

## Comment on “Dynamics of thermal growth of silicon oxide films on Si”

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The paper commented on here [R. M. C. de Almeida, S. Gonçalves, I. J. R. Baumvol, and F. C. Stedile, Phys. Rev. B **61**, 12992 (2000)] claims that the Deal and Grove model of oxidation is unable to describe the kinetics in the thin oxide regime due to two main simplifications: (a) the steady-state assumption and (b) the abrupt Si/SiO<sub>2</sub> interface assumption. Although reasonably good fits are obtained without these simplifications, it will be shown that the values of the kinetic parameters are not reliable and that the solutions given for different partial pressures are erroneous. Finally, it will be shown that the correct solution of their model is unable to predict the oxidation rate enhancement observed in the thin oxide regime and that the predicted width of the interface compatible with the Deal and Grove rate constants is too large.

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### I. INTRODUCTION

Without any doubt the linear-parabolic law derived by Deal and Grove in 1965 (Ref. 1) (DG) to describe the oxidation kinetics of silicon represents a milestone in the field and has established the basis for the study of this important technological process until today. It is usually written in the form

$$\chi^2 + A\chi = B(t - t_0), \quad (1)$$

where  $\chi$  is the oxide thickness,  $t$  is the oxidation time,  $B$  is the so-called parabolic rate constant,  $B/A$  is the linear rate constant, and  $t_0$  accounts for any initial oxide layer. In their original paper,<sup>1</sup> DG already noted that for oxide films thin enough ( $\leq 20$  nm), their law did not work in dry oxidation conditions. The enhanced kinetics in this so-called “thin oxide regime” has been the subject of immense experimental and theoretical research. The paper by Almeida *et al.*<sup>2</sup> (AGB) represents a recent attempt to fit the experimental kinetic curves [ $\chi(t)$ ] under reasonable assumptions. According to their own authors,<sup>2</sup> the paper improves on the DG model in two aspects: (a) their equations are solved in unsteady conditions and (b) the reaction between Si and the diffusing O<sub>2</sub> molecules takes place within the volume of a diffuse interface of finite thickness. They justify this particular model of interface reaction from experimental and theoretical evidence of a reactive layer (Refs. 21–29 in the AGB paper<sup>2</sup>).

The AGB model has two adjustable kinetic parameters: the diffusion coefficient of O<sub>2</sub> in SiO<sub>2</sub>  $D$  and the reaction rate constant  $k$ , which accounts for the reaction that takes place at the diffuse interface. The equations resulting from the model are

$$\frac{\partial \rho_{\text{Si}}}{\partial t} = -k\rho_{\text{O}_2}\rho_{\text{Si}} \quad (2a)$$

and

$$\frac{\partial \rho_{\text{O}_2}}{\partial t} = D \frac{\partial^2 \rho_{\text{O}_2}}{\partial x^2} - k\rho_{\text{O}_2}\rho_{\text{Si}}, \quad (2b)$$

where  $\rho_{\text{O}_2}$  and  $\rho_{\text{Si}}$  are the concentration of O<sub>2</sub> and of unreacted silicon atoms, respectively, normalized to the concentration of Si atoms in *c*-Si.<sup>2</sup> In addition, a boundary condition

is set near the free surface (at  $x=0$ ). The O<sub>2</sub> concentration there is assumed to be proportional to its external partial pressure  $P_{\text{O}_2}$  according to Henry’s law

$$p_0[\equiv \rho_{\text{O}_2}(x=0)] = KP_{\text{O}_2}. \quad (3)$$

From the analysis of their equations, AGB conclude that any oxidation curve merges into a universal curve when the oxide thickness and oxidation time are converted into adimensional variables

$$\tau = t(kp_0) \text{ and } \chi_{\text{th}} = \chi\sqrt{k/D}. \quad (4)$$

From a formal point of view, this is a very elegant solution.

The AGB model is tested against an impressive series of oxidation experiments performed at temperatures ranging from 800 to 1050 °C and  $P_{\text{O}_2}$  in the 0.01–1 atm range (Figs. 4 and 5 of Ref. 2). In view of this success, the paper has been cited in a review article on ultrathin oxide films<sup>3</sup> where it is considered an appropriate description of kinetic data “including the very initial regime” (<4 nm) and it has been considered one of a few successful attempts to fit the experimental pressure dependence in the thin oxide regime.<sup>4</sup> Furthermore, it has been cited as constituting experimental proof of reduced oxygen diffusivity near the Si/SiO<sub>2</sub> interface.<sup>5</sup>

In this Comment, we will show that the agreement between the model and experiment is illusory. In general, the kinetic parameters obtained from the fitting are not reliable enough and, for the  $P_{\text{O}_2}$  series, the calculations are based on an erroneous scaling property. Even when this error is corrected, the AGB model fails to predict the oxidation rate in the thin layer regime, and the interface width compatible with the DG rate constants is thick in excess.

### II. THE STEADY-STATE ASSUMPTION

The DG law [Eq. (1)] was derived under the assumption that the oxidation rate was slow enough to allow a steady-state concentration profile of the oxygen molecules inside the oxide. A simple criterion<sup>1</sup> indicates that, for pure parabolic kinetics [ $\chi^2 = B(t - t_0)$ ], negligible deviations from the steady-state solution are expected. The relative error for  $P_{\text{O}_2} = 1$  atm is given approximately by

$$\psi = C^*/N_1 \approx 10^{-6}, \quad (5)$$

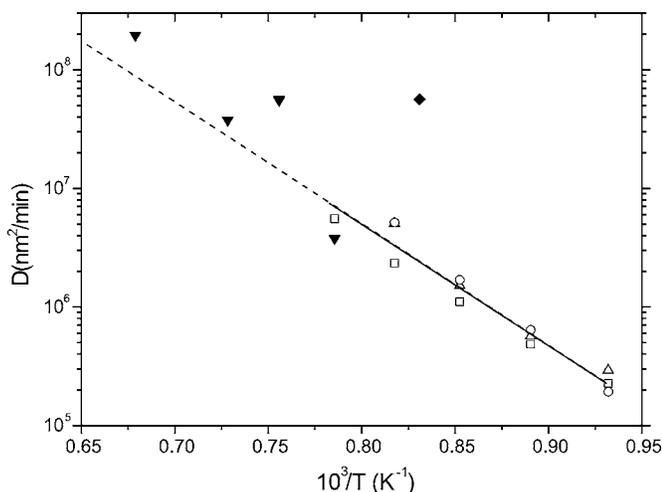


FIG. 1. Arrhenius plot of the diffusivity values obtained from all the experimental curves fitted by AGB (Ref. 2). Only the empty symbols were reported in that paper.

where  $C^* = 5.5 \times 10^{16} \text{ cm}^{-3}$  is the  $\text{O}_2$  concentration in  $\text{SiO}_2$  (Ref. 6) at 1 atm, and  $N_1 = 2.25 \times 10^{22} \text{ cm}^{-3}$  is the number of  $\text{O}_2$  molecules incorporated per unit volume of the oxide.<sup>7</sup> For very thin oxides, the oxidation rate increases considerably and one may wonder if the steady-state approximation is still valid. AGB consider that this is a serious limitation of the DG solution [Eq. (1)] and solve their own equations in an unsteady state (this point of view is also shared by the authors of the review already cited<sup>3</sup>).

We want to stress here that, within the hypothesis of a sharp Si/SiO<sub>2</sub> interface, the steady-state assumption is correct down to very thin oxides. This point has been nicely demonstrated by the quantitative analysis carried out by Mhetar *et al.*<sup>8</sup> Nonsteady effects lead to a first order correction to the thickness given by the DG law lower than  $1/6\psi$  [ $\psi$  of Eq. (5)]. This means that the nonsteady solution given by AGB (Ref. 2) is a requirement of their particular model of diffuse interface because diffusion of  $\text{O}_2$  and reaction coincide in this region of the oxide. However, for all practical conditions of any reported experiment, nonsteady corrections to the DG model are superfluous. In other words, the deviations observed between experiment and the DG law in the thin oxide regime are not due to the steady-state assumption.

### III. RELIABILITY OF THE KINETIC PARAMETERS

Here we will show that, although the calculated  $\chi(t)$  curves fit reasonably well with the experimental points, the values of  $D$  and  $k$  obtained from the fitting are not reliable. Let us first analyze the values of the diffusion coefficient. They are plotted in Fig. 1. Different symbols are used depending on the source of the experimental curves. Even if the point of Rochet *et al.*<sup>9</sup> is omitted (diamond), the dispersion of the remaining points is high. The situation could be worse still if the values of the reaction rate constant  $k$  are considered. Unexpected variations of  $k$  over several orders of magnitude are obtained (Table I of AGB). The authors justify this chaotic behaviour of the fitted values by saying that “... the

kinetic curves are very insensitive to variations in  $k$ . This is caused by the  $k$  dependence of natural units and the scaling properties of the kinetics curve.” However, this is not convincing because, in the limit of oxides much thicker than the interface, the AGB model reduces to the DG law (see Sec. III on Ref. 2), i.e.,

$$\chi^2 + \frac{2D\chi}{k\varepsilon} = 2Dp_0(t - t_0), \quad (6)$$

where  $\varepsilon$  is the effective interface thickness which is defined in the AGB paper (its Sec. III) as

$$\varepsilon \equiv \frac{\int_0^\infty \rho_{\text{O}_2} \rho_{\text{Si}} dx}{\rho_{\text{O}_2}(i)}, \quad (7)$$

where  $\rho_{\text{O}_2}(i)$  is the oxygen concentration at the boundary of the diffuse interface. Within these limits, the kinetics has the same scaling properties and it is sensible to variations of  $k$  through the linear rate constant. We think therefore that if a coherent trend of the values of  $k$  had been sought by the authors, then the resulting dispersion of the  $D$  values would have been even higher. Anyway, we agree with AGB that a significant source of this scattering can be the lack of fine control of the experimental conditions in the thin layer regime (compare, for instance, Figs. 5(b) and 4(c) of Ref. 2).

An additional test for the reliability of the  $(D, k)$  values can be obtained from the essential hypothesis of the AGB model: the thickness of the diffuse interface  $\varepsilon_{10}$ . By  $\varepsilon_{10}$  we mean the thickness of the region where  $0.1 < \rho_{\text{Si}} < 0.9$ . Although  $\varepsilon_{10}$  is proportional to  $\varepsilon$  defined in Eq. (7), they are not identical. For a reference partial pressure of  $p_0 = 1$ , one can extract this value from the profile of the Si concentration detailed in their Fig. 2. Its adimensional value is  $\Delta u_{10} \approx 3.4$ , and the corresponding real value is  $\varepsilon_{10} = 3.4\sqrt{D/k}$  [Eq. (4)]. Now,  $\Delta u_{10}$  is not very sensitive to the value of the partial pressure, so  $\varepsilon_{10}$  can be obtained from the  $D$  and  $k$  values of their Table I. For instance, at 800 °C one obtains  $\varepsilon_{10} = 28$  and 0.6 nm, for a partial pressure of 1 and 0.1 atm, respectively. This enormous variation with pressure is completely unphysical (at 950 °C there is almost no variation). Furthermore,  $\varepsilon_{10} = 28$  nm means that for any time in this particular experiment (800 °C and 1 atm) the reaction takes place in the whole oxide thickness. This clarifies the fact that the kinetics cannot be independent of the  $k$  values.

Before leaving this section, we can conclude that the reasonable agreement between calculated and experimental kinetics is obtained with unreasonable values of the fitting parameters relevant to the AGB’s model ( $D$  and  $k$ ) and to the flexibility afforded by two free parameters not related with the model (the initial time and initial thickness) whose values have not been reported (according to the original paper of Massoud *et al.*,<sup>10</sup> their experiments began with a native oxide layer in the 7–24 Å range). As a consequence, up to this point, it is impossible to extract any reliable value of the key parameter of the AGB model (i.e., the thickness of the interface).

#### IV. DEPENDENCE ON THE OXYGEN PARTIAL PRESSURE

According to AGB, the time axis of the oxidation curves scales linearly with the oxygen partial pressure  $P_{O_2}$ . This property has been used for the calculation of all curves, because the fitting procedure described by the authors involves the calculation of one single universal curve for  $p_0=1$  and then scaling the time axis according to the particular values of  $P_{O_2}$ . It is well established that the parabolic rate constant is proportional to  $P_{O_2}^1$ . However, a sublinear dependence has always been found for the linear rate constant<sup>11–14</sup> and for the thin oxide regime.<sup>10,15</sup> It is thus very surprising that reasonably good fits are obtained for the series of curves corresponding to several of these references.<sup>10,13,15</sup> In particular, it is especially striking that the fits to the curves of Ref. 15 are considered correct [Fig. 5(a) of AGB<sup>2</sup>], because in the original figure of Ganem *et al.*<sup>15</sup> it is clearly stated that the oxidation rate is not proportional to the pressure (0.19 and 0.31 A/s for 40 and 80 mbar, respectively). Anyway, the curves calculated by AGB are not correct because the solution to the model's equations do not scale with the oxygen partial pressure. A simple inspection of the AGB equations [Eqs. (2)] reveals that if  $\rho_{O_2}^{(1)}(x,t)$  and  $\rho_{Si}^{(1)}(x,t)$  are the solutions for  $p_0=1$ , then the scaled profiles

$$\rho_{O_2}^{(2)}(x,t) = \alpha \rho_{O_2}^{(1)}(x, \alpha t) \text{ and } \rho_{Si}^{(2)}(x,t) = \rho_{Si}^{(1)}(x, \alpha t) \quad (8)$$

which would correspond to  $p_0=\alpha$ , are not. Substitution of  $\rho_i^{(2)}$  in Eq. (2b) reveals that the constant  $\alpha$  does not disappear from the resulting equation after  $t$  is rescaled to  $\alpha t$ .

In order to find the correct solution, we have solved these equations for several values of  $p_0$ . We have used an implicit method,<sup>16</sup> which is a customary approach for diffusive equations. The criterion  $\Delta t \leq (\Delta x)^2/D$  ( $\Delta t$  and  $\Delta x$  are the time and space steps, respectively) has been imposed to ensure convergence and stability. Since the implicit system has not an analytical solution, each integration step is solved by an iterative procedure with accuracy (allowed relative error) of  $10^{-5}$ . The space steps of the numerical results given in Fig. 2 were 0.05 and 0.14 for  $p_0=1$  and  $2 \times 10^{-6}$ , respectively. The differences with respect to the results obtained with a step three times smaller were negligible. The curve A ( $p_0=1$ ) is the AGB “universal” curve whereas the curve B ( $p_0=2 \times 10^{-6}$ ) corresponds to an oxygen partial pressure of around 1 atm. For an intermediate value of  $p_0=10^{-3}$ , the curve virtually coincides with that of  $p_0=2 \times 10^{-6}$ . In spite of the fact that Eq. (2) does not scale with  $p_0$ , this coincidence means that when the actual experimental values of  $p_0$  are approached, the oxidation rate is proportional to  $p_0$ . Consequently, the contradiction with the experimental sublinear dependence on  $p_0$ , commented above, remains.

Beyond the quantitative differences between curves A and B, a qualitative difference is revealed when the inverse growth rate is plotted instead (inset of Fig. 2). Within the limit of oxides thick enough, one would expect to find the DG law which, after derivation of Eq. (6), can be written in terms of the inverse growth rate as

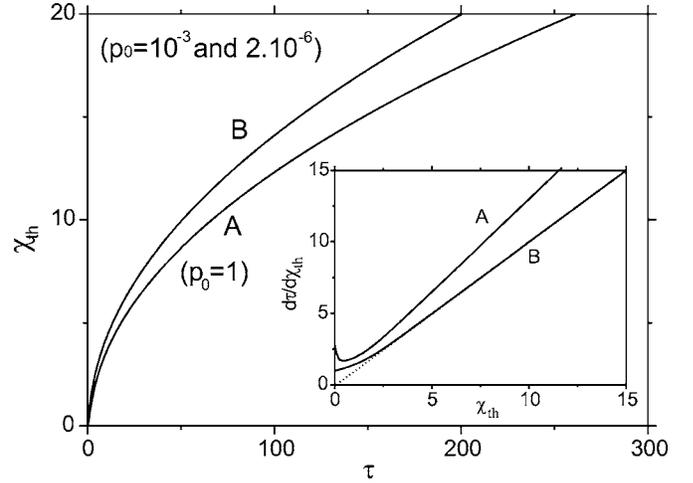


FIG. 2. Kinetic curves obtained theoretically for different values of  $p_0$ . The curves for  $p_0=10^{-3}$  and  $2 \times 10^{-6}$  are indistinguishable (curve B). Inset: inverse growth rate vs oxide thickness. The dashed line is the DG law (slope=1). Note that for thin oxides the predicted oxidation rate is slower than expected.

$$\frac{d\tau}{d\chi_{th}} = \chi_{th} + \frac{1}{\Delta u}, \quad (9)$$

where all magnitudes are normalized to the kinetic parameters and to  $p_0$ . From the inset of Fig. 2, we realize that the DG law (slope=1) is only reached for realistic partial pressures. We think that for the unrealistic value of  $p_0=1$  ( $P_{O_2} \approx 10^6$  atm) this limit is not attained because the parameter  $\psi$  in Eq. (5) approaches unity and, consequently, the steady-state assumption is not valid. This explanation agrees with the fact that for  $p_0=1$ , the  $\rho_{O_2}$  concentration profile does not have a constant slope (Fig. 3).

#### V. VALIDATION OF THE AGB MODEL

Despite the fact that the AGB model is proposed for explaining the observed deviations in the thin oxide regime, it does not. At the initial stages of oxidation, experiments tell us that the oxidation rate is higher than that predicted by the DG law.<sup>1,10</sup> However, the prediction of the AGB model (inset of Fig. 2) is just the opposite.

Finally, we will use our numerical solution of the AGB equations for calculating which would be the thickness of the diffuse interface  $\varepsilon_{10}$  in the case where the AGB model were valid. This calculation will be done in the DG limit because the oxidation kinetics is much better characterized than in the thin layer regime (Sec. III). The DG linear and parabolic rate constants can be expressed in terms of the AGB kinetic parameters through

$$B/A = \Delta u \sqrt{kD} p_0 \text{ and } B = 2Dp_0. \quad (10)$$

$\Delta u$  can be calculated from the definition Eq. (7) (adapted to adimensional parameters) and the  $\rho_i$  profiles corresponding to  $p_0=2 \times 10^{-6}$  (plotted in Fig. 3). For this oxygen partial pressure  $\Delta u=0.65$ . Now, Eqs. (10) can be solved for  $D$  and  $k$ . If we take the values of the linear and parabolic rate con-

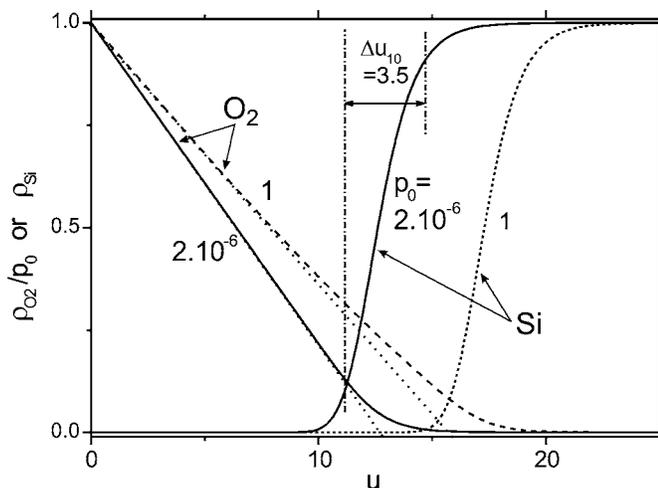


FIG. 3. Concentration profiles calculated for  $p_0=1$  and  $2 \times 10^{-6}$  (i.e.,  $P_{O_2} \approx 0.5 \times 10^6$  and 1 atm, respectively). The thickness of the interface is taken from  $\rho_{Si}=0.1-0.9$ . Note that, outside the interface, the  $\rho_{O_2}$  profile is not a straight line for  $p_0=1$ .

starts from DG,<sup>1</sup> then  $k$  and  $D$  can be obtained for thick oxides. These values allow, finally, to calculate  $\epsilon_{10}(=\Delta u_{10}/\sqrt{k/D})$  provided that the adimensional thickness  $\Delta u_{10}$  is known. It can be extracted from the  $\rho_{Si}$  profile of Fig. 3:  $\Delta u_{10}=3.5$ . The values of  $\epsilon_{10}$  thus obtained are given in Table I. They are enormous (from 50 to 400 nm) in clear contradiction with the experimental determination of reactive layer thicknesses<sup>17</sup> lower than 10 nm. In addition, in the AGB model, deviations from the DG model are expected for oxide thicknesses of the order of  $\epsilon_{10}$  (inset of Fig. 2). This would mean that the thin oxide regime would extend up to several hundreds of nm whereas, from experiment, we know that this region is one order of magnitude lower.<sup>1</sup>

In summary, the analysis of the AGB kinetic equations [Eqs. (2)] leads us to conclude that the corresponding oxidation model is unable to describe two important well established properties of the oxidation kinetics in the thin oxide regime: (a) the enhanced oxidation rate and (b) the sublinear

TABLE I. Thickness of the interface  $\epsilon_{10}$  if the linear ( $B/A$ ) and parabolic ( $B$ ) rate constants are interpreted according to the AGB model.

$T$ (°C)	$B$ ( $\mu\text{m}^2/\text{h}$ )	$B/A$ ( $\mu\text{m}/\text{h}$ )	$\epsilon$ (nm)
1200	0.045	1.12	50
1100	0.027	0.30	100
1000	0.012	0.071	190
920	0.0049	0.021	270
800	0.0011	0.0030	420

dependence on the oxygen partial pressure. In addition, in the limit of oxides thick enough (DG limit), (c) interpretation of the standard values of the linear and parabolic rate constants leads to unrealistic thick values of the reactive layer.

All of these contradictions clearly invalidate the description of the diffuse interface proposed in the AGB model. This conclusion is independent of the success of the model to fit a broad set of experimental curves, which is partly due to the freedom given to the set of constants used in the fitting procedure (Sec. III). In fact, after more than 30 years of kinetic models for silicon oxidation, one is led to conclude that good agreement with the experimental  $\chi(t)$  curves is not a definitive test for the models. We agree with the critical review of kinetic models written by Blanc<sup>18</sup> when he states that "... with the types of data now available, the parameters of models proposed are very badly determined in a statistical sense (even though they may provide excellent fits) and that is not possible to distinguish between distinct models by the quality of fit." In our modest opinion, alternative models<sup>19</sup> developed after the publication of the AGB paper are much more promising.

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