

A Kinetic Model of Silicon Carbide Oxidation Based on the Interfacial Silicon and Carbon Emission Phenomenon

Yasuto Hijikata*, Hiroyuki Yaguchi, and Sadafumi Yoshida

Division of Mathematics, Electronics and Informatics, Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, Japan

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We proposed a kinetic model for thermal oxidation of silicon carbide, termed “silicon and carbon emission model”, taking into account the Si and C emissions from the oxidation interface, which lead to a reduction of interfacial reaction rate. We used this model to calculate oxide growth rates and found that the derived growth rates showed a good fit with the measured rates over the entire oxide thickness for both the C and Si faces. We discussed the difference in oxidation mechanism between these polar faces in terms of the difference in parameter values deduced from the curve fits. © 2009 The Japan Society of Applied Physics

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Among wide-band-gap semiconductor materials, only silicon carbide (SiC) can be thermally oxidized, and a SiO₂ layer, which is widely used as an insulating and passivation layer in electronic devices, can be formed on its surface. In addition, SiC has excellent physical properties, such as a high thermal conductivity and a high breakdown electric field, and is well-suited for high-power and/or high-frequency electronic devices applications.¹⁾ Therefore, SiC metal–oxide–semiconductor field-effect transistors (MOSFETs) have been expected to exhibit excellent electrical characteristics that cannot be obtained with conventional semiconductors like Si or GaAs. However, actual SiC MOSFETs do not have satisfactory electrical characteristics. For example, their on-resistance is one or two orders higher than that predicted from the bulk properties of SiC, which is thought to be due to the low carrier mobility near the SiC–oxide interface.²⁾ Thus, it is important to determine the structure at the interface, which is closely correlated with the oxidation mechanism of SiC.

We have studied the oxidation process of SiC by real-time observations using *in situ* spectroscopic ellipsometry^{3–6)} and, for the first time, found that the oxide growth rates are much larger than those predicted from the Deal–Grove model⁷⁾ in the initial stage of oxidation for the (000 $\bar{1}$) C face^{4,5)} and (0001) Si face.^{5,6)} We applied the empirical equation proposed by Massoud *et al.* for Si oxidation⁸⁾ to SiC oxidation, and found that this equation well reproduces the oxide growth rate of SiC in the entire oxide thickness regime.^{4–6)} In the case of Si oxidation, this empirical relation is explained by an oxidation kinetic model, called the “interfacial Si emission model”.^{9–12)} According to this model, Si atoms are emitted as interstitials into the oxide layers accompanied by oxidation of Si, which is caused by the strain due to the expansion of Si lattices during oxidation. The oxidation rate at the interface is initially large and is suppressed by the accumulation of emitted Si atoms near the interface with increasing oxide thickness, i.e., the oxidation rate is not enhanced in the thin oxide regime but is quickly suppressed with increasing thickness. Because the density of Si atoms in SiC ($4.9 \times 10^{22} \text{ cm}^{-3}$) is almost equal to that of Si, such an interfacial strain would presumably also be generated at the oxidation interface and hence interfacial Si emission is thought to occur in SiC oxidation as well. Thus, we attempted to apply the Si emission model to SiC

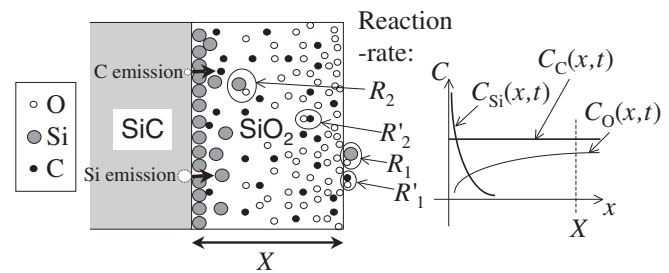
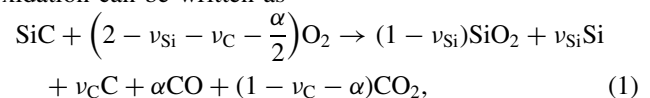


Fig. 1. Schematic illustration of the Si–C emission model.

oxidation,¹³⁾ and found that the model well explains the thickness dependence of the oxidation rate for the C face of SiC, including the high growth rate in the thin oxide regime. However, there are some physical issues that need to be addressed in describing SiC oxidation by the Si emission model, e.g., a different oxygen diffusivity in SiO₂ is required to explain the oxide growth rate of SiC, which may be due to the fact that the presence of carbon atoms is ignored.

In this paper, we have proposed a kinetic model of SiC oxidation on the basis of the interfacial silicon and carbon emission phenomenon, which we will refer to as “silicon and carbon (Si–C) emission model”, derived by adding the processes of C oxidation and emission to the interfacial Si emission model for Si.^{9–12)} We will show that our model can explain the thickness dependence of oxide growth rate in the entire oxide regime for both the C face and Si face of SiC and discuss the difference in oxidation mechanism between the C and Si faces, taking into account the parameters deduced from the curve fits to the measured growth rates.

Figure 1 schematizes the Si–C emission model, where C , x , and X denote the concentration, distance from the interface and oxide thickness, respectively; R_1 and R_2 denote the reaction rate at the oxide surface and in the oxide, respectively; with and without the superscript prime means the value for C and Si interstitials, respectively; and the subscripts Si, C, and O denote the values for the corresponding atoms. Considering Si and C atoms emitted from the interface during the oxidation as well as the oxidation process of C, the reaction equation for SiC oxidation can be written as



where ν and α denote the interfacial emission rate and the

*E-mail address: yasuto@opt.ees.saitama-u.ac.jp

production rate of CO, respectively. In the Deal–Grove model,⁷⁾ the interfacial reaction rate k is assumed to be constant regardless of the oxidation thickness. While in the Si emission model,^{9–12)} since the interfacial reaction rate is suppressed by the accumulation of Si interstitials near the interface, k is given as a decreasing function of C_{Si}^{I} , i.e., $k = k_0(1 - C_{\text{Si}}^{\text{I}}/C_{\text{Si}}^0)$, where C^0 is the solubility limit of the corresponding interstitials in the oxide, k_0 is the interfacial reaction rate in the case of no interstitial accumulation, and the superscript “I” denotes the position at the interface ($x = 0$). For SiC oxidation, the interfacial reaction rate for SiC oxidation is thought to be suppressed by the accumulation of C atoms and Si atoms emitted near the interface. Thus, we assumed that k is given by multiplying decreasing functions for Si and C:

$$k = k_0 \left(1 - \frac{C_{\text{Si}}^{\text{I}}}{C_{\text{Si}}^0}\right) \left(1 - \frac{C_{\text{C}}^{\text{I}}}{C_{\text{C}}^0}\right). \quad (2)$$

A diffusion equation for C atoms is added to the set of diffusion equations for Si interstitials and oxidants in the Si emission model,^{11,12)} that is,

$$\begin{aligned} \frac{\partial C_{\text{C}}}{\partial t} &= \frac{\partial}{\partial x} \left(D_{\text{C}} \frac{\partial C_{\text{C}}}{\partial x} \right) - R'_1 - R'_2, \\ R'_1 &= \eta' C_{\text{O}}^{\text{S}} C_{\text{C}}^{\text{S}}, \quad R'_2 = \kappa'_1 C_{\text{C}} C_{\text{O}} + \kappa'_2 C_{\text{C}} (C_{\text{O}})^2, \end{aligned} \quad (3)$$

where D denotes diffusivity of the interstitials, η' oxidation rate of C atoms at the oxide surface, κ'_1 and κ'_2 oxidation rates of C interstitials in the oxide, and the superscript “S” means the position at the oxide surface ($x = X$). Since it is not only the Si interstitials but also the C interstitials that consume the oxidants in the oxide, the diffusion equation for oxidants^{11,12)} should be modified as,

$$\frac{\partial C_{\text{O}}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\text{O}} \frac{\partial C_{\text{O}}}{\partial x} \right) - R_1 - R_2 - R'_1 - R'_2 - R_3, \quad (4)$$

where R_3 denotes the transportation rate of oxidants at the oxide surface. From eq. (1), the boundary conditions at the interface are given as

$$\begin{aligned} D_{\text{Si}} \frac{\partial C_{\text{Si}}}{\partial x} \Big|_{x=0} &= -\nu_{\text{Si}} k C_{\text{O}}^{\text{I}}, \\ D_{\text{C}} \frac{\partial C_{\text{C}}}{\partial x} \Big|_{x=0} &= -\nu_{\text{C}} k C_{\text{O}}^{\text{I}}, \\ D_{\text{O}} \frac{\partial C_{\text{O}}}{\partial x} \Big|_{x=0} &= \left(2 - \nu_{\text{Si}} - \nu_{\text{C}} - \frac{\alpha}{2}\right) k C_{\text{O}}^{\text{I}}. \end{aligned} \quad (5)$$

It has been believed that the oxidation rate in the thick oxide regime is limited by the in-diffusion of oxidant or out-diffusion of CO. According to recent studies,^{5,14)} the oxide growth rate in the thick oxide regime is proportional to the partial pressure of O_2 , which suggests that the oxide growth rate is limited only by the in-diffusion of O_2 . Therefore, the diffusivity of CO in SiO_2 is thought to be much larger than that of O_2 . Thus, we assumed that CO rapidly diffuses toward the oxide surface and that the diffusion process of CO is insensitive to the oxide growth rate. The oxide growth rate is described as

$$N_0 \frac{dX}{dt} = (1 - \nu_{\text{Si}}) k C_{\text{O}}^{\text{I}}$$

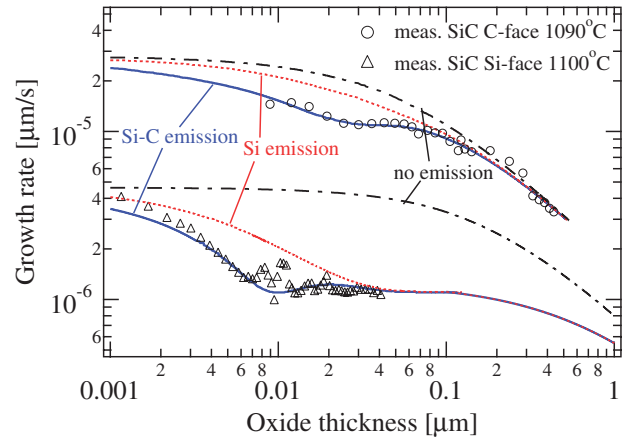


Fig. 2. Oxide thickness dependence of growth rates.

$$+ \int_0^X [\kappa_1 C_{\text{Si}} C_{\text{O}} + \kappa_2 C_{\text{Si}} (C_{\text{O}})^2] dx + \eta C_{\text{Si}}^{\text{S}} C_{\text{O}}^{\text{S}}, \quad (6)$$

where N_0 is the density of Si atoms in SiO_2 .^{9,10)} The right-hand side of eq. (6) is composed of the oxidation rate of Si atoms at the interface (first term), that of Si interstitials in the oxide (second term) and that of Si interstitials at the oxide surface. We approximated the integral term in eq. (6) by the area of a triangle C_{Si}^{I} in height and $\partial C_{\text{Si}}/\partial x|_{x=0}/2$ in gradient of hypotenuse, on the basis of the idea that interstitials are usually distributed according to what resembles a complementary error function or exponential function, and their areal density is given approximately by the area of the triangle.¹⁵⁾ Growth rates were numerically calculated from eqs. (2)–(5) and the diffusion equation for Si atoms using the partial differential equation solver ZOMBIE.¹⁶⁾ The oxide thickness, X , at each time step was obtained from eq. (6). The parameters related to the properties of SiO_2 (D_{Si} , D_{O} , η , κ_1 , κ_2 , and C_{Si}^0) were set to the same values as those obtained for Si oxidation.^{11,12)} The parameters concerning C interstitials (α , ν_{C} , D_{C} , η' , κ'_1 , κ'_2 , and C_{C}^0) as well as the values of k_0 and ν_{Si} were determined by fitting the calculated oxide growth rates to the measured ones.

Figure 2 shows the oxide growth rates observed for 4H-SiC C face at 1090 °C (circles) and Si face at 1100 °C (triangles). The oxide growths were executed under dry oxygen ambient at a pressure of 1 atm. The experimental details can be found in the references.^{4,6)} Also shown in the figure are the growth rates given by the Si–C emission model (blue solid lines), the Si emission model, and the model that does not take account of both Si and C emission, i.e., the Deal–Grove model (red broken line and black double broken line, respectively). We note that the same parameters were used for these three SiC oxidation models.

Figure 2 shows that the Si–C emission model reproduces the experimental values for both the C and Si faces better than the other two models. In particular, the dip in the thickness dependence of the growth rate seen around 0.02 μm for the C face and 0.01 μm for the Si face, which cannot be reproduced by the Si emission model or the Deal–Grove model no matter how well the calculation are tuned, can be well reproduced by the Si–C emission model. These results suggest that the C interstitials play an important role in the reduction of the oxidation rate, similarly to the role of the Si interstitials. Moreover, from the fact that the drop in growth

Table I. The derived parameters for the C face at 1090 °C and the Si face at 1100 °C.

	C face	Si face
α	0.8	0.8*
ν_C	0.050	0.10
η' (cm·s ⁻¹)		5×10^{-8}
D_C (cm ² ·s ⁻¹)		1.6×10^{-11}
κ'_1 (cm ³ ·s ⁻¹)		3.9×10^{-19}
κ'_2 (cm ⁶ ·s ⁻¹)		3.9×10^{-36}
C_C^0 (cm ⁻³)		4.1×10^{20}
k_0 (cm·s ⁻¹)	1.2×10^{-3}	4.0×10^{-4}
ν_{Si}	0.02	0.53

*Assumed value.

rate in the initial stage of oxidation is larger for the Si–C emission model than in the case of taking only Si emission into account, we found that the accumulation of C interstitials is faster than that of Si interstitials and that the accumulation of C interstitials is more effective in the thin oxide regime.

In all three of these models, the oxidation rate in the thick oxide regime is mainly governed by the diffusion of oxidants in the oxide. Figure 2 also reveals that the growth rates for the SiC C face at thicknesses above $\sim 0.2 \mu\text{m}$ are diffusion rate-limited because the growth rate curves predicted by the three oxidation models all roughly coincide with one another. The growth rate in this regime depends on the diffusivity of oxidants in SiO₂ (D_O^{SD}) and α . Thus, it is believed that the different D_O^{SD} from that of Si oxidation was necessary to reproduce the growth rate in the diffusion rate-limiting region¹³ because CO and CO₂ production was neglected. Song *et al.* proposed a modified Deal–Grove model that takes the out-diffusion of CO into account by modifying the parabolic rate constant B by a factor of 1.5 (called “normalizing factor”¹⁴), and through this model, explained the oxidation process of SiC.¹⁷ For the Si–C emission model, the normalizing factor corresponds to the coefficient in the oxidant boundary condition of eq. (5), $(2 - \nu_{Si} - \nu_C - \alpha/2)$. As is explained below, this coefficient is determined to be 1.53, which is almost equal to the value obtained by Song *et al.* (1.5). In the case of the Si face, since the influence of oxygen diffusion was significant at thicknesses above several μm , we could not determine the value of α . The value of α is thought to depend on the areal density of carbon in the substrate. Thus, we used the α value obtained for the C face to calculate the oxide growth rate of the Si face.

The parameters obtained from the fit to the experimental results for the C and Si faces are listed in Table I. The k_0 values for SiC are 10^{-3} cm/s for the C face and 10^{-4} cm/s for the Si face, which are one or two orders of magnitude smaller than that for Si (1.8×10^{-2} cm/s at 1090 °C¹²). This difference can be explained by considering the difference in energy needed to break a bond at the interface. Namely, the binding energy of the Si–C bond (~ 3 eV¹⁸) is larger than that of the Si–Si bond (~ 2 eV⁷). The fact that the k_0 value of the C face is larger than that of the Si face could also be explained by the number of back bonds per Si atom, which is three for the Si face and one for the C face.

Let us consider the reason why the Si emission rate for the Si face is much larger than the corresponding values for the C face (see Table I). It has been believed that in Si oxidation, the Si emission rate depends on the substrate surface orientation because of the variation in the areal density of Si atoms with orientation.¹² However, since the areal density of Si atoms is the same for the C and Si faces, this cannot account for the difference in Si emission rate. Further work is necessary to identify the cause. One possible candidate is the difference in direction of the Si back bonds due to the polar face. In the case of the C face, when the back bond of a Si atom on the topmost layer of the SiC incorporates an O atom, the stress exerted on the SiC substrate is presumably small because the Si–C bond stretches along the [0001] direction. In contrast, the Si–C bond stretches along the [03 $\bar{3}$ 8] direction in the case of the Si face, and thus, the stress generated has an in-plane component. It is believed that, as a result, the stress on the SiC substrate is larger than that for the C face, leading to a higher emission of Si interstitials in the case from the Si face.

In summary, we proposed a kinetic model that accounts for SiC oxidation, termed the “Si–C emission model”, and showed that the model well reproduces the oxide growth rate over the entire thickness range for both the C and Si faces. The results indicated that the oxidation and emission of C and the emission of Si all need to be taken into account to describe the oxide growth process in SiC. A comparison of the parameters obtained for the C and Si faces from the curve fits revealed that the differences in interfacial reaction rate in the case of absence of interstitial accumulation (i.e., surface oxidation rate of SiC substrate) and Si emission rate might be contributing to the large difference in oxide growth rate between these polar faces.

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- 1) S. Yoshida: in *Electric Refractory Materials*, ed. Y. Kumashiro (Marcel Dekker, New York, 2000) p. 437.
- 2) V. V. Afanas'ev *et al.*: *Phys. Status Solidi A* **162** (1997) 321.
- 3) K. Kakubari *et al.*: *Mater. Sci. Forum* **527–529** (2006) 1031.
- 4) T. Yamamoto *et al.*: *Jpn. J. Appl. Phys.* **46** (2007) L770.
- 5) T. Yamamoto *et al.*: *Mater. Sci. Forum* **600–603** (2009) 667.
- 6) T. Yamamoto *et al.*: *Jpn. J. Appl. Phys.* **47** (2008) 7803.
- 7) B. E. Deal and A. S. Grove: *J. Appl. Phys.* **36** (1965) 3770.
- 8) H. Z. Massoud *et al.*: *J. Electrochem. Soc.* **132** (1985) 2685.
- 9) H. Kageshima *et al.*: *Jpn. J. Appl. Phys.* **38** (1999) L971.
- 10) H. Kageshima *et al.*: *Microelectron. Eng.* **59** (2001) 301.
- 11) M. Uematsu *et al.*: *Jpn. J. Appl. Phys.* **39** (2000) L699.
- 12) M. Uematsu *et al.*: *J. Appl. Phys.* **89** (2001) 1948.
- 13) Y. Hijikata *et al.*: *Mater. Sci. Forum* **600–603** (2009) 663.
- 14) E. A. Ray *et al.*: *J. Appl. Phys.* **103** (2008) 023522.
- 15) S. M. Sze: *Semiconductor Devices Physics and Technology* (Wiley, New York, 2002) 2nd ed., Chap. 13, p. 457.
- 16) W. Jügling *et al.*: *IEEE Trans. Electron Devices* **32** (1985) 156.
- 17) Y. Song *et al.*: *J. Appl. Phys.* **95** (2004) 4953.
- 18) L. Pauling: *The Nature of the Chemical Bond and the Structure of Molecule and Crystals* (Cornell University Press, Ithaca, NY, 1960) 3rd ed., p. 85.