A Study on Growth of Ultrathin Silicon Dioxide Films by Rapid Thermal Oxidation

Taofang Zeng[*] and Haris C. Doumanidis[**]

[*]Department of Mechanical and Aerospace Engineering,
North Carolina State University, Raleigh, NC 25695-7910
[**]Department of Mechanical Engineering, Tufts University,
Medford, MA 02155

Abstract

Advanced experimentation such as isotopic labeling and medium-energy ion-scattering spectroscopy has found a hybrid or transitional layer between pure silicon dioxide and pure silicon during silicon oxidation. This paper establishes a consistent model for growth of oxide by considering a volumetric reaction in the transitional layer, in addition to the reaction at the interface of SiO_x/Si. The volumetric reaction plays a more important role for thin films, while the model approaches the Deal-Grove limits for thick films.

1. Introduction

The mechanisms of growth of silicon dioxide have been the focus of research for the last three decades. The prevalent view is based on the seminal paper by Deal and Grove[1]. In this model, the chemical reaction rate controls the growth of very thin films, whereas oxygen diffusion dominates oxide growth when the film is thick. Simple mechanisms lead to a simple and neat expression for the growth rate. For decades nearly all the experimental data have proved the linear-parabolic profile for oxide thickness as a function of the growth time[2,3]. It has been known for a long time, however, that the growth rate for ultrathin films is faster than that would be predicted from the kinetics of the Deal-Grove model. To overcome this shortcoming of the Deal-Grove model, a term has to be added, which could enhance the growth rate in the thin-film regime yet still approach the Deal-Grove behavior asymptotically in the thick-film regime. This was done by Ghez and van der Meulen[4], by adding a reaction term while keeping the diffusion term the same as in the Deal-Grove work. They suspected that there was an additional parallel path for oxidation at the interface, but the physical mechanism for this new path was not clear. Massoud, Plummer and Irene[5] used a similar argument and accounted for the enhancement of growth rate by additional sites of oxidation in the thin-film regime. The concentration of these sites has a profile decaying exponentially with increasing film thickness. They listed oxide structure and oxide stress as possible mechanisms for this effect. Another possible reason is the space charge effect. However, this is a negligible factor, because an externally applied electric field makes little difference for thermal oxidation growth. Realizing that the oxide/Si interface is not a perfect one, Tiller[6] proposed a relaxation or transition layer between pure silicon dioxide and pure silicon. This transitional layer is responsible for the increase of the reaction sites or volume.

The reaction rate was thus increased for thin films, but the model did not approach the Deal-Grove limits.

All the mechanisms in the above-mentioned studies are, however, not based on experimental characterization. Therefore, the prediction of the growth rate failed when extrapolated out of their ranges. Physical characterization by using Auger and X-ray photoelectric spectroscopy found[7,8] that the oxide has suboxide states of Si^{+3}, Si^{+2} and Si^{+1}. Widden at al.[8] added a reaction term for possible intermediate chemical species. Obviously, those intermediate species cannot exist in the pure SiO_2 or pure Si layers, but pertain to a transitional layer. Isotopic mapping was used to find the profile of oxygen across the depth of the oxide and silicon more than twenty years ago[9], and experimental data were consistent with the idea of a transitional or hybrid layer[10]. Murali and Murakra[11] proposed a qualitative model for oxygen diffusion and reaction in silicon substrate based on the framework of a transitional layer.

Thus, the objective of this article is to establish a unified quantitative description of physical phenomena during ultrathin and thicker silicon oxide layer growth, which is consistent with previous experimental evidence. This issue is of fundamental importance to rapid thermal oxidation of silicon in microelectronics fabrication. Before presenting our model, we review the physical processes for silicon oxidation. When a fresh piece of silicon is exposed to oxygen, the outermost layer of silicon will be covered by oxygen and changed into oxide promptly. The immediate adjacent layers will be adjusted in a very short time to bring the system to equilibrium[12]. After that, oxygen penetrates the grown oxide and produces oxide with silicon at a limited rate. All the experiments and some basic numerical simulations[12] have indicated a consistent physical and chemical mechanism for growing very thin films and thick films. Failure of models to predict the growth rate means that some mechanisms are not included in those models. Such a mechanism is the volumetric reaction in the transitional or hybrid layer. Recently, Gusev et al.[13] presented the most comprehensive characterization for oxide on silicon substrate by using isotopic labeling and high-resolution medium-energy ion-scattering spectroscopy (MEIS), which confirmed the existence of the transitional layer. Furthermore, they discovered a volumetric reaction in the transitional/hybrid layer in addition to the reaction at the interface. As will be shown, this transitional layer is very important in the thin-film regime. However, all previous models have not considered this transitional layer. We

believe that this is the reason why previous models fail when extrapolated out of the studied ranges. We include this volumetric reaction in the hybrid layer for the first time and set up a consistent model in this study.

2. Modeling

The fundamental mechanisms of oxidation include oxygen chemsorption, chemical bond formation between oxygen and silicon, bond breakage, lattice deformation etc. Instead of the physics of these basic processes, this study focuses on their kinetics. This allows one to obtain usable expressions for calculating oxide growth rates without sacrificing important physics and chemistry associated with the processes. The process kinetics consists of three major steps. First, oxygen diffuses through oxide. Then some oxygen reacts with silicon at the SiO$_2$/Si interface. The rest will penetrate into the silicon substrate and react with in a layer. Other assumptions of the model include:

1) Oxidation reactions take place in a hybrid layer, in addition to at the interface of oxide/silicon.
2) The concentration of silicon in the hybrid layer is approximately constant. This can be justified by the fact that, the concentration of silicon is much larger than the oxygen concentration. This assumption is also used in the Deal-Grove model. The implication of this assumption is that the reaction rate is only determined by the concentration of oxygen, and the reaction rate can be expressed as

$$dN_O / dt = -K_{hy} \bullet N_O .$$

Where N_O is the oxygen concentration [#/cm^{-3}], K_{hy} in the reaction rate in the hybrid layer [1/s] , which is different from the rate at the interface of oxide/Si.

3) The process is quasi-steady.
4) The system being studied has a uniform temperature even though oxidation is a highly exothermic reaction.
5) All the oxygen diffused through the oxide layer will be consumed to produce oxide.

Figure 1 shows the schematic arrangement of interest to this analysis, which is the hybrid layer in the middle, where oxygen diffuses and reacts with silicon. The controlling equation is

$$D_{O-hy} \bullet \frac{d^2(N_O)}{dx^2} - K_{hy} N_O = 0 , \quad (1)$$

where, D_{O-hy} [cm^2/s] is the diffusivity of oxygen in the hybrid layer. The appropriate boundary conditions for the controlling equation are:

$$N_O(x = 0) = N_O(0) \text{ (to be determined)}, \ N_O(x = L) = N_O(L) .$$
$$(2)$$

Where, $N_o(L) = N_r$, is the resolution of the measurement instrument, for example, secondary ion mass spectroscopy

(SIMS) or MEIS. This resolution defines the thickness L of the measured hybrid layer as:

$$N_r / N_O(0) = \exp(-L / \lambda) , \text{ i.e.} \quad L = \lambda \ln\left(\frac{N_O(0)}{N_r}\right), \text{ where,}$$

$$\lambda = \sqrt{\frac{D_{O-hy}}{K_{hy}}} , \text{ is the characteristic length. The solution to}$$

Eq. (1) can be expressed as:

$$N_O(x) = N_O(0)\exp(-x / \lambda) . \quad (3)$$

The oxygen concentration at the interface of SiO$_2$/Si can be found by applying the continuity condition at the interface:

$$F_1 - F_c = F_2 + F_d,$$

where,

F_1, flux diffused through oxide, $F_1 = -D_{O-ox} \frac{dN_O}{dX_O}|_{x=0^-}$,

F_c, flux associated with moving interface,

$$F_c = N_o(0) \bullet \upsilon_s = N_O(0) \bullet \frac{dx_0}{dt} ,$$

F_2, consumption rate by reaction at the interface, $F_2 = K$ $N_O(0)$, and, F_d, flux diffused through interface into hybrid layer, $F_d = -D_{O-hy} \frac{dN_O}{dx}|_{x=0^+}$.

$$-D_{O-ox} \frac{dN_o}{dx}|_{x=0^-} - N_o(0) \bullet \frac{dx_0}{dt} = K \bullet N_O(0) - D_{O-hy} \frac{dN_o}{dx}|_{x=0^+}$$
.
$$(4)$$

With the same assumption as in the Deal-Grove model, one can write down:

$$-D_{O-ox} \frac{dN_O}{dx}|_{x=0^-} = D_{O-ox} \frac{N^* - N_O(0)}{x_0} .$$

By differentiating Eq. (3), one can have:

$$-D_{O-hy} \frac{dN_O}{dx}|_{x=0^+} = D_{O-hy} \bullet N_O(0)\frac{1}{\lambda} .$$

Where, N^* the oxygen solubility at the interface of oxide/gases (=5.2x10^{16} cm^{-3}). Therefore, Eq. (4) can be written as:

$$D_{O-ox} \frac{N^* - N_O(0)}{x_0} = K \bullet N_O(0) + D_{O-hy} \bullet N_O(0)\frac{1}{\lambda}$$
$$(4a)$$

The oxygen concentration at the interface can be found as:

$$N_O(0) = \frac{N^*}{1 + x_0 \bullet \frac{K + \sqrt{D_{O-hy} \bullet K_{hy}}}{D_{O-ox}}} . \quad (5)$$

Since all diffused oxygen is eventually consumed to form silicon oxide (assumption 5), the continuous equation at the interface can also be written as:

$$F_1 - F_c = \overline{N}\frac{dx_0}{dt} \approx F_1,$$

where $\overline{N}$ is the concentration of oxygen in the oxide ($=2.25 \times 10^{22}$ cm^{-3}). Thus the growth rate is:

$$\frac{dx_0}{dt} = \frac{F_1}{\overline{N}} = \frac{D_{O-ox}}{\overline{N}} \bullet \frac{N^* - N_O(0)}{x_0} = \frac{N^*}{\overline{N}} \bullet \frac{K + \sqrt{D_{O-hy} \bullet K_{hy}}}{1 + x_0 \bullet \dfrac{K + \sqrt{D_{O-hy} \bullet K_{hy}}}{D_{O-ox}}}$$

(6)

The initial condition is
$$x_0 = x_I \text{ at } t = 0.$$
The above equation can be solved as:

$$x_0^2 + \frac{2D_{O-ox}}{K + \sqrt{D_{O-hy} \bullet K_{hy}}} x_0 = \frac{2D_{O-ox}N^*}{\overline{N}}t + \frac{2D_{O-ox}}{K + \sqrt{D_{O-hy} \bullet K_{hy}}} x_I + x_I^2$$

(7)

By defining:

$$A = \frac{2D_{O-ox}}{K + \sqrt{D_{O-hy} \bullet K_{hy}}}, \quad B = \frac{2D_{O-ox}N^*}{\overline{N}},$$

$$\tau = \left[\frac{2D_{o-ox}}{K + \sqrt{D_{O-hy} \bullet K_{hy}}} x_I + x_I^2 \right] / B,$$

this results in:

$$x_0^2 + Ax_0 = B(t + \tau).$$

We then find:

$$\frac{x_0}{A/2} = \left[1 + \frac{t + \tau}{A^2/4B} \right]^{1/2} - 1. \quad (8)$$

3. Results and Discussions

We grew silicon dioxide films in a furnace-based rapid thermal processing system (Axcelis's Summit – 200^{TM}). The sample was then analyzed with Accurel's Atomika SIMS. Figure 1 shows the profile of silicon and oxygen for a sample grown at 1100°C for 40 seconds. It clearly demonstrates that there is a transitional layer with a thickness of 2 nm.

Based on the experiments, a growth process consisting of three major steps is proposed. First, oxygen diffuses through oxide. Then some oxygen reacts with fresh silicon at the SiO$_x$/Si interface. The rest penetrates into the silicon substrate while reacting with oxygen in a layer (Fig.2). Other assumptions of the model include: 1) Oxidation reactions take place in a hybrid layer, in addition to at the interface of oxide/silicon; 2) The concentration of silicon in the hybrid layer is approximately constant. This can be justified by the fact that, the concentration of silicon is much larger than the oxygen concentration; 3) The process is quasi-steady; 4) The system being studied has a uniform temperature even though oxidation is a highly exothermic reaction; and 5) All the oxygen diffused through the oxide layer will be consumed to produce the oxide.

Figure 2 shows the schematic arrangement of interest to this analysis, which is the hybrid layer in the middle, where oxygen diffuses and reacts with silicon. In Fig. (3a), calculation data (lines) are compared to experimental data for oxidation at 1 atm O$_2$. Fig (3b) compares experimental data from ref. (3) and calculation for oxidation at 0.2 atm O$_2$.

4. Conclusions

This paper established a consistent model for the growth of oxide during rapid thermal processing. The physical basis is the transitional or hybrid layer, as discovered and characterized by advanced instrumentation such as isotopic labeling, SIMS and MEIS. Oxidation in this transitional layer accounts for over 4 times the reaction rate at the interface of Si/SiO$_2$.

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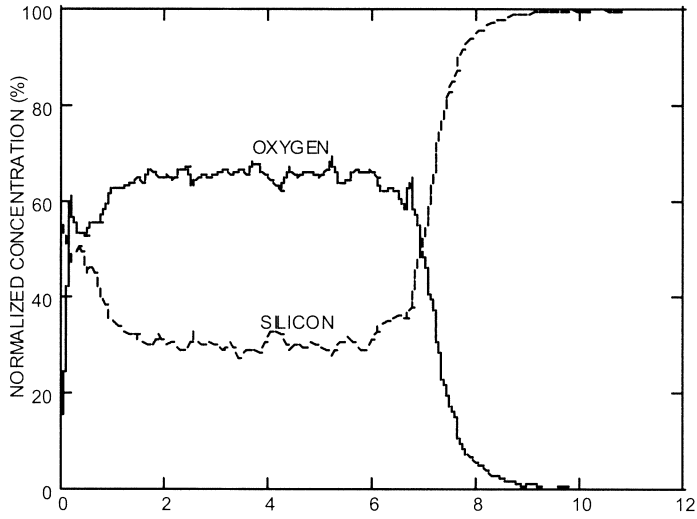
Fig. 1 Profiles of oxygen and silicon in a sample grown in pure oxygen at 1100°C.
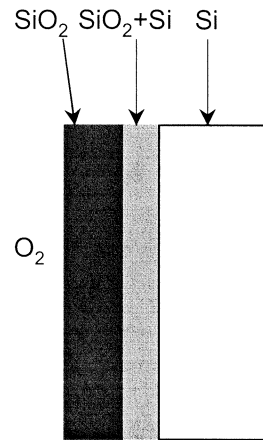
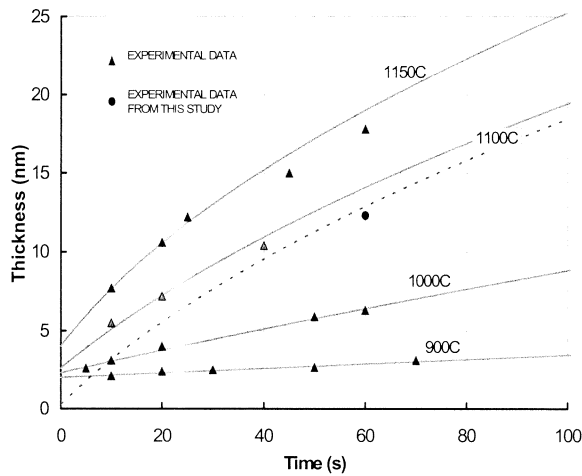Fig. 2 Schematic for oxidation of silicon
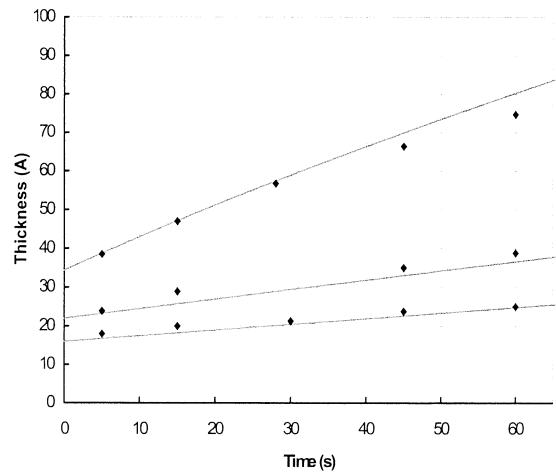
Fig. 3a Comparison between Experiment and Calculation.

Fig. 3b Comparison between Experiment and Calculation. Experimental data are from ref. (2) at 0.2 atm O_2.