

# Fractal Origin of the Thermal Oxidation of Silicon

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The origin of silicon oxidation has been studied using concepts often applied to fractal structures. A model is presented which suggests that silicon oxidation originates when oxygen molecules diffuse into a fractal network structure and determines a power law  $x = at^b$  relating the oxide thickness  $x$ , to the oxidation time  $t$  in agreement with a similar relationship recently proposed by Nicollian and Reisman. The values for the exponent  $b$  are in agreement with the experimental results presented here as well as with those obtained by Nicollian and Reisman through simple mathematical fit of the experimental data of the past thirty years.

## I. Introduction

Due to its importance in silicon technology, the growth of SiO<sub>2</sub> layers by thermal oxidation of silicon has been extensively studied in the past thirty years. Nevertheless, the modeling of silicon oxidation, pioneered by Deal and Grove<sup>[1]</sup> in the mid sixties has yet to be better understood and explained. Although widely used for all these years, the Deal-Grove model fails to explain the oxidation phenomena for oxide films with thicknesses less than 350Å, the so called "anomalous oxidation region"<sup>[2]</sup>.

The Deal-Grove model assumes that is possible to attain steady state in a solid state diffusion process where reaction controlled and diffusion limited specific rate constants can be simultaneously rate limiting in a sequential kinetic process. These ideas were extensively used in the analysis of the silicon oxidation process since then. However, the model does not consider the effects of viscous flow dynamics during oxidation and assumes the diffusion coefficient to be a constant throughout all the oxide layer growth process which has been shown not to be a good approach<sup>[2]</sup>.

Recently Nicollian and Reisman proposed a phenomenological model<sup>[3]</sup> to explain the thermal oxidation of silicon which was shown to fit most existing published experimental data for dry oxidation to a power law. Subsequently a physical mechanism was proposed by them<sup>[4]</sup>. 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. The model suggests that the oxide thickness  $x$ , varies with oxidation time according to  $x=at^b$  where  $a$  and  $b$  are constants obtained from fitting of the experimental data. For values of the time exponent  $b$  in the range of 0.30 to 0.72 they succeed to fit all the existing  $x$  versus  $t$  data with no anomalous oxidation region. Although the agreement between the theory and experimental data is remarkable, they do not have a physical explanation for the observed  $b$  values.

In this work we propose a model based on diffusion of the oxidizing species through a fractal network which leads to a power law similar to the one in their model. Moreover, we obtain values for the exponent  $b$  which agree with those of Nicollian and Reisman and with recent experimental dry oxidation data that we present here.

## II. Fractals and the thermal oxidation of silicon

In order to better understand the thermal oxidation of silicon we consider that the oxidizing O<sub>2</sub> molecules diffuse throughout a fractal network<sup>[5]</sup> formed by the silicon dioxide layer and the silicon surface at the Si/SiO<sub>2</sub> interface before reaching the silicon surface. Further, we assume that the kinetics of the reaction  $\text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s)$  is diffusion controlled into the fractal network with the reaction rate given by:

$$k = At^{\frac{3}{2}-1} \quad (1)$$

where  $\bar{d}$  is the spectral dimension<sup>[6]</sup>

During thermal oxidation of silicon two basic processes occur: (a) the chemical reaction at the Si/SiO<sub>2</sub> interface, and after an initial growth of a thin oxide layer, (b) the transport by diffusion of oxygen from the gas phase through the oxide layer to the Si/SiO<sub>2</sub> interface. Assuming that the oxygen partial pressure at the interface is both time independent and equal to its input partial pressure, the oxidation rate may be written in the form:

$$\frac{dx}{dt} = k_f p^n - k_r p_r^m \quad (2)$$

where  $k_f$  is the forward specific reaction rate coefficient for the reaction  $\text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s)$ ,  $k_r$  is the specific reaction rate coefficient for the reverse reaction  $\text{SiO}_2(s) + \text{Si}(s) \rightarrow 2\text{SiO}(g)$ ,  $p$  is the instantaneous pressure of oxygen,  $p_r$  is the instantaneous partial pressure of SiO at the Si/SiO<sub>2</sub> interface, and  $m$  and  $n$  are the orders of the reverse and forward reactions respectively<sup>[4]</sup>. If no passivation is taking place during the oxidation process, the reverse reaction rate may be considered negligible, in order that equation (2) reduces to :

$$\frac{dx}{dt} = k_f p^n \quad (3)$$

substituting equation (1) into equation (3) we obtain:

$$x(t) = at^{\frac{\bar{d}}{2}} \quad (4)$$

This result reproduces Nicollian and Reisman power law for  $\frac{\bar{d}}{2} = b$ . For one, two and three dimensions<sup>[6]</sup> in Euclidean space the spectral dimension  $\bar{d}$  is calculated to be equal to 1.00, 1.35 and 1.43, which in the present model produces  $b$  values of 0.50, 0.68, and 0.72 respectively. This range of values for  $b$  is in good agreement with the  $0.30 \leq b \leq 0.72$  range coming out from the experimental data fit made by Nicollian and Reisman<sup>[4]</sup>.

In our model we reason that as oxidation is initiated in a clean and bare silicon substrate, the Euclidean dimension of the fractal network formed by the silicon plane and the vertical direction of diffusion of the oxidizing specie (O<sub>2</sub>) is three ( $\bar{d} = 1.43$ ), and as the surface is covered by the newly formed SiO<sub>2</sub> this situation changes to a configuration of Euclidean dimension for the fractal network of two ( $\bar{d} = 1.35$ ) and one ( $\bar{d} = 1.00$ ) as the oxide layer grows and forms a bulky oxide thin film.

This is understood when one recalls that in the early stages of oxidation the random walker (the oxidizing species) reacts almost instantaneously with any free silicon oxidizing site in the plane (reaction limited oxidation in the Deal-Grove model<sup>[1]</sup>,  $b \sim 1$ ). As this plane is being filled by the oxidation process the Euclidean dimensionality changes in the direction that for longer oxidation times it goes into two and one, where the random walker has to diffuse through all the grown oxide (diffusion limited oxidation in the Deal-Grove model<sup>[1]</sup>,  $b \sim 0.5$ ) until it reaches the Si/SiO<sub>2</sub> interface, with these limits being an asymptotic behavior.

### III. Experimental results and discussion

From the previous discussion one may wonder what determines the range of possible  $b$  values for a given oxidation process, and why  $b$  can assume such values for different process conditions as it is demonstrated after careful analysis of oxidation data obtained in different laboratories over the past thirty years<sup>[3]</sup>. In fact, this analysis clearly shows a tendency for  $b$  to decrease for a given set of data when it sweeps many decades of time. In an attempt to clarify some of these questions we performed a simple oxidation experiment as described below.

Silicon wafers (100) oriented, p-type, two inch diameter, and of 1  $\Omega$ -cm resistivity were cleaned following a standard RCA cleaning process<sup>[7]</sup>, except for the last step, where the wafers were immersed in a HF dip solution (2% HF in deionized water) just prior to furnace loading. This procedure is known to leave the silicon surface hydrophobic, therefore aiding in cleaning the surface and removing all possible native oxide. The oxides used in the experiment had thickness in the range of 100-2500  $\text{\AA}$  and were grown in dry O<sub>2</sub> in a Thermco MB-80 furnace at 1000 °C, followed by an in situ dry N<sub>2</sub> annealing at the growth temperature for 30 minutes. Oxidation times were varied between 1 and 500 minutes to obtain a reasonable quantity of data points for the oxidation curve.

The thicknesses of the grown thermal SiO<sub>2</sub> were measured using an Auto El-IV Rudolph Ellipsometer at several wavelengths. For each wafer oxidized ten points were measured along its diameter to verify oxide uniformity, which was better than 3 % in most cases.

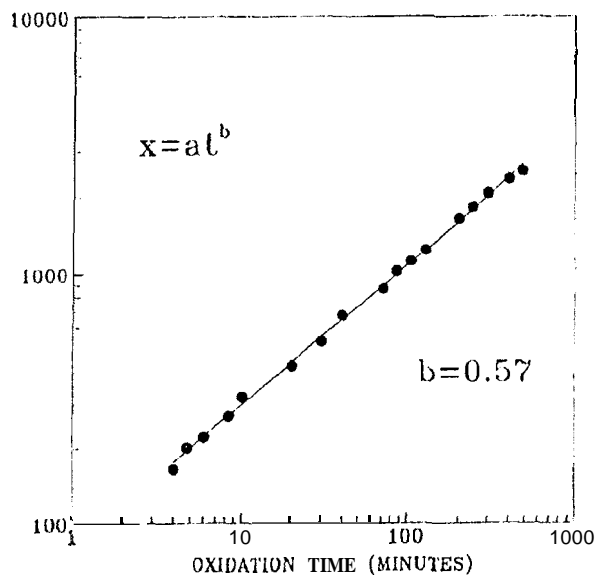


Figure 1: Linear regression for the oxidation data in logarithmic scale of the power law  $x = at^b$ , yielding  $b=0.57$  for data points covering over two decades.

Fig. 1 shows the oxide thickness results for dry oxidation of (100) Silicon wafers for oxidation times between 4 and 480 minutes drawn in a logarithmic scale (power regression of  $x = at^b$ ). From this figure we obtain  $b=0.57$ .

During the process of obtaining these data, and its analysis we observed some differences in behavior (mainly oxidation rate) for samples oxidized for short times (up to a few minutes) and for samples oxidized for a few hundred minutes. Therefore we decided to apply the above discussion for time intervals of oxidation that we have named *short* (less than 20 minutes), *intermediate* (from 20 up to 100 minutes) and *long* (above 100 minutes).

Fig. 2 (a), (b), and (c) show the experimental oxidation results fitted to a power law (least squares) in the form  $x=at^b$  previously discussed. The data clearly show that different  $b$  values are obtained for different oxidation time intervals: *short* ( $b=0.69$ ), *intermediate* ( $b=0.59$ ), and *long* ( $b=0.52$ ). All data fit very well to the power law and it is in good agreement with the calculations from fractal theory, suggesting that during oxidation the dynamics of the reaction in a certain oxidation period is mainly responsible for the observed range of constant  $b$ .

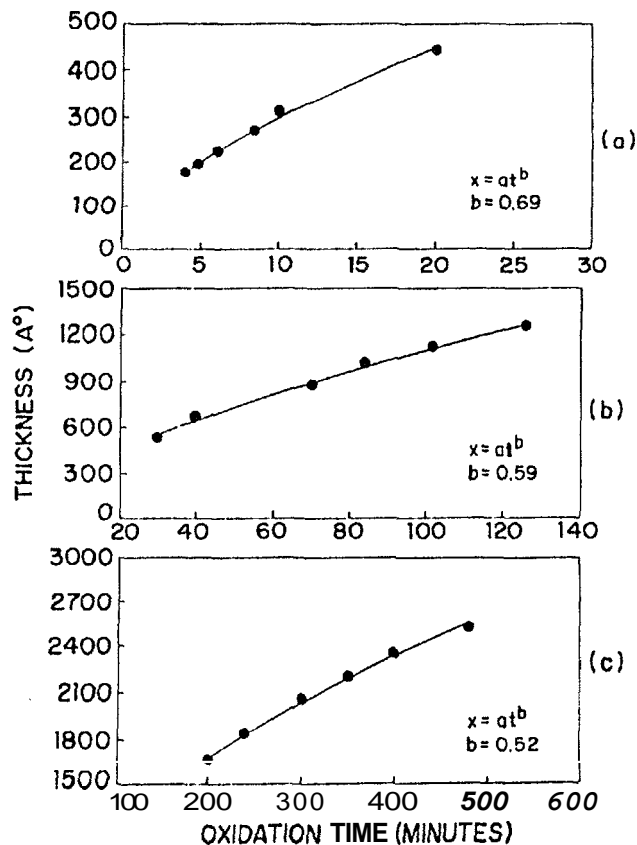


Figure 2: Oxide thickness versus time for dry oxides grown at 1000 °C. (a) *short* oxidation time (less than 20 minutes), (b) *intermediate* oxidation time (from 20 up to 100 minutes), (c) *long* oxidation time (above 100 minutes).

According to our model, one possibility is that during oxide growth, as the  $\text{SiO}_2$  layer gets thicker, the diffusion coefficient varies. This is due to the increasing difficulty that the diffusing specie ( $\text{O}_2$ ) has to perform a random walk throughout the on-growing film and reach the  $\text{Si}/\text{SiO}_2$  interface where reaction takes place. Therefore, the transport of oxygen from the gas phase throughout the oxide layer to the  $\text{Si}/\text{SiO}_2$  interface is altered, possibly by a reduction of the diffusion coefficient, inducing a rate reduction of the chemical reaction at the interface.

The result of this process is a change with time, as the oxidation proceeds, of the euclidean dimension, where for maybe up to a few monolayers of the oxide this dimension is three and as it gets thicker we start to have a random walk in a fractal structure that becomes two or one-dimensional and therefore suggesting that  $b$  values may be in the range 0.50 to 0.72 as found theoretically in the model.

The Nicollian and Reisman model explains the observed values of  $b$  based in the viscous flow in the ox-

ide as the rate limiting mechanism of the surface reaction during growth<sup>[4]</sup>. However, when one considers viscous flow in the oxide, necessarily one has to take into account any diffusion constant changes that may take place during oxide growth, and this necessarily has to take place during this process, as it can be inferred from the fact that intrinsic stress and oxide density<sup>[8]</sup> vary substantially near the Si/SiO<sub>2</sub> interface within ten to fifteen monolayers, the so called "transition region".

Although the model presented here succeeded in obtaining the values of  $b$  consistent with those coming from the power law fit of the experimental data existent from the past thirty years<sup>[3]</sup>, it is not the only interpretation one can follow using the fractal approach. It is possible to show<sup>[9]</sup> that with a random walk over the number of available silicon sites in the "transition region" near the Si/SiO<sub>2</sub> interface one also obtain a similar power law for the time dependence of the oxide thickness.

#### IV. Summary

In summary, we propose a model for the thermal oxidation of silicon based in the concepts of diffusion kinetics in fractal structures. The model suggests that the thermal oxidation of silicon surface is governed by diffusion of oxygen molecules into a fractal network structure which determines a power law that relates oxide thickness  $x$ , to oxidation time  $t$ , in the form  $x(t) = at^b$ . The values for the exponent  $b$ , in the range of 0.50 to 0.72 in the power law coming out from this model, are in good agreement with experimental results for dry oxidation presented, and with those obtained by Nicollian and Reisman through a power law fit of oxidation data from the past thirty years. However, it is inferred that these values are related to changes in the dimensionality of the fractal structure, or to changes in the diffusion coefficient of the oxidizing species during the oxidation process.

The model presents evidence that the exponent  $b$  in the power law is related to the spectral dimension during the diffusion of the O<sub>2</sub> throughout a fractal network which may give us further clues on the physical origin of the constants  $a$  and  $b$  in the power law. Possible mechanisms leading to the observed values for these constants, and parameters that affect their values are being investigated.

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