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Low Temperature Silicon Oxidation Studies

by

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LOW TEMPERATURE SILICON OXIDATION STUDIES

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Several models have been proposed to explain the role of
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these results. It is concluded that the existing models do not
explain all aspects of the data.

Introduction

The scaling of microelectronic devices to smaller sizes and
increased density on a Si chip requires reductions in both the SiO_2
film thickness and the oxidation temperature(1). These VLSI
requirements constrain the oxidation process to an environment in
which the film formation kinetics are not well understood in terms of
both the thickness-time behavior(2,3) and the behavior of the rate
constants with oxidation temperature(4). The initial stage of Si
oxidation (up to several tens of nanometers) displays a faster
oxidation rate than predicted by the Deal-Grove model(2) which
describes the oxidation kinetics observed for thicker films. The
activation energies for both the linear and parabolic rate constants
described in the Deal-Grove model have different values for oxidations
performed at oxidation temperatures below $950^{\circ}C$ than for oxidations at
higher temperatures. In order to explain these results several models
have been proposed which consider the effect of stress and viscous
flow on the oxidation kinetics.

It has been observed that an intrinsic stress develops during
oxidation at temperatures below 950°C (5-8) and that the stress
relaxes via viscous flow at higher temperatures(7). It is therefore
logical to use this observation in a model for low temperature
oxidation where intrinsic stress is the largest. The correlation
between the temperature at which altered activation energies are
observed for the rate constants and the temperature at which an
intrinsic stress develops further supports the idea that stress alters
the reaction kinetics. The proposed stress models differ in principle
on whether stress primarily affects the diffusional transport of O_2 or
the interface reaction between Si and O_2. One model states that the
interface reaction(7,9) is affected by both stress and the number of
Si atoms on the surface. This model results in a modified form for the

linear rate constant as follows:

$$k_1 \propto C_{ox}C_{Si}\sigma/\eta \qquad (1)$$

where C_{ox} and C_{Si} are the concentrations of oxidant and areal density of Si atoms on the surface, respectively, and σ and η are the film stress and viscosity. Another model(10) considers that the stress alters the diffusivity, D as:

$$D = D_L\exp(k\epsilon_o(1-X/L)) \qquad (2)$$

where D_L is the diffusivity when the oxide strain is zero (i.e. at the outer oxide surface), ϵ_o is the maximum strain which exists at the Si-SiO_2 interface (X=0), and L is the SiO_2 film thickness. This model attempts to explain the linear rate constant using the exponential decay of D with distance from the interface and does not consider the interface reaction to be kinetically significant. A third stress related model(11) considers that the diffusivity depends on both the activation energy for diffusion and the activation energy for stress which is given by the relationship:

$$E_\sigma = \sigma\underline{\triangle}V$$

where σ is the intrinsic stress and $\underline{\triangle}V$ is the volume change caused by the application of the stress. This then yields a final form for the diffusivity as follows:

$$D = D_o\exp(-\sigma\underline{\triangle}V/kT) \qquad (3)$$

In the present study we present new kinetic data for the initial regime of oxidation as a function of orientation and oxidation temperature (600-750°C). This data is analyzed in terms of the oxidation rate by a model independent method and then combined with recently reported intrinsic stress data(12) in order to evaluate the models discussed above. The stress related models are compared and judgements concerning the relative merits of the models are presented.

Experimental Procedures

The Si slices were typically 2-10 ohm-cm, chem-mechanically polished, commercially available, device quality Si. Prior to oxidation all samples were cleaned by a slightly modified RCA cleaning procedure(13) followed by a 10 second HF dip. Each step in the cleaning procedure was followed with a thorough deionized H_2O rinse with 18 megaohm H_2O. Oxidations and annealing were performed in thoroughly cleaned fused silica furnace tubes using MOS quality O_2 and N_2 exclusively.

The oxidation kinetics measurements were performed in-situ using a furnace mounted at the focus of an ellipsometer. The experimental apparatus and arrangement as well as operating procedures were similar to those already described(3). The ellipsometer could be operated automatically (using a PCS and rotating analyzer configuration) to obtain rapid and dense data as well as manually (using a conventional PCSA configuration and two zone null measurements) to obtain high accuracy checks on the automatic measurements. All measurements were taken at 70.00 angle of incidence using 632.8nm light.

The SiO_2 film intrinsic stress measurements were obtained using a previously reported(8,12) visible light double beam reflection technique. Calibration standards were used to test the accuracy of the system. This technique actually measures strain from the wafer curvature from which stress is then calculated. These measurements were performed at room temperature and thus the raw data included a thermal expansion stress component which was subtracted from the total measured stress to yield the reported intrinsic stress. The details of this technique, calculations, constants used and results were reported separately(8,12).

Experimental Results and Discussion

Fig. 1 shows typical SiO_2 film thickness, L, versus oxidation time, t, data. This comparison of the manual and automatic data demonstrates the excellent agreement which could be obtained over the range 650-750°C. At 600°C manual measurements were used for analysis purposes since the extremely slow growth rate coupled with instabilities in the automatic measurement decreased the reliability of the data obtained with the automatic analyzer. This data was obtained for four Si orientations: (100), (110), (111), (311), nd at oxidation temperatures from 750°C to 600°C in 50°C increments Figure 2 shows a typical data set. At these low temperatures the thickness range which could be covered on a reasonable time scale was limited to thicknesses between the native oxide obtained after cleaning (about 1nm) to no more than several tens of nanometers for the highest oxidation temperatures. Thus, the initial oxidation regime was emphasized. Similarly dense data for the higher temperature range of 800°C to 1000°C has recently been reported(14). The present data was obtained in the regime where the intrinsic stress is largest, viz. temperatures less than 800°C(15), and thus is specifically aimed at elucidating intrinsic stress effects on the oxidation kinetics.

The data analysis is directed towards a comparison of the above mentioned models. With this intention, a model independent method of data analysis was used which utilized the instantaneous oxidation rates, ie. derivatives of thickness with respect to time. Figure 3 shows typical plots of the derivatives versus oxide thickness. In Figure 3a, which shows the very initial regime, we observe a large

decrease in rate with film thickness up to about 5 nm at 750°C for the (110) and (111) orientations. Similar behavior is observed for the (311) and (100) orientations with rates lower than the (111) orientation. The exponential shape of this regime is in substantial agreement with previous studies(14) in which the decrease in the initial rate was also found to be an exponential. Numerous experimental difficulties associated with the first part of this regime (up to about 2nm) preclude a quantitative interpretation at this time. One difficulty is that the change from N_2 to O_2 to initiate the experiment introduces a time period in which the ambient composition is increasing from 0% to 100% O_2. Another problem is that the error in the automatic ellipsometric measurement is large in this regime and the manual measurement is too slow to obtain reliable data in the time frame. However, for oxides thicker than 2 nm the experimental situation is much improved. Although the analysis is difficult in this region it is reasonable to predict that the early stage of oxidation should be most sensitive to Si orientation since the oxidation reaction occurs at the Si surface. Following the early stage characterized by the rapidly decreasing rate, a more slowly decreasing regime is observed. In order to determine the oxidation rate in this second region, the data in the initial rapid regime was deleted from the data set and a second degree polynomial was fit to the remaining data. The analytic derivative of the polynomial could then be obtained directly. In this stage the rates of oxidation are more parallel although the rate on the (110) orientation decreases more rapidly than the other orientations as seen in Figure 3b. A crossover in the rate for the (110) and (111) orientations at 750°C is observed in the early rapidly decreasing rate regime (see figure 3a). Initially the (110) oriented Si oxidizes fastest under all experimental conditions investigated and up to 1100°C(14). This is followed by the (111) orientation, and the other orientations display nearly the same rates. This crossover effect has been previously explained(15) with the model for the initial oxidation regime summarized in equation (1) above, and will be discussed in the next paragraph. At temperatures of 700°C and below a crossover in the oxidation rates is not observed, but this is likely due to the fact that the limited total SiO_2 growth at these temperatures prevents the oxide from reaching a thickness where the crossover would be observed. The intrinsic stress data shown in Figure 4 also exhibits an orientation dependence. The SiO_2 films grown on (111) oriented Si always have lower intrinsic stress than for the other orientations. With the data in Figures 2-4 we can compare the three stress related oxidation models.

The model proposed by Irene(9) introduces a Si substrate orientation effect directly through both the C_{Si} term and σ term as seen in equation (1) above. The areal densities of Si atoms, C_{Si}, for the orientations studied are given in Table 1. Irene used these numbers with equation (1) to explain that the very initial oxidation

rate should scale with the areal density. Based on the available data for (100), (110), and (111) Si(14), agreement was found(15). From Table 1 the rates should follow the order:

$$R(110) > R(111) > R(100)$$

which is observed in previous(14) and present studies for the very initial regime where the interface should be most dominant. For the region above the crossover this model(15) considers that the film stress dominates and the stress should scale with E/1-v for each orientation where E is Young's modulus and v is Poisson's ratio. From the literature values, Irene calculated that the stress ratios should be:

$$\sigma(111) > \sigma(110) > \sigma(100)$$

which scales with the oxidation rates above the crossover. Not only were the directions for the rates above and below the crossover found to scale qualitatively, but quantitative agreement was found for the (110) and (111) surfaces. However, with the new data reported here we see that although the (311) has a higher density of Si atoms than the (110) its oxidation rate is as slow as the (100) in the very initial regime. Also, Figure 4 shows that the stress for the (111) orientation is less than the measured stress for the other orientations which are about equal. This means that while Irene's model(15), which revises the linear-parabolic model(18), explains some of the trends in the oxidation data and is in accord with anticipated stress results, the (311) orientation rate data and the stress measurements are not explained very well.

The model proposed by Doremus(10) contains the orientation dependence through the strain term in the exponent (see equation (2)). The model proposed by Fargeix et al(11) (see equation (3)), utilizes an exponential dependence of D on stress. Since stress and strain are directly proportional in the elastic limit, the orientation dependence for these latter two models is the same. If the origin of the intrinsic stress is the molar volume change in converting Si to SiO_2, $/\backslash V$, then the resulting force per unit area, the stress, σ, causes a deformation of the oxide. A compressive stress would reduce the oxide volume. The amount of the reduction can be estimated from Hooke's law as:

$$\varepsilon = \sigma/E$$

where E/1-V is used in place of simply E. From the literature values for compliance coefficients(16,17), Fig. 5 shows a plot of calculated E/1-v values for the orientations used in this study. From Figures 4 and 5 we can estimate the effect of orientation. It is easily seen that the smallest stress and large E/1-v value for the (111) plane yield the smallest ε and therefore the largest D in equations (2) and

(3). Using an averaged value for E/1-v for the (110) and nearly constant values for the other orientations from Fig.5, the correct order for the oxidation rates are obtained for film thicknesses above the crossover. The conclusion is that these two stress models for D seem to explain the thicker film orientation dependence but neither can describe the initial regime below the crossover.

Summary and Conclusions

The results presented in this study show that the oxidation rate and the intrinsic stress level developed during oxidation depend on the surface properties of the Si substrate. However, the factors controlling the oxidation rate are more complex than presented in the models considered. None of the proposed stress models sucessfully explain the orientation dependence of the oxidation rate at all stages of the oxidation as a function of the measured intrinsic stress or as a function of the surface density of Si atoms. The orientation dependence of the oxidation rate is not directly related to the surface density of Si atoms as is clear from the results on the (311) orientation. Other factors related to the surface properties such as the angular direction of the surface bonds and the step atom density as well as the electronic properties of the surface may lend further insight into the initial rapid regime. The observed crossover in the oxidation rates between the (111) and (110) orientations indicates a change in the dominant factor controlling the oxidation. Beyond the crossover the orientation with the lowest stress has the highest oxidation rate. This is not the result which would be predicted from the E/1-v values for the various orientations. Further stress measurements are needed to determine what controls the stress level exerted by the oxide. Although the models proposed by Doremus and Fargeix successfully predict the orientation dependence beyond the crossover, they cannot account for the initial regime where the rate decreases exponentially with thickness. A comprehensive model for the oxidation of Si must account for all of the observed trends. While the models considered represent some progress in explaining the complex oxidation kinetics for Si, futher work in this direction is still necessary.

Acknowledgment

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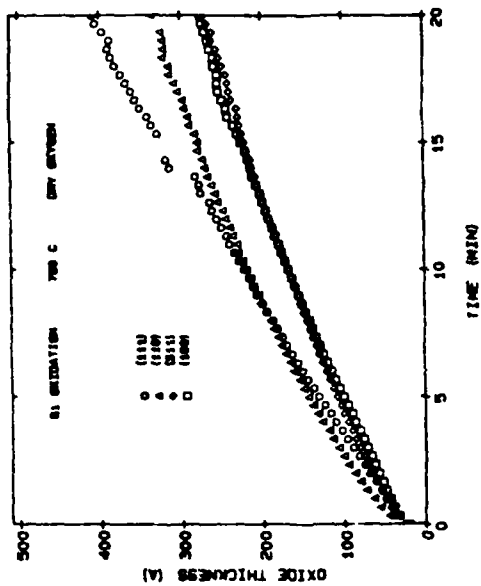18. J.R. Ligenza, J. Phys. Chem., 65, 2011 (1961).

Figure 1. SiO₂ film thickness versus oxidation time from both manual and automatic in-situ ellipsometry.
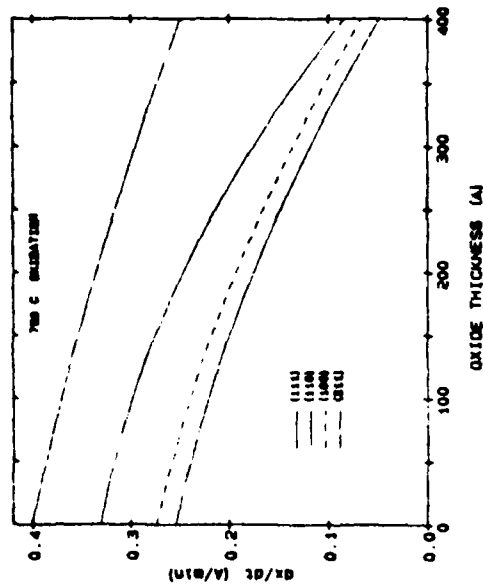

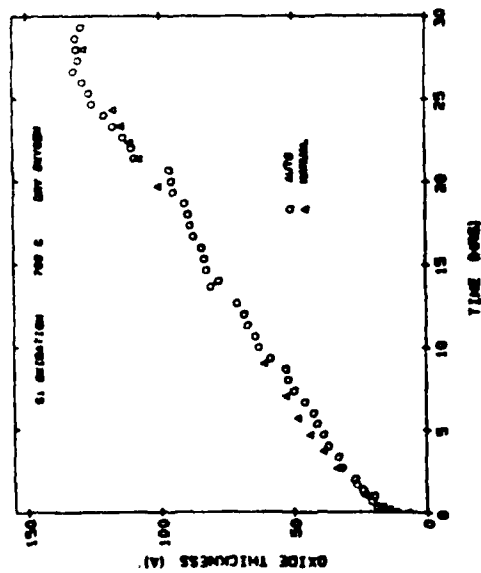Figure 2. SiO₂ film thickness versus oxidation time for four orientations.

Figure 3(a). The oxidation rate versus SiO₂ thickness for (110) and (111) Si.
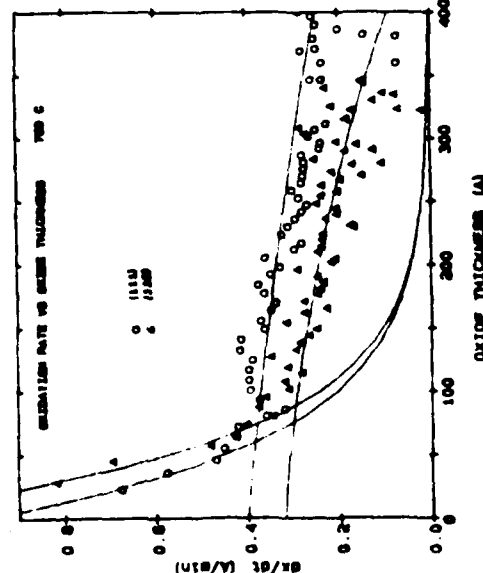

Figure 3(b). The rates for all four orientations (best fit) with the exponential regime deleted.
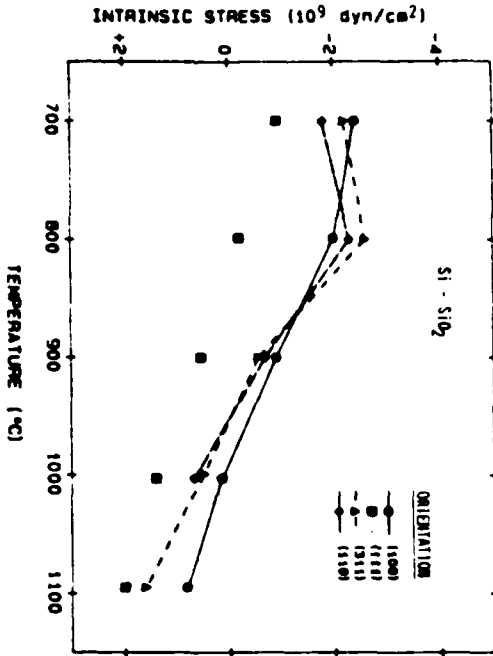
INTRINSIC STRESS $(10^9$ dyn/cm^2)

Si - SiO$_2$

ORIENTATION
(100)
(111)
(311)
(110)

TEMPERATURE (°C)

Figure 4. Intrinsic film stress versus oxidation temperature for four Si orientations.

Table 1

Areal Density of Silicon Atoms on Various Planes (18)

Plane	Areal Density $(\theta/cm^2) \cdot 10^{14}$
(100)	6.8
(110)	9.6
(111)	7.9
(311)	12.0

$E/(1-v)$ $(10^{12}$ DYNES/CM^2)

$E / (1-v)$ for Si

(100)
(111)
(311)
(110)

PHI (DEGREES FROM MAJOR DIRECTION)
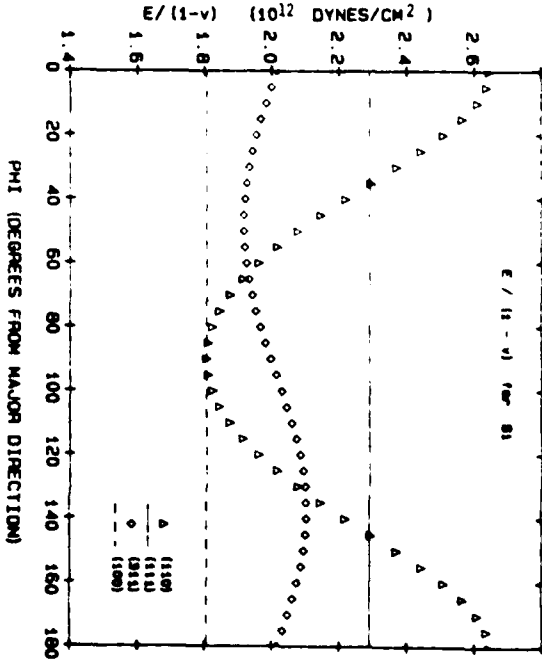
Figure 5. $E/1-v$ for four orientations and for various directions in the plane from the major direction (phi).

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