# Size-dependent oxidation behavior for the anomalous initial thermal oxidation process of Si

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To have a clear insight into the physical origin of the anomalous initial oxidation behavior for silicon oxidation, we proposed a kinetics model by introducing the nanosize effect into the oxidation process. The rate equation of oxide growth was calculated based on our model, and these results are in excellent agreement with experiments. Notably, the present model not only bridges the breakdown of Deal–Grove model [B. E. Deal and A. S. Grove, J. Appl. Phys. **36**, 3770 (1965)] in the anomalous initial region but also accurately describes the oxidation process in the whole oxidation regions over a wide temperature range. © *2009 American Institute of Physics.*
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Although growth kinetics of silicon dioxide ($SiO_2$) films has attracted considerable attention in the past decades as one of the fundamental science issues in Si-based device technology,[1] the understanding about this process is still limited.[2] The often used model proposed by Deal and Grove[3] in 1965 fails to describe the anomalously rapid oxidation process in the thin oxide region.[4] In order to bridge the breakdown of the Deal–Grove model, plenty of efforts have been done.[5–12] Very recently, Watanabe *et al.*[13] proposed a linear-parabolic rate equation, supposing that the growth rate of $SiO_2$ is governed only by the diffusion of the oxidizing species in already grown oxide without the interface oxidation reaction limiting step. Nevertheless, their model shares same prediction with the Deal–Grove model and could not quantificationally describe the anomalous initial oxidation regime. So, it is very necessary to quantificationally reveal the physical origin involved in the anomalous initial rapid oxidation process.

In the present model, we take the nanoscale effect into the oxidation process and quantitatively reveal the physical origin of the anomalous initial regime. In detail, we suppose that the diffusion is suppressed in high density region (*H region*) near the $SiO_2/Si$ interface[13] and increased at initial growth stages due to the size-dependent diffusivity, as indicated in Fig. 1(a). We provide the following kinetics equation for effective diffusivity $D$ as a function of oxidation thickness $x_0$ and the depth $x$ from the oxide surface:

$$D(x_0,x)=\begin{cases} D_0 \exp\left[-\dfrac{E_{sd}}{k_B T}\right], & 0 < x < x_0 - H \\[2mm] D_0 \exp\left\{\dfrac{-[E_{sd} + \Delta E \rho(x) f(x_0)]}{k_B T}\right\}, & x_0 - H < x < x_0, \end{cases}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1)$$

$$E_{sd} = E_d f(x_0), \qquad\qquad\qquad\qquad (2)$$

where $D_0$, $T$, $k_B$, $E_{sd}$, $E_d$, and $\Delta E$ denote a pre-exponential constant, oxidation temperature in $K$, the Boltzmann con-

stant, size-dependence activation energy in eV, the activation energy of $O_2$ diffusion in bulk $\alpha$-$SiO_2$ in eV, and the maximum of incremental diffusion barrier in eV in $H$ region, respectively; $f(x_0)$ is the no dimension function which is
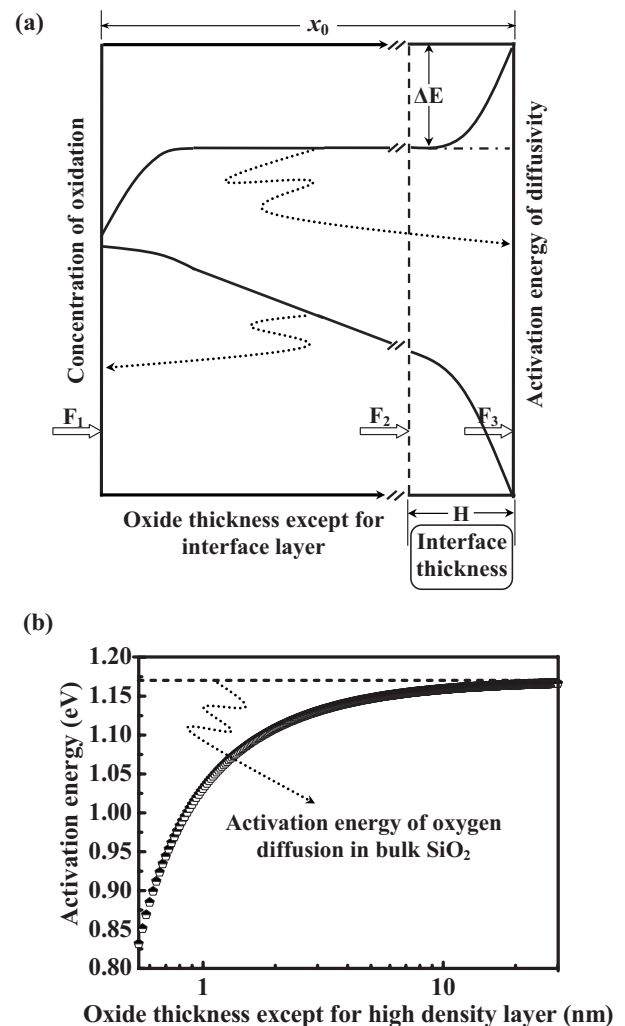


FIG. 1. The effective activation energy of $O_2$ diffusion in the oxide and depth profiles of oxidant concentration (a) and the size-dependence diffusion activation energy (b).

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relative to size-dependence activation energy, $\rho(x)$ is the space-dependence mass density of $H$-region oxide in $g/cm^3$, which is proportional to the increase in diffusion barrier,[14] and $k$ is a constant in $cm^3/g$. In this formula, we emphasize the size-dependent diffusivity, which is not considered in any past model of Si oxidation.

We assume a steady-state diffusion process with $F=F_1=F_2=F_3$.[15] According to Fick's law, the constant flux will be given as $F=-D(x_0,x)[dC(x)/dx]$, where $C(x)$ is the concentration of oxidant at depth $x$ and the oxide thickness $x_0$. Solving the differential equation by integrating from 0 to $x_0$, we attain

$$F = \frac{(C_0 - C_i)D_0 \exp\left[-\dfrac{E_d f(x_0)}{k_B T}\right]}{x_0 - H + H\displaystyle\int_{x_0-H}^{x_0} \exp\left[\dfrac{\Delta E k \rho(x) f(x_0)}{k_B T}\right]dx}, \quad (3)$$

where $C_0$ and $C_i$ are the concentrations at the oxide surface and the $SiO_2/Si$ interface, respectively. Due to rapid interface reaction with the lower interface reaction activation energy,[16,17] we set $C_i=0$. The flux of the oxidant from the gas to the vicinity of the outer surface is taken to be $F=F_1=h(C^*-C_0)$,[3] where $h$ is a gas-phase transport coefficient and $C^*$ denotes the equilibrium concentration of the oxidant in the oxide. So, one can attain the flux expression as following:

$$F = \frac{C^* D_0 \exp\left[-\dfrac{E_d f(x_0)}{k_B T}\right]}{x_0 + H\displaystyle\int_{x_0-H}^{x_0} \exp\left[\dfrac{\Delta E k g(x) f(x_0)}{k_B T}\right]dx - H + \dfrac{D_0 \exp\left[-\dfrac{E_d f(x_0)}{k_B T}\right]}{h}}. \quad (4)$$

The kinetic rate equation of oxide layer growth can be described as $dx_0/dt = F/N_1$, where $N_1$ is the number of oxidant molecules incorporated into a unit volume of the oxide layer. So, we can give a kinetics rate equation

$$\frac{dx_0}{dt} = \frac{B}{A + x_0}, \quad (5)$$

where

$$B = \frac{C^*}{N_1} D_0 \exp\left[-\frac{E_{sd}}{k_B T}\right],$$

$$A = H\int_{x_0-H}^{x_0} \exp\left[\frac{\Delta E k g(x) f(x_0)}{k_B T}\right]dx - H$$

$$+ \frac{D_0 \exp\left[-\dfrac{E_{sd}}{k_B T}\right]}{h}.$$

We have simply proposed size-dependence activation energy of $O_2$ diffusion in the $SiO_2$ in the above deduction, and therefore it is necessary to verify the reliability of the approximation. It is well known that the effective diffusivity of atoms (molecule) diffusion in nanosized materials is significantly higher than the corresponding bulk materials.[18,19] Very recently, we had introduced nanosize effect to reveal the origin of self-limited oxidation behavior of silicon
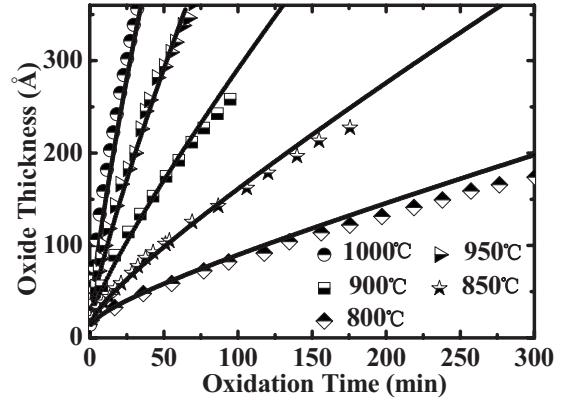


FIG. 2. Oxide thickness as a function of time for the initial growth stages under the relative low growth temperature, together with the theoretical and experimental data (Ref. 4).

nanowires.[15] Based on the diffusion equation in nanoscale films,[20] the $f(x_0)$ in Eq. (2) can be expressed as

$$f(x_0) = \exp\left(\frac{-2S}{3k_B}\frac{n_s}{n_v}\right), \quad (6)$$

where $S$ and $n_s/n_v$ are the melting entropy for $O_2$, and the ratio of $SiO_2$ molecule numbers of surface and bulk, respectively. Considering the existing of $H$ region in oxide, we calculate $n_s/n_v$ shown as following:

$$\frac{n_s}{n_v} = \frac{r_0 \rho_{2.2}}{(x_0 - H - r_0)\rho_{2.2} + \displaystyle\int_{x_0-H}^{x_0} \rho(x)dx}, \quad (7)$$

where $r_0$, $H$, and $\rho_{2.2}$ are a thickness where almost all atoms are located on the surface, the thickness of $H$ region near the $Si/SiO_2$ interface, and the mass density of normal $\alpha$-$SiO_2$ ($\sim 2.2$ $g/cm^3$), respectively. The dry $O_2$ diffuses in $\alpha$-$SiO_2$ by jumping among interstitial cages offered by the oxide network,[21,22] and the mean distance of the adjacent interstitial sites is about 0.27 nm,[23] so we set $r_0 = 0.27$ nm. Recently, x-ray reflectivity study has quantitatively revealed the existence of thin and high mass density (2.2–2.4 $g/cm^3$) region at the $SiO_2/Si$ interface and found the thickness of this region changes with the oxidation temperature.[24] Moreover, Bongiorno and Pasquarello[25] found the distribution of mass density in $H$ region by constructing atomistic models of
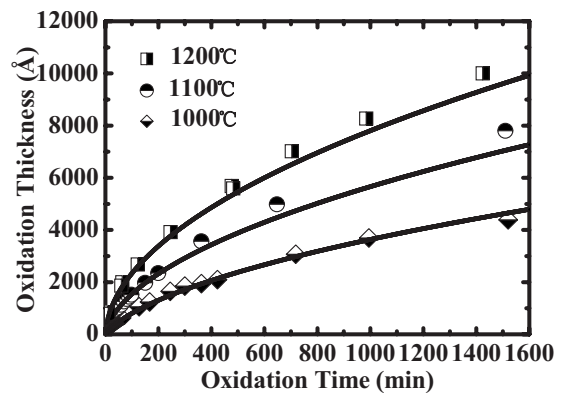


FIG. 3. Oxide thickness as a function of time for the whole oxidation process under the relative high growth temperature, together with the theoretical curves and experimental data (Refs. 3 and 4).
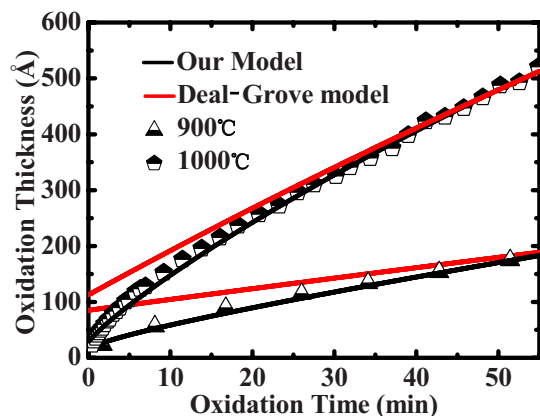
FIG. 4. (Color online) Growth kinetics for Si thermal oxidation by the Deal–Grove model (Ref. 3) (red solid line) compared with the present theory (black solid line) in the initial growth regime, together with the conventional experiment data (Refs. 3 and 4).

the Si–SiO$_2$ interface from crystalline silicon to disordered SiO$_2$.[25] In light of the experimental and theoretical data mentioned above, we have obtained the quantitative dependence of the *H*-region thickness on the oxidation temperature and space-dependence $\rho(x)$ in *H* region by the nonlinear power function curve fitting method.[26] Based on Eqs. (2), (6), and (7), together with those in Ref. 26, one could obtain the relationship curve between the thickness of oxide and activation energy of O$_2$ diffusion in the oxide, as shown in Fig. 1(b). As expected, the diffusion activation energy exponentially decreases with the oxide thickness diminishing and reduced to 0.83 eV at given the initial oxidation thickness (0.54 nm), which is well compared with 0.76 eV obtained by experiment.[27] The size-dependence activation energy goes to the bulk value when the thickness is bigger than ~10 nm, as is consistent with the results of atom-size modeling for the Si oxidation process.[28]

One can obtain the oxidation thickness as a function of time by numerically integrating Eq. (5) and applying conventional experimental data[3,4,29] in a wide size and temperature range, as shown in Figs. 2–4. Figure 2 gives the dependence of the oxidation thickness on oxidation time at given temperatures of 800, 850, 900, 950, and 1000 °C. Obviously, at the initial growth stages (<20 nm), the present model is in excellent agreement with the experimental data. Moreover, at the high oxidation temperature (950 and 1000 °C), the model curve can be well consistent with experimental data even in the high oxidation thickness. Contrary, at the low oxidation temperature (800 and 850 °C), when the thickness of oxide layer exceeds 20 nm, the growth rate of the oxide is higher than the experimental values. It is expected that due to the different molar volume between Si (12 cm$^3$/mol) and SiO$_2$ (26 cm$^3$/mol), there will exist a compression stress at the Si/SiO$_2$ interface when the oxidation temperature is below 900 °C, and the stress will influence the diffusion of O$_2$ in the grown oxide, as has been well observed and qualitatively discussed by many researchers.[8,30]

Figure 4 shows the contrast between the present and the Deal–Grove models together with the experiment data. It is apparent that the present model not only solves the breakdown of the Deal–Grove model but also is consistent with experiment data in the growth of thick oxide just as the

Deal–Grove model has done. The findings suggested that the size- and space-dependence activation energies of O$_2$ diffusion in the oxide may be the physical origin of Si thermal oxidation.

In conclusion, we have derived a kinetics model for the thermal oxidation of silicon by assuming that the diffusion is size- and space-dependence, which accounts for oxidation process in both the thin- and thick-oxide regions over a wide temperature range. Our model indicates that the size-dependence activation energy of O$_2$ diffusion in the oxide may be the physical origin of anomalous initial growth stages. The present approach may not be restricted to Si oxidation but may be applicable to the oxidation process of various metal or semiconductor materials.

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