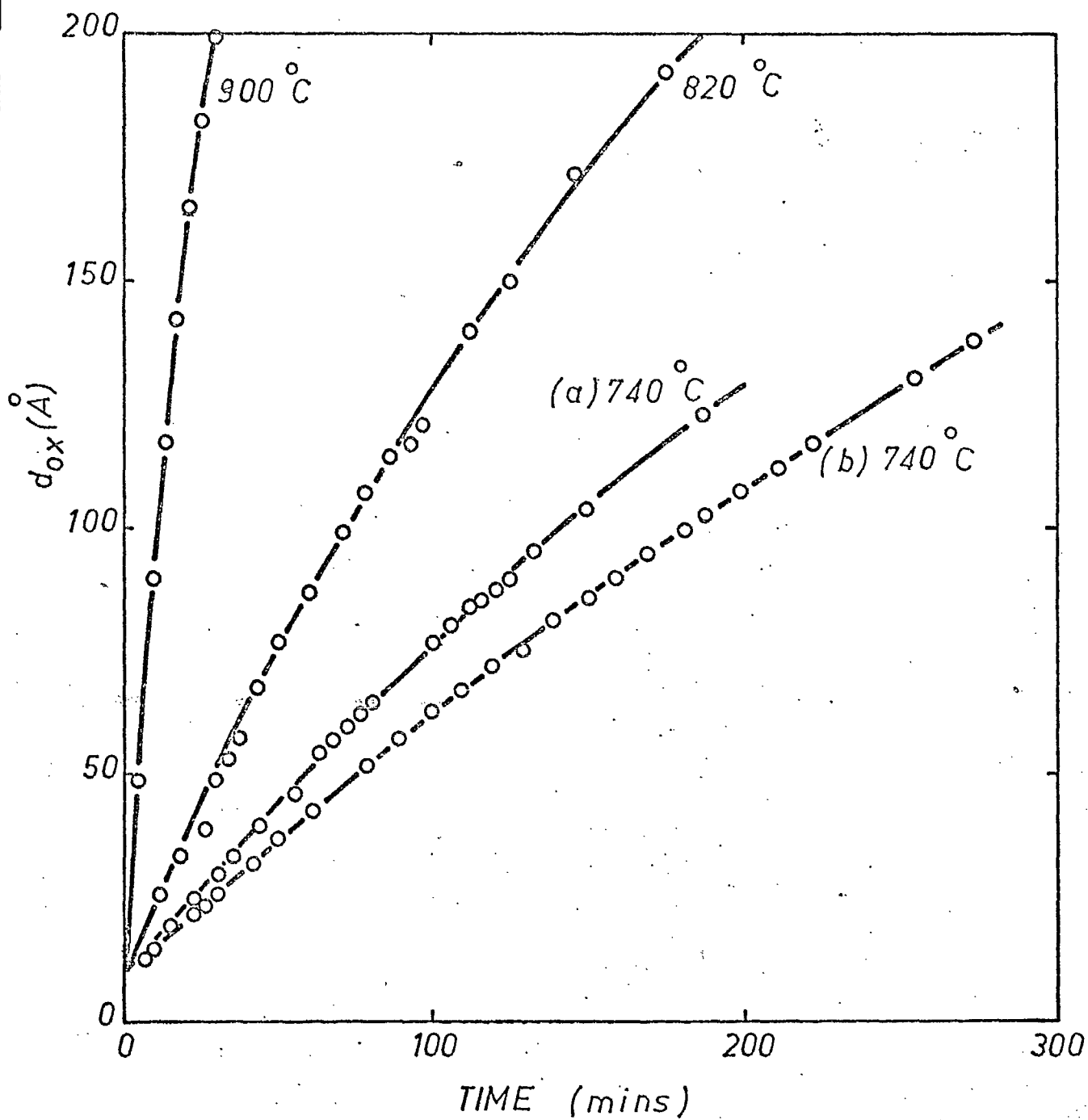


Fig. 4 b) Typical oxidation kinetics data (circles) in the thin film region. Oxide thickness vs. time is plotted for a number of samples at different temperatures.

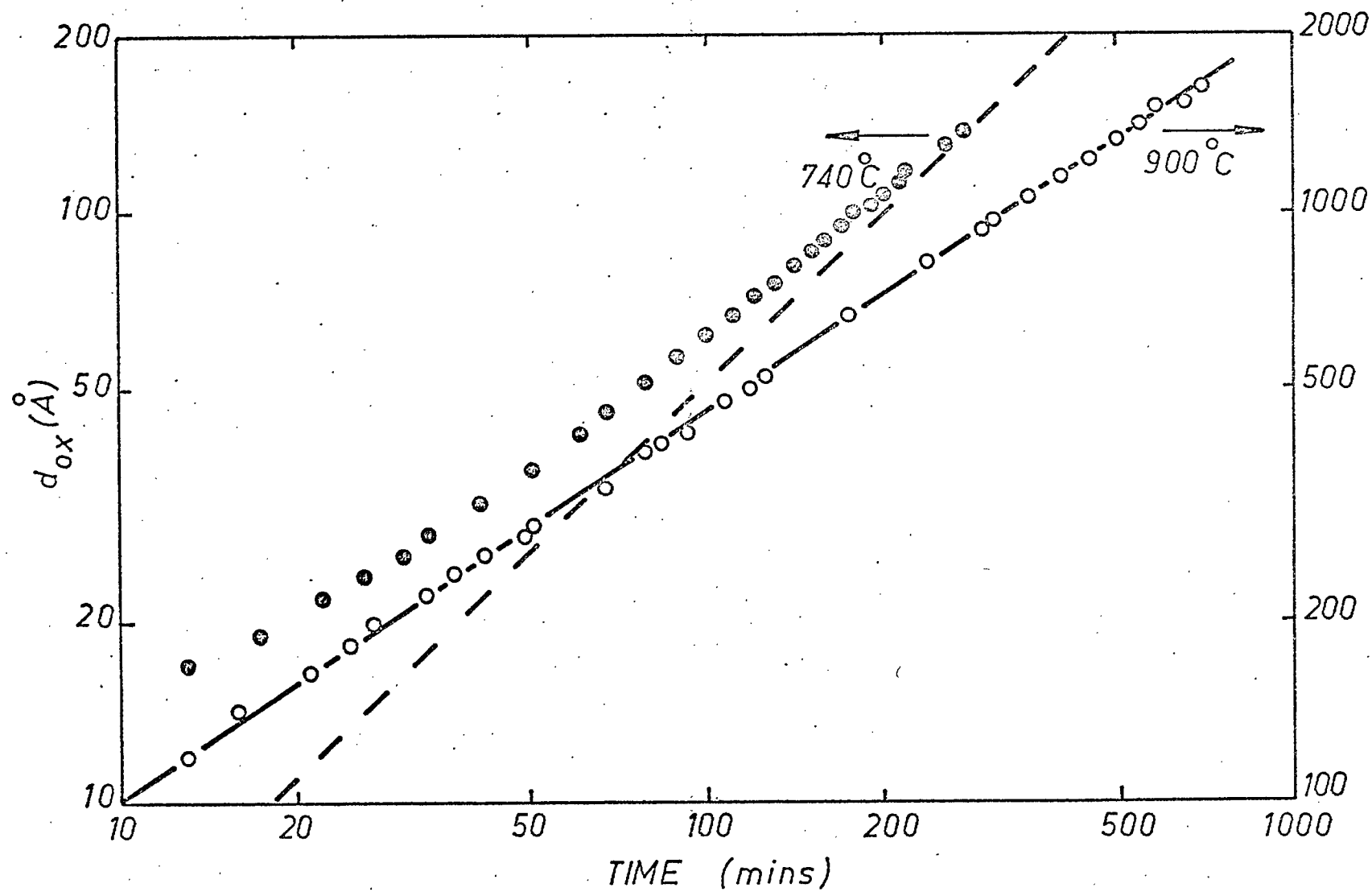


Fig. 4 c) Plot of  $\log d_{ox}$  vs.  $\log t$  for two samples. For sample at 900°C,  $n = 1.5$  for  $100\text{Å} < d_{ox} < 1600\text{Å}$  while for the 740°C sample (after subtraction of 10Å from each thickness dashed line),  $n \sim 1$  for  $20\text{Å} < d_{ox} < 100\text{Å}$ .

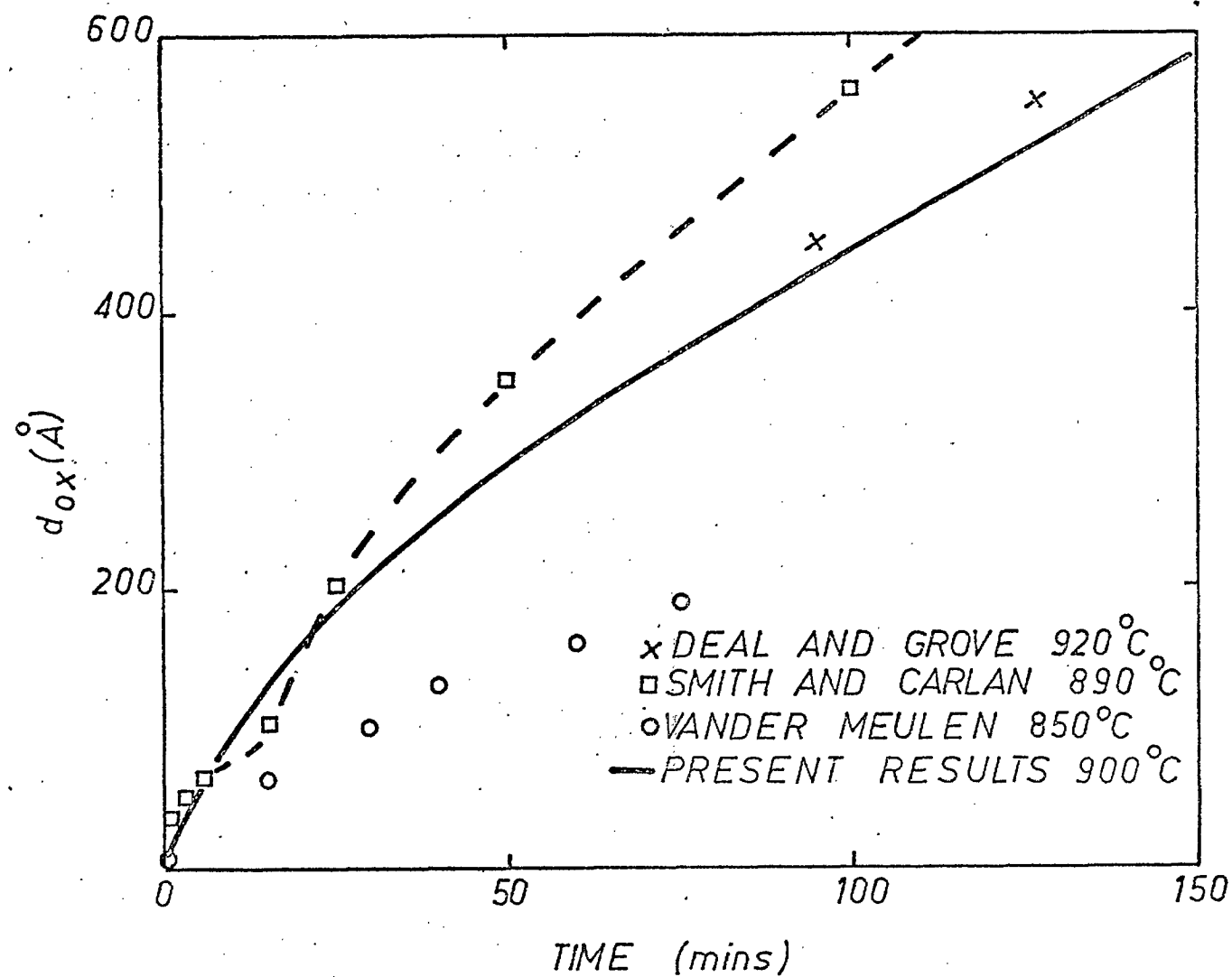


Fig. 5 Comparison of oxidation kinetics data from Deal and Grove<sup>14</sup> (x - 920°C), Smith and Carlan<sup>26</sup> (□ - 890°C), Van der Meulen<sup>24</sup> (○ - 850°C) and present results (— 900°C).

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