

New Linear-Parabolic Rate Equation for Thermal Oxidation of Silicon

Takanobu Watanabe,^{1,2,3,*} Kosuke Tatsumura,¹ and Iwao Ohdomari^{1,2}

¹Faculty of Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

²Institute for Nanoscience and Nanotechnology, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

³PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan

(Received 4 March 2006; published 17 May 2006)

We propose a new oxidation rate equation for silicon supposing only a diffusion of oxidizing species but not including any rate-limiting step by interfacial reaction. It is supposed that diffusivity is suppressed in a strained oxide region near the SiO_2/Si interface. The expression of a parabolic constant in the new equation is the same as that of the Deal-Grove model, while a linear constant makes a clear distinction with that of the model. The estimated thickness using the new expression is close to 1 nm, which compares well with the thickness of the structural transition layers.

DOI: 10.1103/PhysRevLett.96.196102

PACS numbers: 81.65.Mq, 68.35.Fx, 68.47.Fg, 81.15.Aa

Thermal oxidation of silicon is among the most fundamental processes in the fabrication of silicon devices. Although industry has nowadays started to replace silicon dioxide with other specialized dielectric materials for some applications [1], silicon oxidation is still indispensable to easily forming an excellent interface to silicon substrate with low density of interface states.

Ever since the work of Deal and Grove [2], the thermal oxidation process of silicon has generally been assumed to occur through two processes in series: (i) the diffusion of oxidizing species through the oxide film already formed, and (ii) the chemical reaction at the SiO_2/Si interface. According to the Deal-Grove equation, oxide thickness increases linearly with time for relatively small oxidation times. This is the linear regime, in which the rate-limiting process is the interfacial oxidation reaction. At longer oxidation times, the limiting process is the diffusion of oxidant, and the thickness increases parabolically with time. This is the parabolic regime. When silicon is oxidized in dry oxygen ambient, the growth rate of oxide film thinner than about 25 nm deviates from linear-parabolic kinetics. To interpret this anomalous initial regime, many hypotheses [3–6] have been proposed keeping the basic concept of the Deal-Grove model, however. On the contrary, it has been pointed out that there is no convincing evidence that the linear regime is dominated by the interfacial oxidation reaction [7,8].

Recent theoretical studies have brought again the subject of the physical model for the linear regime to the attention of researchers. First-principles calculations [9] have revealed that the activation barrier for the interfacial oxidation reaction is negligibly small. Furthermore, it has been found that the layer-by-layer oxidation of silicon surfaces, which has been observed by various experimental methods [10], is simulated by the diffusion-limited oxidation model when it can be supposed that the reaction occurs immediately upon the arrival of the oxidant at the SiO_2/Si interface [11]. These findings suggest that the linear regime is governed by the oxidant diffusion as well as the parabolic regime, and therefore reconsideration of the Deal-Grove

model is necessary. In this Letter, we propose a new linear-parabolic rate equation for thermal oxidation of silicon, in which any rate-limiting process of oxidation reaction is excluded.

In the present oxidation model, we suppose a compressively strained oxide layers with a thickness of L localized in the proximity of SiO_2/Si interface and that the oxidant diffusivity is suppressed in the strained layers, as indicated in Fig. 1. We provide the following model for the diffusivity D as a function of the depth x from the oxide surface:

$$D(x) = \begin{cases} D_0, & 0 < x < x_0 - L \\ D_0 \exp\left[-\frac{\Delta E}{k_B T}\left(\frac{x-x_0+L}{L}\right)^2\right], & x_0 - L < x < x_0 \end{cases} \quad (1)$$

where x_0 is the total thickness of the oxide film, ΔE is the incremental barrier of the diffusivity at the SiO_2/Si interface, and D_0 is the diffusivity in the oxide film except for the interfacial strained region. This formula means that the activation energy of the oxidant diffusivity is raised monotonically in the strained region with approaching to the SiO_2/Si interface.

To find the oxidation rate equation, we assume that a steady-state diffusion profile results, as well as the Deal-Grove theory [2]. The constant flux F of oxidant across the oxide film is given by Fick's law, $F = -D(x) \frac{dC(x)}{dx}$, where $C(x)$ is the concentration of oxidant at depth x . The differ-

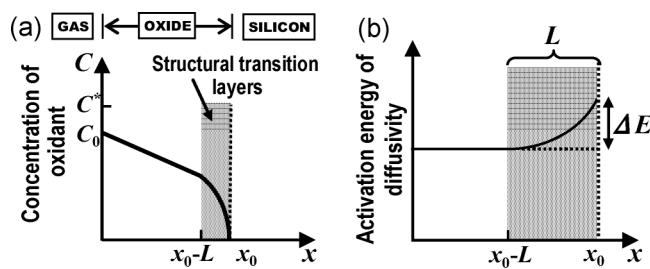


FIG. 1. Depth profiles of oxidant concentration (a) and activation energy of diffusivity (b) in the new oxidation model.

ential equation is integrated over x in the oxide film to give

$$F = \frac{D_0(C_0 - C_i)}{\frac{L}{2} \sqrt{\frac{\pi k_B T}{\Delta E}} \operatorname{erfi}(\sqrt{\frac{\Delta E}{k_B T}}) - L + x_0}, \quad (2)$$

where C_0 and C_i are the concentrations at the oxide surface and at the SiO_2/Si interface, respectively. $\operatorname{erfi}(z)$ is the *imaginary error function* defined by $\operatorname{erfi}(z) = -i\operatorname{erf}(iz)$. Since the interfacial oxidation reaction is regarded to occur nearly spontaneously [9], the oxidant concentration at the interface should be negligibly small in the steady-state condition. It is therefore a good approximation to set $C_i = 0$.

After the Deal-Grove theory, the flux of the oxidant from the gas to the vicinity of the oxide surface is taken to be

$$F = h(C^* - C_0), \quad (3)$$

where h is the gas-phase transport coefficient, and C^* is the equilibrium concentration in the oxide film. By solving simultaneous equations of (2) and (3) under the condition of $C_i = 0$, the following expression is obtained for the flux of oxidant:

$$F = \frac{2D_0C^*}{L\sqrt{\frac{\pi k_B T}{\Delta E}} \operatorname{erfi}(\sqrt{\frac{\Delta E}{k_B T}}) - 2L + \frac{2D_0}{h} + 2x_0}. \quad (4)$$

The growth rate of the oxide film is described by the differential equation $dx_0/dt = F/N_1$, where N_1 is the number of oxidant molecules incorporated into a unit volume of the oxide film. From this equation and Eq. (4), the next linear-parabolic type equation [2] is obtained:

$$\frac{dx_0}{dt} = \frac{B}{A + 2x_0}, \quad (5)$$

$$A = L\sqrt{\frac{\pi k_B T}{\Delta E}} \operatorname{erfi}\left(\sqrt{\frac{\Delta E}{k_B T}}\right) - 2L + \frac{2D_0}{h}, \quad (6)$$

$$B = 2D_0C^*/N_1. \quad (7)$$

The expression of parabolic constant B is exactly the same as that of the Deal-Grove model. The difference between the present equation and the Deal-Grove equation lies within the expression of A . In the Deal-Grove equation, the constant A is given by $A_{DG} = 2D_0/k + 2D_0/h$, where k is the reaction constant of interfacial oxidation. In the present theory, the reaction constant is replaced by the expression involving the thickness of strained layers L , and the incremental barrier of diffusion ΔE .

There have been reported experimental values for the constant A and B [2]. From the Arrhenius plots of linear constant B/A and parabolic constant B , ΔE is determined as the difference of their activation energies. As discussed by Deal and Grove [2], the term $2D_0/h$ in Eq. (6) takes a negligibly small value. Therefore, the unknown variable in Eq. (6) is only L , and we estimate the thickness L so as to reproduce the measured values of A .

The estimated values of L at various temperatures are shown in Table I. The experimental values for A are of the oxidation in dry oxygen ambient [2]. The estimated values of L are close to 1 nm, which compare well with the thickness of the structural transition layers near the SiO_2/Si interface [12].

Here we set $\Delta E = 0.76$ eV, which is the difference in the typical experimental activation energy between 2.0 eV [2] for the linear constant and 1.24 eV [2] for the parabolic constant. It has been revealed by x-ray reflectivity measurement [12] that the mass density of oxide layers near the SiO_2/Si interface is increased to about 2.4 g/cm³. According to a Monte Carlo simulation [13] on the O₂ diffusion in an amorphous SiO₂ (*a*-SiO₂) model, the effective activation energy for diffusion was 1.12 eV in a normal *a*-SiO₂ sample with the density of 2.2 g/cm³, and it increased to 2.0 eV in a sample with the higher density of 2.4 g/cm³. In view of these reports, the adopted value for ΔE is considered to be appropriate.

Since we have simply assumed a homogeneous oxide model in the above derivation, it is necessary to verify the quantitative reliability of the approximation. In dry oxidation, the dominant diffusing oxidant species is the O₂ molecule, which jumps among interstitial cages offered by the oxide network [13,14]. Supposing the ideal pseudocrystobalite model on Si(100) substrate [15], the mean distance of the adjacent interstitial sites projected to the surface normal axis is about 0.27 nm. The thickness of the strained oxide layers is about 1 nm, which corresponds to only 3 or 4 layers of interstitial sites. To estimate quantitatively the thickness of the thin strained layers, it is necessary to take into account the microscopic picture of an O₂ molecule jumping among the potential minima in the oxide film.

From this paragraph, we derive the rate equation based on an atomistic model. Figure 2 shows schematics of the potential energy profile of an O₂ molecule near the SiO_2/Si interface assumed in this model. The gradient of oxide strain introduces bias into the diffusion process by increasing the barrier toward the interface. The net flux of the oxidant from a potential minimum at x to an adjacent minimum at $x + a$ is given by

$$F = C(x)a\Gamma^+(x) - C(x + a)a\Gamma^-(x + a), \quad (8)$$

TABLE I. Estimated thickness of interfacial strained layers so as to reproduce the experimental values of A . Equations (6) and (16) are used to estimate L and la , respectively.

T °C	A nm [Ref. [2]]	L nm	la nm
800	370	0.76	0.93
920	235	0.92	0.99
1000	165	1.03	0.98
1100	90	0.86	0.96
1200	40	0.55	0.68

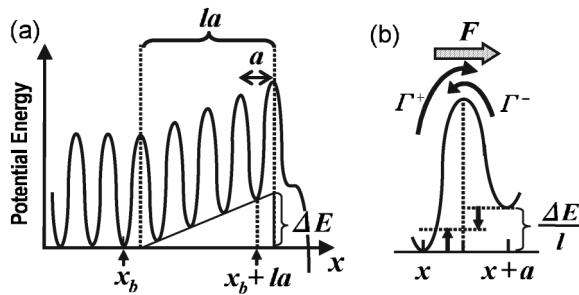


FIG. 2. (a) Microscopic potential energy profile of oxidant around the interfacial strained layers. (b) Flux of oxidant through a barrier in the oxide film.

where a is the mean distance of the adjacent potential minima, and $\Gamma^+(x)$ and $\Gamma^-(x)$ are the jumping rates of oxidant at x toward the SiO_2/Si interface and the oxide surface, respectively. Since Eq. (8) is valid for any adjacent potential minima, the following recursive formula is derived

$$C(na) = \frac{F}{a\Gamma^+(na)} + C[(n+1)a] \frac{\Gamma^-[(n+1)a]}{\Gamma^+(na)}, \quad (9)$$

where n is an integer number. We define x_b as the position of a potential minimum just before the starting point of the interfacial strained region.

By solving the recursive formula (9) from x_b over l layers, the next expression is obtained

$$\begin{aligned} C(x_b) &= \frac{F}{a\Gamma^+(x_b)} \left[1 + \sum_{i=1}^l \prod_{j=1}^i \frac{\Gamma^-(x_b + ja)}{\Gamma^+(x_b + ja)} \right] \\ &\quad + \frac{\Gamma^-[x_b + (l+1)a]}{\Gamma^+(x_b)} \prod_{j=1}^l \frac{\Gamma^-(x_b + ja)}{\Gamma^+(x_b + ja)} \\ &\quad \times C[x_b + (l+1)a]. \end{aligned} \quad (10)$$

Here we set $x_0 = x_b + la$; i.e., the interfacial strained oxide region is l layers in thickness. Since it is assumed that an O_2 molecule is immediately consumed to oxidize the silicon if it reaches the substrate, it is a good approximation to set $C[x_b + (l+1)a] = 0$, so that the second term of the right side of Eq. (10) is eliminated. Γ^-/Γ^+ in Eq. (10) is the ratio of the jumping rate toward the oxide surface to that toward the SiO_2/Si interface. If we assume a linear slope of potential energy in the strained oxide layers, Γ^-/Γ^+ takes a constant value in that region. In this case, the activation barrier of Γ^- is lowered by the half value of $\Delta E/l$, and that of Γ^+ is increased by the same value, as shown in Fig. 2(b). Therefore, $\Gamma^-/\Gamma^+ = \exp[\Delta E/lk_B T]$. At the position x_b , since there is no longer exists the potential gradient, $\Gamma^+(x_b)$ is same as that in the remaining part of oxide film. Hence $\Gamma^+(x_b) [= \Gamma^-(x_b)] = D_0/a^2$. Therefore, from Eq. (10) the oxidant flux F is derived to be

$$F = \frac{C(x_b)D_0}{a} \left\{ \frac{\text{Ex}(\frac{1}{l}) - 1}{\text{Ex}(\frac{l+1}{l}) - 1} \right\}, \quad (11)$$

where $\text{Ex}(z) \equiv \exp[z\Delta E/k_B T]$ as a simple notation.

It should be noted that the SiO_2/Si interface moves forward as the oxidation reaction progresses. Since the thickness of interfacial strained layers is regarded as nearly constant, the potential profile in the strained region changes periodically with the period of one monolayer oxidation, as illustrated in Fig. 3. The potential profile shown in Fig. 2 corresponds to the phase with highest barrier at the SiO_2/Si interface, and the flux given by Eq. (11) is the minimum estimate. To estimate the mean value for the oxidant flux, we must take the intermediate phases with lower barriers into account. The maximum flux in the case of the lowest barrier shown in Fig. 3(b) is obtained in the same way:

$$F_{\max} = \frac{C(x_b)D_0}{a} \left\{ \frac{\text{Ex}(\frac{1}{l}) - 1}{\text{Ex}(\frac{1}{l}) + \text{Ex}(1) - 2} \right\}. \quad (12)$$

Taking the average of Eqs. (11) and (12), the mean flux \bar{F} in the interfacial strained region is obtained:

$$\bar{F} = C(x_b)D_0\bar{\kappa}/a, \quad (13)$$

$$\bar{\kappa} = \frac{[\text{Ex}(\frac{1}{l}) - 1][\text{Ex}(\frac{l+1}{l}) + \text{Ex}(\frac{1}{l}) + \text{Ex}(1) - 3]}{2[\text{Ex}(\frac{1}{l}) + \text{Ex}(1) - 2][\text{Ex}(\frac{l+1}{l}) - 1]}. \quad (14)$$

By equating the mean flux Eq. (13) with the flux from the gas to the oxide surface given by Eq. (3), and with the flux in the remaining part of the oxide given by

$$F = -D_0 \frac{C(x_b) - C_0}{x_0 - la}, \quad (15)$$

the same differential equation with Eq. (5) is obtained. Here

$$A = 2a/\bar{\kappa} - 2la + 2D_0/h, \quad (16)$$

and B is just the same expression as with Eq. (7). The thickness of the interfacial strained layers la estimated by

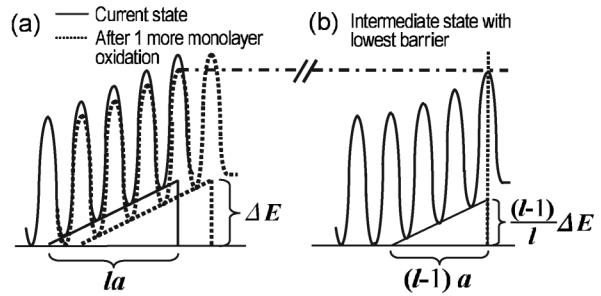


FIG. 3. Potential energy profiles of oxidant in the transition layers. (a) States with an additional potential energy of ΔE at the interface. (b) Intermediate state in which the potential is decreased by $\Delta E/l$ at the interface.

using Eq. (16) is shown in Table I. Here we set $a = 0.27$ nm, providing the pseudocristobalite oxide structure [15]. The estimated thickness is closer to the reported value of 1 nm for the dense oxide layer at the SiO_2/Si interface [12], supporting the validity of the present theory.

An essential difference from Deal-Grove's equation is that the linear constant B/A in the present theory is proportional to the oxidant diffusivity D_0 . From Eq. (16), B/A is given by

$$\frac{B}{A} = \frac{D_0 C^*}{aN_1(1/\bar{\kappa} - l)}, \quad (17)$$

where $2D_0/h$ in A is omitted. On the other hand, the linear constant in the Deal-Grove theory is $B/A_{\text{DG}} = kC^*/N_1$, which does not depend on D_0 . This difference produces a substantial change in the interpretation of the anomalous initial regime as discussed as follows.

Fargeix *et al.* [16] have confirmed that the inverse oxidation rate dt/dx_0 against the oxide thickness x_0 has deviated from a linear dependence predicted by the linear-parabolic rate equation, in the initial oxidation regime. The tendency of the deviation was attributed to either an increase in B/A or a decrease in B . In the Deal-Grove scheme, that means either an increase in the reaction constant k or a decrease in the diffusivity D_0 . In the present model, however, B/A is proportional to D_0 as well as B , and the deviation can be attributed to the increase in D_0 . Providing that D_0 depends on x_0 , the differential coefficient of the inverse oxidation rate is

$$\frac{d}{dx_0} \left(\frac{dt}{dx_0} \right) = \frac{N_1}{D_0 C^*} - \frac{N_1}{2D_0^2 C^*} (A + 2x_0) \frac{dD_0}{dx_0}, \quad (18)$$

where the second term on the right side corresponds to the deviation from the linear-parabolic relationship. Experimental results show that the deviation in the differential coefficient takes positive values [16]. Hence dD_0/dx_0 must be a negative number, i.e., D_0 increases as x_0 decreases [17]. Thus the hypothesis of enhanced diffusion [2,3], which was once dismissed in the context of Deal-Grove equation [4,16], comes back again via the present theory.

It should be noted that the enhanced diffusion hypothesis for the anomalous initial regime does not contradict the present model. While the diffusivity in the interfacial strained layers is assumed to be suppressed, it is possible that the diffusivity given by Eq. (1) is enhanced entirely due to the increase in D_0 . Microchannels in the oxide film for diffusing species [3] is one of the possible explanations for the increase in D_0 .

The present model argues that the linear region is caused by the strained oxide region near the interface. The linear

region is expected to disappear if the interfacial stress is vanished, although it may be difficult to realize such a system experimentally. Contrary, according to the Deal-Grove model, the linear region should exist regardless of the extent of the stress at the interface.

In conclusion, we have derived a new linear-parabolic rate equation for the thermal oxidation of silicon without the rate-limiting step of interfacial oxidation reaction, assuming that the oxidant diffusivity is suppressed in the thin strained layers near the SiO_2/Si interface. The thickness of the strained layers estimated by our model is close to that of the structural transition layers, and we have found that the anomalous initial regime can be explained by the enhanced diffusion hypothesis.

We acknowledge support from a Grant-in-Aid for COE Research and the 21st-Century COE program "Center for the Practical Nano-Chemistry" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and a grant from JST-PRESTO.

*Electronic address: watanabe-t@waseda.jp

- [1] International Technology Roadmap for Semiconductors 2005 edition (<http://public.itrs.net/>).
- [2] B. E. Deal and A. S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).
- [3] A. G. Revez *et al.*, *J. Phys. Chem. Solids* **30**, 551 (1969).
- [4] H. Z. Massoud *et al.*, *J. Electrochem. Soc.* **132**, 2685 (1985).
- [5] A. M. Stoneham *et al.*, *Philos. Mag. B* **55**, 201 (1987).
- [6] H. Kagesima *et al.*, *Jpn. J. Appl. Phys.* **38**, L971 (1999).
- [7] R. H. Doremus, *Thin Solid Films* **122**, 191 (1984); *J. Appl. Phys.* **66**, 4441 (1989).
- [8] N. F. Mott *et al.*, *Philos. Mag. B* **60**, 189 (1989).
- [9] A. Bongiorno *et al.*, *Phys. Rev. Lett.* **93**, 086102 (2004); T. Akiyama *et al.*, *Surf. Sci.* **576**, L65 (2005).
- [10] F. M. Ross *et al.*, *Phys. Rev. Lett.* **68**, 1782 (1992); M. Ohashi *et al.*, *Jpn. J. Appl. Phys.* **36**, L397 (1997); H. Watanabe *et al.*, *Phys. Rev. Lett.* **80**, 345 (1998).
- [11] T. Watanabe *et al.*, *Appl. Surf. Sci.* **237**, 125 (2004).
- [12] N. Awaji *et al.*, *Jpn. J. Appl. Phys.* **35**, L67 (1996).
- [13] A. Bongiorno and A. Pasquarello, *Phys. Rev. B* **70**, 195312 (2004); *Phys. Rev. Lett.* **88**, 125901 (2002).
- [14] T. Hoshino *et al.*, *Jpn. J. Appl. Phys.* **42**, 3560 (2003).
- [15] T. Hattori *et al.*, *Jpn. J. Appl. Phys.* **28**, L1436 (1989); T. Takahashi *et al.*, *J. Phys. Condens. Matter* **5**, 6525 (1993); K. Tatsumura *et al.*, *Phys. Rev. B* **69**, 085212 (2004).
- [16] A. Fargeix *et al.*, *J. Appl. Phys.* **54**, 2878 (1983).
- [17] See EPAPS Document No. E-PRLAO-96-030622 for the graphical explanation of the dependency of the inverse oxidation rate on D_0 . For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.