

Universal Theory of Si Oxidation Rate Taking Account of Interfacial Si Emission

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1. Introduction

The design and control of thermal oxide formation on silicon surfaces are important for developing new generation devices such as highly integrated metal-oxide-semiconductor field-effect transistors (MOS FET), and single-electron devices. Especially, the pattern-dependent-oxidation (PADOX) method, in which the nano scale 2-dimensional distribution of the oxidation rate is controlled by the pattern, is a promising process for fabricating Si single-electron devices [1]. For this reason, we have theoretically studied the atomistic mechanism of the silicon oxidation by using first-principles calculation [2]. From previous studies, we have found that the emission of Si atoms from the interface plays a very important role in the oxidation. The accumulation of the strain due to the large volume expansion during oxidation cannot be released efficiently without the emission. Therefore, the emission is inevitable during oxidation. This is consistent with already known phenomena such as the oxidation-induced stacking faults (OSF) [3] and the oxidation-enhanced diffusion (OED) [4]. However, we have also found that the emission rate is too large to conclude that all emitted Si atoms become the self-interstitials in the substrate as the source of the OSF and OED.

In this work, we study the behavior of the emitted Si atoms, and propose a universal theory for the oxide growth rate at all range of oxide thickness.

2. Behavior of Emitted Si Atoms

There are many candidates for the possible locations of the emitted silicon atoms. To clarify where the emitted Si atoms go, we estimated the reaction energies of all possible locations by using first-principles calculation with ultrasoft pseudopotentials [5]. The details of the method are similar to those in Ref. 2. To estimate the total energy change of the emission at the interface, we used a H-terminated super-slab model with $c(2 \times 2)$ unit cell. For molecules, the supercell geometry is used. The theoretically estimated results are shown in Fig. 1. For estimating the reaction energy for the A and E cases, we used the values reported by Car, *et al.* [6]. The figure clearly shows that the self-interstitials (I_{Si}) are hardly formed from the silicon emission. Piling up on the oxide surface does not occur often. Emission from the surface as SiO molecules and recombination with Si vacancy (V_{Si}) occur more often. However, absorption into the oxide layer by oxidation occurs the most frequently. This could occur even during the oxidation because the oxide has large holes between the Si-O-Si networks, which could make the diffusion of Si atoms easy. In addition, oxide that is far from the interface could be very soft due to the viscous flow, which could make the absorption into the Si-O-Si network easy as well. Therefore, we can conclude that the atomic processes for the emitted silicon atoms during oxidation are as follows (Fig. 2): (1) When the oxide layer is very thin, the Si atoms diffuse through the oxide to the surface, and they

emit as SiO molecules or grow as an oxide layer there. (2) When the oxide layer is thick, the Si atoms mostly diffuse into the oxide layer and absorb there through oxidation, while only a part of the Si atoms diffuse into the substrate and become the self-interstitials. The diffusion into and through the oxide is consistent with recent experiments [7], and the absorption into the oxide is supported by previous studies [8].

3. Oxide Growth Rate

Based on the above conclusions, we construct a theory for the silicon oxidation rate. Since the emission of Si atoms releases the accumulated stress during the oxidation, the emission can control the oxidation rate itself.

We assumed the following two atomic processes are necessary in addition to the general processes assumed in the Deal-Grove model [9]: (1) Creation of interstitial silicon atoms requires oxidation reactions to occur at the oxide/silicon interface. (2) The emitted interstitials always diffuse into the oxide layer and are absorbed there by forming a Si-O-Si network. Then, we introduce the following equation as the interfacial-reaction-rate constant,

$$k = k_0 \left(1 - C_{Si}^I / C_{Si}^0\right),$$

where C_{Si}^I is the density of Si interstitials in the oxide around the interface, C_{Si}^0 is the maximum density of Si interstitials in the oxide, and k_0 is the maximum interfacial-reaction-rate constant. We also introduce the following equations for the diffusion equation with boundary conditions for emitted Si atoms density, $C_{Si}(x)$,

$$D_{Si} \frac{\partial^2 C_{Si}(x)}{\partial x^2} = \kappa C_{Si}(x), \quad k C_{Si}^I v = \int_0^x dx \kappa C_{Si}(x) + k' C_{Si}^S,$$

and the density flow equation for oxidant,

$$h(C_o^* - C_o^S) = \frac{D_o}{X} (C_o^S - C_o^I) = k C_o^I.$$

Here, $x = 0$ is the interface and $x = X$ is the surface of the oxide, which means X is the thickness of the oxide layer. D_{Si} and D_o are the diffusion coefficient in the oxide for Si and O atoms, κ is the oxidation rate of Si atoms in the oxide, v is the emission rate of Si atoms from the interface, k' is the oxidation rate of Si atoms at the oxide surface, h is the gas phase mass-transfer coefficient, and C_o^* is the solubility of the oxidant in the oxide. C_o^S and C_o^I are the density of oxidant at the oxide surface and at the interface. Here, we assumed that κ is constant for simplicity though it should generally depend on the density of oxidant. We also assumed that the density flow of oxidant is not affected by the reaction with the emitted Si atoms. The growth rate is,

$$N_o \frac{dX}{dt} = k C_o^I (1 - v) + \int_0^x dx \kappa C_{Si}(x) + k' C_{Si}^S,$$

where N_o is the number density of oxidant incorporated into a unit volume of the growing oxide. Here we neglected SiO emission from the surface.

By solving the above equations, we can obtain the following equation for the oxide growth rate.

$$\left(N_o \frac{dX}{dt}\right)^{-1} = \frac{1}{2k_o C_o^*} \left[F_1 + F_2 + \sqrt{(F_1 - F_2)^2 + 4F_2} \right],$$

where,

$$F_1 = 1 + k_o/h + k_o X/D_o, \quad F_2 = k_o C_o^* v / C_{Si}^0 F, \\ F = k'' + (k' - k'') e^{-X/L_s}, \quad L_{Si} = \sqrt{D_{Si}/\kappa}, \quad k'' = \kappa L_{Si}.$$

When the oxide is thick, this equation is completely the same as that derived by Deal and Grove [9]. In addition, when the oxide is thin, it is the same as the empirical equation for the initial enhanced growth proposed by Massoud, *et al.* [10],

$$\frac{dX}{dt} = \frac{B}{A + 2X} + K e^{-X/L},$$

under the condition of $k_o C_o^* v \gg k' C_{Si}^0, k'' C_{Si}^0$, i.e. the maximum emission rate of Si atoms at the interface is far larger than the absorption rate in the oxide layer or on the surface. By comparison, we can obtain $L = L_{Si}$ and

$K = (k' - k'') C_{Si}^0 / v N_o$. Furthermore, $B/A = k'' C_{Si}^0 / v N_o$, which is different from that of Deal-Grove model, $B/A = C_o^* / (k_o^{-1} + h^{-1})$.

These results come only from our assumptions about the interfacial reaction rate. The density of Si atoms at the interface exponentially increases up to the maximum value with the increase in the oxide thickness. As a result, the interfacial reaction rate is quickly reduced. However, since a further increase of the oxide thickness results in the decrease of the oxidant density at the interface, the diffusion of the oxidant begins controlling the oxide growth rate.

Thus, the initial enhancement of oxidation can be explained only by the behavior of the emitted Si atoms from the interface during oxidation. This suggests that the initial interface reaction is governed by the emission and saturation of Si atoms. Our model for the oxide growth is supported by the previous experimental studies [11]. Since the Si-atom diffusion through the oxide should be far more difficult than the oxidant diffusion due to their atomic radii, it should be far more sensitive to the strain. This means that the growth process for PADOX would be strongly affected by our model. The reliability against the insulation breakdown of the formed oxide should be also strongly affected by our model because the emitted Si atoms into the oxide would possibly cause the O defects in the oxide [12]

4. Conclusions

We theoretically found that the emitted Si atoms are mostly absorbed into the oxide layer and that the behavior of the emitted Si atoms governs the oxidation process itself. Based on these results, we derived a new equation for the oxide growth rate, which can naturally explain the empirical equation for the initial enhanced growth proposed by Massoud, *et al.*

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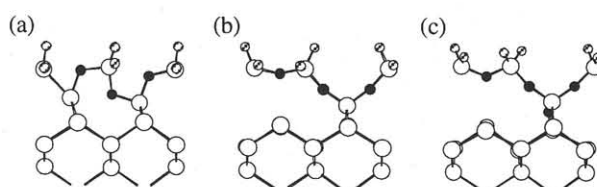
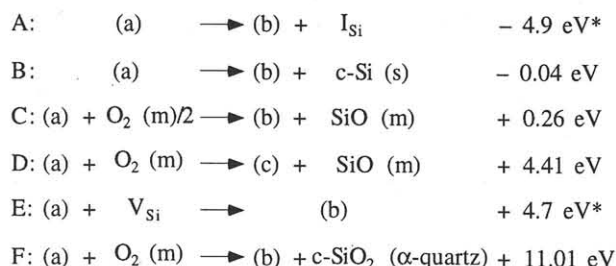


Fig. 1: Comparison of reaction energies estimated by first-principles calculation.

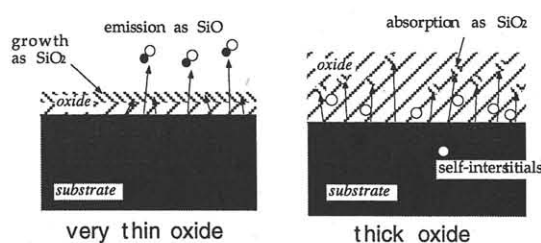


Fig. 2: Schematic view for the atomic processes of emitted silicon atoms during oxidation based on first-principles calculations. The open circles are Si atoms, and the filled circles are O atoms.