Oxidation of silicon: Further tests for the interfacial silicon emission model

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The classical description of Si oxidation given by Deal and Grove has well-known limitations for thin oxides (below 200 Å). Among the large number of alternative models published so far, the interfacial emission model has shown the greatest ability to fit the experimental oxidation curves. It relies on the assumption that during oxidation Si interstitials are emitted to the oxide to release strain and that the accumulation of these interstitials near the interface reduces the reaction rate there. The resulting set of differential equations makes it possible to model diverse oxidation experiments. In this paper, we have compared its predictions with two sets of experiments: (1) the pressure dependence for subatmospheric oxygen pressure and (2) the enhancement of the oxidation rate after annealing in inert atmosphere. The result is not satisfactory and raises serious doubts about the model's correctness. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2773693]

I. INTRODUCTION

A. Deal and Grove kinetics

Oxidation of silicon is an essential step in microelectronics processing. Owing to its technological interest, it has been the subject of continuous research for more than 40 years. Most studies take as reference the seminal paper by Deal and Grove (DG),[1] in which the Si oxidation kinetics was described with a simple diffusion–reaction model leading to the DG kinetic equation

$$X^2 + AX = B(t + \tau), \tag{1}$$

where X is the oxide thickness, t is time, and τ is a parameter that takes into account any initial deviation from the DG kinetics. The oxidation rate depends on two kinetic parameters: the parabolic rate constant, B, and the linear rate constant, B/A. B basically accounts for the diffusion of oxidant molecules (O_2 or H_2O) from the free oxide surface to the SiO_2–Si interface, and is expressed as

$$B = \frac{2D_O C_O^*}{N_0}, \tag{2}$$

where D_O is the oxidant diffusivity, C_O^* its solubility, and N_0, the number of SiO_2 molecules in a unit volume of oxide. The linear rate constant B/A accounts for the oxidation reaction at the interface. It is expressed as

$$B/A = \frac{k_0 C_O^*}{N_0}, \tag{3}$$

where k_0 is the rate constant of the (first-order) reaction between silicon and the oxidant molecules.

Equation (1) gives a good description of oxidation by water vapor (wet oxidation) for any temperature of practical interest and down to virtually zero thickness. However, serious discrepancies arise for oxidation by oxygen (dry oxidation) when oxides are thin enough (thin oxide regime). DG already realized that the oxidation rate was higher than ex-

pected with thicknesses less than several hundred angstroms (initial oxidation enhancement). Two reviews published at the end of the 1980s (Refs. 2 and 3) account for the theoretical and experimental efforts done to elucidate the origin of this discrepancy. In fact, further detailed experiments revealed additional weak points of the DG kinetics. Some of them will be described in the next subsection.

B. Interfacial emission model

Among the kinetic models that have been proposed since 1990, the one that has been tested against the widest number of experiments is that by Uematsu's group. The entire set of equations is reproduced in the Appendix. Here we will comment on those aspects that are most characteristic of the model.

The interfacial emission model invokes the crucial role of silicon interstitials emitted from the interface into the oxide during oxidation.[4] Emission of interstitials is said to release the strain at the interface that develops due to the large volume mismatch between Si and SiO_2.[5] According to this model,[4] the flux of interstitials, F_{Si}^I, at the Si–SiO_2 interface is proportional to the reaction rate at the interface through the so-called emission rate constant, v,

$$F_{Si}^I = D_{Si} \left. \frac{\partial C_{Si}}{\partial x} \right|_{x=0} = -kv C_O^I, \tag{4}$$

where D_{Si} and C_{Si} are the interstitial Si diffusivity and concentration, respectively, and k is the oxidation rate constant which relates the oxygen flux at the interface with its concentration there, C_O^I:

$$F_O^I = D_O \left. \frac{\partial C_O}{\partial x} \right|_{x=0} = k C_O^I. \tag{5}$$

k in Eq. (5) is essentially k_0 of DG [Eq. (3)] but modified by the Si interstitial concentration. In all the equations, coordinate x is the distance to the interface. At the oxide free surface $x=X$. It is argued that Si interstitials reduce the oxidation rate because C_{Si} cannot exceed its equilibrium concentration in SiO_2 (i.e., its solubility, C_{Si}^0) and, conse-

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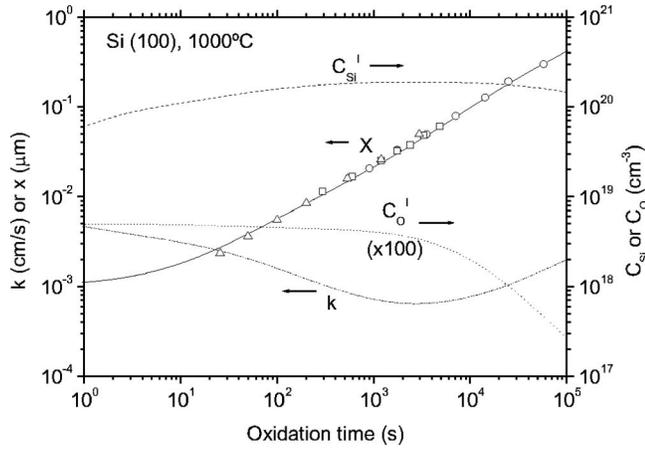
FIG. 1. Time dependence of various quantities during dry oxidation at 1000 °C calculated with the interfacial emission model equations. The theoretical $X(t)$ curve fits the experimental results of various authors (symbols). These curves compare well with those published in Fig. 3 of Ref. 6.

quently, a relationship between k and C_{Si} at the interface (C_{Si}^I) is proposed:

$$k = k_0 \left(1 - \frac{C_{Si}^I}{C_{Si}^0} \right). \tag{6}$$

This relationship couples the Si interstitial emission phenomenon with the oxidation rate (dX/dt) :

$$N_0 \frac{dX}{dt} = k C_O^I, \tag{7}$$

and has important consequences that account for most of the observed deviations between the experiment and the DG kinetics. Uematsu *et al.* have succeeded in fitting several series of $X(t)$ curves with very good accuracy: Series 1, dry oxidation of Si(100) at 1 atm measured by several authors in the 800−1200 °C temperature range,[6,7] notably the experimental points by Massoud *et al.*[8] in the thin oxide regime; Series 2, the oxygen pressure dependence in the 1–20 atm range and thickness above 100 Å (Refs. 7 and 9) measured by Lie *et al.*;[10] Series 3, dependence on Si substrate orientations (100) and (111) at several temperatures and oxygen pressures[11] measured by Massoud *et al.*[8] and Lie *et al.*;[10] and Series 4, a similar series for wet oxidation.[7]

The enhanced initial oxidation and the sublinear dependence on the oxygen partial pressure of the linear rate constant (revealed in Series 1 and 2) are accounted for by the interfacial emission model in an elegant and unified way. Let us explain first the initial enhanced oxidation with the help of Fig. 1. As oxidation proceeds and the oxide gets thicker, the diffusion of Si interstitials away from the interface becomes more difficult. As a result, its concentration at the interface (C_{Si}^I) increases and k diminishes [Eq. (6)]. In Fig. 1 we see that at $X = 0.03$ μm, $k \approx k_0/7$. According to this explanation, it is more accurate to say that the oxidation becomes slower for thick oxides rather than enhanced for thin oxides. This interpretation agrees with concluding experiments by Ajuria *et al.*,[12] although the proposed underlying physical mechanism is completely different. Concerning the sublinear dependence on the oxygen partial pressure, P_{O_2}, it can easily be

related to the emission of Si interstitials. When P_{O_2} increases, the O_2 concentration at the interface increases in proportion. Consequently, more interstitials are emitted and reduce the value of k, making the product kC_O^I [Eq. (5)] and the oxidation rate sublinear on P_{O_2}.

The oxidation curves, $X(t)$, for substrates with orientations (111) (Series 3 and 4) are fitted with the same parameters used to fit the (100) orientation but changing the emission rate constant v [Eq. (4)]. It is said that the ratio $v_{111}/v_{100} = 0.4$ agrees with indirect experimental quantifications of the fluxes of Si interstitials.[11] This explanation for the dependence of $X(t)$ curves on substrate orientation avoids the need to consider different O_2 diffusivities in the oxide [the DG parabolic rate constant of Eq. (2)].

Finally, the absence of any oxidation rate enhancement for thin films during wet oxidation is interpreted by lower Si interstitial emission [$v(\text{wet}) = 0.2$ $v(\text{dry})$] and it is argued that this interpretation agrees with independent experiments.[7]

Apart from these features (initial oxidation enhancement in O_2 but not in H_2O, sublinear dependence on P_{O_2}, dependence on substrate orientation) already highlighted by Uematsu *et al.*, we have identified additional experimental results that can be qualitatively explained by the interfacial emission model. These are the experiments showing an enhancement of the oxidation after annealing of thin oxides in inert atmosphere.[12] This effect is easily explained because, after annealing, the distribution of Si interstitials becomes smoother, its concentration at the interface diminishes, and consequently, k increases [Eq. (6)].

We consider that the ability of the interface emission model to quantitatively reproduce the experimental facts described above (which could not be explained within the elementary DG model) is impressive and probably unmatched by any other model published so far. Perhaps, 40 years after publication of the DG model, it will be substituted by a more refined, widely accepted model that contains the classical DG model in the $v \rightarrow 0$ limit.

C. Motivation for the present work

Several years ago, we struggled to find a convincing explanation for the sublinear dependence on P_{O_2} for thin oxides and thought that the results of the interface emission model (notably, those published in Figs. 2 and 7 of Ref. 7) provided the correct explanation. However, a serious doubt arose when we considered subatmospheric pressure. In fact, for low O_2 pressure, the oxidation rate is slow and, consequently, few Si interstitials are emitted. This leads to the unexpected prediction that the pressure dependence should recover proportionality and the initial oxidation enhancement should disappear for O_2 pressure that is low enough. Fortunately, there are several experiments at subatmospheric pressure[13–15] ready to test this prediction. This point will be addressed in Sec. II.

As commented in the previous subsection, we also realized that the interfacial emission model could account for the experiments published by Ajuria *et al.*[12] We must remark that the explanation for these kinds of annealing experiments has always been qualitative.[12,16] What is really new with the in-
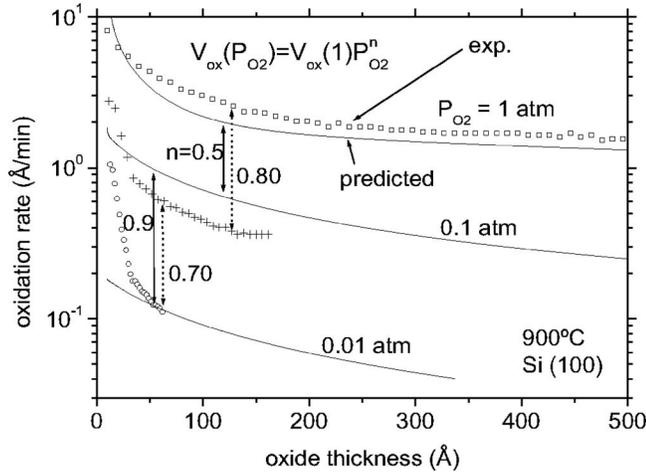
FIG. 2. Oxidation rate vs. oxide thickness at 900 °C for Si(100) at several oxygen pressures. Experimental points are from Ref. 8. Solid curves at 0.1 and 0.01 atm are predicted by the interfacial emission model with the parameters obtained from the fit to the $X(t)$ curve at 1 atm.

terfacial emission model is that these experiments can be modeled quantitatively with the parameters of the model already obtained from the fits to independent experiments [the $X(t)$ curves of isothermal oxidation]. This point will be addressed in Sec. III.

We have solved the equations of the model with the parameters already published by Uematsu *et al.*[7] Some technical details of our calculations are given in the Appendix, and the results corresponding to the particular experiments are given in Secs. II and III. A general discussion and conclusions will be the contents of Secs. IV and V, respectively.

II. DEPENDENCE ON P_{O_2} AT SUBATMOSPHERIC PRESSURE

A. Experiments

Pressure and temperature are experimental parameters that have an obvious influence on the oxidation kinetics of silicon, and consequently, can deliver important information for understanding its microscopic mechanisms. Just after the DG paper,[1] several groups worked intensively on the sublinear dependence on P_{O_2} observed for thin oxides.[8,14,15] The *in situ* ellipsometry measurement of the oxide thickness by Massoud *et al.*[8] allowed determination of $X(t)$ with an unprecedented density of experimental points. Their $X(t)$ curves are those that have been most used to test new kinetic models. In Fig. 2 we have plotted a series of the Massoud curves corresponding to the oxidation rate versus oxide thickness at 900 °C for $P_{O_2}=1$, 0.1 and 0.01 atm. At any pressure, dX/dt increases quickly for X below 200 Å. This is the oxidation rate enhancement in the thin oxide regime. To highlight this behavior, it is better to plot the inverse of the oxidation rate because in the DG regime dt/dX follows a linear dependence on X, as revealed by taking the derivative of Eq. (1):

$$\frac{2X}{B} + \frac{A}{B} = \frac{dt}{dX}.$$ (8)
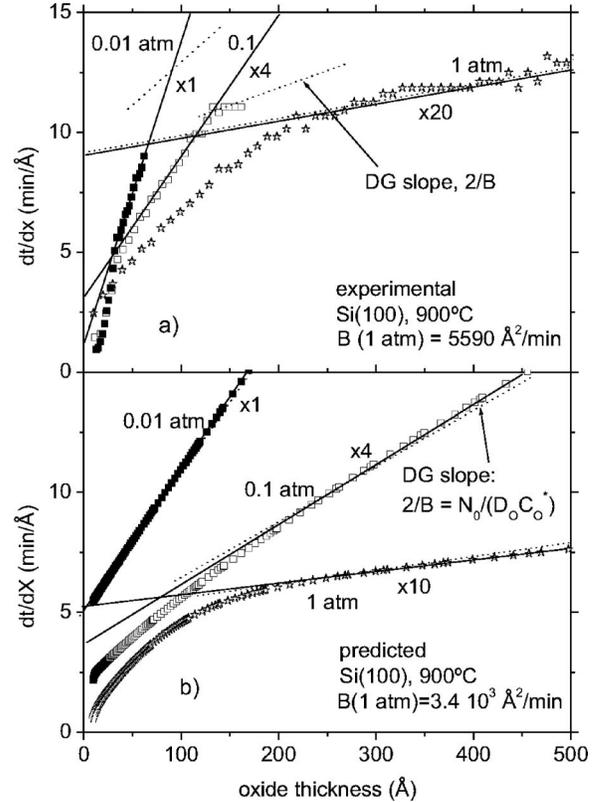
FIG. 3. Plots of the inverse oxidation rate (from Fig. 2) showing deviations from the Deal and Grove model for thin oxides: (a) experimental points; (b) prediction by the interfacial emission model. Solid lines indicate the apparent DG limit for large X. Dashed lines indicate the expected slope in the DG limit. Note that at 0.01 atm the enhanced oxidation region is lost in the predicted curve.

In Fig. 3(a), a clear deviation from linearity is observed at 1 atm below 200 Å. At greater thicknesses, the slope agrees with the value of Eq. (8), $2/B$ (dashed line). Although at first sight one could think that for low pressure DG fails only for very thin thicknesses below ~40 Å (deviation from the solid lines), this is not correct. In fact, all the experimental points measured at 0.1 and 0.01 atm are within the enhanced oxidation regime. This can be proved by simply plotting the DG slope, $2/B$ (dashed lines), which according to all experiments[9,10,17] is proportional to P_{O_2} [$B(1$ atm) $=5590$ Å²/min].[8] The slopes of the 0.1 and 0.01 atm points in Fig. 3(a) (solid lines) are much higher than the expected DG slopes (dashed lines).

The pressure dependence of the oxidation rate can be characterized by an exponent n relating the oxidation rates measured at the same thickness:

$$dX/dt(P_{O_2}) = dX/dt(P_{O_2}=1) \cdot P_{O_2}^n.$$ (9)

We see from Fig. 2 that $n \approx 0.80$ and 0.70 in the 1–0.1 and 0.1–0.01 atm pressure ranges, respectively.

B. Prediction of the interfacial emission model

The equations of the interfacial emission model have been solved with the same parameters used for fitting the

Si(100) oxidation curves at 1 atm,[7] except for C_O^*, which is proportional to P_{O_2}. The predicted dX/dt versus X curves are plotted as solid lines in Fig. 2.

First of all, let us analyze if they exhibit the typical oxidation enhancement for small thicknesses already revealed by the experimental curves. Below 200 Å the dt/dX plot [Fig. 3(b)] shows an acute deviation from linearity for 1 atm and a moderate deviation for 0.1 atm. However, the points of 0.01 atm are perfectly aligned. Furthermore, the expected DG slopes (dashed lines) with the value of $B(1 \text{ atm})=3.4\times10^3$ Å^2/min (Ref. 7) agree fairly well with those of the linear regions in Fig. 3(b) (solid lines) for all pressures, thus confirming that at low pressure the interface emission model tends to DG. In fact, our calculations show that at 900 °C this limit is reached at a pressure between 0.1 and 0.01 atm.

Concerning the pressure dependence, a pronounced deviation with respect to the experiment is observed below 150 Å in the 1–0.1 atm range: the predicted n value of 0.5 is clearly lower than the experimental value of 0.8. In the 0.1–0.01 range, the predicted dependence is nearly linear (n =0.9) in contrast to the experiment (n=0.7).

C. Analysis

The present comparison of the experimental curves with those predicted by the interfacial emission model has been done without any free parameter. So, one does not expect an accurate agreement between both sets of curves in Fig. 2. We consider that the discrepancies observed at 1 atm are not significant. They could probably be minimized by slight modifications of the parameters used in the calculations detailed in Ref. 7. In fact, these parameters were chosen by Uematsu *et al.* because they provided the best fit to two series of $X(t)$ curves: Series 1 (1 atm at several temperatures) and Series 2 (the oxygen pressure dependence for $1<P_{O_2}$ <20 atm). Consequently, the good fit obtained by Uematsu *et al.* for the P_{O_2} series[7] does not provide a solid argument for the validity of the model. Furthermore, as detailed in their paper devoted to the pressure dependence,[9] good fitting did not only require choosing the appropriate values of the parameters; it also required modifying the oxidation kinetics of the Si interstitials, which was finally written as

$$R_2 = \kappa_1 C_O C_{Si} + \kappa_2 (C_O)^2 C_{Si}, \qquad (10)$$

where κ_i are the reaction rate constants and C_i are the concentrations in the oxide. The second reaction term, proportional to C_O^2, is difficult to justify and will be discussed in the next section.

In contrast to the quantitative discrepancies at 1 atm, we consider the predictions of the model concerning (1) the sublinear dependence on P_{O_2} and (2) the disappearance of the initial enhancement of the oxidation rate at low pressure (0.1–0.01 atm) to represent a serious qualitative discrepancy with the experiment. Although measurements at low pressure show quantitative discrepancies among different authors, as far as we know, no one has observed the predicted trend n $\rightarrow 1$. In addition to the results of Massoud *et al.*,[8] those of Kamigaki *et al.*,[15] Ganem *et al.*,[18] von der Meulen *et al.*,[14]
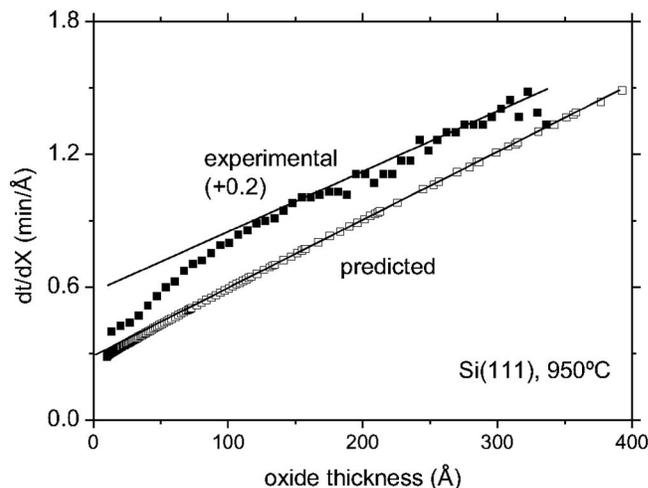
FIG. 4. Plot of the inverse oxidation rate at 950 °C for Si(111) at 0.1 atm. Experimental points by Massoud *et al.* (Ref. 8). Solid lines: apparent DG limit for large X. For oxides thinner than 100 Å, the model fails to predict the enhanced oxidation region.

and Ludstek *et al.*[19] exhibit values of n clearly lower than 1 for oxygen pressures below 0.1 atm in oxidation experiments on Si(100). On the other hand, we have found no experimental curve where the DG limit is reached at low pressure. This discrepancy is even more acute when we consider the Si(111) surface because for this orientation the emission rate constant is smaller [$v_{111}=0.4 \ v_{100}$ (Ref. 11)]. Our calculations at 950 °C indicate that, for this orientation, the DG limit is already reached at 0.1 atm (empty symbols in Fig. 4) in clear contradiction with Massoud's results,[8] where a clear deviation from linearity is observed below 100Å (solid symbols in Fig. 4) and with those of Hopper *et al.* at 870 °C (Ref. 17) [these $X(t)$ curves are published in detail in Ref. 20]. It is worth noting that these discrepancies are not only quantitative but qualitative. In other words, the fact that the interfacial emission model tends to DG kinetics (and n=1) at low pressure is intrinsic to the model and does not depend on the particular set of kinetic parameters.

III. REOXIDATION RATE AFTER THERMAL ANNEALING

A. Experiments

In 1990 Taniguchi *et al.*[16] did a series of original experiments showing that a thick oxide ($\approx$1000 Å) reoxidizes at a faster rate after annealing in an inert atmosphere. They correlated the reoxidation rates with changes in the oxide's refractive index. After annealing, the oxide was less dense, and consequently, more permeable to the oxygen molecules. Within the DG model, their experiments were formally explained as due to an increase in the parabolic rate constant during annealing. Four years later, Ajuria *et al.*[12] extended these kinds of experiments to the thin oxide regime. Typical results are shown in Fig. 5. Si(100) wafers were preoxidized at 850 °C up to an initial thickness, X_0, and then annealed at 950 or 1000 °C during 1 h. Afterwards, reoxidation was done during 50 min at 850 °C and the average reoxidation rate between 15 and 50 min was calculated. In Fig. 5 we have plotted it versus the mean oxide thickness, i.e.,
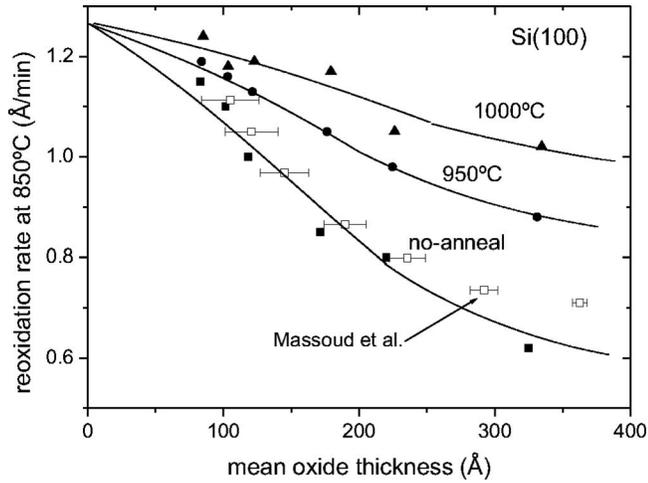
FIG. 5. Reoxidation rate at 850 °C of Si(100) wafers previously oxidized at the same temperature to various thicknesses and annealed in an inert atmosphere during 1 h at 950 and 1000 °C. The lower series of points were not annealed (Ref. 12). This last series is compared with the results by Massoud *et al.* (Ref. 8).

$$X_{\text{mean}} \equiv X_0 + \frac{\Delta X}{2}, \tag{11}$$

where ΔX is the oxide grown during reoxidation. The lower series of solid symbols in Fig. 5 corresponds to a series of experiments without any annealing period. One can identify the initial regime of enhanced oxidation rate lasting up to 300 Å (compare it with the results of Massoud *et al.* in Fig. 2). The effect of 1 h annealing is to increase the oxidation rate, which tends to recover the value measured at zero thickness. Ajuria *et al.*[12] measured the kinetics of this phenomenon by varying the annealing time. Their results, for an initial thickness of 200 Å, are plotted as solid symbols in Fig. 6. Time constants of 80 and 15 min are obtained for annealing at 950 and 1000 °C, respectively.

Before comparing these results with the prediction of the interfacial emission model, let us provide proof for the accuracy of Ajuria's measurements. Without the intermediate an-
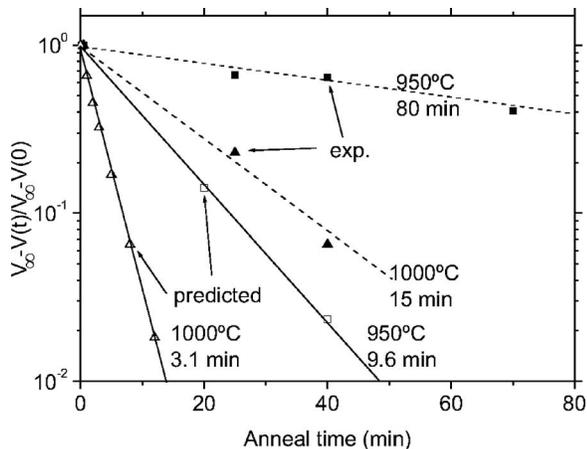
FIG. 6. After annealing in an inert atmosphere, the oxidation rate $v(t)$ tends asymptotically to a value v_∞ similar to the oxidation rate for zero thickness (Fig. 5). The prediction of the interfacial emission model delivers much shorter time constants. Predicted oxidation rates were computed at a reoxidation time of 1000 s.

nealing period, the reoxidation rate should agree with the oxidation curves of Massoud *et al.*[8] Fortunately, Massoud *et al.* measured the instantaneous oxidation rate at the same temperature as Ajuria (850 °C). If we average this oxidation rate during the thickness interval corresponding to the reoxidation time period of 15–50 min (error bars in Fig. 6), then the agreement of Ajuria's points with Massoud's results is excellent (Fig. 5). Consequently, we consider that Ajuria's results can be used for quantitative comparison with kinetic models with the same degree of confidence as the usual $X(t)$ curves. Furthermore, any model able to describe Massoud's curves in the thin layer regime should describe Ajuria's results with a similar degree of accuracy, because both experiments show complementary views of the same phenomenon: the initial enhanced oxidation (which, in fact, is the reduced oxidation rate as the oxide gets thicker).

B. Prediction of the interfacial emission model

As we have already pointed out in the Introduction, Ajuria's results can be easily explained with the interfacial emission model. During preoxidation, a spatial distribution of Si interstitials develops in the oxide with maximum concentration, C_{Si}^I, at the interface. Although most Si interstitials react with dissolved oxygen molecules [Eq. (10)], a small fraction arrives at the free surface where they oxidize quickly [$C_{\text{Si}}^S \equiv C_{\text{Si}}(X) = 0$]. This profile of interstitials evolves during annealing due to diffusion. The essential point is that its concentration diminishes at the Si–SiO$_2$ interface, and consequently [Eq. (6)], the reaction rate increases, as was experimentally observed.

Now, the question is whether the interfacial emission model is able to predict the value of the time constants obtained by Ajuria *et al.*[12] To answer this, we have solved the diffusion equation for the Si interstitials

$$D_{\text{Si}} \frac{\partial^2 C_{\text{Si}}}{\partial x^2} - \frac{\partial C_{\text{Si}}}{\partial t} = 0, \tag{12}$$

during the annealing period with a condition of zero flux at the boundaries of the oxide (Si–SiO$_2$ interface and the free SiO$_2$ surface). This condition follows from the fact that, in the absence of oxygen, Si atoms cannot escape by evaporation to the atmosphere and Si diffusivity is highly reduced in crystalline silicon.[21] The initial distribution after preoxidation, $C_{\text{Si}}(x, t = 0)$, and the reoxidation rate after several annealing periods are obtained by solving the equations of the interfacial emission model. In Fig. 6, the predicted reoxidation rates are plotted as empty symbols. Reoxidation rates tend much more quickly to the asymptotic value than experimentally observed. The predicted time constants are eight and five times shorter at 950 and 1000 °C, respectively, than the corresponding experimental values.

C. Analysis

In contrast with the conventional oxidation curves, $X(t)$, which have been used to test a large number of kinetic models, we know of no attempt to predict the evolution of the oxidation rate after annealing in inert atmosphere. At present, with the exception of the interfacial emission model, the cur-

rent explanation of these experiments was that annealing modified the oxygen transport in the oxide. We consider this interpretation to be convincing in the case of thick oxides.[16] In fact, it predicts[22] an abrupt change for the activation energy of the parabolic rate constant, B, around 1100 °C, which has been indeed observed[8] Uematsu et al.[7] consider an alternative mechanism also related with the oxide relaxation. According to them, the oxide stress would have a higher influence on v than on the diffusivity. For the case of thin oxides, the lack of refraction index measurements in the paper by Ajuria et al.[12] makes it difficult to correlate the reoxidation rate with the oxide properties. Thus, the interfacial emission model is the only model that allows a quantitative prediction of these results. Unfortunately, the discrepancy between the experimental and predicted time constants is notorious (Fig. 6). One could argue that, although the interfacial emission model does predict an increment of the reoxidation rate after annealing, this mechanism may not be the only one at work. In other words, another mechanism parallel to Si emission could explain the longer experimental time constants. However, if this interpretation were correct, the experimental time constant should be shorter, which is not the case (Fig. 6).

Finally, let us say that a slight modification of the calculation delivers reasonable values of the time constants. If the zero flux condition at the free surface is substituted by a zero Si concentration, then the predicted time constants would be 30 and 12 min at 950 and 1000 °C, respectively. Despite a better agreement with the experiment, this alternative boundary condition entails important consequences for the interfacial emission model. Zero concentration at the free surface means that this surface is a sink for Si interstitials. If in oxidizing conditions interstitials disappear by fast reaction with oxygen, in an inert atmosphere, they can only escape by evaporation. Thermodynamic arguments as well as experimental evidence[23,24] show that the only volatile species of the Si−SiO$_2$ system is the SiO molecule. Consequently, agreement with Ajuria's results would require the diffusing species to be SiO molecules.

In a recent paper,[25] Uematsu et al. report on experiments devoted to measure the diffusivity of Si atoms ionically implanted in SiO$_2$ layers thermally grown on Si. The profile of the implanted atoms evolves on annealing in inert atmosphere at different rates depending on the distance from the profile to the Si−SiO$_2$ interface, it being faster when the interface is nearer. It is concluded that SiO molecules, created by thermal decomposition of the oxide at the interface, are responsible for the enhanced Si diffusivity. Thermomigration experiments in SiO$_2$ (Ref. 26) are also explained in terms of SiO$_2$ decomposition and SiO diffusion. So, it seems reasonable to propose that during oxidation the emitted species at the Si−SiO$_2$ interface are SiO molecules and not Si interstitials.

Although at first sight one may think that this proposal simply changes the meaning of the model equations, where C_{Si} should be replaced by C_{SiO}, this is not the case. As commented on in Sec. II, the reaction of Si interstitials with oxygen molecules contains a strange term proportional to the product $C_O^2 C_{Si}$ [Eq. (10)], which was introduced to fit the
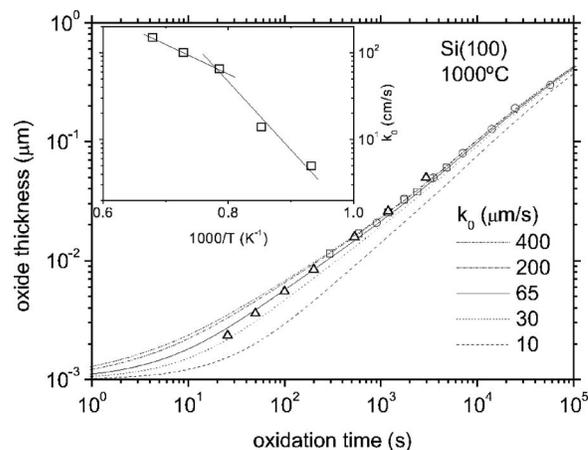
FIG. 7. Dependence of the initial region of the predicted oxidation curves on the reaction rate constant at the interface, k_0. Inset: values of k_0 obtained from fitting to experimental $X(t)$ curves.

pressure dependence for $P_{O_2} > 1$ atm. Such a term indicates that oxidation proceeds through a step where the simultaneous collision of two oxygen molecules and one silicon atom occurs. Stoichiometry considerations make this term even more unphysical if SiO molecules are considered instead.

IV. DISCUSSION

In this section, we want to discuss general aspects of the interfacial emission model to get additional criteria about its correctness, namely (1) its ability to fit the oxidation curves, $X(t)$, measured at various experimental conditions; and (2) the physical justification of some of its key assumptions.

The authors indicate that only four parameters were left for the fitting procedure:[6,7] the oxidation rate constants of Si interstitials, κ_1 and κ_2 [Eq. (10)]; the emission rate constant, v [Eq. (4)]; and the oxidant diffusivity, D_O [Eq. (5)]. As we have shown in the Appendix (Fig. 7), the reaction rate constant at the interface, k_0, has a negligible influence for thick oxides but is relevant in the thin oxide regime. So, five parameters have been left free for the fitting. We consider that it constitutes a large number of parameters that render the model flexible enough to fit the experimental curves. Consequently, one should not be surprised by the good fitting to Series 1 of Si(111) dry oxidation curves at 1 atm and to Series 2 of curves for $P_{O_2} > 1$ atm.[6,7] The same consideration applies to Series 4 of wet oxidation curves.[7] At this stage, and similar to what has been said for many other kinetic models,[20] good fit to experiment cannot be taken as proof of model correctness. A more stringent test is the ability of the model to predict the results of other experiments without free modification of the parameters. Such an exercise has been partially done by Uematsu et al. with Series 3 of the Si(111) oxidation curves. In this case, v was the only free parameter and the result was satisfactory.[9] In this context, we consider that the additional tests introduced by us in the present work are appropriate. The results are not satisfactory and raise serious doubts about the correctness of the model. Perhaps, in view of the flexibility of the model, one could reach better agreement with experiment with another set of

parameters. However, we feel that the boundary condition of zero flux at the free surface, unavoidable if the diffusing species are Si atoms, constitutes a serious barrier to getting reasonable agreement with the annealing experiments of Ajuria et al.[12]

Concerning the physical justification for the model equations, in addition to the comments already addressed to the oxidation kinetics of Si interstitials [Eq. (10)], we want to comment on the effect of Si interstitials on the oxidation rate constant at the interface, k [Eq. (6)]. It is not clear why an accumulation of Si interstitials at the interface should reduce the oxidation rate between two other species (Si atoms in the silicon crystal and the oxygen molecules). Let us accept that this is an effect that could be elucidated in the future and simply focus our attention on the assumption behind the functional form of Eq. (6). It is explicitly assumed that C_{Si}^I cannot exceed its solubility in SiO_2, C_{Si}^0. In fact, C_{Si}^0 is the concentration of Si interstitials when SiO_2 is in thermodynamic equilibrium with the Si substrate[21] in an inert atmosphere. The definition of C_{Si}^0 has no relationship with oxidation. So, there is no reason why C_{Si}^0 should enter into the equation governing the oxidation rate. Furthermore, as it occurs for the solubility of any species, C_{Si}^0 can be surpassed (supersaturation)[21] in out-of-equilibrium conditions such as those met during oxidation. We consider that if there exists any reduction of k due to the Si interstitials, it cannot be described through its solubility in the oxide.

V. CONCLUSIONS

In the present paper we have tested the interfacial emission model of silicon oxidation with two series of experiments: (1) oxidation at subatmospheric oxygen pressure and (2) reoxidation experiments after annealing in inert atmosphere. Although the model qualitatively explains the experimental dependencies (sublinear dependence on oxygen pressure and faster oxidation rate after annealing), it fails to predict them quantitatively. In particular, the model predicts that DG kinetics should be recovered for any thickness when oxygen pressure is below 0.1 atm. This trend has never been observed. In addition, several key assumptions leading to the model equations are shown to be poorly justified. Despite the expectations we had for the interfacial emission model, we are led to conclude that the large discrepancies detected by means of our tests make it difficult to trust the model's correctness.

ACKNOWLEDGMENT

APPENDIX: INTEGRATION OF THE MODEL EQUATIONS

The transport equations of the interfacial emission model are

$$\frac{\partial C_{Si}}{\partial t} = D_{Si}\frac{\partial^2 C_{Si}}{\partial x^2} - R_1 - R_2, \tag{A1}$$

$$\frac{\partial C_O}{\partial t} = D_O\frac{\partial^2 C_O}{\partial x^2} - R_1 - R_2 - R_3, \tag{A2}$$

where R_i are reaction terms, C_i are concentrations of Si interstitials and oxidant molecules, and D_i are their diffusivities. In oxidizing conditions, the boundary conditions at the interface are:

$$D_{Si}\left.\frac{\partial C_{Si}}{\partial x}\right|_{x=0} = kvC_O^I \quad \text{and} \quad D_O\left.\frac{\partial C_O}{\partial x}\right|_{x=0} = kC_O^I, \tag{A3}$$

where the reaction rate constant, k, depends on the Si concentration at the interface through the interstitial solubility, C_{Si}^0:

$$k = k_0(1 - C_{Si}^I/C_{Si}^0). \tag{A4}$$

As already noted in the body of this paper,

$$R_2 = \kappa_1 C_O C_{Si} + \kappa_2 (C_O)^2 C_{Si}. \tag{A5}$$

Finally, according to Uematsu et al.,[7] the reaction terms R_1 and R_3 can be substituted by a boundary condition at the free surface for the Si interstitials and for the oxidant molecules, respectively:

$$C_{Si}^S = 0 \quad \text{and} \quad C_O^S = C_O^*. \tag{A6}$$

Once the equations are solved and C_O^I is known, the oxidation rate is calculated:

$$N_0\frac{dX}{dt} = kC_O^I, \tag{A7}$$

where N_0 is the number of SiO_2 molecules per unit volume of the oxide.

We have calculated the solutions of the above equations with the same values of model parameters used by Uematsu et al. and detailed in Ref. 7 except for k_0, whose value was not detailed. In Fig. 7, we see that variations of k_0 have an effect on thin oxides. The values of k_0 detailed in the inset of Fig. 7 have been obtained by fitting the experimental points of Si(100) dry oxidation curves at 1 atm. We should remark that, in view of (1) D_O being much greater than D_{Si} and (2) the number of emitted Si interstitials being below 1 or 2% of the arriving oxidant molecules, the model equations can be further simplified. We have verified for all calculations that the oxidant profile changes almost instantaneously as compared to the slower variations of the Si profile. Consequently, the oxidant profile is in steady-state conditions, i.e., instead of solving Eq. (A2) one can take the value

$$C_O(x) = C_O^I + \frac{C_O^* - C_O^I}{X}x. \tag{A8}$$

No significant difference has been found between the exact solution and that obtained by using this approximation.

Finally, an implicit method[27] has been used to solve the partial differential equations numerically. The criterion $\Delta t \leq \Delta x^2/D$, where Δt and Δx are the time and space steps, respectively, has been imposed to ensure convergence and stability. Since the implicit system does not have an analyti-

cal solution, each integration step is solved by an iterative procedure with an accuracy (allowed relative error) of 10^{-14}.

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