# A Simulation System for Diffusive Oxidation of Silicon: One-Dimensional Analysis

Ulrich Weinert and Ernst Rank
Siemens AG, München, Germany

Z. Naturforsch. **46a,** 955–966 (1991); received April 30, 1990

Thermal oxidation of silicon is described as a three-component thermodynamic local process involving silicon, silicon oxide, and oxygen molecules. A simplified system of model equations is used to demonstrate the evoluton of the Si–$SiO_2$ interface. For the one-dimensional case the equivalence with the model of Deal and Grove could be shown analytically. For that purpose effective interface coordinates have been introduced which establish the connection between the conventional concept of sharp interfaces and our "diffusive" interface, i.e., a transition region between pure silicon and pure silicon oxide.

## 1. Introduction

Thermal oxidation of silicon is one of the most important processing steps during the production of semiconductor devices. The historic development of the theoretical formalism for its description can be represented as a three-stage process. Based upon the fundamental work of Deal and Grove [1], which appeared as early as 1965, one-dimensional simulations of thermal oxidation process steps could be carried out with remarkable success. One of the basic ideas of the method was the concept of a sharp interface between the silicon and the oxide region. Oxide growth was supposed to occur solely along the direction of simulation. Because of these restrictions due to one-dimensionality, the physical development of the formalism was mainly on the side of reacton kinetics [2–4]; stress effects, for instance, could not be taken into account properly.

With decreasing dimensions of the semiconductor devices the latter assumption became more and more invalid; lateral oxide growth and movement had to be taken into account, e.g., for the treatment of shaped surfaces [5] or for the familiar "bird's beak". So a generalization of the Deal-Grove concept to two dimensional simulations was necessary; an excellent representation can be found in the fundamental paper of Chin et al. [6].

Now that a two-dimensional formalism had been established, a variety of physical phenomena could and had to be taken into account. The most important aspects were the incorporation of stress effects (see, for instance, the papers of Kao et al. [7, 8]) and the viscous-flow properties of the silicon oxide material [9–11].

With the growing need of small structures and thin oxide layers, the interface between silicon and silicon oxide is becoming more and more important. Here we enter the last one of the three stages mentioned at the beginning of our discussion. Microscopic properties of the transition region between Si and $SiO_2$ have to be studied in detail [12–16], and a proper formalism has to be made available for their incorporation.

Not only on the microscopic level mentioned above, a higher resolution of the interface representation seems necessary, but also on a slightly enlarged scale where, due to roughness effects of the silicon surface, a certain "transition" layer has turned out to be a useful model concept [17–20]. We note in passing that the difference between the two scales, i.e., the molecular scale of about 2 nm on the one hand and the roughness scale on the other hand, eventually decreases to less than a single order of magnitude. It turns out that our formalism can be easily adjusted to either scale by tuning a model parameter; more details can be found in Section 4.4.

The main reason for our own attempts to set up a simulation system for the thermal oxidation process of silicon was a certain lack of uniqueness and consistence of what we shall call the sharp-interface model. Instead of separating the two materials silicon and silicon oxide from each other into different spatial regions, we consider it more natural to permit a continuously varying coexistence of both at any point

---

Reprint requests to Dr. U. Weinert, Siemens AG, Otto-Hahn-Ring 6, W-8000 München 83.

0932-0784 / 91 / 1100-0955 $ 01.30/0. – Please order a reprint rather than making your own copy.

(this is what we call the "diffusive" oxidation regime). In essence, we have to describe the entire system under consideration as a thermodynamic mixture of (at least) three components: Silicon, silicon oxide, and oxygen. The macroscopic interface between silicon and silicon oxide should then appear automatically as a result of the basic set of "kinetic equations"; all of its properties should be derivable from the result as well.

The elaborate task to produce a simulation system like the one mentioned above, can be divided into two parts. For checking most of the basic concepts, a one-dimensional version of the formalism seems much more adequate than the full two-dimensional apparatus. A one-dimensional treatment provides its results faster and in a more transparent way, and moreover, it should be compatible with the classical Deal-Grove model. Then, after satisfactory results of the simplified one-dimensional version, the extension to two dimensions can be attacked with all the variety of particular problems due to the two-dimensionality; they have been mentioned above, as far as physical aspects are concerned. In correspondence to this subdivision of problems, we have projected a set of two papers. In the present work we shall start with presenting some preliminary one-dimensional considerations.

In Sect. 2 we set up the theoretical frame for the following discussions. Then, in Sect. 3 a brief introduction is given into the particular model concepts for a derivation of expressions for the diffusion coefficient and for the oxidation rate. It should be emphasized that the formalism is not restricted to the models introduced in Section 3; these have been utilized only in the sense of a lowest-order approximation.

The numerical studies discussed in Sect. 4 are the straight-forward attempt to solve the one-dimensional problem on an equally spaced space-time grid. As the main numerical problem without any doubt, can be found on the two-dimensional side of our formalism, we have not put very much effort into refining the one-dimensional technique. Moreover, the problem turned out to be exactly solvable by means of a similarity solution, which is in good agreement with the numerical results of Section 4.

The basic shortcoming of the similarity solution discussed in Sect. 5 is its only asymptotic validity [21, 22]. However, in our particular application this range of validity is sufficiently large: Any initial condition is, considered from the physical point of view, rather arbitrary, and a solution for these short times cannot be of significance.

One of the most interesting results of the present paper is derived in Sect. 6, where it is shown that the similarity solution of Sect. 5 has as a consequence the same oxide growth formula as the one derived from the Deal-Grove model. This rather satisfying agreement is an encouraging motivation for further two-dimensional considerations [25].

## 2. Definitions and Basic Equations

Consider a three-component mixture of oxygen $O_2$, silicon Si of an initially crystalline structure, and silicon oxide $SiO_2$. The corresponding concentrations are the silicon concentration $C_{Si}(x, t)$, the silicon oxide concentration $C_{Ox}(x, t)$, and the oxygen concentration $C(x, t)$. By an additional index 0 we characterize reference values: $C_{Si0}$ is the silicon concentration in the pure crystal, $C_{Ox0}$ is the oxide concentration in the pure-oxide region, and $C_0$ is the oxygen concentration outside the $Si-SiO_2$ system.

The one-dimensional space where this mixture develops, is decomposed into three parts:

1. the range $0 \leq x < \infty$, initially filled by the silicon crystal.
2. the range $-x_0(t) \leq x \leq 0$, filled up with oxide, and
3. the range $x < -x_0(t)$ which is of no concern for our considerations; from this range we only take the boundary condition that the oxygen concentration at the $SiO_2-O_2$ interface has the constant value $C_0$.

The silicon material is treated as immobile, i.e., the only variations of its concentration $C_{Si}(x, t)$ are due to oxidation processes. Furthermore, the silicon as well as the silicon oxide are treated as incompressible substances. Hence, as the volume expansion during the oxidation process is assumed to be constant, we have the equation

$$\alpha C_{Ox}(x, t) + C_{Si}(x, t) = C_{Si0}; \tag{1}$$

the experimental value for $\alpha$ is 2.2.

The equation of change for the silicon concentration can now be written as

$$\frac{\partial C_{Si}}{\partial t} = -R(C, C_{Si}, C_{Ox}) \tag{2}$$

with the reaction term $R$ due to oxidation of silicon to silicon oxide. The same reaction term appears in the equation of change for the oxygen concentration: Any oxygen molecule in a certain volume of space can be lost either by diffusion or by reaction, i.e., oxidation. Hence, the equation for the oxygen concentration is

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}D(x,t)\frac{\partial C}{\partial x}-R(C,C_{\mathrm{Si}},C_{\mathrm{Ox}})\,, \tag{3}$$

i.e., the diffusion equation with the diffusion coefficient $D(x,t)$ and with the additional reaction term $R$.

Studying the time dependence of the solution of this diffusion equation, we notice that there are two time scales. The short time scale is given by the time derivative in (3). On the large time scale, which is the interesting scale in our context, we therefore assume that the solution of (3) has always reached its steady state. Hence, for our actual problem we are left with the steady-state equation

$$\frac{\partial}{\partial x}D(x,t)\frac{\partial C}{\partial x}=R(C,C_{\mathrm{Si}},C_{\mathrm{Ox}})\,. \tag{4}$$

Now we have two partial differential equations for the two unknown functions $C(x,t)$ and $C_{\mathrm{Si}}(x,t)$ (the oxide concentration $C_{\mathrm{Ox}}$ is eliminated by means of (1)); with proper initial and boundary conditions the system is complete and can be solved. As initial condition we consider a situation with no silicon eaten away by oxidation. We thus have a sharp Si$-$O$_2$ interface at $x=0$, no silicon oxide whatsoever, and constant values of the silicon and oxygen concentrations,

$$C_{\mathrm{Si}}(x,t)=\begin{cases}C_{\mathrm{Si0}} & \text{for}\quad x>0\\ \frac{1}{2}C_{\mathrm{Si0}} & \text{for}\quad x=0\,,\\ 0 & \text{for}\quad x<0\end{cases} \tag{5}$$

and

$$C(x,0)=\begin{cases}0 & \text{for}\quad x>0\\ \frac{1}{2}C_0 & \text{for}\quad x=0\,,\\ C_0 & \text{for}\quad x<0\end{cases} \tag{6}$$

respectively. With increasing time, the oxide layer develops with its upper boundary at $x=-x_0(t)$, $x_0(t)>0$. (Note that the $x$ axis points downwards into the crystal.)

Basically, the oxide is treated as an incompressible fluid. Every volume element has a velocity $v_{\mathrm{Ox}}(x,t)$, and the oxide concentration is actually determined by a continuity equation of the form

$$\frac{\partial C_{\mathrm{Ox}}}{\partial t}+\frac{\partial}{\partial x}v_{\mathrm{Ox}}(x,t)\,C_{\mathrm{Ox}}(x,t)=R(C,C_{\mathrm{Si}},C_{\mathrm{Ox}})\,, \tag{7}$$

disregarding any diffusion flux of oxide particles. Substituting the right-hand side of (7) by the equation of change for the silicon concentration, (2), using the incompressibility relation, (1), and integrating over $x$ from $x_0(t)$ to infinity and over $t$, we end up with

$$x_0(t)\,C_{\mathrm{Si0}}=(\alpha-1)\int_0^{\infty}[C_{\mathrm{Si0}}-C_{\mathrm{Si}}(x,t)]\,\mathrm{d}x\,. \tag{8}$$

Clearly,

$$\frac{\mathrm{d}x_0}{\mathrm{d}t}=v_0(t)=-\,v_{\mathrm{Ox}}(x_0(t),t)\,. \tag{9}$$

Here already one of the boundary conditions has been used: There is never any pure silicon to be found in the upper half space (with $x<0$), i.e.,

$$C_{\mathrm{Si}}(x,t)=0\quad\text{for}\quad x<0\,. \tag{10}$$

Furthermore, there is no silicon oxide in the space above $x_0(t)$, i.e.

$$C_{\mathrm{Ox}}(x,t)=0\quad\text{for}\quad x<-x_0(t)\,. \tag{11}$$

In the same region, i.e., for $x<-x_0(t)$, the oxygen concentration is assumed to be constant,

$$C(x,t)=C_0\quad\text{for}\quad x<-x_0(t)\,. \tag{12}$$

There are another two remaining boundary conditions to be added, both of them concerning the solution for large values of $x$. From the intuitive point of view both are trivial; however, they are essential for picking out the correct solution. The conditions can be written in the form

$$\lim_{x\to\infty}C_{\mathrm{Si}}(x,t)=C_{\mathrm{Si0}}\,, \tag{13}$$

and

$$\lim_{x\to\infty}C(x,t)=0\,. \tag{14}$$

There is another way to derive (8); it demonstrates explicitely the initial condition involved (cf. (5)): At starting time there is no silicon oxide yet to be found, i.e., all the oxide is generated during the process under consideration. Then the total number of oxide particles at time $t$ is

$$\int_{x_0(t)}^{\infty}C_{\mathrm{Ox}}(x,t)\,\mathrm{d}x=\frac{1}{\alpha}\left(C_{\mathrm{Si0}}\,x_0(t)+\int_0^{\infty}[C_{\mathrm{Si0}}-C_{\mathrm{Si}}(x,t)]\,\mathrm{d}x\right). \tag{15}$$

The same number of silicon atoms, however, has been consumed by oxidation. Hence, the right-hand side of (15) is equal to the number of silicon particles removed from the initial state,

$$C_{\mathrm{Si}0}\, x_1(t) = \int_0^{\infty} [C_{\mathrm{Si}0} - C_{\mathrm{Si}}(x, t)]\, \mathrm{d}x\, . \tag{16}$$

Equating the right-hand sides of (15) and (16), we once again arrive at (8).

Actually, (16) is a possible definition for the coordinate $x_1$ of an "effective" interface between silicon and silicon oxide. It is the very same coordinate which a sharp interface would have to have in order to describe the same process kinetics as we are concerned with here.

In this section we have introduced the system of differential equations to be solved; such a solution, however, can only be attempted if the diffusion coefficient $D(x, t)$ and the reaction (oxidation) term $R(C, C_{\mathrm{Si}}, C_{\mathrm{Ox}})$ are known. In the next section some models for their determination will be discussed briefly.

## 3. Model Concepts

### 3.1. Diffusion Coefficient

From a kinetic theory point of view the diffusion coefficient can be derived from an equation of motion. In a lowest-order approximation this equation of motion for the oxygen molecules can be written in the form

$$-\frac{k_{\mathrm{B}}T}{m}\frac{\partial C}{\partial x} = (B_{\mathrm{Si}}\, C_{\mathrm{Si}}(x, t) + B_{\mathrm{Ox}}\, C_{\mathrm{Ox}}(x, t))\, j(x, t)\, . \tag{17}$$

In this equation, $k_{\mathrm{B}}T/m$ is the Boltzmann factor for the oxygen molecules. $B_{\mathrm{Si}}$ and $B_{\mathrm{Ox}}$ are collision elements for the characterization of the collisions between the oxygen molecules on the one hand and the silicon atoms and oxide molecules, respectively, on the other hand, $j(x, t)$ is the particle flux density of the oxygen, caused by the concentration gradient on the left-hand side.

Equation (17) is valid for gaseous materials of small densities, an assumption which is certainly not correct in our case of rather densely packed silicon atoms. Hardly any oxygen molecule will be able to penetrate even the outmost layers of the crystal. Only after some initial oxidation has taken place, some holes will have been created and a certain "diffusive" regime might have developed. Thus for no oxide molecules present there will be supposedly no oxygen molecules penetrating the silicon material. As an ansatz we shall account for this idea by changing (17) to

$$-\frac{k_{\mathrm{B}}T}{m}\frac{\partial C}{\partial x} = \left(B_{\mathrm{Si}}\frac{C_{\mathrm{Si}0}}{C_{\mathrm{Ox}}(x, t)}\, C_{\mathrm{Si}}(x, t) + B_{\mathrm{Ox}}\, C_{\mathrm{Ox}}(x, t)\right) j(x, t)\, . \tag{18}$$

This equation can be considered the simplest way to describe an infinite number of collisions between the oxygen molecules and the silicon atoms, i.e., to model the impossibility for an oxygen molecule to penetrate into pure silicon.

In the oxide material the diffusion coefficient is supposed to be known. With Fick's law we then have

$$j(x, t) = -D_{\mathrm{Ox}}\frac{\partial C}{\partial x}\, . \tag{19}$$

Comparing with (17) or (18), we then obtain

$$\frac{k_{\mathrm{B}}T}{m} = D_{\mathrm{Ox}}\, B_{\mathrm{Ox}}\, C_{\mathrm{Ox}0}\, . \tag{20}$$

(Note that in the pure-oxide region we have $C_{\mathrm{Si}}(x, t) = 0$ and, hence the constant value

$$C_{\mathrm{Ox}0} = \frac{1}{\alpha}\, C_{\mathrm{Si}0} \tag{21}$$

for the oxide concentration.) With the abbreviating notation

$$\beta' = \frac{B_{\mathrm{Si}}}{B_{\mathrm{Ox}}} \tag{22}$$

the result of (17) can be written as

$$D_{\mathrm{Ox}}\, C_{\mathrm{Si}0} = \alpha\, D(x, t)\, (\beta'\, C_{\mathrm{Si}}(x, t) + C_{\mathrm{Ox}}(x, t))\, . \tag{23}$$

Finally, we define the normalized silicon concentration

$$\eta(x, t) = \frac{C_{\mathrm{Si}}(x, t)}{C_{\mathrm{Si}0}} \tag{24}$$

and obtain

$$D(x, t) = D_{\mathrm{Ox}}\frac{1}{1 + \beta\, \eta(x, t)} \tag{25}$$

with

$$\beta = \alpha\, \beta' - 1\, . \tag{26}$$

After this detailed discussion of the transition from (17) to (25) the implications of the modified version (18), can be dealt with more briefly. In analogy to (23) we have

$$D_{Ox}\, C_{SiO} = \alpha\, D(x, t) \left( \beta' \frac{C_{Si}(x, t)\, C_{SiO}}{C_{Ox}(x, t)} + C_{Ox}(x, t) \right), \quad (27)$$

which can be written in the form

$$D(x, t) = D_{Ox} \frac{1-\eta}{(1-\eta)^2 + \gamma\eta} \quad (28)$$

with

$$\gamma = \alpha^2 \beta'. \quad (29)$$

By construction, this formula has the desired property: In the region with pure silicon with $\eta = 1$ the diffusion coefficient $D(\eta)$ vanishes; no oxygen molecule can move in this region. On the other side, in the region with pure oxide with $\eta = 0$ the diffusion coefficient has the oxide value $D_{Ox}$. It is interesting to note that (25), while yielding the same oxide diffusivity, results in a nonvanishing diffusion coefficient in the pure-silicon region. Figure 1 shows the characteristic features of our simplified models in a comprehensive way.

For analytical purposes a last diffusion coefficient shall be given; it has, however, a purely hypothetical character: Both properties mentioned above, are satisfied by the extremely simple formula

$$D(\eta) = D_{Ox}(1-\eta), \quad (30)$$

which will be used in a later part of this paper.

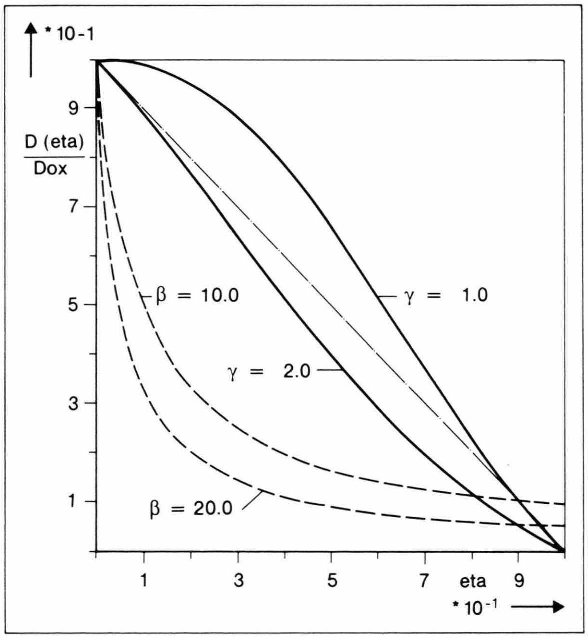

Fig. 1. Normalized diffusion coefficients for different values of the parameters $\beta$ and $\gamma$. The dashed-dotted line shows the linear model, Eq. (30).

### *3.2. Reaction Term*

For the determination of the reaction term we apply a rather crude model on the basis of a hypothetical one-stage process: Let $k$ be the (constant) reaction rate for the oxidation

$$\mathrm{Si} + \mathrm{O}_2 \rightarrow \mathrm{SiO}_2;$$

in lowest-order approximation we then write

$$R(C, C_{Si}, C_{Ox}) = k\, C(x, t)\, \eta(x, t). \quad (31)$$

It is important to note that the inverse process, i.e., the reduction has been neglected. A more detailed discussion of this topic is necessary if the influence of the (tensorial) stress on the chemical reaction is to be studied. This aspect, however, shall be put aside for the moment.

Our introduction of the reaction rate is different from the conventional treatment where a surface reaction rate on the (sharp) $\mathrm{Si}-\mathrm{SiO}_2$ interface is used. The connection between both types of reaction rates will be established in Section 6.

Now we have supplied all model functions necessary for a numerical treatment of our problem. This will be our objective in the following sections.

## 4. Numerical Solution

### *4.1. Scaling*

The basic equations for a solution of our problem are (2) and (4) of Section 2. With the reaction term of Sect. 3.2 inserted, they read

$$\frac{\partial \eta}{\partial t} = -k \frac{C_0}{C_{SiO}} \psi(x, t)\, \eta(x, t) \quad (32)$$

and

$$\frac{\partial}{\partial x} \Delta(\eta) \frac{\partial \psi}{\partial x} = \frac{k}{D_{Ox}} \psi(x, t)\, \eta(x, t). \quad (33)$$

Apart from the normalized silicon concentration $\eta(x, t)$, defined in (24), we have introduced here the normalized oxygen concentration

$$\psi(x, t) = \frac{C(x, t)}{C_0} \quad (34)$$

and the normalized diffusion coefficient

$$\Delta(\eta) = \frac{D(\eta)}{D_{\mathrm{Ox}}} . \tag{35}$$

The use of these dimensionless quantities exhibits a natural scaling for the variables $x$ and $t$. Equation (33) gives us a reference length for the variable $x$: With

$$x_{\mathrm{ref}} = \sqrt{\frac{D_{\mathrm{Ox}}}{k}} \tag{36}$$

we define the normalized spatial variable

$$\xi = \frac{x}{x_{\mathrm{ref}}} . \tag{37}$$

Similarly, (32) yields a scaling quantity for the time,

$$t_{\mathrm{ref}} = \frac{1}{k} \frac{C_{\mathrm{SiO}}}{C_0} . \tag{38}$$

We use this reference time and define

$$\tau = \frac{t}{t_{\mathrm{ref}}} . \tag{39}$$

By means of the normalized variables defined here, we rewrite the basic equations in the form

$$\frac{\partial \eta}{\partial \tau} = -\psi(\xi, \tau)\, \eta(\xi, \tau) \tag{40}$$

and

$$\frac{\partial}{\partial \xi} \Delta(\eta) \frac{\partial \psi}{\partial \xi} = \psi(\xi, \tau)\, \eta(\xi, \tau) . \tag{41}$$

Correspondingly, the initial and boundary conditions are (we omit the obvious condition at $\xi \to \infty$)

$$\psi(-\xi_0(\tau), \tau) = 1 \tag{42}$$

and

$$\eta(\xi, \tau) = 0 \quad \text{for} \quad \xi < 0 . \tag{43}$$

Eventually, we can derive matching conditions from requiring a continuous oxygen particle flux density, i.e., the quantity

$$\Delta(\eta) \frac{\partial \psi}{\partial \xi}$$

is supposed to be continuous on the whole range of interest. Finally, the spatial coordinate of the $SiO_2$–$O_2$ interface, i.e., the upper boundary of the oxide region can be read from (8); we obtain

$$\xi_0(\tau) = (\alpha - 1) \int_0^\infty [1 - \eta(\xi, \tau)]\, d\xi . \tag{44}$$

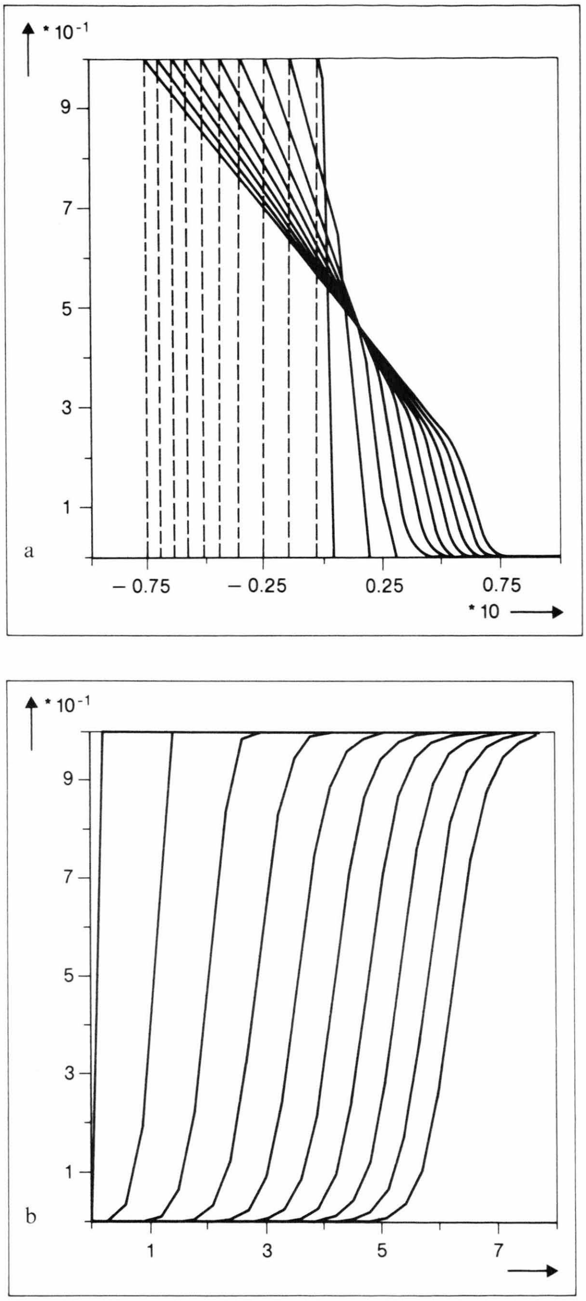

Fig. 2. Time evolution of the normalized oxygen (left) and silicon (right) concentration. The dashed lines indicate the upper oxide boundary.

### 4.2. Discussion

Some results of the numerical calculations can be found in Figs. 2a and 2b. For a set of times the computed profiles are presented for the (normalized) concentrations of oxygen (Fig. 2a) and silicon (Figure 2b). The upper oxide boundary is indicated in Fig. 2a by a dashed vertical line.

For our numerical demonstration we have used the model parameter $\beta = 10$, i.e., the hypothetical diffusion constant in the pure-silicon region is set to 1/11 of its oxide value. This is certainly not a physically realistic choice. However, for increasing values of $\beta$ all our statements remain valid; the only variation due to the increase of $\beta$ (and $\gamma$) is a decrease of the width of the transition zone. Our figures indicate a transition width of about $1.5\,x_{\text{ref}}$, going down to about $0.02\,x_{\text{ref}}$ for $\beta = 10^5$.

For the determination of the numerical values for our reference quantities $x_{\text{ref}}$ and $t_{\text{ref}}$, we need the reaction rate $k$ for the oxidation process (cf. (31)). After its connection with the surface reaction rate of Deal and Grove has been established (see Sect. 6.2, (83)), we are able to extract all physical numbers needed from a comparison between our results (in the normalized version) and applications of the Deal-Grove formula in the literature [23, 24]. The results are reference lengths varying with temperature $T$ roughly between 500 nm (for $T = 900$ °C) and 50 nm (for $T = 1100$ °C). Correspondingly, the reference time $t_{\text{ref}}$ varies between 7 h and 90 sec, respectively.

The dependence of the numerical results on the particular type of model for the diffusion coefficient (see Sect. 3.1) is rather unsignificant; only the shape of the interface profile varies slightly due to changes of the model diffusivities (see Figs. 3a and 3b, Section 5). Therefore we have restricted ourselves to just presenting the case of (25). This choice has the advantage of being compatible with the two-dimensional calculations to be discussed in a parallel paper [25].

In Fig. 2a the linear regime of the oxygen concentration $\psi(\xi, \tau)$ can be seen. It extends over the region where the silicon concentration $\eta(\xi, \tau)$ is practically 0, i.e., over the pure-oxide region. Figure 2b exhibits an important invariance property of the solution. After a small initial period an interface profile has evolved which moves along the $\xi$ axis with time-dependent velocity and invariant shape. This property gives rise to the considerations in the subsequent sections. The resulting thickness of the oxide layer is discussed in Sect. 6 in comparison with the results of the Deal-Grove model. In Sect. 5 an ordinary differential equation is derived, which allows the immediate determination of the invariant interface profile appearing in Figure 2b.

The extension of the "diffusive" interface region can be estimated roughly by inspecting Figure 2b. In our special case we have chosen for the parameter $\beta$ (cf. (25)) the value 10, which yields an interface range of about 1.5 (in units of $x_{\text{ref}}$). With increasing values of $\beta$ the width of the diffusive region decreases; by means of the choice $\beta = 10^5$, for example, the width of the transition regime could be reduced to about 0.025. In connection with the values for $x_{\text{ref}}$ given above, we realize that we are able to cover a vast variety of physical orders of magnitude. A more specific fit of the parameters $\beta$ or $\gamma$, i.e., the choice of the particular physical scale, shall be left open for the time being. Earlier investigations (see, for instance, [26] and [13, 14]) suggest an interface width of about 2.5–4 nm.

## 5. Similarity Solutions

The starting point for any discussion of similarity solutions is the basic assumption that there exists a set of similarity variables such that the number of independent variables of the partial equation can be reduced. In our case the set $(x, t)$ or $(\xi, \tau)$, respectively, of independent variables is reduced by the assumption that there is a similarity variable $\zeta(\xi, \tau)$. With this variable we make the ansatz

$$\eta(\xi, \tau) = F(\zeta) \tag{45}$$

and

$$\psi(\xi, \tau) = g(\tau)\, N(\zeta)\,. \tag{46}$$

The first part of this ansatz, (45), can be partially justified by inspecting the shape of the function $\eta(\xi, \tau)$: For $\xi \to \infty$, for example, the value of $\eta$ becomes 1, no matter at what time it is considered. Therefore a time dependent factor like $g(\tau)$ in (46) is not necessary in (45). The second part of our ansatz, (46), is more general; actually, it means an ordinary separation of the variable $\zeta$ from the time $\tau$. Empirically, the results of the numerical studies discussed in the previous section give rise to assuming that the function $\eta(\xi, \tau)$ is shift-invariant with respect to the spatial coordinate. This means that at time $\tau_1$ the function $\eta(\xi, \tau_1)$ is the same as the function at time $\tau_0$, shifted by a certain coordinate difference $\xi_1$, i.e., $\eta(\xi - \xi_1, \tau_0)$. This empirical fact is taken into account by a second assumption,

$$\zeta(\xi, \tau) = \xi - \xi_1(\tau)\,. \tag{47}$$

As has been demonstrated, there is strong evidence for our special similarity ansatz; the final proof for its correctness, however, can only be supplied by verification.

We start with the silicon continuity equation (40). Inserting the functions $F(\zeta)$, $N(\zeta)$, $g(\tau)$, and $\xi_1(\tau)$, we obtain

$$g(\tau) = \frac{\mathrm{d}\xi_1}{\mathrm{d}\tau} \tag{48}$$

as well as the ordinary differential equation

$$\frac{\mathrm{d}F}{\mathrm{d}\zeta} = N(\zeta)\, F(\zeta)\,. \tag{49}$$

Correspondingly, we obtain from the (stationary) diffusion equation (41),

$$\frac{\mathrm{d}}{\mathrm{d}\zeta}\, \Delta(F(\zeta))\, \frac{\mathrm{d}N}{\mathrm{d}\zeta} = N(\zeta)\, F(\zeta)\,. \tag{50}$$

We have now constructed a system of ordinary differential equations for the determination of the functions $F(\zeta)$ and $N(\zeta)$. It can be solved formally, as will be demonstrated in the following considerations.

To prepare the first integration step, we eliminate the reaction term on the right-hand sides of (49) and (50). Thus we obtain a single equation,

$$\frac{\mathrm{d}}{\mathrm{d}\zeta}\, \Delta(F(\zeta))\, \frac{\mathrm{d}N}{\mathrm{d}\zeta} = \frac{\mathrm{d}F}{\mathrm{d}\zeta}\,, \tag{51}$$

which can be integrated easily. Without any particular assumption about the function $\Delta(F)$ we note that the $\zeta$ derivative of $N(\zeta)$ vanishes for large values of the argument. Hence, the constant of the first integration is fixed, and we have

$$\Delta(F(\zeta))\, \frac{\mathrm{d}N}{\mathrm{d}\zeta} = F(\zeta) - 1\,. \tag{52}$$

Now we are able to eliminate the function $N(\zeta)$. We combine (52) with the silicon continuity equation (49) and obtain

$$\Delta(F)\, \frac{\mathrm{d}}{\mathrm{d}\zeta}\, \frac{1}{F}\, \frac{\mathrm{d}F}{\mathrm{d}\zeta} = F(\zeta) - 1\,. \tag{53}$$

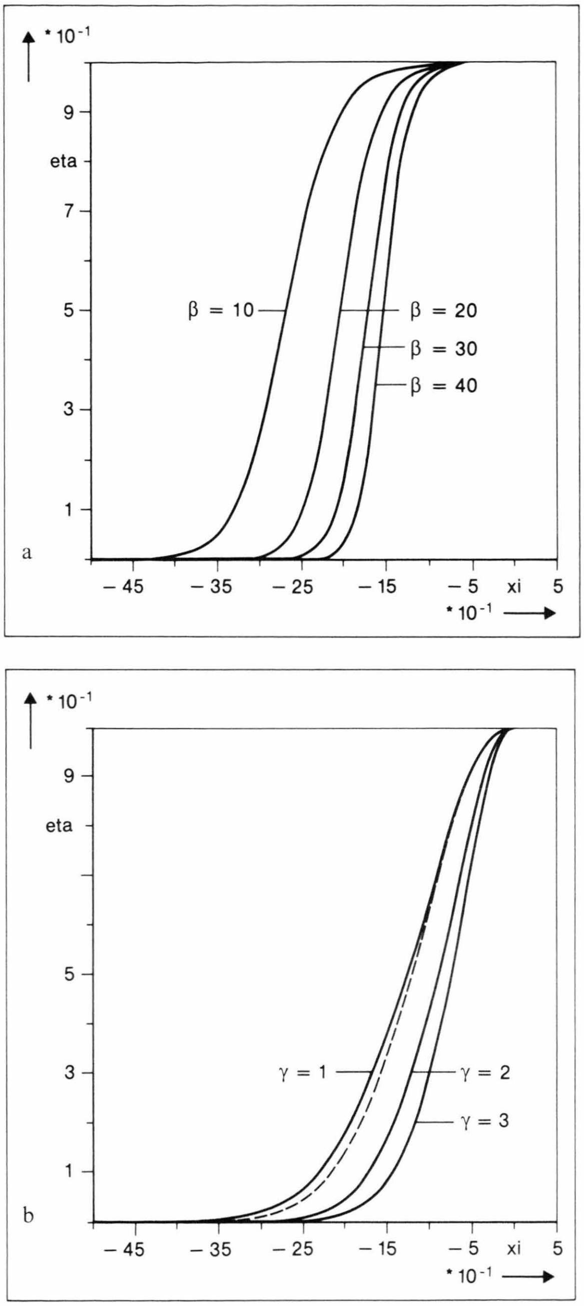

Fig. 3. Normalized silicon concentration profiles from similarity solutions for various values of the parameters $\beta$ and $\gamma$. The dashed line indicates the linear model, Eq. (30).

Figures 3a and 3b show the numerical solution of this differential equation for the model diffusion coefficients given in Sect. 3.1 with various parameters $\beta$ and $\gamma$. In Sect. 4.4 we have discussed the case shown in Fig. 3a with $\beta = 10$. It is easily compared with the profiles appearing in Fig. 2b and demonstrates the validity of our similarity solution. Obviously, the model described by (25), i.e., with a finite diffusivity in the silicon region, yields solutions with a quality slightly different from the linear model, (30), and the model described by (28), i.e., with no diffusion in the pure-silicon region. Both Figs. 3a and 3b again exhibit the dependence of the thickness of the transition regime on the choice of the parameters $\beta$ and $\gamma$ that has been mentioned already at the end of the previous section.

For a general analytic discussion of the second integration step we proceed as follows: We exchange the roles of $\zeta$ and $F$. Thus let $\zeta$ be a function of $F$, i.e., $\zeta = \zeta(F)$. Then we define a function $z(F)$ as

$$z(F) = \left\{ F \frac{d\zeta}{dF} \right\}^2 . \tag{54}$$

Using this function, we can rewrite (53) in the form

$$\frac{dz}{dF} = 2 \frac{F-1}{F \Delta(F)} . \tag{55}$$

With $\Delta(F)$ given as suggested in the models discussed in Sect. 3, this equation can be integrated analytically. For the most simplified model given by (30) we obtain, for instance,

$$z(F) = -2 \log F . \tag{56}$$

Inserting this result on the left-hand side of (54), we end up with a differential equation whose integration constitutes the third integration step; we have to solve the equation

$$\left( \frac{d\zeta}{d \log(1/F)} \right)^2 = \frac{1}{2 \log(1/F)} . \tag{57}$$

The integration of this equation is easy; we obtain two branches,

$$\zeta - \zeta_0 = \pm \sqrt{2 \log(1/F)} . \tag{58}$$

At $\zeta = \zeta_0$ we have $F = 1$. Moving along the positive direction of the $\zeta$ axis means moving downward in the silicon material; we have to restrict the $\zeta$ interval to $-\infty < \zeta \le \zeta_0$. Finally, we rewrite (58) in a more familiar form as

$$F(\zeta) = e^{-\frac{1}{2}(\zeta - \zeta_0)^2} . \tag{59}$$

As mentioned above, the result is valid for negative arguments $\zeta$. Thus (59) represents the profile of the "soft" interface between silicon and silicon oxide in a frame of reference moving with the (normalized) velocity $g(\tau)$. From (49) we obtain

$$N(\zeta) = \zeta_0 - \zeta . \tag{60}$$

There is a certain freedom in the choice of $\zeta_0$. As only the product of $N(\zeta)$ and $g(\tau)$ has physical significance, there is in principle the possibility to choose one "constant of integration" at wish. In later discussions we need the quantity $N(0)$, which we now fix as

$$N(0) = 1 . \tag{61}$$

This choice for $N(0)$ is not restricted to any particular choice of the model for the diffusion coefficient. For our special example, (59) and (60), we then have

$$N(\zeta) = 1 - \zeta . \tag{62}$$

It is interesting to note that the function $g(\tau)$ or the velocity $v_1(t)$ has not yet entered our considerations explicitly. The similarity variable $\zeta$ contains the reference coordinate $\xi_1$. In view of subsequent discussions, we identify this reference coordinate with the effective interface coordinate (cf. (16)). At the same time, we have established the connection with the upper oxide boundary $-\xi_0$. The entire process of determining the function $g(\tau)$ is thus closely connected with satisfying the boundary conditions. As this is a problem of its own, its discussion will be given in the next section.

## 6. Oxide Growth

### 6.1. Rigorous Treatment

At the beginning of our discussions we assume that the transition regime, i.e., the thickness of the soft interface is small compared to the total oxide thickness. It then seems a reasonable lowest-order approximation to substitute our "diffusive" interface by a sharp one at a certain spatial coordinate. After the considerations of the previous sections, there appears a useful choice for such an interface coordinate: The reference coordinate $\xi_1(\tau)$. Talking about a sharp interface means (cf. Sect. 2) to assume that there is no silicon in the interval $\xi < \xi_1(\tau)$ and no silicon oxide at any $\xi > \xi(\tau)$. Then, however, we obtain from (8) and (16):

$$\xi_0(\tau) = (\alpha - 1)\, \xi_1(\tau) . \tag{63}$$

Accordingly, the (normalized) oxide thickness then reads

$$\delta(\tau) = \xi_1(\xi, \tau) + \xi_0(\tau) = \alpha\, \xi_1(\tau) . \tag{64}$$

With the model concept of a sharp interface we are now at the basics of the Deal-Grove model; there we can find a way to evaluate the oxide growth. However, a more rigorous treatment should be possible on the basis of our previous considerations. Note, for instance, that during the numerical studies in Sect. 4 there was no further information necessary to obtain the desired oxide growth. Here we are going to discuss the question how such a growth could be obtained on the basis of the similarity solution.

Suppose that we have calculated the functions $F(\zeta)$ and $N(\zeta)$. Note that after $F(\zeta)$ has been found, the function $N(\zeta)$ can be read from the silicon continuity equation as

$$N(\zeta)=\frac{1}{F(\zeta)}\frac{\mathrm{d}F}{\mathrm{d}\zeta}. \tag{65}$$

The problem now is to determine the function $\xi_1(\tau)$ such that the boundary conditions at the $SiO_2$–$O_2$ interface are satisfied. Thanks to the normalization of the function $\psi$, (34), we have at this boundary $\psi(-\xi_0(\tau), \tau)=1$. Hence,

$$1=g(\tau)\,N(-\xi_0(\tau)-\xi_1(\tau)). \tag{66}$$

The assumption that a similarity solution has any significance, is in accordance with the above assumption of a small transition regime. Hence, we can take (63) serious and are thus left with a single differential equation for $\xi_1(\tau)$:

$$1=g(\tau)\,N(-\alpha\,\xi_1(\tau)). \tag{67}$$

With the function $N(\zeta)$ given, the problem is thus reduced to the integration of an ordinary nonlinear differential equation. Taking the time derivative on both sides of (67), we obtain

$$\frac{1}{g(\tau)}\frac{\mathrm{d}g}{\mathrm{d}\tau}=\alpha\,g(\tau)^2\,\frac{\mathrm{d}N}{\mathrm{d}\zeta}(\zeta=\alpha\,\xi_1(\tau)). \tag{68}$$

The derivative of $N(\zeta)$ can be taken from (52):

$$\frac{\mathrm{d}N}{\mathrm{d}\zeta}=\frac{1}{\Delta(F)}(F-1). \tag{69}$$

For $F(\zeta)\ll 1$, i.e., for sufficiently large times, (69) yields the constant value

$$N'=-1. \tag{70}$$

(See the linear or quasi linear regime of the oxygen concentration in Section 4.) Upon substituting the constant value of (70) into the differential equation for $g(\tau)$, (68), we have

$$\frac{\mathrm{d}g}{\mathrm{d}\tau}=-\alpha\,g(\tau)^3. \tag{71}$$

The solution of this differential equation is easy; the result is

$$g(\tau)=\left(2\alpha\tau+\frac{1}{g(0)^2}\right)^{1/2}. \tag{72}$$

Initially, at time $\tau=0$, both interfaces coincide and we have

$$1=g(0)\,N(0), \tag{73}$$

yielding (cf. (61))

$$g(0)=1. \tag{74}$$

A final integration over $\tau$ then yields the (normalized) oxide thickness,

$$\delta(\tau)=\sqrt{2\alpha\tau+1}-1 \tag{75}$$

(the initial condition for $\delta(\tau)$ was assumed to be $\delta(0)=0$). This result can be compared with the results of the Deal-Grove model which is discussed briefly in the next subsection.

### 6.2. Deal-Grove Model

The Deal-Grove model starts from the assumption that at the (sharp) Si–$SiO_2$ interface the particle flux is balanced, i.e., there are as many oxygen molecules moving in from above as are consumed by silicon oxidation. As the latter number is the same as the number of silicon atoms consumed by oxidation, we obtain

$$D_{\mathrm{Ox}}\frac{C_0-C(x_1(t),t)}{x_0(t)+x_1(t)}=C_{\mathrm{SiO}}\frac{\mathrm{d}x_1}{\mathrm{d}t}. \tag{76}$$

In our normalized notation this reads (again with $N(0)=1$)

$$\frac{1-g(\tau)}{\delta(\tau)}=g(\tau). \tag{77}$$

It should be mentioned that in the original version of the Deal-Grove model, the right-hand side of (76) is expressed in terms of a surface reaction rate $k_s$ for the silicon oxidation. The connection between this original version and (76) is established by the relation

$$C_{\mathrm{SiO}}\frac{\mathrm{d}x_1}{\mathrm{d}t}=k_s\,C(x_1(t),t); \tag{78}$$

the meaning of the equation is obvious after the foregoing remarks.

It is interesting to elaborate the relation between the surface reaction rate $k_s$ and the conventional (volume) reaction rate $k$ introduced in (31). For that purpose we start from the definition of the effective $SiO_2$–Si interface (cf. (16)),

$$x_1(t)=\int_0^\infty\{1-\eta(x,t)\}\,\mathrm{d}x. \tag{79}$$

Taking the time derivative of this equation and substituting the derivative of $\eta$ by the silicon continuity equation (32), we obtain

$$C_{\mathrm{SiO}} \frac{\mathrm{d}x_1}{\mathrm{d}t} = k\, C_0 \int_0^{\infty} \{\psi(x,t)\, \eta(x,t)\}\, \mathrm{d}x\,. \tag{80}$$

We insert the similarity ansatz, (45) and (46) as well as (50), which enables us to evaluate the integral in (80):

$$C_{\mathrm{SiO}} \frac{\mathrm{d}x_1}{\mathrm{d}t} = \alpha\, C_0\, x_{\mathrm{ref}}\, g(\tau) \int_0^{\infty} \frac{\mathrm{d}F}{\mathrm{d}\zeta} (\zeta = \xi - \xi_1(\tau))\, \mathrm{d}\zeta\,. \tag{81}$$

Neglecting $F(\xi - \xi_1(\tau))$ at $\zeta = 0$ (see the transition from (69) to (70)), we can substitute the integral in (81) by 1. Finally, we insert $x_{\mathrm{ref}}$ from (36) and compare the result with (78). Thus we obtain the relation (again with $N(0) = 1$)

$$k_s = \sqrt{k\, D_{\mathrm{Ox}}}\,. \tag{82}$$

After this brief excursion we continue to discuss (76). With

$$\frac{\mathrm{d}\delta}{\mathrm{d}\tau} = \alpha\, g(\tau), \tag{83}$$

we rewrite (77) as

$$1 - g(\tau) = g(\tau)\, \delta(\tau)\,. \tag{84}$$

The simple solution of this differential equation is

$$\alpha\tau - \delta(\tau) = \tfrac{1}{2}\, \delta(\tau)^2, \tag{85}$$

which can be rewritten in form of (75), i.e., we have shown that the assumptions of the Deal-Grove model are essentially equivalent to assuming the existence of similarity solutions combined with the asymptotic condition contained in (70). The remark should be added that, as far as the constants $N(0)$ and $g(0)$ are concerned, the match between the similarity solution and the Deal-Grove model is even more general than demonstrated in this brief discussion.

For a comparison of the numerical results shown in Sect. 4.4 with the Deal-Grove formula, we have to restrict ourselves to times $\tau \geq \tau_0$, $\tau_0$ being the time needed for the evolution of the invariant interface profile. In this period of time, however, an initial oxide pad of thickness $\delta_0$ has been built up. According to the Deal-Grove model, we then have instead of (85) the solution

$$\alpha(\tau - \tau_0) - \{\delta(\tau) - \delta_0\} = \tfrac{1}{2}\, \{\delta(\tau)^2 - \delta_0^2\}\,. \tag{86}$$

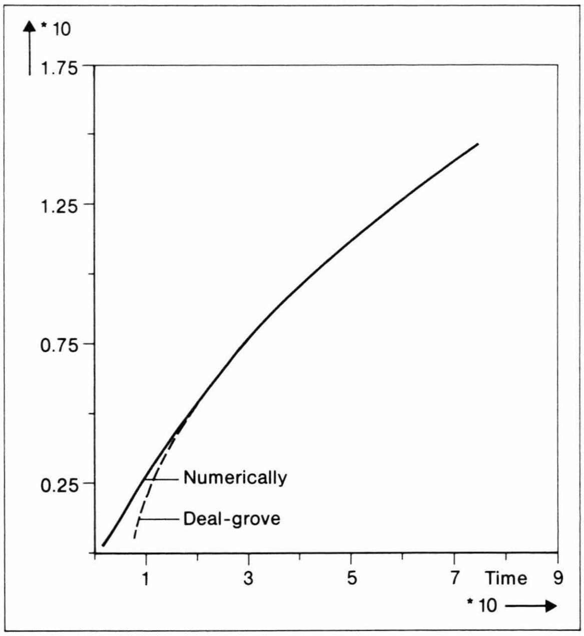

Fig. 4. Oxide growth. Comparison of our numerical results with the Deal-Grove formula.

The time shift $\tau_0$ has to be picked empirically in such a way that at times $\tau \geq \tau_0$ the interface profile is practically independent of the initial profile at $\tau = 0$. After this time $\tau_0$ has been extracted from the result of the numerical calculations, the thickness $\delta_0$ of the oxide layer has to be matched between the numerical results and the Deal-Grove formula. Figure 4 presents the comparison between the Deal-Grove formula, (86), with suitably adjusted parameters $\tau_0$ and $\delta_0$ and the time dependent oxide thickness extracted from the numerical solution discussed in Section 4.

## 7. Concluding Remarks

In the foregoing sections we have developed a formalism which describes the thermal oxidation of silicon. In a natural way the free boundary of the oxide as well as the Si–SiO$_2$ interface evolve from the solution of the fundamental system of partial differential equations. It is understood that the basic physics underlying this system of equations is all but complete; the models that have been used (see Sect. 3) are rather restricted and unsophisticated. However, they are sufficient for a discussion of the main features of our formalism. After the method has been established, a generalization to more realistic models should not be too difficult.

The concept of a "diffusive" $Si-SiO_2$ interface has been introduced, emphasizing in each step the close correspondence to the classical model of Deal and Grove. This connection could be established after defining the coordinates of an "effective interface" representing the conventionally used sharp boundary between the silicon and the silicon oxide region. We have the strong feeling that this concept of a soft transition not only results in a more consistent and unique formalism from the mathematical point of view (note, for instance, that no a priori movement of the interface in any direction whatsoever has to be assumed!), but also allows an easier incorporation of more developed future model concepts within the interface region. While these conceptual advantages remain somewhat hidden in a one-dimensional treatment, they become much more essential within the framework of a two-dimensional consideration.

The important tool for establishing the logical connection between our results on the one hand and the Deal-Grove relation on the other hand turned out to be the similarity solution of our rather transparent set of partial differential equations. Reversely, this equivalence between the similarity solution and the Deal-Grove technique exhibits the basic features of the latter formalism. For that reason we have dedicated a whole section to working out the similarity solution which could be shown to be even exactly solvable, inspite of the fact that such a solution might be of only academic interest in the context of realistic applications.

The next step towards the development of the formalism, which goes far beyond the scope of the Deal-Grove method, is the appropriate extension of our basic ideas to the two-dimensional case. Such a generalization has been attacked successfully and is the object of a further paper [25].

[1] B. E. Deal and A. S. Grove, J. Appl. Phys. **36** (12), 3770 (1965).

[2] Y. J. van der Meulen, J. Electrochem. Soc. **119** (4), 531 (1972).

[3] R. Ghez and Y. J. van der Meulen, J. Electrochem. Soc. **119** (8), 1101 (1972).

[4] J. Blanc, Appl. Phys. Lett. **33** (5), 424 (1878).

[5] R. B. Marcus and T. T. Sheng, J. Electrochem. Soc. **129** (6), 1278 (1982).

[6] D. Chin, S.-Y. Oh, S.-M. Hu, and R. W. Dutton, IEEE Trans. Electron Dev. **ED-30** (7), 744 (1983).

[7] D.-B. Kao, J. P. McVittie, W. D. Nix, and K. C. Saraswat, IEEE Trans. Electron Dev. **ED-34** (5), 1008 (1987).

[8] D.-B. Kao, J. P. McVittie, W. D. Nix, and K. C. Saraswat, IEEE Trans. Electron Dev. **ED-5** (1), 25 (1988).

[9] W. A. Tiller, J. Electrochem. Soc. **127** (3), 619 (1980).

[10] W. A. Tiller, J. Electrochem. Soc. **127** (3), 625 (1980).

[11] R. H. Doremus, J. Electrochem. Soc. **134** (8A), 2001 (1987).

[12] A. Redondo, W. A. Goddard III, C. A. Swarts, and T. C. McGill, J. Vac. Sci. Technol. **19** (3), 498 (1981).

[13] K. Hübner, E.-D. Klingenberg, and A. Stern, phys. stat. sol. (b) **135,** 475 (1986).

[14] K. Hübner, A. Stern, and E.-D. Klingenberg, phys. stat. sol. (b) **136,** 211 (1986).

[15] E. A. Lewis and E. A. Irene, J. Electrochem. Soc., **134** (9), 2333 (1987).

[16] V. I. Sokolow and N. A. Fedorovich, phys. stat. sol. (a) **99,** 151 (1987).

[17] J. S. Johannessen, W. E. Spicer, and Y. E. Strausser, J. Vac. Sci. Techno. **13** (4), 849 (1976).

[18] C. R. Helms, N. M. Johanson, S. A. Schwarz, and W. E. Spicer, J. Appl. Phys. **50** (11), 7007 (1979).

[19] A. H. Carim and R. Sinclair, J. Electrochem. Soc. **134** (3), 741 (1987).

[20] J. Sune, I. Placencia, E. Farres, N. Barniol, and X. Aymerich, phys. stat. sol. (a) **109,** 497 (1988).

[21] G. I. Barenblatt and Y. B. Zel'dovich, Ann. Rev. Fluid Mech. **4,** 285 (1972).

[22] G. I. Barenblatt, Similarity, self-similarity, and intermediate asymptotics, Plenum Press, New York 1979.

[23] B. E. Deal, J. Electrochem. Soc. **125** (4), 576 (1978).

[24] M. J. Needs, V. Jovic, C. Taylor, K. Board, and M. J. Cooke, Linear elastic model for the local oxidation of silicon using the boundary element method. In: Simulation of conductor devices and processes. Proc. 2nd Int. Conf., Swansea (U.K.) 1986, Vol. 2, p. 412.

[25] E. Rank and U. Weinert, IEEE Trans. Computer-Aided Design. **9** (5), 543 (1990).

[26] C. R. Helms, N. M. Johnson, S. A. Schwarz, and W. E. Spicer, Auger Sputter Profiling Studies of the $Si-SiO_2$ Interface. In: The Physics of $SiO_2$, Proc. Int. Top. Conf., Yorktown Heights, New York 1978, p. 366.