# Temporal Logarithmic Oscillations in Self-Similar Multilayer Aggregation: Shlesinger−Hughes Renormalization with Application to the Tunnel-Assisted Wet Oxidation of Silicon

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A renormalization group approach to self-similar multilayer aggregation processes is suggested on the basis of the following assumptions. 1. The aggregate is generated by a layer-by-layer process, the rate of growth of a given layer being proportional to the number of free sites in the preceding layer. 2. The process is self-similar, that is, from layer to layer the rates of growth are scaled by a subunitary positive Grossmann factor *a*. It is shown that this mechanism of growth leads to temporal scale invariance. For large times the total rate of the process decreases in time according to a hyperbolic law modulated by oscillations occurring on a logarithmic time scale, with a period equal to the logarithm of the reciprocal value of the scaling factor *a*. In the long run the time-dependence of the total mass of the aggregate is given by a logarithmic function of time also modulated by logarithmic oscillations. The model is applied to the tunnel-assisted wet oxidation of silicon. It is assumed that multiple layers of silicon oxide are generated by a mechanism that involves a tunneling process through the silicon oxide layers. In this case Grossmann's scaling factor and the period of logarithmic oscillations have simple physical interpretations: the scaling factor is the transparency of a layer of silicon oxide, and the period of logarithmic oscillations is a measure of the tunneling length. The logarithmic oscillations of the model give a theoretical description of the stepped behavior of the oxidation process observed in the experiments reported in the literature. The presented results are of interest both from the points of view of statistical physics of fractals and nonlinear chemical kinetics.

## 1. Introduction

The study of chemical oscillations is a field of major importance in theoretical and applied chemical kinetics.[1−3] A large number of oscillatory chemical reactions have been investigated both experimentally and theoretically. Moreover, systematic techniques are available for providing mechanistic explanations of the experimental data and for projecting a given oscillatory system. The literature on this subject is enormous; we mention only three recent reviews.[1−3] It is usually assumed that two different conditions are necessary for the occurrence of a chemical oscillation: (1) The system should be operated far from thermodynamic equilibrium and (2) The corresponding kinetic equations must be nonlinear. Although these conditions are not sufficient they are assumed to be necessary for ideal homogeneous chemical systems described by the mass-action law. Recent research, however, goes beyond the ideal chemical systems described by the mass action law; for instance, for nonideal systems some unexpected phenomena may occur, such as chemical oscillations in the immediate vicinity of thermodynamic equilibrium.[4]

In this paper we investigate a class of linear kinetic models for multilayer aggregation that may display a new type of temporal chemical oscillations, which occur on a logarithmic time scale, rather than in real time. The occurrence of logarithmic oscillations for a linear kinetic model contradicts the above mentioned nonlinearity paradigm encountered in the literature. The logarithmic oscillations are characteristic for the renormalization group theory. They were first noticed by theoreticians in the sixties and seventies in connection with the study of energy cascades in turbulent flow[5] and in the real space renormalization of the energy for the Ising model.[6] They also occur for systems described in terms of the Shlesinger−Hughes stochastic renormalization scheme[7−8] and for transport processes in ultrametric spaces.[9,10] The renormalization group logarithmic oscillations have been identified in fluid mechanics[11,12] and in the physiology of the lung.[13−15] As far as we know they have not been reported yet in chemical kinetics.

The renormalization group model for multilayer aggregation suggested in this paper may be used for the description of the chemical process of the wet oxidation of silicon.[16,17] Our theoretical approach is based on the combination of the renormalization procedure of Grossmann[18] with a stochastic version of the Shlesinger−Hughes renormalization method suggested by us for the study of transport processes in disordered systems,[19−21] in ultrametric spaces,[22] and for the study of recycle flows in porous media.[23] Our model is equivalent to a linearized version of the nonlinear kinetic equations suggested by Cerofolini[16,17] for explaining the stepped behavior of the wet oxidation of silicon.[24]

The structure of the paper is as follows. In section 2 we give a general formulation of the problem. Sections 3 and 4 deal with the physical and mathematical self-similar features of the model, respectively. In section 5 the relationships between the suggested approach and the description of the wet oxidation of silicon are investigated and a comparison between our theoretical

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predictions and the experimental data is made. Finally in section 6 the physical and chemical implications of the model are outlined from the points of view of both chemical kinetics and fractal physics.

## 2. Formulation of the Problem

We consider a plane surface on which many identical particles may aggregate in a regular fashion. On the first layer of particles a second layer may be formed by aggregation and so on, layer by layer, up to infinity. This aggregation is similar to the ones used in statistical physics for generating random fractal structures, for instance with diffusion-limited aggregation.[25] We assume that there is an infinite supply of particles and that the kinetics of the process can be described by the mass action law. We assume that initially there are $N_0$ identical sites on the surface and that the process of aggregation starts at the initial time $t = 0$. The kinetic evolution of the process is simply described, to a good approximation, by the equations

$$dN_u(t)/dt = k^{\mathrm{u}}[N_{u-1}(t) - N_u(t)] \qquad u = 1, 2, ... \tag{1}$$

with the initial condition

$$N_0(0) = N_0(t) = \text{constant} \qquad N_u(0) = 0 \qquad u = 1, 2, ... \tag{2}$$

where $N_u$, $u = 1, 2, ...$ are the numbers of particles from the layers 1, 2 and $k_u$, $u = 1, 2, ...$ are the rate coefficients of aggregation corresponding to the different layers. The evolution equations (1) are based on the assumption that the rate of aggregation of the $u$th layer is proportional to the number $N_u - N_{u-1}$ of unoccupied (free) sites in the $(u - 1)$th layer. We are interested in the determination of the time evolution of the total rate of aggregation $r(t)$ expressed in terms of the average number of aggregated particles corresponding to a site on the initial surface. We have

$$r(t) = \frac{1}{N_0}\sum_{u=1}^{\infty}\left[\frac{dN_u(t)}{dt}\right] = \sum_{u=1}^{\infty} r_u(t) \tag{3}$$

where

$$r_u(t) = \frac{1}{N_0}\frac{dN_u(t)}{\mathrm{d}t} \qquad u = 1, 2, ... \tag{4}$$

are the specific rates of growth of the different layers. We are also interested in the evaluation of the time dependence of the total average size $R(t)$ of the aggregate corresponding to an initial lattice center:

$$R(t) = \int_0^t r(t)\,dt = \sum_{u=1}^{\infty}[N_u(t)/N_0] \tag{5}$$

where the terms in the sum express the contributions of the different layers.

Since eqs 1 are linear their integration is very simple. Each function $N_u(t)$ can be written as a linear combination of exponentials of the form $\exp(-k_u t)$, $u = 1, 2, ...$ expressing the contributions of the growth processes of the different layers. At first sight the dynamics of such a process may seem trivial because a combination of exponentials cannot express any self-similar features of the growth process. This claim is however not true. In a general study of the dynamics of the linear evolution equations of the type (1), Grossmann[18] has shown that the system may display self-similarity if the rate coefficients $k_u$, $u = 1, 2, ...$ obey the scaling condition

$$k_u = ka^u \qquad u = 1, 2, ... \tag{6}$$

where $a < 1$ is a scaling factor smaller than unity and $k$ is a reference rate coefficient. In general Grossmann's scaling condition (eq 6) may seem rather formal. We shall see, however, that in the case of the wet oxidation of silicon eq 6 has a straightforward physical meaning, which is related to the reaction mechanism.

The purpose of the present article is to study the scaling behavior of the total specific reaction rate $r(t)$ and of the average size of the aggregate $R(t)$ per lattice center in the case when the growth rates are given by eq 6.

## 3. Physical Approach to Renormalization Group

As far as we know the scaling behavior of the solutions of the evolution equations (eq 1−3) has not been investigated in the literature. In this section we suggest a physically oriented approach to this problem by analogy with the renormalization group scheme suggested by Shlesinger and Hughes for random walks.[7,8] By means of Laplace transformation eqs 1−3 lead to a formal series expansion for the Laplace transform of the specific total growth rate:

$$\bar{r}(s) = \mathrm{L}_s r(t) = \int_0^{\infty} e^{-st} r(t)\,dt \tag{7}$$

where $s$ is the Laplace variable conjugate to the time t and $\mathrm{L}_s$ and the overbar denote the Laplace transformation. By applying the Laplace transformation to eqs 1−3 and by eliminating from the resulting equations the Laplace transforms of the numbers of particles from the different layers, after some elementary algebra we obtain

$$\bar{r}(s) = \sum_{u=1}^{\infty}\prod_{m=1}^{u}\left[\frac{a^m}{a^m + (s/k)}\right] \tag{8}$$

This equation displays some self-similar features that can be outlined by rewriting it in the following form:

$$\bar{r}(s) = \bar{g}_1(s) + \bar{g}_1(s)\bar{g}_2(s) + \bar{g}_1(s)\bar{g}_2(s)\bar{g}_3(s) + ... \tag{9}$$

where

$$\bar{g}_m(s) = [a^m/(a^m + (s/k))] \qquad m = 1, 2, ... \tag{10}$$

are transfer functions, which describe the growth kinetics of the different layers, $m = 1, 2, ...$ It is easy to check that these transfer functions have the property

$$\bar{g}_{m+1}(s) = \bar{g}_m(s/a),\ m = 1, 2, ... \tag{11}$$

and therefore eq 9 can be rewritten as

$$\begin{aligned}\bar{r}(s) = \bar{g}_1(s)[\bar{g}_1(s/a) + \bar{g}_1(s/a)\bar{g}_2(s/a) +{} \\ \bar{g}_1(s/a)\bar{g}_2(s/a)\bar{g}_3(s/a) + ...] = \bar{g}_1(s)\bar{r}(s/a) ={} \\ [a/(a + (s/k))]\{1 + \bar{r}(s/a)\}\end{aligned} \tag{12}$$

from which, coming back to the time variable by means of an inverse Laplace transformation we obtain

$$r(t) = \int_0^t \psi(t')r[a(t - t')]\,dt' + \psi(t) \tag{13}$$

where

$$\psi(t)\, dt = \exp[-(ka)t](ka)\, dt$$

with

$$\int_0^\infty \psi(t')\, dt' = 1 \tag{14}$$

is the probability density of the time $t'$ necessary for the completion of the first layer.

Equations 12 and 13 have a structure typical for a renormalization group equation; they express the self-similarity of the growth process due to the scaling condition (eq 6) for the rate coefficients of growth corresponding to the different layers. From the physical point of view these equations express the fact that the growth process would have exactly the same dynamics if the first layer were removed from the system; the only effect of leaving out the first layer would be a change of the time scale in the evolution equations by a multiplicative factor $a$. Moreover, if the first $n$ layers were removed from the system, the only effect of such a change would be a change of the time scale in the evolution equations by a multiplicative factor $a^n$. By making an analogy with the renormalization group theory, such a physical behavior should lead to temporal scale invariance for the specific growth rate $r(t)$ in the limit of large times. There is a simple physical approach for investigating the self-similar behavior of simple renormalization group equations of the type[7−8]

$$y(x) = b\, y(ax) + f(x) \tag{15}$$

where $f(x) \to 0$ as $x \to \infty$. The solution of this equation is made up of the sum of a nonanalytic component, $w(x)$, which has the main contribution as $x \to \infty$ and by transient analytic contribution $z(x)$ which decreases quickly to zero for large values of $x$:

$$y(x) = w(x) + z(x) \tag{16}$$

The expression for the nonanalytic contribution, $w(x)$, can be evaluated from the homogeneous part of eq 15, which is valid in the limit $x \to \infty$

$$w(x) = bw(ax) \text{ as } x \to \infty \tag{17}$$

by using an interaction representation of the solution of the form:

$$w(x) = x^H Q(x) \tag{18}$$

where $H$ is an unknown real number and $Q(x)$ is an unknown function, respectively. By inserting eq 18 into eq 17, a straightforward calculation shows that $H$ must be given by the relationship

$$H = \ln(b)/\ln(1/a) \tag{19}$$

and that $Q(x)$ must be a periodic function of $\ln x$ with a period $\ln(1/a)$; indeed, the function given by eq 18 is a solution of eq 17 only if $H$ is given by eq 19 and $Q(x)$ fulfills the condition:

$$Q(\ln(x)) = Q(\ln(x) + \ln(1/a)) \tag{20}$$

which expresses the periodicity of $Q(x)$ on a logarithmic, $\ln x$, scale. Even though eq 13 does not have a form given by eqs 15 or 17, the asymptotic behavior of its solutions can however be investigated by using this physical approach. If the time $t$ is larger than the average time necessary for the completion of the first layer,

$$\langle t'\rangle = \int_0^\infty t'\psi(t')dt' = 1/(ka) \tag{21}$$

Then in this region for the computation of the time integral in eq 13 we can approximate the probability density $\psi(t')\, dt'$ by a delta function:

$$\psi(t')\, dt' \approx \delta(t')\, dt' \text{ for } \langle t'\rangle \gg t \tag{22}$$

This approximation is justified by the fact that for large values of the ratio $t/\langle t\rangle$ on the time scale $t$, the exponential probability density (eq 14) for $\psi(t)$ is very sharp, with a large height $ka = 1/\langle t\rangle$ and very narrow, with a small width $\langle t\rangle = 1/(ka)$, and therefore the delta function (22) is a very good approximation for it.

By inserting eq 22 into eq 13 we come to a functional equation for the specific total growth rate $r(t)$, which is a particular case of eq 17 corresponding to $b = a$:

$$r(t) = ar(at) \tag{23}$$

Its solution is given by eq 18 where, according to eq 19 the fractal exponent $H$ is equal to $[\ln a]/[\ln(1/a)] = -1$. Thus we have

$$r(t) = t^{-1}Q(\ln t) \tag{24}$$

where, as in eq 18, $Q(\ln t)$ is a periodic function of $\ln t$ with a period $\ln(1/a)$. In order to evaluate the total specific size per lattice center $R(t)$ of the aggregate, it is advantageous to decompose the periodic function $Q(\ln t)$ into a constant term equal to its logarithmic time average:

$$Q_0 = \frac{1}{\ln(1/a)}\int_0^{\ln(1/a)} Q(b)\, db \tag{25}$$

and into a periodic term in $b = \ln t$ with average value zero:

$$Q_1(\ln t) = Q(\ln t) - Q_0$$

with

$$\int_0^{\ln(1/a)} Q_1(b)\, db = 0 \tag{26}$$

By inserting eqs 24 and 15 into eq 5 and evaluating the time integral for large times we get the following expression for the total specific average size of the aggregate at time $t$:

$$R(t) = Q_0(\ln t) + \Xi(\ln t) \qquad \text{as } t \to \infty \tag{27}$$

where

$$\Xi(b) = \int_0^b Q_1(b')\, db' \tag{28}$$

is also a periodic function of $\ln t$ with a period $\ln(1/a)$. We notice that for large times the total average specific size of the aggregate increases slowly in time according to a logarithmic law modulated by logarithmic oscillations.

In summary in this section we have shown that, due to the assumed Grossmann scaling condition (eq 6) of the rate coefficients attached to the different layers, the growth of the aggregate is self-similar and characterized by a scaling exponent $H = -1$. For large times the specific rate of growth $r(t)$ decreases according to a hyperbolic law ($t^{-1}$) modulated by slow oscillations occurring on a $\ln t$ scale. Similarly, the specific average total size of the aggregate $R(t)$ increases slowly in time according to a logarithmic law of the Elovich[26] type modulated by logarithmic oscillations. The physical approach presented in this paper shows without doubt that the logarithmic growth of the aggregate and the logarithmic oscillations are generated by the self-similarity of the growth process, layer by layer. Unfortunately this technique cannot be used for evaluating the constant and the periodic functions entering eqs 24 and 27 for the total specific rate of growth and for the total size of the aggregate, respectively. These functions can be determined by using a mathematical approach based on the use of the Poisson summation technique;[27] this approach is presented in the following section.

## 4. Explicit Integration of the Evolution Equations

The explicit time dependence of the total rate of growth $r(t)$ can be evaluated by means of an inverse Laplace transformation of eq 8. After lengthy but straightforward calculations eq 8 leads to

$$r(t) = \sum_{u=1}^{\infty} ka^u A_u(a) \exp[-a^u kt] \tag{29}$$

where

$$A_u(a) = S(a)/S_{u-1}(a) \qquad u = 1, 2, ... \tag{30}$$

and

$$S_0(a) = 1,\ S_u(a) = \prod_{m=1}^{u}(1 - a^m), u = 1, 2, ...$$
$$S(a) = \lim_{u\to\infty} S_u(a) \qquad 1 > a > 0 \tag{31}$$

Note that $S(a)$ is a well-known convergent infinite product commonly used in astrophysics as well as in number theory.[28] In order to investigate the asymptotic behavior of the rate of growth $r(t)$, we use the Poisson summation technique,[27] that is, we use the identity

$$\sum_{-\infty}^{+\infty} f(n) = \sum_{-\infty}^{+\infty} C_n \tag{32}$$

where the coefficients

$$C_n = \sum_{-\infty}^{+\infty} f(y) \exp(2i\pi ny)\, dy \tag{33}$$

can be expressed in terms of the Fourier transform of the function $f(y)$. We change in eq 29 the summation label from $u$ to $n = u - 1$ and evaluate the resulting series with the help of eqs 32–33. By noticing that the imaginary part of the result vanishes, after some algebra we obtain

$$\begin{aligned} r(t) = {} & \frac{1}{2} akA_1(a) \exp(-akt) + \\ & \int_0^{\infty} dy A(1 + y,a) \exp(-a^{1+y}kt) + \\ & 2\sum_{u=1}^{\infty} \int_0^{\infty} dy ka^{1+y} A(1 + y,a) \exp(-a^{1+y}kt) \cos(2\pi\, uy) \end{aligned} \tag{34}$$

where $A(u,a)$ is an analytic continuation of the function $A_u(a)$ given by eq 30 for real values of the label $u$. In particular we have

$$A(u,a) = A_u(a) \qquad u = \text{integer} \tag{35}$$

By using the new integration variable

$$x = ka^{1+y}t \tag{36}$$

after a succession of elementary transformations, eq 34 can be rewritten in a more convenient form:

$$\begin{aligned} r(t) = {} & \frac{1}{2} kaA_1(a) \exp(-akt) + \frac{\mathrm{G}_0(akt,a)}{t[\ln(l/a)]} + \\ & \frac{2}{t[\ln(1/a)]} \sum_{u=1}^{\infty} \left\{ \mathrm{G}_u^{+}(akt,a) \cos\left[\frac{2\pi\, u \ln(akt)}{\ln(1/a)}\right] + \right. \\ & \left. \mathrm{G}_u^{-}(akt,a) \sin\left[\frac{2\pi\, u \ln(akt)}{\ln(1/a)}\right] \right\} \end{aligned} \tag{37}$$

where

$$\mathrm{G}_0(z,a) = \int_0^z A\left[1 + \frac{\ln(z/x)}{\ln(1/a)},a\right] \exp(-x)dx \tag{38}$$

and

$$\mathrm{G}_u^{\pm}(z,a) = \int_0^z A\left[1 + \frac{\ln(z/x)}{\ln(1/a)},a\right] \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \left[\frac{2\pi\, u \ln(x)}{\ln(1/a)}\right] \times \exp(-x)dx \tag{39}$$

Equation 37 can be used for investigating the asymptotic behavior of the total rate of growth $r(t)$ for large times. For $t \gg \langle t \rangle = 1/(ka)$, in eqs 38 and 39 the $A$ functions can be approximated by unity because for large $u$ we have

$$A(u,a) \approx A_{[u]}(a) \approx \lim_{[u]\to\infty} [S(a)/S_{[u-1]}(a)] = 1 \qquad \text{for } u \gg 0 \tag{40}$$

and therefore

$$\mathrm{G}_0(akt,a) \approx \int_0^{akt} \exp(-x)\, dx = 1 - \exp(-akt) \approx 1 \qquad \text{for } t \gg \langle t \rangle = 1/(ak) \tag{41}$$

and

$$\mathrm{G}_u^{\pm}(akt,a) \cong \int_0^{akt} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \left[\frac{2\pi\, u \ln(x)}{\ln(1/a)}\right] \exp(-x)dx \cong \mathrm{F}^{\pm}\left(1,\frac{2\pi\, u}{\ln(1/a)}\right) \qquad t \gg \langle t \rangle \tag{42}$$

where with

$$\mathrm{F}^{\pm}(b,c) = \begin{Bmatrix} \mathrm{Re} \\ \mathrm{Im} \end{Bmatrix} \Gamma(z = b + \mathrm{i}c)$$
$$\Gamma(z) = \int_0^{\infty} t^{z-1} \exp(-t)\, dt \tag{43}$$

are the real and imaginary parts of the gamma function of complex argument, respectively.

By using the approximate equations 41 and 42 we recover from eq 37 the asymptotic scaling law (eq 24) where the components $Q_0$ and $Q_1(\ln(akt))$ of the function

$$Q(\ln t) = Q_0 + Q_1(\ln(akt)) \tag{44}$$

are given by

$$Q_0 = 1/[\ln(1/a)] \tag{45}$$

and

$$Q_1[\ln(akt)] = \frac{2}{\ln(1/a)} \times \sum_{u=1}^{\infty} \left\{ F^{+}\left(1, \frac{2\pi u}{\ln(1/a)}\right) \cos\left[\frac{2\pi u \ln(akt)}{\ln(1/a)}\right] + F^{-}\left(1, \frac{2\pi u}{\ln(1/a)}\right) \sin\left[\frac{2\pi u \ln(akt)}{\ln(1/a)}\right] \right\} \tag{46}$$

Similarly, by considering two large times, $t$ and $t_0$, integrating the expression (eq 24) from $t_0$ to $t$ and making use of eqs 44–46, we recover the expression (eq 27) for the asymptotic behavior of the total specific size of the aggregate, where the periodic contribution $\Xi(\ln t)$ is given by

$$\begin{aligned} \Xi[\ln(kat)] = R(t_0) - & \sum_{u=1}^{\infty} \frac{1}{\pi u} \left\{ F^{+}\left(1, \frac{2\pi u}{\ln(1/a)}\right) \sin\left[\frac{2\pi u \ln(akt_0)}{\ln(1/a)}\right] + F^{-}\left(1, \frac{2\pi u}{\ln(1/a)}\right) \cos\left[\frac{2\pi u \ln(akt_0)}{\ln(1/a)}\right] \right\} + \\ & \sum_{u=1}^{\infty} \frac{1}{\pi u} \left\{ F^{+}\left(1, \frac{2\pi u}{\ln(1/a)}\right) \sin\left[\frac{2\pi u \ln(akt)}{\ln(1/a)}\right] + F^{-}\left(1, \frac{2\pi u}{\ln(1/a)}\right) \cos\left[\frac{2\pi u \ln(akt)}{\ln(1/a)}\right] \right\} \end{aligned} \tag{47}$$

In conclusion, the direct integration of the evolution equations leads to results consistent with the physical approach presented in section 3. We have recovered the Elovich logarithmic law for the total size of an aggregate, as well as the oscillatory logarithmic modulation. The mathematical approach presented in this section leads to analytic expressions for the proportionality factors, the characteristic frequencies, and the Fourier series representing the logarithmic oscillations.

## 5. Application to the Wet Room Temperature Oxidation of (100) Silicon

Silicon oxidation at room temperature has been the subject of many experimental studies in the past years. The literature on this subject is rather large and we do not intend to review it here. For information on these experimental studies see refs 16, 17, 24, 29–31. The room-temperature oxidation in wet air of the (100) face of a single crystal of silicon creates multiple layers of silicon oxide, each layer being generated after the almost complete generation of the previous layer. The thickness $x$ of the $SiO_2$ layer grown during wet oxidation is a stepped function of time, which can be described by a main logarithmic trend

$$x(t) - x(t_1) \propto \ln(t/t_1) \tag{48}$$

where $x_1$ is the thickness of the first layer and $t_1$ is the time at which the first layer is completely formed. This main trend is modulated by oscillations which occur on a logarithmic time scale (Figures 1 and 2).

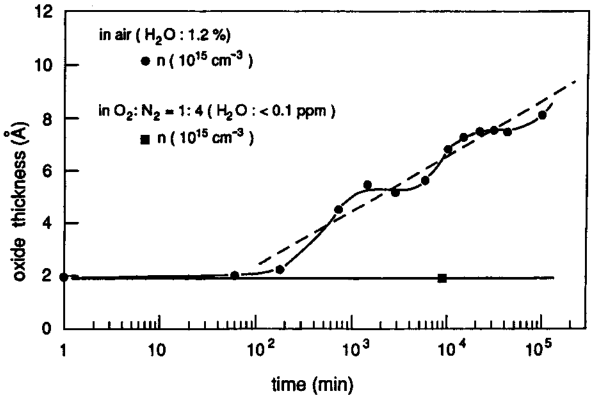

**Figure 1.** Oxide thickness $z$ grown during room temperature oxidation of a single crystal, (100) oriented, of $n$-type silicon in wet and dry air. The dopant concentration $n$ was $10^{15}$ $cm^{-3}$. A similar behavior is also observed for wet oxidation of heavily doped $p$ type silicon and, with a higher rate, for $n$ type silicon (after Ohmi et al.[24]).

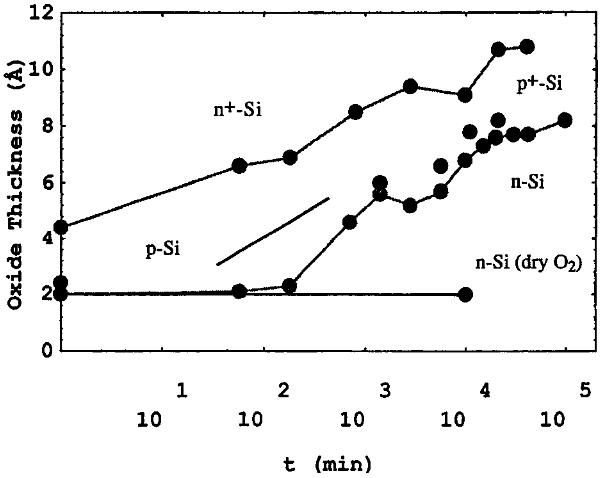

**Figure 2.** Linear-logarithmic plot of the experimental oxidation kinetics of $p$, $p^+$, $n$, and $n^+$ type (100) silicon resulting from exposure to wet air. Data for $p$ type silicon are taken from Mende et al.[29] The other data are taken from Morita et al.[30] Lines have been drawn as done in refs 29 and 30.

One of the present authors, in collaboration with other researchers, has suggested a number of reaction mechanisms for explaining the experimental data.[24,29,30] Although the assumptions concerning the detailed reaction mechanisms are different for these three models, the main kinetic equations are the same for all the models. The initial model was based on the assumption that molecular oxygen and the adsorbed water on the surface are involved in sequences of different cycles, each cycle corresponding to one layer of oxide. Each cycle involves three steps:[16] 1. The molecular oxygen $O_2$ reacts with Si–Si bonds to form siloxanic centers Si–O–Si. 2. The siloxanic centers Si–O–Si react with the absorbed water $H_2O$ on the surface to form Si–OH groups, thus rendering new silicon atoms to react with oxygen. 3. The water is readsorbed on each hydroxyl group.

The first step is assumed to be very fast and not limited by the oxygen diffusivity inside the formed oxide and, similarly, $H_2O$ is assumed to give an almost complete coverage of the surface. On the other hand, water may reasonably be assumed to be bonded at the superficial hydroxylic groups and unable to diffuse to the reaction interface. For this reason it is assumed that starting from the second cycle the reaction of adsorbed water

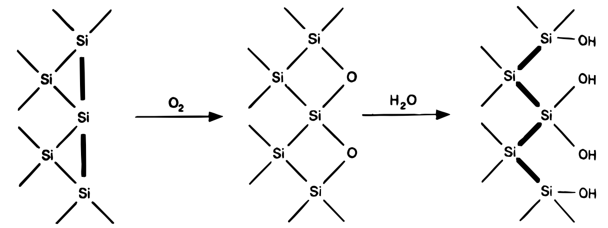

**Figure 3.** First model. Sketch of the oxidation−hydroxylation cycle.

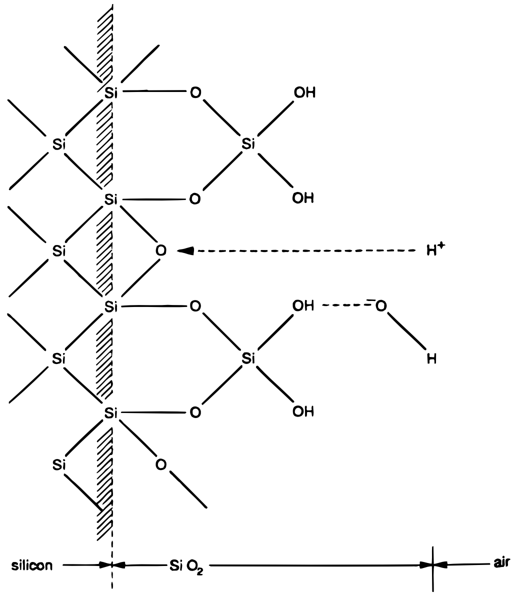

**Figure 4.** First model. Mechanism showing the proton transfer from adsorbed water to disiloxanic interface oxygen via tunneling through a grown-in oxide layer.

with an Si−O−Si at the interface occurs via a tunnel effect through a thermally excited state. It is assumed that this tunneling step is the rate-determining step of the process. Quantum mechanical tunneling requires that the mass of the tunneling particle is sufficiently small. In ref 16 it is suggested that the proton is the tunneling particle. This assumption is justified by the fact that $H_2O$ is a weak Brønsted acid, i.e., a proton donor. The following microscopic model has been suggested: 1. The oxide is characterized at each point by its thickness expressed in terms of the number $n$ of layers; 2. Water is adsorbed on the hydrophilic sites at the surface of the $SiO_2$; 3. Because of thermal excitation water partially dissociates as $OH^-$ and $H^+$; 4. In a thermally excited state the proton tunnels with a transmission coefficient $\mathscr{T}_n$ to a neutral Brønsted basic site at the interface; 5. Under the action of the Coulombic attraction the $OH^-$ ion migrates to the proton-hosting site at the interface, eventually forming therein hydroxyl groups; 6. The migration of the $OH^-$ ion restores the surface site, which becomes available to adsorb another $H_2O$ molecule.

Figure 3 displays the oxidation reactions during the first cycle, and Figure 4 illustrates the proton tunneling from absorbed water to siloxanic oxygen during the following cycles. Ref 16 provides qualitative and quantitative arguments in favor of such a mechanism, based on energetic considerations.

The analysis of this model is resumed in a later publication.[17] In this article further evidence is provided suggesting that the hydroxylation is produced by the hydration of a peroxidic bridge rather than of a siloxanic bridge. Otherwise the main steps of the process are assumed to be the same. In Figure 5 we give a schematic representation of the main reactions involved in the second mechanism.

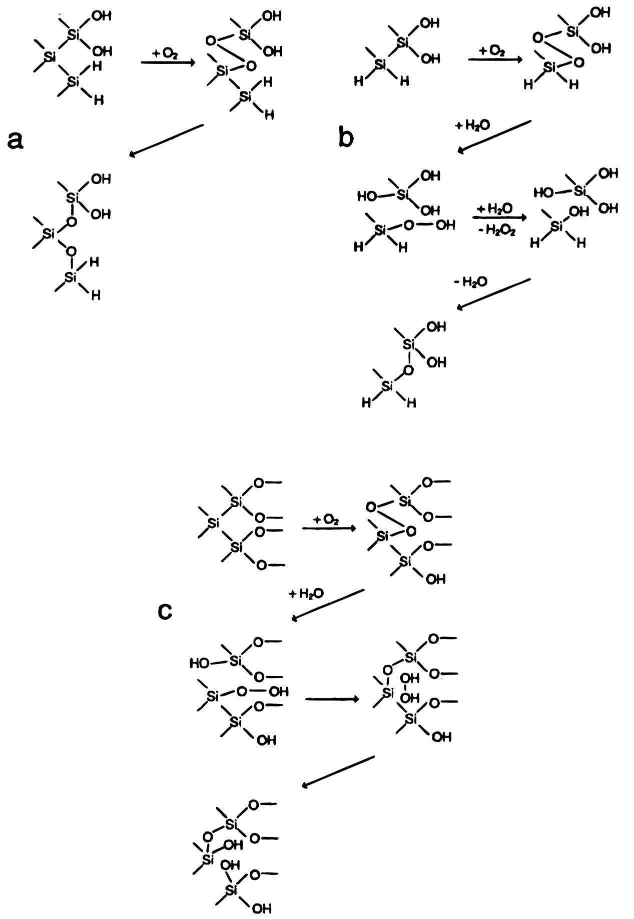

**Figure 5.** Second model. The superficial oxidation of silicon (a) in dry air and (b) in wet air and (c) the oxidation of silicon in wet air at the $Si-SiO_2$ interface.

For both models preliminary computations have shown that the experimental data are compatible with tunneling (transparency) factors of the order of magnitude $10^{-2}$, which are rather large for proton tunneling. This observation has generated a third version of the model, by assuming that the rate-determining step is electron tunneling from a negatively charged center at the $Si-SiO_2$ surface to adsorbed oxygen. The details of this third mechanism are presented elsewhere.[31] Here we give only the main steps of the process: 1. Water diffuses easily from the adsorbed state at the $SiO_2$ surface to the $Si-SiO_2$ interface. 2. Water at the $Si-SiO_2$ interface reacts to form $(-O)_3Si^+ \leftarrow OH_2$ $^-Si \equiv$ centers. 3. The electron charge on silicon tunnels to physically adsorbed $O_2$ to form $O_2^{\bullet-}$. 4. Under the Coulombic attraction, $O_2^{\bullet-}$ drifts to the positively charged $(-O)_3Si^+ \leftarrow OH_2$ sites, where it initiates a new reaction cycle.

The main steps of this third model are represented in Figure 6. The overall reaction corresponding to the reaction mechanism from Figure 6 is

$$2 \equiv \mathrm{Si}-\mathrm{Si} \equiv +\mathrm{O}_2 \xrightarrow{\mathrm{H_2O}} 2 \equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}$$

Water is necessary for initiating the multilayer oxidation process and for allowing it to proceed, but there is no net consumption of $H_2O$; water behaves as a catalyst and it may activate the oxidation cycle even in traces.

These three models share an important feature: in all cases a succession of tunneling processes through the different layers of silicon oxide is the rate-determining process. Because of this

$$\equiv \mathrm{Si}\text{-}\mathrm{Si}\equiv + \mathrm{H_2O} \rightarrow \equiv \mathrm{Si}^{+} \leftarrow \mathrm{OH_2}\ {}^{-}\mathrm{Si}\equiv$$

$$\equiv \mathrm{Si}^{+} \leftarrow \mathrm{OH_2}\ {}^{-}\mathrm{Si}\equiv + \mathrm{O_2} \rightarrow \equiv \mathrm{Si}^{+} \leftarrow \mathrm{OH_2}\ {}^{\bullet}\mathrm{Si} + \mathrm{O_2^{\bullet-}}$$

$$\equiv \mathrm{Si}^{+} \leftarrow \mathrm{OH_2}{}^{\bullet}\mathrm{Si}\equiv + \mathrm{O_2^{\bullet-}} \rightarrow \equiv \mathrm{SiOO}^{\bullet}\ {}^{\bullet}\mathrm{Si}\equiv + \mathrm{H_2O}$$

$$\equiv \mathrm{SiOO}^{\bullet}\ {}^{\bullet}\mathrm{Si}\equiv \rightarrow \equiv \mathrm{SiOOSi}\equiv$$

$$\equiv \mathrm{SiOOSi}\equiv + \mathrm{H_2O} \rightarrow \equiv \mathrm{SiOH}\ \ \mathrm{HOOSi}\equiv$$

$$\equiv \mathrm{SiOH}\ \ \mathrm{HOOSi}\equiv + \mathrm{H_2O} \rightarrow \equiv \mathrm{SiOH}\ \ \mathrm{HOSi}\equiv + \mathrm{H_2O_2}$$

$$\equiv \mathrm{Si}\text{-}\mathrm{Si}\equiv + \mathrm{H_2O_2} \rightarrow \equiv \mathrm{SiOSi}\equiv + \mathrm{H_2O}$$

$$\equiv \mathrm{SiOH}\ \ \mathrm{HOSi} \rightarrow \equiv \mathrm{SiOSi}\equiv + \mathrm{H_2O}$$

**Figure 6.** Third model. Mechanism showing the electron transfer from $\mathrm{Si}^{-}$ centers to adsorbed oxygen $\mathrm{O_2}$.

common feature they all lead to the same type of kinetic equations, even though the physical meaning of the variables involved is different. In the following we consider the case of model 2, for which a detailed kinetic analysis has been presented in the literature.[17] In the first place we write an evolution equation for the generation of the first layer. We introduce the following notations: $f$ for the fraction of peroxidic sites covered by water; $\nu_0$ for frequency of vibration along the configuration, which allows $H_2O$ and $(\equiv Si)_2O$ to react; and $P_0$, the probability that this process occurs. In terms of these parameters, the kinetic equation for the formation of the first layer, can be expressed as

$$d\theta_0/dt = \nu_0 P_0 f\eta(1 - \theta_0) \tag{49}$$

where $\eta$ and $\theta_0$ are the fraction of the silicon atoms from the surface bonded to peroxidic oxygen and disiloxanic oxygen, respectively. The condition that oxidation follows hydroxylation almost immediately is

$$\eta(t) = \xi\theta_0(t) \tag{50}$$

where $\xi$ is a constant factor of the order of unity. These two assumptions lead to the following kinetic equation:

$$d\theta_0/dt = E_0\theta_0(1 - \theta_0)$$

with

$$E_0 = \xi\nu_0 P_0 f \tag{51}$$

The evolution equations for the following layers have a similar structure

$$d\theta_n/dt = (1 - \theta_n)\theta_{n-1} f\nu P_n \qquad n = 1, 2, ...; \theta_0 = 1 \tag{52}$$

where $\theta_0(t)$ is the solution of eq 51, $\nu$ is the proton vibration frequency perpendicular to the surface, and $P_n$ is the probability of proton transfer from the $n$th layer to the interfacial layer. Since this process results from the combination of a thermal excitation, with probability $\exp(-\Delta E^*/k_BT)$, and proton tunneling from the surface to interface, we have

$$P_n = \mathcal{T}_n \exp(-\Delta E^*/k_BT) \tag{53}$$

where $\mathcal{T}_n$ is the barrier transparency from the $n$th layer to the surface layer. According to quantum mechanics[32] the barrier transparency $\mathcal{T}_n$ can be expressed as

$$\mathcal{T}_n = \exp(-\chi\lambda n) \tag{54}$$

where $\lambda$ is the average tunneling length per layer and $\chi$ is a shape factor depending on the form of the potential barrier.[32]

We introduce the notations

$$E_* = \xi\nu f \exp(-\Delta E^*/k_BT) \tag{55}$$

and

$$a = \mathcal{T}_1 = \exp(-\chi\lambda) \tag{56}$$

and rewrite eqs 52 in the following form:

$$d\theta_n/dt = E_* a^n(1 - \theta_n)\theta_{n-1} \tag{57}$$

Now we make use of the approximation that the completion of one layer of silicon oxide starts after the preceding layer is practically completed. Under these circumstances the $\theta$-dependent factor in eq 57 can be approximated by observing that, during the completion of the $n$th layer, the $(n - 1)$th layer is almost filled up and $\theta_n$ is close to unity. Therefore in eq 57 the factor $(1 - \theta_n)\theta_{n-1}$ can be approximated by the difference of the coverages of the two layers, i.e.,

$$(1 - \theta_n)\theta_{n-1} = \theta_{n-1} - \theta_{n-1}\theta_n \cong \theta_{n-1} - \theta_n \tag{58}$$

By using this approximation we can put eq 57 in a form similar to the general evolution equation (eq 1) for multilayer aggregation derived in section 1:

$$d\theta_n/dt = k(t)a^n(\theta_{n-1} - \theta_n) \tag{59}$$

where $k(t)$ is a time-dependent rate coefficient, which can be evaluated analytically by integrating eq 51. We have

$$k(t) = \xi\nu f \exp(-\Delta E^*/k_BT) \times \left[1 + \frac{1 - \theta_0(0)}{\theta_0(0)} \exp(-\xi\nu_0 P_0 ft)\right]^{-1} \tag{60}$$

We notice that in the case of multilayer silicon oxidation, the scaling condition of the Grossman type given by eq 6 has a simple physical interpretation: it is due to the quantum mechanical tunneling of multiple layers of silicon oxide. The scaling factor $a$ is the transparency of a layer of oxide, which, according to eq 56 varies exponentially with the tunneling length $\lambda$. We notice that there is however a difference between the general model for multilayer aggregation developed in section 1 and the process of silicon oxidation. In section 1 the rate coefficient $k$ is independent of time whereas for silicon oxidation it is a function of time given by eq 60. However, since the factor

$k(t)$ enters all equations (eq 57), we can introduce an intrinsic time scale, $\tau(t)$, given by

$$\tau(t) = \int_0^t k(t)dt = \xi\nu f \exp(-\Delta E^*/k_BT) \times \left\{t + \frac{\ln[\theta_0(0) + (1 - \theta_0(0)) \exp(-\xi\nu_0 P_0 f t)]}{\xi\nu_0 P_0 f}\right\} \quad (61)$$

In terms of the intrinsic time scale $\tau(t)$, eq 57 can be written is a form which is identical to eq 1

$$d\theta_n/d\tau = a^n(\theta_{n-1} - \theta_n) \quad (62)$$

where the time $t$ is replaced by $\tau(t)$ and the numbers of particles from the different layers are replaced by the corresponding partial coverages.

It follows that the general theory developed in section 1 can be easily applied to silicon oxidation. In particular the logarithmic law observed experimentally for large times as well as the logarithmic oscillations which modulate it are derived as straightforward consequences of our approach. Strictly speaking, from our theory we derive these dependencies in terms of the intrinsic time scale $\tau(t)$ rather than in terms of the real time $t$. However, the difference between the two time scales is important only for short times. From eq 61 we notice that the relationship between the two time scales is nonlinear only for short times; for times larger than $1/(\xi\nu_0P_0f)$, the dependence between the two time scales becomes linear

$$\tau(t) \cong \frac{\nu \exp(-\Delta E^*/k_BT)}{\nu_0 P_0 f} t \qquad \text{for } t \gg 1/(\xi\nu_0 P_0 f) \quad (63)$$

In the particular case of silicon oxidation, the period of logarithmic oscillations, $\Theta = \ln(1/a)$, is proportional to the tunneling length $\lambda$. From eq 56 we have

$$\Theta = \ln(1/a) = \chi\lambda \quad (64)$$

Equation 64 illustrates the physical origin of logarithmic oscillations in the case of silicon oxidation: the oscillations are generated by a succession of tunneling events across successive layers of silicon oxide.

The main problem connected to the application of the renormalization group approach to the study of silicon oxidation is related to the approximation (eq 58), which is physically reasonable. The approximation is very good if the scaling factor is small, i.e., less than $a < 10^{-1}$. In order to check the validity of our theoretical approach we have solved numerically the nonlinear evolution equations (eq 57) expressed in terms of the intrinsic time scale $\tau$

$$d\theta_n/d\tau = a^n(1 - \theta_n)\theta_{n-1} \quad (65)$$

and computed the total production of silicon oxide per site, $R_{\text{nonlinear}}(\tau)$ as a function of the intrinsic time $\tau$. We have compared the result with the analytic expression for the average size of an aggregate, $R(\tau) = R(t = k/\tau)$, expressed as a function of the intrinsic time, which in the case of our general approach from sections 2−4 is simply equal to $\tau = kt$. Figure 7 displays the dependence of the difference between these two functions

$$\Delta R(x,\Theta) = R_{\text{nonlinear}}(\tau = \exp(x)) - R(\tau = \exp(x)) \quad (66)$$

as a function of the period $\Theta = \ln(1/a)$ of logarithmic oscillations and of the logarithm of dimensionless time $x = \ln \tau$. We notice that our approximation is excellent for large values of $\Theta$ and $x$, but is very bad for low values of these two variables, where huge oscillations occur. For a period of logarithmic oscillations bigger than three, $\Theta > 3$, which corresponds to $a < 10^{-1}$, the approximation is very good even for moderately large values of the dimensionless time.

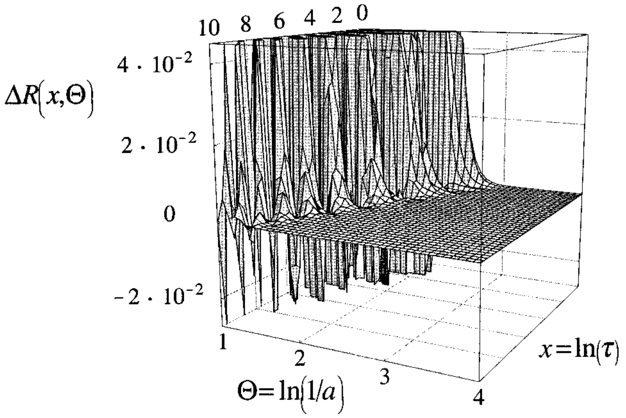

**Figure 7.** Surface representation of the difference $\Delta R(x,\Theta)$ between the aggregate size per unit site obtained from the numerical integration of the nonlinear model and the approximate analytic expression obtained by applying the renormalization group theory. The figure shows a surface plot of the difference $\Delta R(x,\Theta)$ as a function of the period of logarithmic $\Theta = \ln(1/a)$ oscillations and the logarithm of dimensionless time, $x = \ln(\tau)$.

In order to compare the theory with experiment it is necessary to compute the experimental observable, which is usually the oxide thickness $z(t)$ grown at time $t$. In its present form, our theory is able to give the amount of oxide $W(t)$ per unit area of oxidized silicon

$$W(t) = N_s\eta + N_{\text{Si}}^{\text{ox}}\sum_{m=0}^{\infty}\theta_m(t) = N_s[(1 + \kappa)\theta_0(t) + \kappa\sum_{m=1}^{\infty}\theta_m(t)] \quad (67)$$

where $N_s$ and $N_{\text{Si}}^{\text{ox}}$ are the numbers, per unit area, of silicon atoms in silicon and SiO$_2$, respectively, and $\kappa = N_{\text{Si}}^{\text{ox}}/N_s$. For the (100) surface of silicon one has $N_s = 6.8 \times 10^{14}$ cm$^{-2}$, whereas $N_{\text{Si}}^{\text{ox}}$ depends on the structure of silicon oxide. The order of magnitude of $N_{\text{Si}}^{\text{ox}}$ can be evaluated from $N_{\text{Si}}^{\text{ox}} = (s\,\rho_{\text{Si}}^{\text{ox}})^{2/3}$ where $\rho_{\text{Si}}^{\text{ox}}$ and $s$ are the density and the packing fraction of silicon oxide, respectively. Assuming for $s$ a value between that of the diamond cubic lattice and that of the face-centered cubic lattice we have $s = 0.7-0.8$. We consider that only a fraction $1 - \beta$ of this surface can be described by the model presented here and that the remaining fraction $\beta$ is already covered at $t < 1/(\xi\nu_0P_0f)$ by $h$ layers of silicon oxide. Under these circumstances eq 67 becomes

$$z(t) = W(t)/\rho_{\text{Si}}^{\text{ox}} = \lambda^0[(1 - \beta)((1 + \kappa)\theta_0(t) + \kappa\sum_{m=1}^{\infty}\theta_m(t)) + \beta h] \quad (68)$$

where $\lambda^0 = N_s/\rho_{\text{Si}}^{\text{ox}} = 3.1$ Å.

Equation 68 depends on seven independent parameters: the effective rate coefficient of the first oxidation−hydroxylation process,

$$R_0 = \xi\nu_0 P_0 f \quad (69)$$

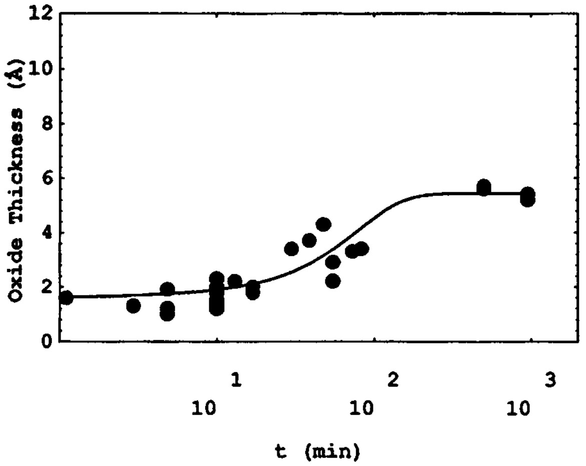

**Figure 8.** Comparison between experimental data (dots) and the theoretical expression (line) for the oxide thickness for the oxidation of *p* type silicon.

**TABLE 1: Kinetic Parameters Characterizing the Multilayer Growth of Silicon Oxide on Different Substrates (for definitions of the parameters see eqs 49−64)**

| | *p*-Si | *n*-Si | $p^+$-Si | $n^+$-Si |
|---|---|---|---|---|
| $\kappa$ | 0.7 | 0.7 | 0.85 | 0.7 |
| $R_0(s^{-1})$ | $4.2 \times 10^{-4}$ | $5.6 \times 10^{-5}$ | $5.6 \times 10^{-5}$ | $5.6 \times 10^{-5}$ |
| $R(s^{-1})$ | | $6.0 \times 10^{-5}$ | $6.0 \times 10^{-5}$ | $6.0 \times 10^{-5}$ |
| $a$ | | $2.0 \times 10^{-2}$ | $2.0 \times 10^{-2}$ | $2.0 \times 10^{-2}$ |
| $\theta_0(0)$ | 0.29 | 0.37 | 0.40 | 0.37 |
| $\beta$ | 0 | 0 | 0 | 0.2 |
| $h$ | | | | 7 |

the transparency of a layer of silicon oxide, $a$; the effective rate coefficient

$$R_n = \nu f \exp(-\Delta E^*/(k_B T)) \tag{70}$$

which describes the oxidation of the following layers; the fraction $\theta_0(0)$, which describes the initial oxidation state of the surface; the fraction $\kappa$, which depends on the oxide structure, and $\beta$ and $h$, which describe the effect of other oxidation processes. Suitable choices for these parameters which provide a satisfactory description of the experimental data presented in the literature are given in Table 1, for the particular case of $p$, $p^+$, $n$, and $n^+$ type (100) silicon. The physical basis for the choice of these parameters is going to be presented in another paper. Figures 8−11 give a comparison of the experimental data presented in the literature with the theoretical prediction of the model. We notice a satisfactory agreement between theory and experiment. The logarithmic oscillations show up clearly in the stepped behavior of the oxidation curves for the $p^+$, $n$, and $n^+$ type (100)silicon, presented in Figures 9, 10, and 11.

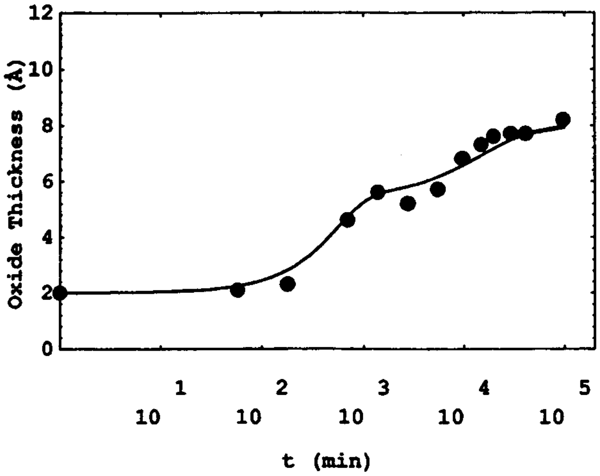

**Figure 9.** Comparison between experimental data (dots) and the theoretical expression (line) for the oxide thickness for the oxidation of *n* type silicon.

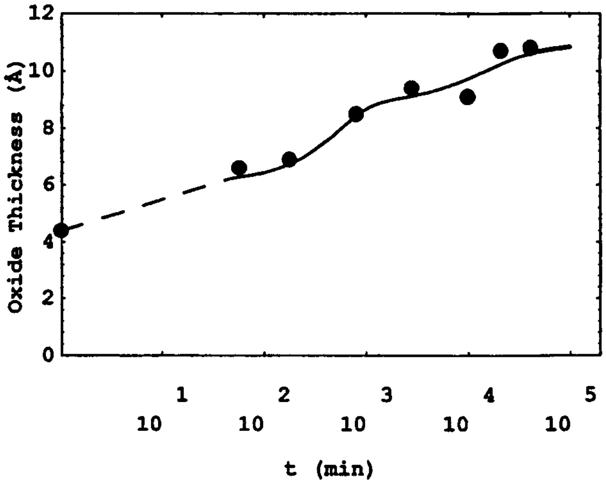

**Figure 10.** Comparison between experimental data (dots) and the theoretical expression (line) for the oxide thickness for the oxidation of $p^+$ type silicon.

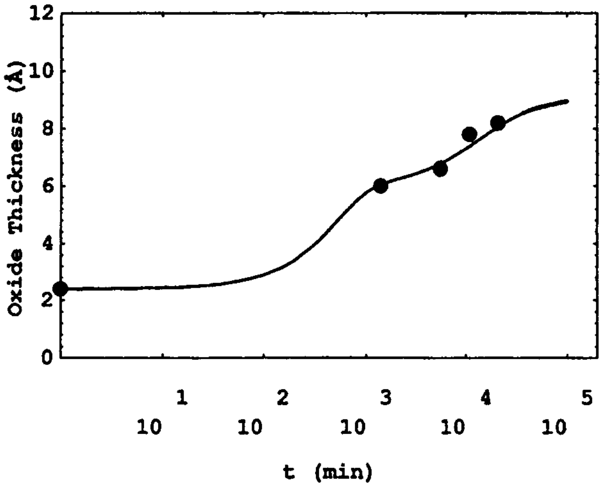

**Figure 11.** Comparison between experimental data (dots) and the theoretical expression (line) for the oxide thickness for the oxidation of $n^+$ type silicon.

## 6. Conclusions

In this article we have suggested a simple kinetic model of layer-by-layer aggregation. We have proved that for a self-similar system, obeying a scaling condition of the Grossmann type, in the long run the total size of the aggregate obeys a growth law of the logarithmic type, modulated by oscillations on a logarithmic time scale. We have shown that our model is capable of describing the main features of the chemical process of the wet oxidation of the (100) face of a single crystal of silicon, where the logarithmic oscillations show up in the stepped behavior of the kinetic curves. We have suggested that for the wet oxidation of silicon, the Grossmann scaling condition is due to a process of quantum tunneling across multiple layers of silicon oxide. We have shown that the model provides a satisfactory description of the experimental data presented in the literature.

Our research is an interdisciplinary study of interest both for nonlinear chemical kinetics and the statistical physics of fractal systems. In nonlinear kinetics the study of oscillations has a long history. In this article we have reported the existence of a new type of chemical oscillations for which the oscillatory process takes place on a logarithmic time scale rather than in real time. The oscillations reported here are not conventional oscillations in the sense that the kinetic curves are not going up and down but rather present a stepped behavior. Nevertheless, the kinetic process has a periodic component which is responsible for the stepped behavior and which is described by a periodic function of the logarithm of real time.

In the statistical physics of fractal systems the study of aggregation processes is a subject of topical interest: these processes provide a lot of interesting examples of statistical and geometrical fractals. In this field the logarithmic oscillations are well known theoretically, they enter the solutions of the equations of the renormalization group. However, for most systems they are considered to be only a mathematical artifact and are usually discarded in the description of real physical or chemical processes. There are only few examples for which there is no doubt that the logarithmic oscillations of the renormalization group exist in the real world. In this paper we have enriched this small collection with a new example, the wet oxidation of silicon.

From the point of view of fractal physics our model is rather unusual because our law of growth has a main logarithmic trend rather than a power law trend. However, there is no doubt that for our model the mathematical origin of logarithmic oscillations is in the renormalization group equations. Our kinetic equations for the rate of growth are hyperbolic and modulated by logarithmic oscillations, which corresponds to a fractal exponent equal to $-1$, a value which is unusual in fractal statistics; this special value of the fractal exponent generates the main logarithmic trend in the integral kinetic equations. A slight modification of the model of aggregation presented in this article leads to “true” statistical fractal kinetics with logarithmic oscillations with fractal exponents smaller than $-1$. This generalized model also displays some interesting new kinetics features, such as the existence of logarithmic oscillations occurring on a double iterated logarithmic time scale, $\ln \ln t$. Work on this problem is in progress and the results will be presented elsewhere.

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