

Reply to “Comment on ‘Dynamics of thermal growth of silicon oxide films on Si’ ”

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In a Comment on “Dynamics of thermal growth of silicon oxide films on Si” [Phys. Rev. B **61**, 12992 (2000)], Roura and Farjas argue that the values of the kinetics parameters obtained from the model proposed in that paper are not reliable and that the solutions given for different partial pressures are erroneous. Moreover, that the solution from such model is unable to predict the oxidation rate experimentally observed in the thin oxide regime neither the width of the interface. Resorting to experimental results, and old and new results obtained from our model, we show in this Reply that none of the criticisms are solid and that the results of the original paper represent indeed an improvement over the Deal-Grove model. Finally, motivated by one of the issues raised by Roura and Farjas, we present here new fittings of experimental data using our model together with experimental estimates for the interface width between the oxide layer and the silicon substrate. This turned a two parameter fitting problem into a much simpler one parameter procedure.

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I. INTRODUCTION

In a previous paper¹ we presented a nonlinear reaction diffusion equation to describe the profiles of nonreacted silicon, silicon oxide, and diffusing oxygen in a silicon wafer exposed to an oxidant atmosphere at high temperature, whose asymptotic solution is equivalent to the Deal and Grove model for silicon oxide growth on silicon.² In that paper, we rewrote the equations using natural units, namely $\sqrt{D/k}$ for length and $1/k$ for time, where D is the diffusion coefficient of oxygen in SiO_2 , and k is the rate controlling the reaction $\text{O}_2 + \text{Si} \rightarrow \text{SiO}_2$, assumed to be a one step reaction. The model is hence left with only one free parameter, associated to the oxygen pressure at the surface of the sample. The same happens in the Deal and Grove model, when the grown oxide layer thickness $\chi(t)$ is shown to present a further scaling with pressure, such that by doubling the pressure, the required time to obtain the same amount of oxide is halved. The result is a universal curve for $\chi(t)$, whose fit to experimental data would, in principle, yield physical parameters as D and k . We successfully fitted several experimental curves, measured by different authors and obtained values for D and k in different temperatures and conditions. Among the results of that paper, we clearly stated that although the fitting procedure shed values of D vs temperature, yielding a sensible Arrhenius plot, the scattering in the obtained values of k rendered these estimates not reliable.

In the Comment³ Roura and Farjas (RF) raise a series of criticisms to the results of our paper. For example, concerning the fitted values of the kinetics parameters, specifically the reaction rate constant k , RF are right in saying that they “are not reliable.” This, in turn, yields consequences mainly for the prediction of the interface width. However, as we said before, the uncertainty in the determination of the reaction rate constant has been clearly stated in the original paper. Nevertheless, the implicit suggestion in the RF Comment of using the experimental interface width as an input parameter to feed our model greatly enhances the accuracy of the method. We will show this in Sec. IV.

Other issues in the Comment are related to the necessity of a nonsteady state solution, the correction of the numeri-

cally obtained solutions, and the dependence of $\chi(t)$ on the oxygen partial pressure and the consequent time renormalization for different pressures. In what follows we discuss separately each one of these issues and demonstrate that they either originate in a nonrealistic parameter range or in a poor numerical solution to the model equations, probably due to too large time or space steps. We approach then the kinetics parameters issue in the last section.

II. THE STEADY STATE ASSUMPTION

We agree with RF in stressing that “... within the hypothesis of a sharp Si/SiO₂ interface, the steady-state assumption is correct down to very thin oxides.” But this is almost obvious: in such assumption there is not a length scale to compare with the oxide thickness and hence both Deal and Grove criteria² and Mhetar results⁴ apply to all ranges of oxide thickness. However, in all experimentally investigated cases so far, there is always a finite interface width, which influences the dynamics of the system. Then, the assumption of sharp interfaces applies only for oxide layers much thicker than the interface width. In fact, the Deal and Grove model is an asymptotic thick oxide solution to many nonlinear reaction diffusion equations, which do not present analytical solutions. Our model is the simplest case we could think of, since it considers constant diffusion and reaction coefficients, and the transient leading to a Deal and Grove-like solution is compatible with experimental data. As typical interfaces widths are between 0.5 and 3 nm,⁵⁻⁷ we expect that for oxide thickness larger than 7 to 10 times the interface width, the sharp interface assumption would apply. This roughly corresponds to the onset of validity of Deal and Grove fitting, presenting a further argument to validate the model.

Therefore, although the Deal and Grove criteria and Mhetar’s results regarding the steady state assumption are flawless, they just do not apply to the initial stages of oxide growth when the interface width is non-negligible compared to the oxide thickness.

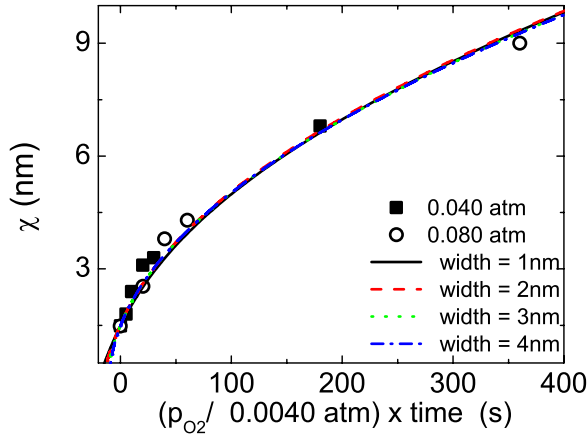


FIG. 1. (Color online) Symbols: growth kinetics by Ganem *et al.* (Ref. 8) with rescaled time using O_2 partial pressure. Lines: fits using different values for the interface width (see text).

III. DEPENDENCE ON THE OXYGEN PARTIAL PRESSURE

RF do not agree with the scaling presented by both experimental and theoretical kinetics curves $\chi(t)$ with partial O_2 pressure.³ We start by presenting in Fig. 1 a modified version of Fig. 5(a) of Ref. 1, where we plot the experimental data by Ganem *et al.*⁸ as a function of rescaled times using O_2 partial pressure: a scaled kinetics curve is clearly suggested by the experimental data *per se*. RF objection to this scaling is based on the oxidation rate obtained by Ganem *et al.*,⁸ within the assumption of the Deal and Grove model. As there are several experimental points in the region of very thin oxide layers, where one expects divergences from sharp interfaces solutions, this discrepancy is not surprising.

As far as the theory is concerned, Eqs. (16) of Ref. 1 clearly state that multiplying O_2 partial pressure by a constant value α and simultaneously rescaling time will change the diffusive oxygen profile while leaving untouched nonreacted silicon profile and the oxide thickness χ . These equations are

$$\begin{aligned} \phi_{O_2}^{(2)}(u, \tau) &= \alpha \phi_{O_2}^{(1)}(u, \alpha\tau), \\ \phi_{Si}^{(2)}(u, \tau) &= \phi_{Si}^{(1)}(u, \alpha\tau) \\ \chi^{(2)}(\tau) &= \chi^{(1)}(\alpha\tau), \end{aligned} \quad (1)$$

where $\phi_{O_2}^{(2)}$ and $\phi_{Si}^{(2)}$ are normalized concentration profiles of, respectively, diffusive O_2 and nonreacted silicon in the sample. u and τ are nondimensional variables giving, respectively, length in units of $\sqrt{D/k}$ and time in units of $1/k$. However, this scaling cannot be proved analytically. It does not apply to all ranges of oxidation pressures, indeed. Nonetheless, the pressure scaling works in a very wide range of oxidation pressures, that contemplates by far any experimental setup. In fact the implicit approximation is that in the interface region, where reaction is taking place, the amount of reactive oxygen atoms is much smaller than that of reactive silicon atoms, allowing the metaphor of reactive oxygen atoms dispersed in an infinite sea of reactive silicon atoms.

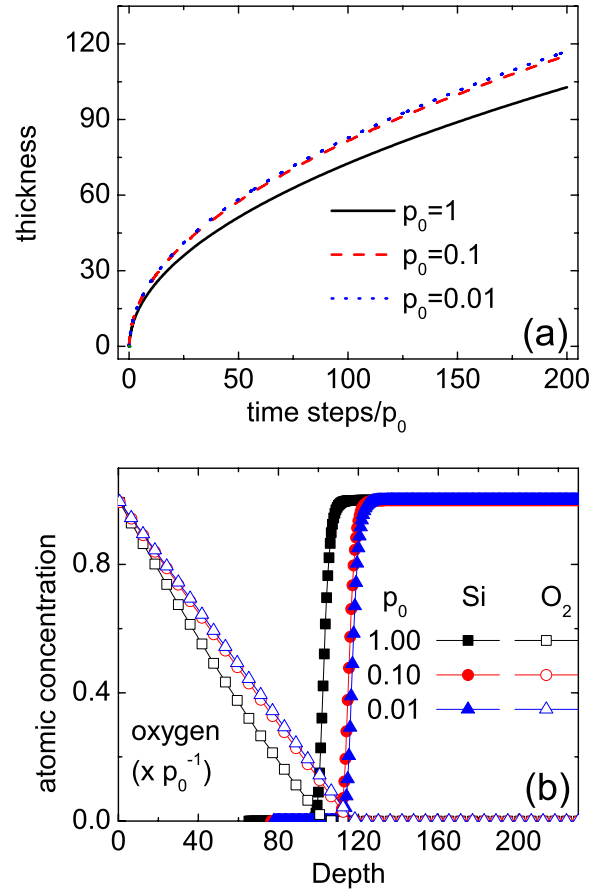


FIG. 2. (Color online) (a) Growth kinetics and (b) O_2 and Si profiles at $t=200/p_0$ time steps for different values of p_0 . In (b), O_2 profiles have been multiplied by $1/p_0$. D and k are the same for all numerical solutions, and all quantities are given in natural units.

In this approximation, doubling the amount of oxygen atoms (i.e., the oxidation pressure at the surface) is equivalent to doubling the reaction rate, yielding the pressure scaling, as we will show numerically below. Figure 2 shows numerical solutions for the following model equations, for different values of pressure p_0 :

$$\begin{aligned} \frac{\partial \phi_{O_2}}{\partial \tau} &= \frac{\partial^2 \phi_{O_2}}{\partial u^2} - \phi_{O_2} \phi_{Si}, \\ \frac{\partial \phi_{Si}}{\partial \tau} &= -\phi_{O_2} \phi_{Si} \end{aligned} \quad (2)$$

together with initial and boundary conditions given by

$$\phi_{Si}(x, 0) = 1, \quad \forall x \geq 0$$

$$\phi_{O_2}(0, t) = \frac{c_{gas} f_v}{c_{Si}^{bulk}} = p_0, \quad \forall t \geq 0, \quad (3)$$

where c_{gas} is the O_2 concentration in the gas phase and f_v is the ratio between the accessible free volume for O_2 in the silica network and the unit volume of the solid.⁹ It is clear that for $p_0 < 0.1$ pressure scaling is already valid. p_0 is a nondimensional quantity and using Eq. (3) we can estimate the pressure scaling validity range:

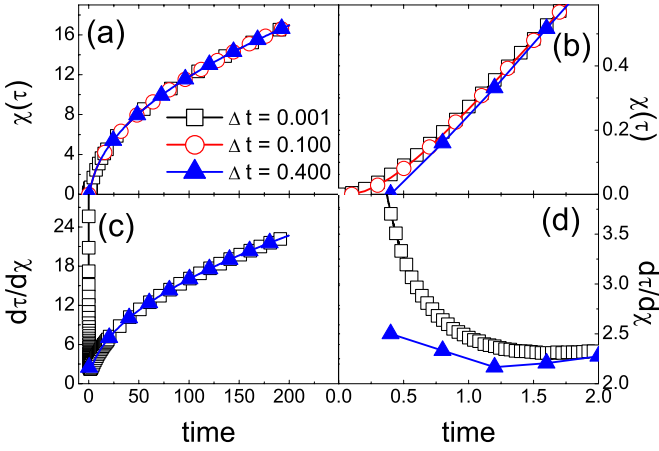


FIG. 3. (Color online) Numerical solutions $\chi(\tau)$ and the reciprocal of its time derivative obtained using finite time steps $\Delta\tau$. For all curves $p_0=1$. All quantities are given in natural units. Zoomed plots in the right column.

$$P_{O_2} < 0.1 \frac{1}{f_v} \frac{RTd_{Si}}{\mu_{Si}}, \quad (4)$$

where P_{O_2} is the partial O_2 pressure, R is the universal gas constant, d_{Si} is the bulk silicon density (2.33 g/cm^3), T is temperature, and μ_{Si} is silicon molar mass (28.09 g/mol). Assuming $T=1200 \text{ K}$ and $f_v=0.01$, we estimate that the requirement for the pressure scaling to hold is equivalent to assuming that $P_{O_2} < 79\,300 \text{ atm}$ which, to say the least, is a comfortable O_2 pressure range for experimental setups.

One more comment on the numerical solutions. They always involve finite time and space iterations, which should be small enough in order to yield good approximations to a continuous problem. For pressures differing by three orders of magnitude, care should be taken in defining the steps sizes, especially when nonlinear equations are considered. Figure 3 presents different numerical solutions for the scaled problem given in Eqs. (2) considering $p_0=1$ with different sizes for time steps $\Delta\tau$. The convergence to a unique solution is clear as $\Delta\tau$ decreases. Figure 3 also shows the reciprocal of the time derivative of the kinetics curve, $d\tau/d\chi$. As $\Delta\tau$ decreases, the $\tau \rightarrow 0$ limit of $d\tau/d\chi$ approaches infinity. In fact, this behavior is expected and can be analytically proved: at $\tau=0$, the amount of oxide formation at the sample surface in an infinitesimal time interval $d\tau$ is proportional to the product of the amount of O_2 diffusing into the sample and to the reaction probability. This yields a thickness increase $d\chi$ of order $d\tau^2$, resulting in $d\chi/d\tau=0$ at $\tau=0$. We also show the effect of different space steps Δu in numerical solutions. Figure 4 presents the plot of $d\tau/d\chi$ vs χ for different space steps and $p_0=0.1$. Again, the deviation from the continuous time solution is clear, and so is the divergence in $d\tau/d\chi$ as $\chi \rightarrow 0$.

We emphasize, however, that experimental data regarding growth kinetics of silicon oxide on silicon never present the bending upwards shown by the theoretical curves. This is so because the bending happens for very early stages, when there should be a free silicon surface exposed to an oxidizing

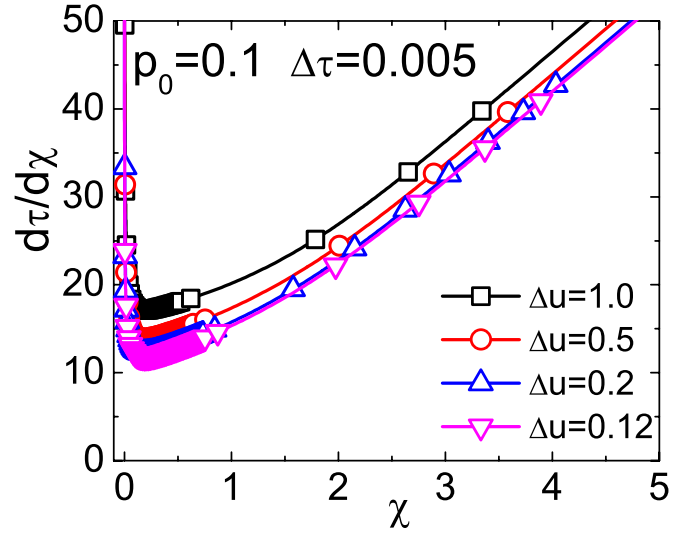


FIG. 4. (Color online) $d\tau/d\chi$ derivative vs χ obtained using finite space steps Δu . For all curves, $p_0=0.1$. All quantities are given in natural units.

atmosphere. These extremely early stages are not accessible with any reported experimental technique. Besides, we do not claim our mean field model would be valid in that regime, where fluctuations should dominate.

Summarizing, the discrepancies found by RF in their numerical solutions regarding O_2 pressure scaling in $\chi(t)$ are probably due to high (unrealistic) values of p_0 . They can also be due to numerical errors in considering too large time and/or length steps in the numerical iteration of the nonlinear model equations. Criteria for numerical integration of linear (diffusion) equations are not necessarily valid in nonlinear cases.

IV. KINETICS PARAMETERS

We finally approach the issue regarding the determination of kinetics parameters D and k from the experimental data fitting. As we have clearly stated, the values for k in Ref. 1 are not reliable and they were presented in order to reproduce the fits in diverse figures of that reference, although the obtained values for D yield a sensible Arrhenius plot. The point here is that, in the appropriate O_2 pressure range, the theoretical growth kinetics curve $\chi(t)$ obtained from our model equations can be approximated by an homogeneous function, provided time and space are continuous variables. In fact, this property yields the scaling in pressure, described by Eqs. (1). However, it also produces a sensitivity lack in the fittings, producing scattered values for the reaction rate.

Nevertheless, the implicit suggestion by RF of using the experimental interface width as an input parameter turned out to be extremely useful by reducing the number of fitting parameters from two to one, greatly enhancing the fitting accuracy, which is now performed as follows.

(1) Iterate the model equations for fixed theoretical parameters, keeping $p_0 < 0.1$, to obtain a theoretical growth kinetics in nondimensional units $\chi_{th}(\tau_{th})$.

(2) A relation between the experimental values D_{ex} and

k_{ex} is obtained by observing that the theoretical interface width stabilizes at some value w_{th} . Using the experimental value for the interface width, w_{ex} , we have

$$\sqrt{\frac{D_{ex}}{k_{ex}}} = \frac{w_{ex}}{w_{th}}. \quad (5)$$

(3) Using the experimental initial oxide thickness, χ_{ex}^0 , we can obtain the theoretical time τ_0 necessary to build an oxide layer corresponding to

$$\chi_{th}^0 \sqrt{\frac{D_{ex}}{k_{ex}}} = \chi_{ex}^0.$$

(4) From each experimental point $\chi_{ex}(t_{ex})$, it is possible to obtain the corresponding theoretical point:

$$\chi_{th} = \frac{w_{th}}{w_{ex}} \chi_{ex}(t_{ex}),$$

$$\tau_{th} - \tau_0 = k_{ex} p_0 t_{ex}. \quad (6)$$

(5) The above equations yield values for D_{ex} and k_{ex} . Average over points where $\chi_{ex} > 5$ nm, to reduce experimental errors, obtaining D_{av} and k_{av} .

(6) Build the fitting curve using $\chi_{fit} = \chi_{th} \sqrt{\frac{D_{av}}{k_{av}}}$ and $t_{fit} = \frac{(\tau_{th} - \tau_0)}{p_0 k_{av}}$.

This procedure has been used to build the fits presented in Fig. 1, for different estimated experimental interface widths. Observe that we have used experimental kinetics curves at two different oxygen pressures and, to obtain D_{av} and k_{av} , we have considered only two points (above 5 nm), besides the native oxide thickness. Even so, the very early oxidation kinetics behavior has been correctly predicted.

The model cannot discriminate between the different fitting curves, meaning that the information concerning interface width is necessary to calculate the kinetics parameters. Table I presents the values of D_{av} and k_{av} considering different interface widths. Observe the small variation in D_{av} .

V. CONCLUSIONS

The Comment by Roura and Farjas³ raised several objections to the model presented in Ref. 1. We have demonstrated here that a substantial portion of this criticism originated

TABLE I. Calculated values of the kinetics parameters obtained from the fit functions presented in Fig. 1.

Interface width (nm)	D_{av} (nm ² /min)	k_{av} (min ⁻¹)
1	7.14×10^6	8.22×10^6
2	7.20×10^6	2.84×10^6
3	7.44×10^6	0.95×10^6
4	7.56×10^6	0.54×10^6

either in a nonrealistic parameter range or in a poor numerical solution to the model equations, probably due to too large time or space steps. In particular, the divergence in $d\tau/d\chi$ as $\chi \rightarrow 0$ is an analytical result, expected for all ranges of p_0 and, in fact, may be used as a criterium to control the adequate size of time and space steps in numerical solutions.

However, the criticisms related to the nonreliability of the kinetics parameters is relevant. We used the implicit suggestion of using the experimental estimates for the interface widths between the oxide layer and the silicon substrate: this turned a two parameter fitting problem into a much simpler one parameter procedure. Nevertheless, interface widths are not strictly controlled as well as there are uncertainties⁵⁻⁷ in their determination. Therefore there is still some uncertainty in the estimate of the reaction rate.

Moreover, we want to stress that some experimental data, as, for example, the growth kinetics presented 20 years ago by Massoud and collaborators,¹⁰ show a clear deviation from constant diffusion coefficient D and/or reaction rate k , when long oxidation processes are considered. This fact may imply different phenomena, which could range from a real nonconstant parameter diffusion reaction phenomena to H₂O contamination of the oxidizing atmosphere, or some other experimental artifact.

The present procedure assumes a constant D and k process. When this is not the case, the result corresponds to average values of D and k , suitable to the used data interval. However, given that an even simpler solution as the Deal and Grove model yields a good approximation to the silicon oxide thermal growth in a wide range of oxide thickness, we think that taking D and k as constants during the growth of thin films of silicon oxide is a sensible assumption.

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