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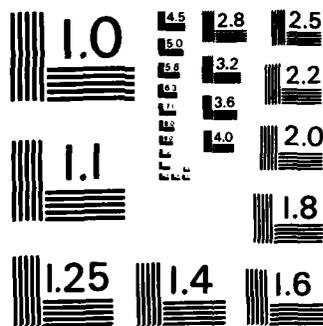
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Silicon Oxidation Studies: Silicon Orientation Effects
on Thermal Oxidation

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Abstract

The initial stage of the thermal oxidation of various crystallographic orientations of silicon reveals a complex rate behavior. This behavior is not understood within the conventional linear - parabolic model. A recently revised model which explicitly contains the areal density of Si atoms and mechanical stress effects is shown to provide both a qualitative and somewhat quantitative explanation of the complex substrate orientation effects.

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Introduction

Recently, we reported new initial regime silicon oxidation data in terms of film thickness, L , versus time t , (1,2,3) which shows a crossover in the oxidation rate, ie. the slope of the L - t data, with the major Si surface orientations. An example of this crossover effect is shown in Fig. 1a and b and it was found for all temperatures studied (800°C to 1150°C). For the three low index orientations ((100), (110), (111)) the rates of oxidation, R , have the initial order:

$$R_{(110)} > R_{(111)} > R_{(100)}$$

but at greater oxide film thicknesses the order of the rates changes to:

$$R_{(111)} > R_{(110)} > R_{(100)}$$

Within the widely accepted linear-parabolic, L-P, model(4) the initial rates are governed by the linear rate constant, k_1 , which contains orientation information for each Si orientation and which is essentially a first order chemical rate constant for the reaction of Si with oxidant. It is clear that the L-P model is incapable of explaining the crossover.

The purpose of this study is to analyze the crossover effect in terms of a recently proposed viscous flow model for Si oxidation(5,6). This model utilizes the notion of mechanical stress and viscous relaxation in SiO_2 which occur as a result of the oxidation process on a Si substrate(5,7,8) in addition to the other assumptions in the L-P model(4) such as a steady state between the interface reaction and the transport of oxidant through the oxide. It is reported herein that the new viscous flow model provides a

reasonable qualitative explanation for the crossover effect and in some instances a quantitative correlation of the effect.

Previous studies of the orientation dependence of the oxidation rate of Si have shown a variety of behavior. The most recent report(11) is a crossover effect between (111) and (100) orientations near an oxygen pressure of about 0.1 atm. Below $P_{O_2} = 0.1$ atm the (100) oxidation rate was found to be greater than the (111) rate, while above that pressure the (111) oxidized faster. This crossover was also reported for oxidation in reduced pressures of H_2O . The results were qualitatively attributed to a complex orientation dependent reaction at the Si-SiO₂ interface. Two earlier studies using steam oxidation showed different behavior. In one study(12) for thick SiO₂ films (several tens of nm and thicker) on Si grown near 1000°C in 1 atm steam the order for the oxidation rate was found to be (111) > (110) > (100). This order is the same as for thicker films in dry O₂ as reported here(1-3). No model was proposed for this behavior. In another steam oxidation study(13), but in high pressure steam (up to 150 atm) at temperatures up to 800°C and for films thicker than about 150nm, the (110) was reported to display a faster rate than the (111). For this behavior the author used a model based on the number of chemical bonds oriented parallel to the surface to be oxidized and the steric aspects of H₂O on the differently oriented Si surfaces. In another oxidation model(14) in which vacant cation sites are required for the oxidation to proceed, the surface reaction rate would increase with a decreasing atomic density of surface atoms for Si oxidation in the thin film regime. This would yield the rate order (100) > (111) > (110) which is the opposite of our experimental observations(1-3). This of course may indicate a direct proportionality between the oxidation rate and the areal density of Si atoms at the outset of the oxidation reaction. Such a proportionality is physically sensible for the earliest stage of oxidation and provides the starting point for the presently proposed model. The other studies (11-13) provide little guidance for the present work except to

demonstrate that the orientation behavior is quite complex and little understood at the present time. The L-P model offers no explanation for the complex orientation behavior that is observed.

The Revised Linear Rate Constant

Within the L-P model(4), the rate of reaction at the Si-SiO₂ interface is given by the relationship:

$$\text{Rate} = k_1 C_2$$

where k_1 is the first order rate constant for the reaction between Si and the concentration of oxidant at the interface, C_2 . This rate constant also contains the orientation information about the Si surface such as the areal density of Si atoms on a given Si surface orientation which can alter the oxidation rate. The recently revised oxidation model(6) explicitly introduces the effective Si atom concentration on a surface, C_{Si}^* as:

$$\text{Rate} = k' C_2 C_{Si}^*$$

C_{Si}^* is obtained from the actual number of Si atoms on a Si surface orientation, C_{Si} , by reducing C_{Si} by a fraction proportional to the rate at which the film of SiO₂ which is forming, viscously flows away from the interface, thereby uncovering a new layer of Si atoms to oxidation. If we consider the plane of the Si surface to be the (X,Y) plane then we obtain for C_{Si}^* :

$$C_{Si}^* \propto C_{Si} \dot{\epsilon}_z$$

where $\dot{\epsilon}_z$ is the rate of viscous relaxation in the Z direction which is normal to the Si surface and is obtained from the linear Maxwell model for a viscoelastic solid(5). From this relationship and the Maxwell model it was shown(5,6) that $\dot{\epsilon}_z$ is a function of the stress in the (X,Y) plane, σ_{xy} , and the SiO₂ viscosity, η_{SiO_2} as:

$$\dot{\epsilon}_z = \sigma_{xy} / \eta_{SiO_2}$$

Therefore, one obtains for the linear rate constant of the L-P model, k_1 , a revised form as:

$$k_1 = k^* C_{Si} \sigma_{xy} / \eta_{SiO_2}$$

In the revised model k_1 is no longer a first order rate constant for an elementary reaction step, but rather it is a composite coefficient for a complex process. The revised linear rate constant is directly proportional to the stress and inversely proportional to oxide viscosity. We now can use the revised relationship for k_1 to analyze the initial regime of Si oxidation, viz. the crossover regime.

Analysis of The Crossover Data

For the purpose of this study we focus our attention on those variables in the revised model that directly relate to the orientation of the Si surface. These variables are C_{Si} which is the number of Si atoms per unit area of surface, and σ_{xy} which in the elastic limit depends on Youngs modulus, E, which is orientation dependent. For the very early stage of oxidation the reaction between Si and for example O₂ must depend on the

number of Si atoms per area, C_{Si} . For the orientations used in this study Table 1 shows that the (110) has the greatest areal density of Si atoms, followed by the (111) and then the (100). Qualitatively, this is precisely the order for the initial oxidation rates seen in Fig. 1 as well as all our data from 800° to 1150°C.

As the oxide film grows thicker than about 5nm, the SiO_2 network develops in the Z direction. The onset of the mechanical influence of a film with the substrate should only be observed when the film network or structure is developed sufficiently to exert a mechanical influence on the substrate. Very thin films merely reflect the mechanical properties of the substrate until such films are thick enough to become mechanical entities with different properties. At that thickness the film stress, an intrinsic stress which exists under oxidation conditions, is assumed to influence the oxidation rate as shown in the revised relationship for k_1 above, ie. a direct proportionality. Since the elastic stress is directly proportional to the strain with the orientation dependent constant of proportionality being Youngs modulus, E, it is useful to examine the orientation dependence of E or better $E/1-v$, where v is the Poisson ratio. It has been found (9,10) that the decreasing order for $E/1-v$ shown in Table 3 parallels the decreasing oxidation rate for films greater than about 10nm, viz. (111) > (110) > (100) again in qualitative agreement with the data for films thicker than the crossover value. It is now useful to examine the quantitative aspects of the revised model in relation to the orientation dependence of the oxidation rates.

For the very early stage of oxidation prior to the crossover, we calculate oxidation rate ratios relative to the initially fastest oxidizing rate for the (110) orientation. The ratios are reported in Table 2 for SiO_2 film thicknesses between about 2 and 5 nm. The rates below 2nm are very high and somewhat non-reproducible and the rates above 7nm may be significantly affected by the stress mechanism. While it is clear that the rates change up to 10nm, the rate ratios hardly change at all (less than 10%). It is seen that

the agreement between the ratio of the areal densities of Si atoms and the oxidation rate ratios is quite good for the (111) orientation (better than 4%) but not nearly so close for the (100) orientation (about 37%).

For the regime above the crossover, we observe from Fig. 1 that the (111) rate is greatest and if the film stress is important according to the revised oxidation model(6) as briefly outlined above, then the oxidation rates should scale with the orientation dependence of Youngs modulus or more specifically $E/1-\nu$. This is so because the volume change across the interface is always the same hence any differences in stress is due to differences in the accomodation of the same strain by the Si which varies with Si orientation according to $E/1-\nu$ for the various orientations. Table 3 shows the ratio of $E/1-\nu$ values for the (100) and (111) orientations relative to the (110). Also in Table 3 are experimental rate of oxidation ratios for the (100) and (111) orientations relative to the (110) orientation as before, but here the rate values are selected from the 30 to 50nm SiO_2 film thickness range which is above the crossover. Since it is important that these ratios be reflective of the initial regime rather than the transport limited thicker growth regime, the derivative values were limited to the thicknesses from the crossover thickness to about 50nm. It is observed that the agreement between the rate ratios and the $E/1-\nu$ ratios is about 10% for the (111) orientation but more than 25% for the (100).

In summary, previous and recent oxidation data on Si substrate orientation effects of the Si oxidation rate cannot be understood within the L-P model. Recently reported high precision oxidation data for the initial growth regime in dry O_2 at 1 atm display a orientation crossover effect that is qualitatively and somewhat quantitatively explained by a recently proposed oxidation model(6). Within this recent revision to the L-P model, the initial stage of oxide growth is governed by the areal density of Si atoms which is explicit in the revised model; but as the oxide grows to become three dimensional with a

network normal to the Si surface, the mechanical effects of the SiO_2 on Si dominates and the observed crossover in oxidation rates for the major orientations scale with the stress which is proportional to Young's modulus. This model appears successful in quantitatively predicting the relationship between the (111) and (110) orientations but not for the (100) Si surface. At the present time we have no explanation for this. It may be that there are other not yet accounted for effects such as steric effects as proposed by previous authors(11,13). Further studies that include other orientations, still lower oxidation temperatures, and higher oxidation pressures are in progress to further elucidate this problem.

Several recent reports (15,16) have attempted to model the initial growth regime using a stress altered diffusivity. While we agree that intrinsic oxide stress will alter diffusivity and oxidation kinetics, there seems to be considerable evidence in favor of the very initial regime being dominated by the Si surface orientation. We have shown the qualitative correlation and for the (110) and (111) orientations, good quantitative agreement with simply the number of Si atoms on a surface. Furthermore, the reversal in rate order for thicker films, to an order that does correlate with stress, supports the idea that the early stage is dominated by the interface reaction.

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 and (111) Planes
- Table 2 Experimental Rate Ratios for the Initial Oxidation
 Regime
- Table 3 Experimental Rate Ratios after the Crossover

Table 1

Orientation	Areal Density of Si Atoms (#/cm ²).	Relative to (110)
(100)	6.8 X 10 ¹⁴	.71
(110)	9.6 X 10 ¹⁴	1
(111)	7.85 X 10 ¹⁴	.82

Table 2

Experimental Rate Ratios At About 5mm

Oxidation Temperature (°C)	Rate(100)/Rate(110)	Rate(111)/Rate(110)
800	0.39	.76
850	0.42	.91
900	0.47	.90
950	0.47	.90
1000	<u>0.48</u>	<u>.78</u>
	Av 0.45	0.85

Ratios of the Areal Density of Si Atoms

0.71 0.82

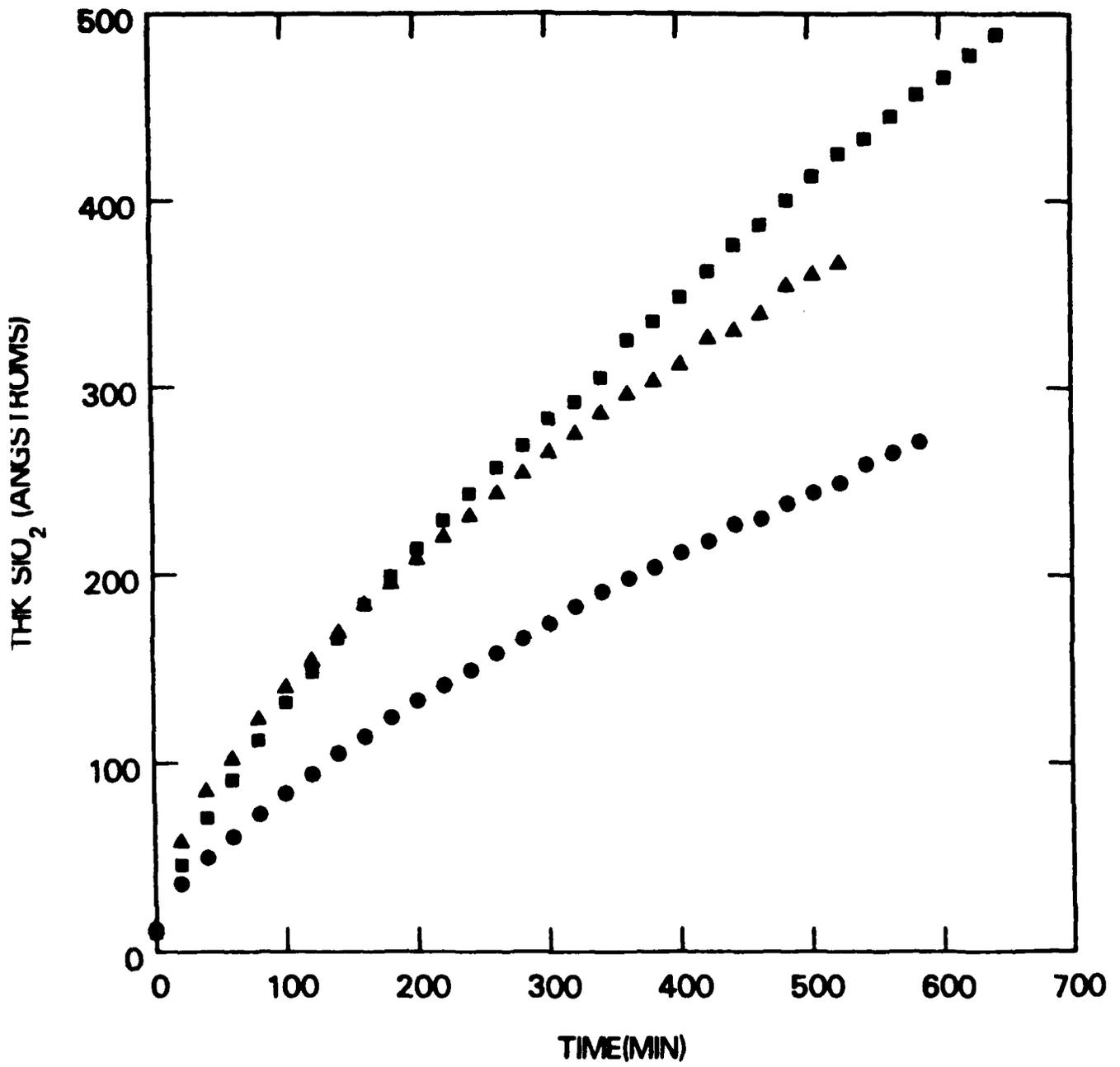
Table 3

Experimental Rate Ratios Between 30 - 50mm

Oxidation Temperature (°C)	Rate(100)/Rate(110)	Rate(111)/Rate(110)
800	0.54	1.26
850	0.67	1.36
900	0.60	1.27
950	0.69	1.32
1000	0.64	0.90
	Av	0.63
		1.22
Ratios of E/l-v	0.86	1.09

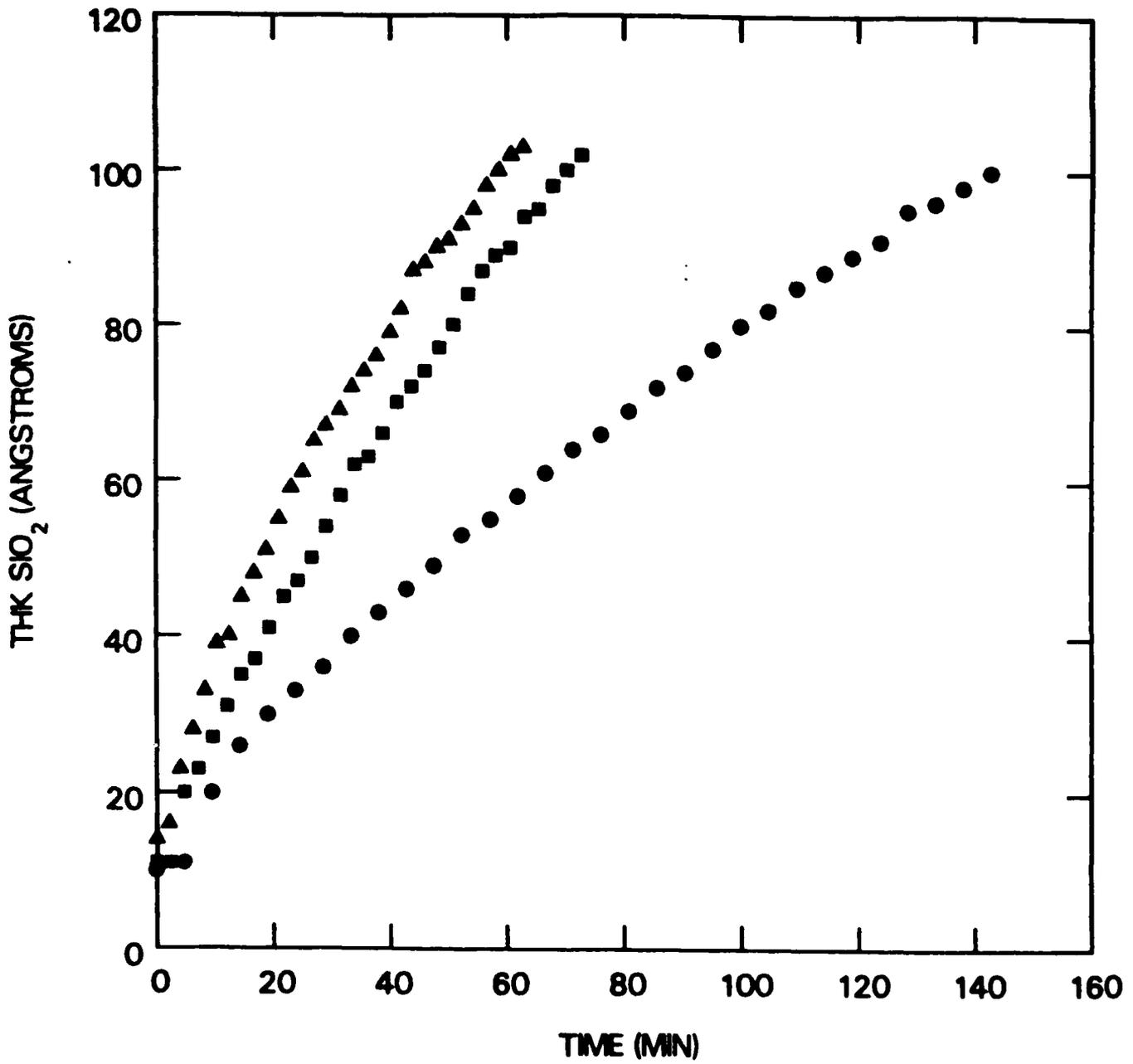
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Figure 1 SiO_2 film thickness, L , versus oxidation time, t , at 800°C , in dry O_2 for the (100), (110) and (111) Si orientations. In a) is a closeup of the early stage of oxidation and b) is the overall oxidation.



(100)DO, (110)TR, (111)S SI, 1ATM O₂, 800C

Fig 1 a



(100)DO, (110)TR, (111)S SI, 800C, INITIAL GROWTH

Fig 1b

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