

Model Calculation of SiC Oxidation Rates in the Thin Oxide Regime

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Abstract. To explain the growth rate enhancement of SiC oxidation in the thin oxide regime, which was recently found from the real time monitoring experiments of the initial oxidation stage of SiC (000-1) C-face using an *in-situ* spectroscopic ellipsometer, we tried to apply the interfacial Si emission model, which has been originally proposed for Si oxidation, and found that the Si emission model successfully reproduced the SiC oxidation rates at the whole range of oxide thickness and at oxidation temperatures measured. By comparing with the simulations for Si oxidation, we have discussed the oxidation mechanism of SiC.

Introduction

Among wide-gap semiconducting materials, only silicon carbide (SiC) can be thermally oxidized and SiO₂ layers, known as a superior insulator for metal-oxide-semiconductor (MOS) applications, can be formed on it. In addition, the physical properties of SiC, such as high break-down voltage, high saturated electron drift velocity and high thermal conductivity, make SiC an attractive material for applying to high-power and/or high-frequency electronic devices. However, despite of many active developments, SiC MOSFETs still have serious problems, such as higher on-resistance than that expected from the physical properties of SiC and low reliability of the oxide films. Moreover, the oxidation mechanism of SiC is not understood well compared with that of Si, which makes the problems more difficult to be solved.

In the previous work, we have successfully obtained the time dependence of oxide thickness during thermal oxidation by using an *in-situ* ellipsometer [1]. We found that Deal-Grove (D-G) model [2], which was originally proposed for the explanation of Si oxidation, can account for the SiC oxidation as well, as pointed out by Song *et al.* [3]. However, by the detailed analysis, we have found the growth rate enhancement phenomena in the thin oxide regime ($< ca. 20$ nm) [4], which cannot be explained by D-G model as reported for Si oxidation [5]. For the explanation of the growth rate enhancement phenomena in Si oxidation, several models have been proposed [5-9], including the interfacial Si emission model.

In this report, we applied the Si emission model [7] to the SiC oxidation, and showed that the calculated values based on the Si emission model can be fitted to the experimental values of SiC oxidation rate well. Through these model calculations, we discuss the oxidation mechanisms of SiC.

Calculation of SiC oxidation rates

We have tried to fit the oxidation rates of SiC as a function of oxide thickness calculated from the Deal-Grove model and the interfacial Si emission model with those obtained from the *in-situ* ellipsometric measurements [1]. The experimental values of the oxidation rate at various

temperatures were derived from the oxidation-time dependence of oxide thickness, as shown in Ref. [1].

2.1 D-G model

According to the D-G model, the oxidation rate, dX/dt , is expressed by the following equation:

$$\frac{dX}{dt} = \frac{B}{2X + A} \quad (1)$$

where B/A and B denote the linear rate constant and parabolic rate constant, respectively. The values of B/A corresponds to the oxidation rate when $X = 0$. Namely, B/A value is the reaction-rate at the SiC surface. On the other hand, the value of B corresponds to the diffusivity of oxidant in the oxide. We have tried to fit the calculated values with the observed ones by adjusting two parameters, B/A and B . However, as reported in Ref. [4], a good fitting could not be achieved with any values of B/A and B , though the fittings are well in the oxide thickness larger than *ca.* 20 nm [4].

2.2 Interfacial Si emission model

According to the Si emission model [7], the interfacial Si emission into SiO_2 occurs due to the stress caused by the difference in the density of Si atoms between Si ($5.0 \times 10^{22} \text{ cm}^{-3}$) and SiO_2 ($2.3 \times 10^{22} \text{ cm}^{-3}$). Because the density of Si atoms for SiC ($4.9 \times 10^{22} \text{ cm}^{-3}$) is almost equal to that of Si, it is plausible that the interfacial Si emission occurs also in SiC oxidation.

Figure 1 shows the schema of Si emission model. When oxide thickness X is small, the emitted Si atoms can easily arrive at the oxide surface. However, when the oxide is getting thick, the emitted Si atoms cannot reach the surface and then they accumulate near the oxidation interface. Because such an accumulated Si atom prevents the following Si emission, interfacial-reaction-rate (k), i.e. oxidation rate, decreases. This behavior can be expressed by the following equation:

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

where k_0 and C_{Si}^0 denote maximum interfacial-reaction-rate constant and solubility of Si atom in SiO_2 , respectively. C with the subscript 'Si' and the superscript 'I' means the concentration of Si atom at the position $x = 0$ (oxidation interface). Using the diffusion theory, the distribution of C_{Si} and C_{O} can be written as:

$$\frac{\partial C_{\text{Si}}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\text{Si}} \frac{\partial C_{\text{Si}}}{\partial x} \right) - R_{\text{Si}}, \quad \frac{\partial C_{\text{O}}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\text{O}} \frac{\partial C_{\text{O}}}{\partial x} \right) - R_{\text{O}}, \quad (3)$$

where R denotes the reaction-rate between Si and O atoms, and D is the diffusivity. Considering separately x into three zones, i.e., inside oxide ($0 < x < X$), a surface layer of 1 nm in thickness at the oxide surface ($x = X$) and gas phase region ($x > X$), R is expressed as follows,

$$\begin{aligned} 0 < x < X: & \quad R_{\text{Si}}, R_{\text{O}} = \kappa_1 C_{\text{Si}} C_{\text{O}} + \kappa_2 C_{\text{Si}} (C_{\text{O}})^2 \\ x = X: & \quad R_{\text{Si}}, R_{\text{O}} = k' C_{\text{O}}^{\text{S}} C_{\text{Si}}^{\text{S}} \\ x > X: & \quad R_{\text{Si}} = 0, R_{\text{O}} = h(C_{\text{O}}^{\text{S}} - C_{\text{O}}^*) \end{aligned} \quad (4)$$

where κ_1 and κ_2 denote reaction-rate coefficients in SiO_2 with respect to SiO and SiO_2 , and k' , h and C_{O}^* denote reaction-rate at the oxide surface, gas phase mass-transfer coefficient and solubility of oxidant in SiO_2 , respectively. The superscript 'S' means the position at $x = X$ (oxide surface). The boundary conditions for the Si interstitials and the oxidant are given by:

$$D_{\text{Si}} \frac{\partial C_{\text{Si}}}{\partial x} \Big|_{x=0} = -\nu C_{\text{O}}^{\text{I}}, \quad D_{\text{O}} \frac{\partial C_{\text{O}}}{\partial x} \Big|_{x=0} = -k C_{\text{O}}^{\text{I}}, \quad (5)$$

where ν denotes the emission-rate of Si atoms. The oxidation rate is described as:

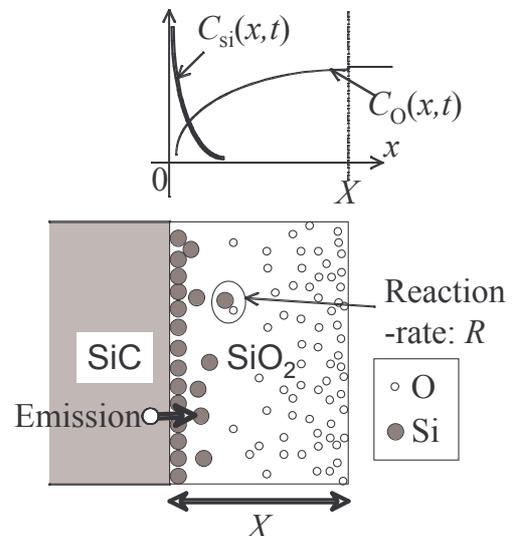


Fig. 1 Schema of interfacial Si emission model.

$$N_0 \frac{dX}{dt} = kC_o^l, \quad (6)$$

where N_0 is the density of Si atoms in SiO_2 . Equations (1)–(5) were solved numerically by a commercial partial differential equation solver 'FlexPDE' [10], and dX/dt and X at each time step were obtained by eq. (6).

In the simulation based on the interfacial Si emission model, we adjusted two parameters, i.e., oxidant self-diffusivity D_o^{SD} ($=D_o C_o^*/N_0$), which corresponds to $B/2$ [7], and k_0 . The other parameters were assumed as the same as those for Si (100)-face dry oxidation [7]. Because the value of k_0 is dominant to decide the oxidation rate in the thin oxide regime, the value was derived from the fitting of calculated oxidation rates to the experimental values thinner than 40 nm. The common sense of the above two models is that the rate-controlling reaction in the thick oxide regime is oxygen diffusion-limited process. Thus, D_o^{SD} is determined by fitting the oxidation rate calculated from Si emission model to that from D-G model at $X > 40$ nm.

Results and Discussion

Figure 2 shows the oxidation rates at various temperatures observed (circles), and those given by the D-G model (broken line) and the Si emission model (solid line). The figure indicates that the D-G model cannot explain the SiC oxidation rates at the oxide thickness less than *ca.* 20 nm at any temperature, similarly to the case of Si oxidation [5]. While, the Si emission model can explain well the growth enhancement of SiC oxidation rate in the thin oxide regime, as well as the SiC oxidation rate in all the oxide thickness range at all the temperatures measured.

Figure 3 shows Arrhenius plots of the adjusted two parameters k_0 and D_o^{SD} in the simulation as well as these values for Si (100)-face oxidation [7]. In the Arrhenius plots of k_0 for Si, we diverted the activation energy of Si (100)-face wet oxidation and determined its pre-exponential factor from the k_0 value for dry oxidation at 900°C (1.4×10^{-3} cm/s [7]) because of absence of the Arrhenius behavior of k_0 value for Si dry oxidation in the literature. The broken lines in Fig. 3 denote the fitted lines for the experimental values. As shown in the figure, both of the experimental values of k_0 and D_o^{SD} are well on the fitted lines. From the gradients of the fitted lines, the activation energy of k_0 and D_o^{SD} was found to be -2.20 and -3.36 eV, respectively. It is found that activation energy for SiC of k_0 and D_o^{SD} is a little larger and about 2 times larger, respectively, than those for Si.

As shown in Fig. 3, the values and the temperature dependence of k_0 between SiC and Si are almost similar. This suggests that the surface reaction-rate k_0 value is not related to the existence of carbon. For the difference in activation energy of D_o^{SD} , as suggested by Song *et al.* [3], the CO or CO_2 out-diffusion through the oxide during SiC oxidation might change the activation energy.

In the previous work [1], we found that activation energy of linear rate constant B/A for SiC was smaller than that for Si. However, the activation energy of k_0 , corresponding to that of B/A in the D-G model, for SiC is larger than that for Si, which is reasonable because of the difference in the binding energy between Si-C

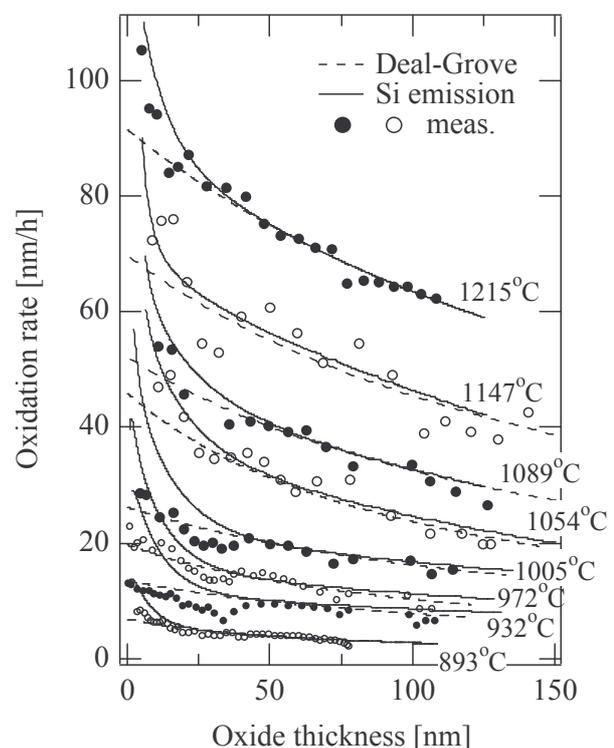


Fig. 2 Thickness dependence of oxidation rate for 4H-SiC (000-1) face at various temperatures.

and Si-Si. These results also indicate the fault in the D-G model in the thin oxide regime, as in the case of discrepancy of oxidation rate in the thin oxide regime.

At present we do not have any explanation for the differences in k_0 and D_o^{SD} between SiC and Si. In future, by studying other oxidation cases, such as pressure dependence [11] or surface orientation dependence, we try to clarify the meanings of modification of these parameters and to establish a unified SiC oxidation model.

Summary

We have investigated the oxidation mechanism of SiC in terms of the two Si oxidation models. It is found that the Si emission model represents the SiC oxidation well at the whole range of oxide thickness, at any temperature, by adjusting only two parameters,

maximum interfacial reaction-rate k_0 and oxidant self-diffusivity D_o^{SD} . Arrhenius behaviors of k_0 are almost similar between SiC and Si, and the difference in activation energy of D_o^{SD} is probably due to the influence from the out-diffusion of CO or CO₂ through the oxide.

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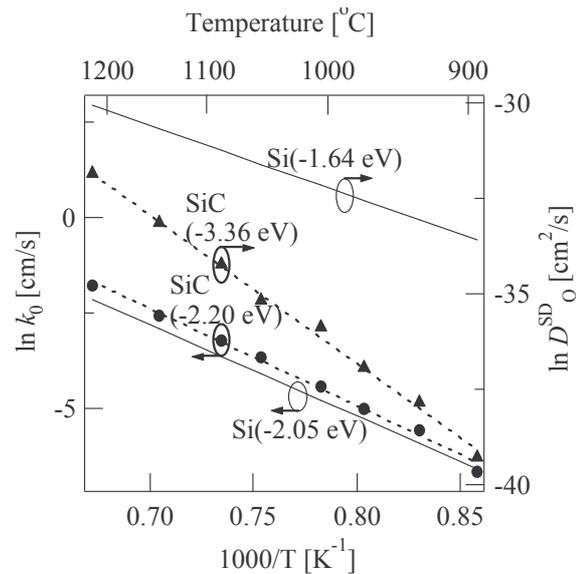


Fig. 3 Arrhenius plots of k_0 and D_o^{SD} values for 4H-SiC (000-1) face as well as those for Si (100)-face.