Microscopic Properties of the SiO_2/Si Interface Growth Based on Numerical Simulations

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To improve the understanding of the microscopic properties of the silicon oxidation process, we perform numerical simulations of thermal SiO_2 thin film growth. Therefrom, we analyze the growth kinetics as well as the evolution of the SiO_2/Si interface formation. The oxidation rate in the early stages of growth is governed by two processes: the rapid initial formation of the oxidation front, and its subsequent diffusion. The corresponding oxidation kinetics, arising from the simulations, provides a rather good description of a large variety of experimental data, with the minimum number of variable parameters. The effect of external parameters, such as temperature and pressure, can be explained in terms of scaling concepts. It is found that the temporal evolution of SiO_2 concentration at a given fixed crystalline cross section is continuous, while the spatial distribution at any given time shows abrupt (step like) behavior, decaying from 100 % to zero concentration within just a few lattice constants. The results of the simulations suggest a very simple phenomenological approach for modeling of microstructural aspects of the SiO_2/Si system.

I. Introduction

Thermal SiO_2 thin films and the SiO_2/Si interface have been among the most studied systems in condensed matter physics, ever since the first successful experimental realisation[1] of the metal-oxide-semiconductor field effect transistor (MOSFET). This great interest arose due to the fact that the SiO_2/Si interface represents the heart of metal-oxide-semiconductor (MOS) devices, and also because a large variety of diverse physico-chemical phenomena govern the interfacial physical and electrical properties. The experimental achievement of producing highly reliable interfaces, with very low concentrations of electrically active defect densities, has been the turning point of technological advancements that led towards deep submicron size MOSFETs and a number of advanced MOS technologies in the ultra large scale of integration (ULSI).

The improvements accomplished in the physical and electrical properties of thermal SiO_2 and the SiO_2/Si interface (despite the volume expansion which occurs during thermal growth) have led to the development of transistors which operate with thermally grown gate oxides to thicknesses below 10 nm. However, the physics and chemistry of thermal SiO_2 layers with thicknesses under 20 nm are still not yet well understood, and represent a very important current research line in the materials science field. The leading role of the SiO_2 system in these advanced technologies is due, in great part, to the ease and low cost of silicon dioxide production (from the silicon substrate), and to its excellent insulating characteristics. New insights are still needed, to better understand the physical mechanisms responsible for the growth kinetics of very thin SiO_2 films on silicon, and the dynamics of the SiO_2/Si interface formation. This represents one of the requirements for further advancements in MOS technologies, and other

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applications of the SiO_2/Si system related to state of the art microelectronic devices and integrated circuits.

Over the past two decades[2−29], we have witnessed a number of important developments in the chemistry and physics of SiO_2 thin films, mainly due to advances in probing and measuring techniques that originated refined experiments, and revealed a variety of new phenomena in the SiO_2/Si system. During this period, the microstructure of the SiO_2/Si system has been probed by dozens of experimental techniques in order to examine its intrinsic properties, as well as the chemical and physical nature of defects and atomic bonding formation. This has led to important information related to the SiO_2/Si interface extent and its roughness. These techniques include Auger spectroscopy[2], ellipsometry[3], Rutherford backscattering[4], low-energy electron diffraction[5], x-ray photoelectron spectroscopy[6], transmission electron microscopy[7], scanning tunneling microscopy[8], x-ray scattering[9], synchrotron spectroscopy[10], and a variety of other spectroscopical and electrical probing techniques[11]. Despite the availability and diversity of information on the microstructural properties of the SiO_2/Si system which arose from these experiments, the reported values for the spatial extent of the SiO_2/Si interface presently range from atomically sharp to about 3-5 nm wide[10]. The variations observed may be due, in part, to the different processing used during sample fabrication, and on the other side to the resolution and data analysis methodology associated with each probing technique. In the theoretical aspect, the models proposed to explain the growth kinetics of thermal SiO_2 films still seem to lack consistency to explain all experimental results. In particular, discrepancies in the very thin film growth regime (thicknesses less than 20 nm) are superficially discussed or at most explained phenomenologically[10,21], and are often based on experimental data originating from samples prepared under a large variety of processing or substrate preparation conditions[11,21].

Extensive experimental and theoretical research on the thermal SiO_2 growth has been conducted since 1965, when Deal and Grove[12] proposed the linear-parabolic model to describe thermal SiO_2 growth kinetics, which has been widely accepted up to date. More recent theoretical advances[13−29] have called attention to the so-called "anomalous oxidation region" and the growing importance of oxides with thickness less than 20 nm, where the linear-parabolic model fails to explain the experimental data for dry oxides. A number of attempts have been made to model the silicon oxidation process taking into account the apparent fractal geometry of bulk SiO_2[24−25], and the SiO_2/Si interface[26−29]. In many of these approaches however, the enhancement of the oxidation rates in the very thin film regime has not been properly addressed. Also, at this point it is not clear what comprises the minimum set of parameters necessary for successful description of the growth process, and what are the basic ingredients responsible for the dynamics of the SiO_2/Si system.

In order to clarify some of the microstructural properties of the SiO_2/Si system we perform numerical simulations of the thermal SiO_2 growth process, which may be expected to provide additional insight into the details of the growth kinetics of SiO_2 very thin films, as well as to the dynamical evolution of the SiO_2/Si interface. In this work we briefly describe the simulation technique used, and comment on the various local rules that we have explored in order to gain a deeper understanding of the thermal SiO_2 growth process[28,29]. The results of numerical simulations are presented, analyzed, and compared with the experimental data. We show that a concept of "temporal scaling" can be introduced to unify the data obtained for different values of external parameters (such as temperature and pressure) on a single growth kinetics curve, and discuss the nature of the SiO_2/Si interface formation based on the details of its spatial and temporal evolution. These observations lead to a simple phenomenological description of the growth process, taking into account the discrete nature of interface propagation.

In the next Section we briefly comment on a few (of many) experimental and theoretical models which have attempted to describe the thermal SiO_2 growth kinetics over the past decades. In Section 3 we recapitulate the recently developed[29] approach used to perform numerical simulation of very thin SiO_2 film growth. In Section 4 we present the results of the simu-

lations. We first provide evidence that a temporal scaling assumption may be used to unify the data obtained at different temperatures on a single scaled growth rate curve. Then we present our findings concerning the microstructure (temporal evolution and spatial distribution) of the interface, governing the dynamics of thin SiO_2 film growth. Finally in Section V we draw the conclusions and discuss the implications of the simulation results.

II. Modeling the thermal SiO_2 growth: a brief review

In their pioneering work[12], Deal and Grove presented the first model of thermal SiO_2 growth, using the basic assumption that the oxidizing species are dissolved interstitialy in SiO_2 and during growth diffuse towards the SiO_2/Si interface. Their model assumes that it is possible to attain steady state in a diffusion process where reaction controlled and diffusion limited specific rate constants can be simultaneously rate limiting in a sequential kinetic process. Their work is still widely accepted, and has been generally referred to in the literature as the "linear-parabolic law". The model is in excellent agreement with a large variety of observed experimental data for both dry and wet oxidations. However, it fails to explain the oxidation phenomena for dry oxide films with thicknesses less than 20 nm, the so called "anomalous oxidation region". Further, it does not consider effects of viscous flow dynamics, and assumes the diffusion coefficient to be a constant throughout the oxide layer growth process.

In the seventies Breed and Deremus[13] refined the Deal and Grove theory in order to account for the possibility of chemical interaction of the mobile species (H^+, OH^-, H_2O) during the oxidation process with the SiO_2 network. Later, Wolters[14] extended the idea in order to allow for the presence of an arbitrary type of impurity during oxidation. Simultaneously, Revesz[15] for the first time proposed the idea of channel formation near the interface for very thin oxide films, suggesting that this channeling may be responsible for the observed enhancement of dry oxidation rates.

In the eighties Fargeix et al[16,17] and Tiller[18] incorporated the concept of a varying diffusion coefficient throughout the on growing SiO_2 layer and simultaneously Agius et al[19] attributed variations in the diffusion coefficient to the high compressive stress present at the SiO_2/Si interface (due to the volume expansion during the SiO_2 growth). In the late eighties Nicollian and Reisman[20,21] proposed a phenomenological model to explain the thermal oxidation of silicon which was shown to fit most of existing published experimental data for dry oxidation to the power law $x = at^b$ where x is the thickness of the oxidized region, t is the oxidation time, and a and b are variable fitting parameters. Fitting available experimental data accumulated over the past thirty years[21] indicated the values of b to lie in the range 0.30 to 0.72. They assumed that the thermal oxidation of silicon is surface reaction limited, and that the reaction rate is controlled by the viscous flow of newly formed oxide to accommodate the volume expansion that occurs when silicon oxidizes[20]. Although the agreement between the theory and experimental data is remarkable, they failed to provide a simple and clear physical explanation for the observed b values.

In the early nineties, studies performed using atomic force microscopy[22,23] have indicated that silicon surfaces may be highly irregular, suggesting that Si/SiO_2 interfaces probably have a complex fractal nature. Verdi et al[24,25] attempted to model the silicon oxidation process by taking into account the fractal geometry of bulk SiO_2, while da Silva Jr. et al[26] and Gomes et al[27] the fractal geometry of the SiO_2/Si interface.

In short, a large variety of physical phenomena has been incorporated into the theoretical models in the attempt to explain the nature of the silicon oxidation process. A common feature of most of these phenomenological approaches however, is the fact that they are often based on defining a large number of independent variable parameters. In fact, as many as eight independent parameters[25] have been used to model the silicon oxidation process. Despite of the diversity of the existing models, they have not been successful to account for all of the experimental results available in the literature (at least for some of its aspects) especially in the very thin film regime. Presently, a simple model that would simultaneously describe the growth kinetics of very thin SiO_2 films and the SiO_2/Si interface for-

mation dynamics is still lacking. In order to further explore these important aspects of the SiO_2/Si system, these authors have developed[28,29] a simple numerical simulation algorithm, as described in the following sections.

III. Numerical simulations

In the numerical simulations we employ a simple picture of many simultaneous three dimensional random walkers (oxygen atoms) diffusing through the silicon substrate. The walk is performed on the cubic lattice, with variable "granularity" g, underlying the Si diamond structure (g denotes the number of cubic lattice constants per one lattice constant of the diamond structure). This numerical simulation setup is illustrated in Fig. 1 for the case of $g = 4$. One complete lattice update, or "time step", consists of random conditional repositioning of all the oxygen atoms inside the system to their neighboring positions. The first oxygen atom that reaches a given silicon site is bonded, and thereafter prevented from moving. The other atoms that reach the same site may freely move to one of the randomly chosen neighboring positions. At every time step the surface of the silicon crystal is supplied with new oxygen atoms at the rate proportional to pressure, to compensate for the ones that have moved into the interior.

At the very beginning of the simulation a self-affine oxidation interface front of several crystalline lattice constants (typically 2-4) is rapidly formed. The depth of the front saturates as soon as the layers close to the surface begin to consolidate, and thereafter remains practically constant. This is a consequence of the fact that the rate of consolidation becomes equal to the rate of oxidation. The result is a subsequent effective drifting of the oxidation front at the random walk rate of diffusion. We thus differentiate between two elementary processes: the rapid initial formation of the oxidation front, and its subsequent diffusion. It is the superposition of these two processes that produces the crossover[29] from the so called "anomalous oxidation region" behavior to the linear-parabolic law. On a very short time scale it is only the formation of the front that matters, on an intermediate time scale both processes are important, while on a long time scale the rapid formation of the front is seen just as an additive constant (the non-consolidated interface region). We will next demonstrate that a variety of experimental data may be well fitted within this picture to the simulation predictions, as well as that new insights emerge concerning the nature of the oxidation process.

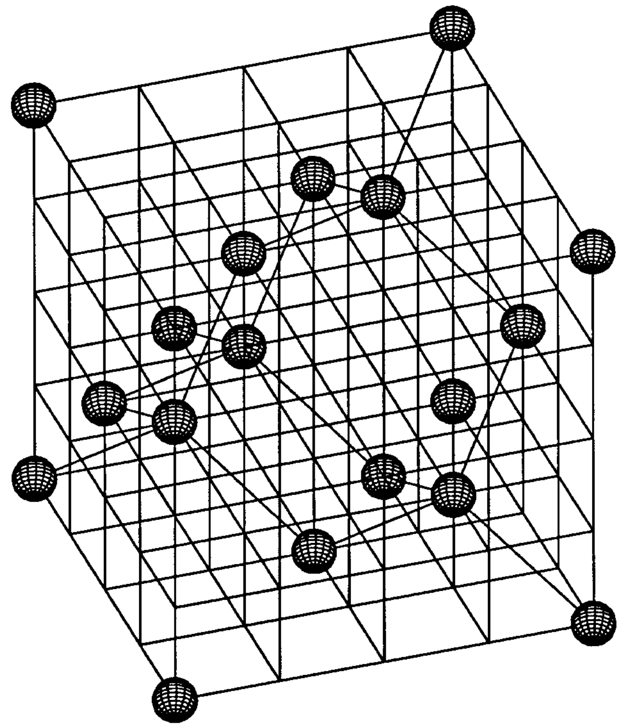

Figure 1. In the numerical simulation the silicon atoms reside on the sites of the diamond lattice, while the oxygen atoms perform random walk on the underlying cubic lattice with granularity g=4.

IV. Results and discussion

IV.1. Universal Behavior of the Oxidation Process

In the very early stages of the simulation the oxide front grows at a power law rate, but as soon as the region on the surface begins to consolidate, it levels off to a practically constant value (transition layer width)[29]. The end of the consolidated region (beginning of the oxide front) on the other hand, shows parabolic behavior typical for the random walk problem. Since the integral rate of oxidation corresponds to superposition of these two constituent curves, it follows that fitting of this data to a power law for different time scales should

yield a range of different exponents, corresponding to the crossover from the "anomalous oxidation region" behavior to the linear-parabolic law.

The basic properties of these curves remain the same if the more involved local rules are taken into consideration. In particular, stochastic treatment of the oxygen diffusion process affects mainly the time scale (number of Monte Carlo Steps[30] (MCS) needed to grow a film of a certain depth), but not the shape of the resulting integral oxidation rate curve represented on arbitrary scale. To be more precise, decreasing temperature slows down both the front formation and the advance of the consolidated region, so that the resulting integral oxide curve is effectively "stretched". This implies that experimental data obtained for *different* temperatures can be compared with the *same* simulation data by rescaling the time to match the experiment. On the other hand, it also follows that experimental data obtained for different temperatures should collapse onto a single curve if appropriate temperature dependent temporal scaling is introduced. Stochastic treatment of the chemical oxidation process as well as the different diffusion schemes affect mainly the depth and the rate of formation of the oxidation front. Since in all the cases the oxidation front is in the range of 2-4 crystal lattice constants, the integral oxidation curve is affected by changing the local rules mainly in this region, where there is shortage of reliable experimental data for comparison.

Comparison of the numeric simulation results with experimental data, obtained for silicon oxidation in dry atmosphere, is shown in Fig. 2 for three different temperatures. Details of sample fabrication process are given elsewhere[28]. The experimental data is represented on the scale $t' = t/\tau(T)$, where the "characteristic time" $\tau(T)$ is a variable parameter used to adjust the time scale of experimental data obtained at different temperatures to match the simulation data. Simulation results are represented by small open circles, while the experimental data for temperatures of 900, 1000, and 1100 °C are represented by large open circles, triangles and squares, respectively. It follows that rather high quality comparison of the experimental and simulation data is obtained despite the simple simulation scheme. The temporal scaling assumption seems to be justified, while the form of the $\tau(T)$ function remains to be established through more elaborate analysis of massive experimental data under varying processing conditions[12,20,21].

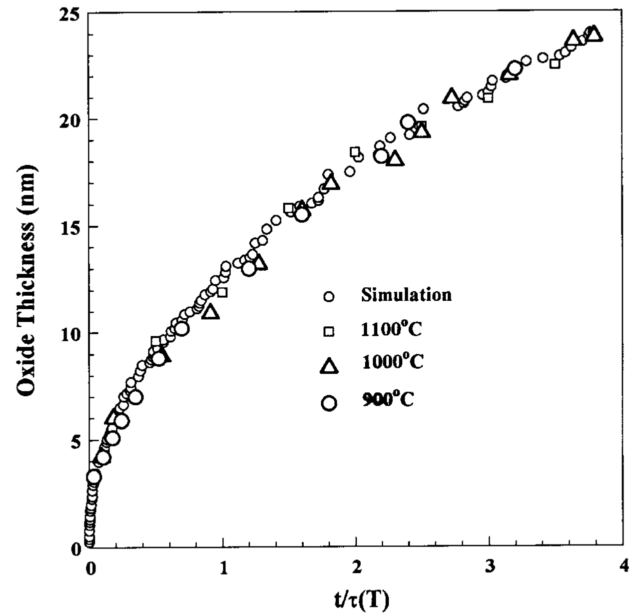

Figure 2. Comparison of experimental data for the SiO_2 growth rate at three different temperatures, presented on different time scales, with the simulation data from a single run (g=4). The data is represented in scaled form to demonstrate the universal behavior of the oxidation rate (time was scaled with temperature, for each experimental curve, to match the simulation data). For the values of the scaling function $\tau(T)$ we have used $\tau(900^oC) = 1min$, $\tau(1000^oC) = 4.75min$, and $\tau(1100^oC) = 25min$, while for the simulation data we used $\tau = 7926MCS$.

IV.2. Dynamic Evolution of the SiO_2/Si Interface

Numeric simulations also provide means to study the SiO_2/Si interface (the self-affine oxidation front) at the microscopic level. To study the SiO_2 concentration spatial distribution, measured along the axis of oxide growth (perpendicular to the crystal surface), in Fig. 3 we show the crystal cross section at the interface. The non-oxidized Si sites are represented by white, and the oxidized sites by black dots. It is seen that at any given time step the interface is comprised of only a few crystal layers (those with concentration significantly different from 100% and zero), while on the other hand, the time dependence of SiO_2 concentration of any given layer is continuous. This observation suggests that theoretical models for SiO_2 growth dynamics should take into account the discrete nature of the oxide front spatial distribution: they *should not* be based only on first order

differential equations for oxide thickness[12–27], which assume that the oxide thickness changes continuously in both space and time. Instead, the dynamics of SiO_2 concentration change should be established for distinct separate layers, wherefrom the integral oxide growth rate should be deduced.

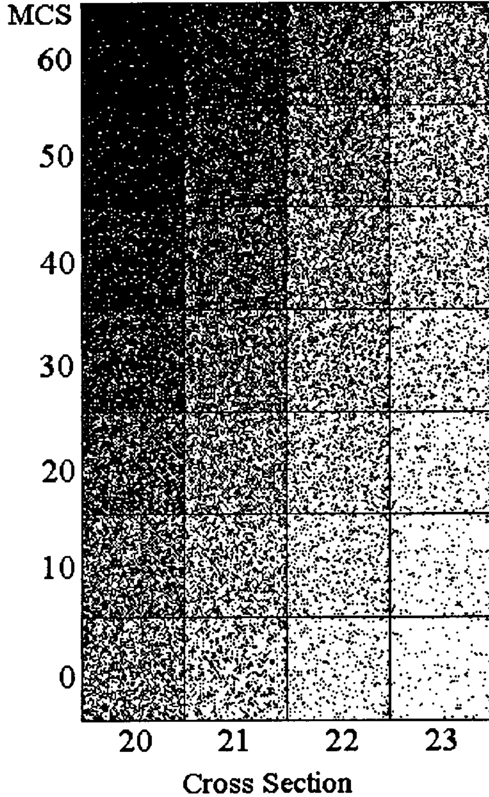

Figure 3. The crystalline silicon cross section at the interface (four fixed successive crystal layers at seven time steps, ten MCS apart). The non-oxidized Si sites are represented by white, and the oxidized sites by black dots. The individual crystal layers are labeled by integer numbers. The initial time $t = 0$ corresponds to the cross-sections displayed in the bottom row.

Next, we describe a simple phenomenological approach for modeling of the SiO_2 thin film growth process, in accordance with the above numerical simulation results. In Fig. 4 we show the normalized SiO_2 density time dependence obtained from the simulations, for the first ten crystal layers, where each of the curves corresponds to a different layer. It turns out that the individual layer concentration time dependence curves from Fig. 4 can be well fitted to the Boltzmann formula

$$C_n(t) = \frac{1}{1+\exp\left(\frac{t-t_n}{\sigma_n}\right)}, \tag{1}$$

where n is the layer order number, t_n is the central line position (time step at which $C_n = \frac{1}{2}$), and σ_n is the line halfwidth. The values t_n for $n = 1, 2, \ldots, 22$, obtained by fitting the layer concentration curves (obtained in the simulations) to phenomenological equation (1), are shown in Fig. 5. It follows that the line centers obey equation

$$t_n = \delta n^2, \tag{2}$$

where $\delta = 0.904MCS$, corresponding to a simple random walk with $n \sim t^{\frac{1}{2}}$. On the other hand, the line halfwidths σ_n shown if Fig. 6 for $n = 1, 2, \ldots, 22$, contain the information associated with the initial front formation. The data is well fitted to the form

$$\sigma_n = \alpha + \beta n - \alpha e^{-\gamma n}. \tag{3}$$

with $\alpha = -5.56$, $\beta = 1.99$, and $\gamma = 0.31$. The exponentially decaying term in (3) reflects the rapid initial formation of the oxidation front, relevant for the "anomalous region" of the oxidation process. Inserting (2) and (3) into (1), we finally find the general phenomenological formula for the layer concentration time dependence

$$C_n(t) = \left[1+\exp\left(\frac{t-\delta n^2}{\alpha[1-exp(-\gamma n)]+\beta n}\right)\right]^{-1}. \tag{4}$$

It remains to establish the connection between the individual layer concentration curves $C_n(t)$ and the integral oxide depth growth rate. If we define the interface position to be the location of the last crystal layer with SiO_2 concentration above some (arbitrary) threshold value C_c, it follows from Fig. 4 that the oxide depth actually displays discontinuous behavior: the interface is pinned to a given crystal layer (the last layer with SiO_2 concentration above C_c) for a given amount of time, and then 'jumps' to the next layer (when SiO_2 concentration of this layer rises above the threshold). For the special choice $C_c = 0.5$ the jumps occur at time steps given by (2), where the units MCS (Monte Carlo Steps) need to be adjusted to the experimental data for each set of external parameter values. The obtained value $n \sim t^{\frac{1}{2}}$ corresponds to the "parabolic regime", that is, the simple random walk. The "anomalous region" can be probed by choices of $C_n \sim 1$, where the time steps of interface "jumps" may be calculated from (4) as

$$t = \delta n^2 + \beta n \ln\left(\frac{1-C_n}{C_n}\right) + \alpha \ln\left(\frac{1-C_n}{C_n}\right)(1-e^{-\gamma n}). \tag{5}$$

For $C_n \sim 1$, the quadratic term in (5) becomes negligible, and for intermediate n we reproduce the "linear regime", while for very small n the exponential term dominates, and $n \sim \ln(t)$, corresponding to the "anomalous region".

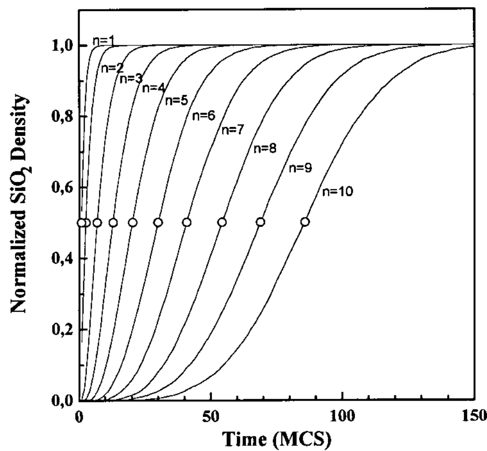

Figure 4. The normalized SiO_2 density time dependence obtained from the simulations, for the first ten crystal layers. Each of the curves, corresponding to a different layer, is labeled by an integer number. Open circles represent the points where concentration is equal to half of its maximum value.

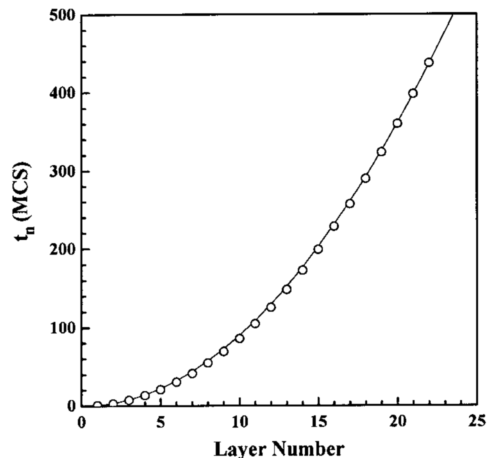

Figure 5. The positions of centers t_n (open circles) of layer concentration lines from Fig. 5, versus layer number, for $n = 1, 2, \ldots, 22$. The full line represents the parabola δn^2, where only one variable parameter $\delta = 0.904 MCS$ was used to fit the simulation data.

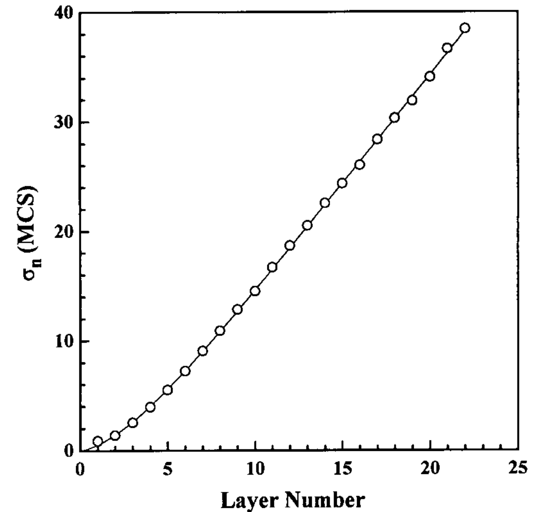

Figure 6. Halfwidths σ_n (open circles) of layer concentration lines from Fig. 5, versus layer number, for $n = 1, 2, \ldots, 22$. The data fit well to a superposition of a straight line, and an exponentially decaying term, which apparently contains the information associated with the initial front formation.

In summary, the numerical simulations lead to a phenomenological approach with parameters reflecting different aspects of the growth dynamics on the microscopic time and length scales, as opposed to other phenomenological models[20,24-27] which employ a larger number of parameters associated with macroscopic properties of the oxidation process.

V. Conclusions

Despite of the diversity of theoretical models which attempt to explain the kinetics of SiO_2 films and the dynamics of the SiO_2/Si interface formation, a simple model that would simultaneously describe the growth kinetics of very thin SiO_2 films (thicknesses under 20 nm) and the SiO_2/Si interface dynamics (its extent, and spatial/temporal evolution) is still lacking. The existing models successfully describe the experimental data in the region above 20 nm, basically reproducing the Deal and Grove linear-parabolic law, while the discrepancies are found in the very thin film regime (the so called "anomalous region"), where there is also shortage of reliable experimental data.

To complement the existing theoretical understanding and the experimental results in the thin film regime,

we perform numerical simulations of the oxidation process, providing some new insights into the dynamics of the interface formation. It is found that the kinetics of thin SiO_2 film growth is governed by simple properties of the oxygen diffusion itself, rather than by more complicated time (or depth) dependence of the diffusion constant or other associated parameters. A phenomenological approach arising from these simulations allows for probing different aspects of the growth dynamics on the microscopic time and length scales.

Acknowledgments

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