

Oxide Growth Rate Enhancement of Silicon Carbide (0001) Si-Faces in Thin Oxide Regime

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Thermal oxidation process of silicon carbide (SiC) has been studied by performing *in-situ* spectroscopic ellipsometry. In our previous work, we, for the first time, found that the growth rates of SiC(000 $\bar{1}$) C-face at oxidation thicknesses less than around 20 nm are much higher than those given by the Deal-Grove (D-G) model. In this report, we show that such a growth rate enhancement occurs also in the oxidation of SiC(0001) Si-face. By applying the empirical equation proposed by Massoud *et al.* [J. Electrochem. Soc. **132** (1985) 2685] to the oxidation of SiC Si-face and comparing the temperature and oxygen partial pressure dependences of oxidation rate parameters obtained with those for C-face, we discuss the difference in oxidation mechanism between SiC Si- and C-faces.

KEYWORDS: silicon carbide (SiC), (0001) Si-face, oxidation, *in-situ* spectroscopic ellipsometry, Deal-Grove model, Massoud empirical equation

1. Introduction

Silicon carbide (SiC) has attractive properties, such as wide band gap, high thermal conductivity, and high breakdown electric field, for high-power and high-frequency electronic devices, whose specifications cannot be obtained using Si and GaAs.¹⁾ In addition, by thermal oxidation, a SiO₂ layer can be formed as the gate insulator for metal-oxide-semiconductor (MOS) applications similarly to Si. SiC-MOS field-effect transistors (FETs) are expected to have an on-resistance two orders of magnitude lower than that of Si-MOSFETs at the same breakdown voltage. Therefore, SiC-MOSFETs have been ardently researched and developed.

However, SiC-MOSFETs have some problems to be solved before practical use, such as their higher on-resistance than that predicted from bulk properties. This poor electrical characteristic is attributed to high interface state density at the SiC-oxide interface.²⁾ To elucidate the origin of interface states, it is important to study the oxidation mechanism of SiC. We have studied the oxidation of SiC(000 $\bar{1}$) C-face by real time observation using *in-situ* ellipsometry.³⁾ Although it has been reported that^{3,5-7)} the oxidation time dependence of oxide thickness can be generally represented by the Deal-Grove (D-G) model proposed for Si oxidation,⁴⁾ we have, for the first time, found that the growth rates in the initial stage of oxidation are much higher than those predicted by the D-G model by analyzing the growth rate of SiC(000 $\bar{1}$) C-face precisely.^{8,9)}

Thus far, SiC(0001) Si-face is widely used for the fabrication of SiC devices, partly because high-quality Si-face epiwafers are available. It is well known that the oxide growth rate of Si-face is about 1/10 that of C-face. Because the reason for such a large difference in growth rate is considered to give some important information on the elucidation of the SiC oxidation mechanism, it is important to study precisely the growth rate of SiC Si-face, as well as that of C-face.

In this study, we have observed the oxidation of

SiC(0001) Si-face by *in-situ* spectroscopic ellipsometry. We have measured growth rates at various oxidation temperatures and oxygen partial pressures, and derived the oxidation rate parameters by applying Massoud's empirical equation.¹⁰⁾ We have discussed the difference in oxidation mechanism between SiC Si- and C-faces from the temperature and oxygen pressure dependences of the oxidation rate parameters.

2. Experiment procedure

Epitaxial layers grown on 4H-SiC(0001) Si-face with 8° off-angles (*n*-type, $N_d - N_a = 5 \times 10^{15} \text{ cm}^{-3}$) were used in this study. After RCA cleaning, an epiwafer was placed in a chamber equipped with an *in-situ* spectroscopic ellipsometer and heated at temperatures between 1050 and 1200°C in the oxygen flow of 1 slm at 1 atm. The oxidation was performed also at oxygen partial pressures between 0.1 and 1.0 atm at 1200°C. Prior to the oxidation, ellipsometric parameters (Ψ , Δ) were measured in the argon atmosphere to determine the optical constants of SiC at the oxidation temperatures. Then, oxygen gas was introduced into the chamber and the oxidation time dependence of (Ψ , Δ) was monitored during dry oxidation. Spectroscopic ellipsometric measurements were carried out at wavelengths between 310 and 410 nm, and at an angle of incidence of 75.8°. In the evaluation of oxide thickness from the ellipsometric measurements, we assumed a three-layer structure, i.e., the sample is composed of a SiO₂ layer, an interface layer and a SiC substrate. We have evaluated the thickness of SiO₂ layers under the assumption that the interface layer is 1 nm in thickness and has the optical constants obtained in the previous study.¹¹⁾ The details of the spectroscopic ellipsometric measurements and the evaluation of oxide thickness were described elsewhere.^{3,8)}

3. Results and Discussion

Figure 1 shows the growth rate dX/dt of SiC(0001) Si-face as a function of the oxide thickness X at various oxidation temperatures. By the D-G model, the relation between the growth rate dX/dt and the oxide thickness

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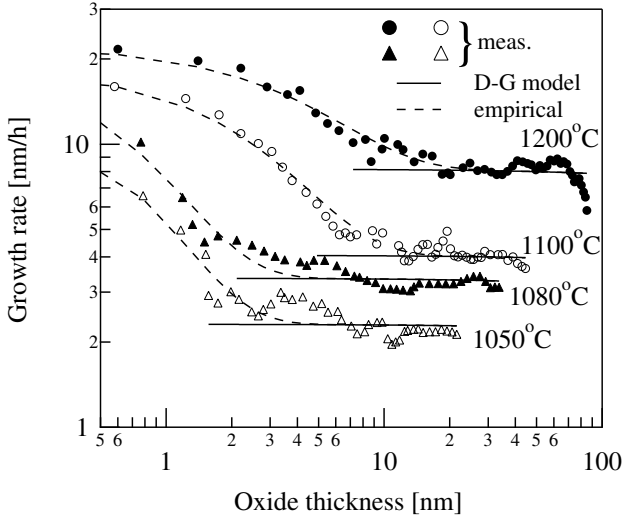


Fig. 1. Oxide thickness dependence of growth rate for SiC Si-face at various oxidation temperatures. The solid and dashed lines denote the values derived from the Deal-Grove model given by eq. (1) and those derived from the Massoud's empirical relation given by eq. (2), respectively.

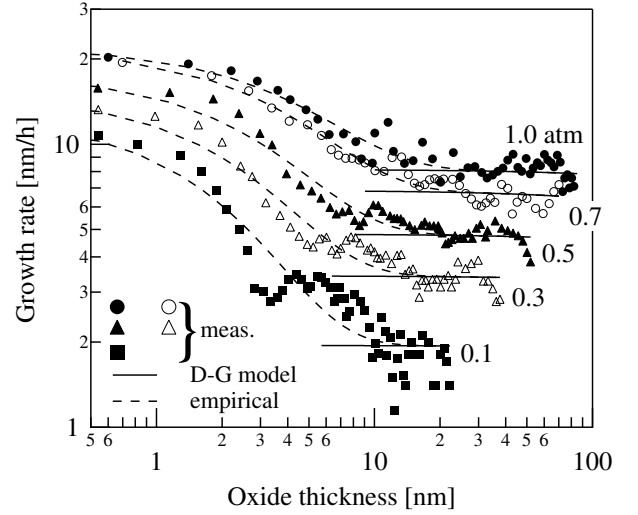


Fig. 2. Oxide thickness dependence of growth rate for SiC Si-face at various oxygen partial pressures. The solid and dashed lines denote the same values as those in Fig. 1.

X in the thermal oxidation of Si is given as⁴⁾

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

where B/A and B denote the linear and parabolic rate constants of oxidation, respectively. When $X \ll A$, i.e., in the small thickness range, the oxidation is limited by the reaction rate at the interface, and the values of dX/dt are constant in this thickness range. The figure shows that the values obtained are almost constant in the larger thickness range in this study at any oxidation temperature. However, in the smaller thickness range, the values of dX/dt are not constant but increase with decreasing oxide thickness, i.e., the oxide growth rate enhancement occurs at any temperature in this study, as in the case of C-face.⁸⁾ Figure 2 shows the oxide thickness dependence of dX/dt at various oxygen partial pressures. This figure also shows that the oxide growth rate enhancement occurs at any partial pressure, as in the case of C-face.⁹⁾ These experimental results for Si-face reveal that the oxidation enhancement is not peculiar to the C-face but occurs also in the case of Si-face.

In the case of Si oxidation, it has been known that the growth rate enhancement occurs in the thin oxide regime. To fit with the measured oxide thickness dependence of the growth rate of Si, Massoud *et al.*¹⁰⁾ have modified the D-G model by adding the exponential term $C \exp(-X/L)$ as

$$\frac{dX}{dt} = \frac{B}{A + 2X} + C \exp\left(-\frac{X}{L}\right), \quad (2)$$

where C and L denote the pre-exponential constant and characteristic length of the growth rate enhancement, respectively. We have applied this empirical equation (2) to the growth rate of SiC. The dashed lines shown in Figs. 1 and 2 indicate the calculated curves using eq. (2) fitted to the observed ones by adjusting the four param-

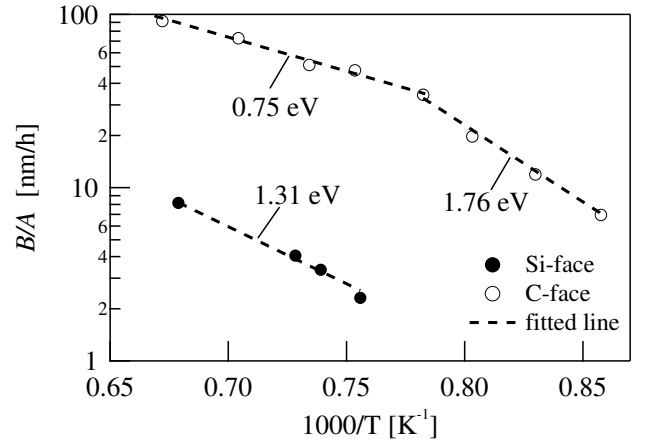


Fig. 3. Arrhenius plots of the linear rate constant B/A for Si-face. The values for C-face reported in ref. 8 are also plotted in the figure.

eters B/A , B , C , and L . As shown in the figures, the calculated curves fit well to the observed ones in the entire thickness range measured for all the studied oxidation temperatures and oxygen partial pressures, as in the case of C-face.^{8,9)} Therefore, the growth rate of SiC for both polar faces can be well represented by the empirical equation proposed by Massoud *et al.*

We discuss the temperature and oxygen partial pressure dependences of the four parameters B/A , B , C , and L below. Figure 3 shows the Arrhenius plots of the linear rate constant B/A for Si-face. The previously reported values for C-face⁸⁾ are also plotted in the figure. The values of B/A for Si-face are one order of magnitude smaller than those for C-face at any studied temperature, which is in agreement with the well-known experimental result indicating that the growth rate of Si-face is about 1/10 that of C-face. In the case of Si-face, the observed values of B/A are on a straight line with an activation energy of

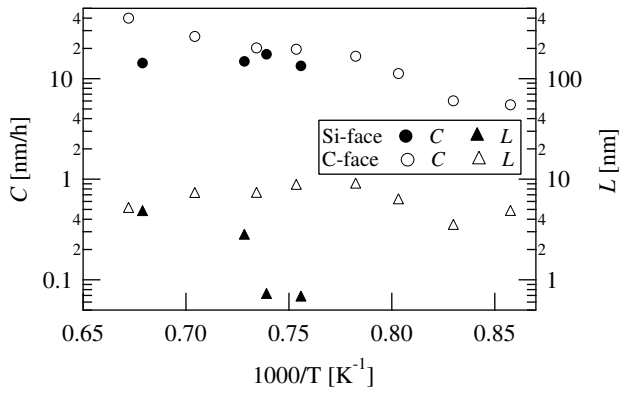


Fig. 4. Arrhenius plots of characteristic length and pre-exponential constant of the growth rate enhancement C , and L for Si- and C-faces.

1.31 eV. While for C-face, the values are on two straight lines, suggesting the existence of two activation energies, i.e., 0.75 and 1.76 eV, and the break point in the activation energy is around 1000°C . As we have measured the growth rates of SiC Si-face in the oxide thickness range less than 100 nm, the diffusion limiting-step regime, in which the growth rate is inversely proportional to X , does not appear regardless of the temperatures used in this study. Therefore, the precision in determining the values of B , related to the diffusion coefficient, is not sufficient, and thus, we do not discuss the values of B for Si-face in this report.

The values of $C/(B/A)$, which mean the magnitude of oxide growth enhancement, are around 2–6 for Si-face in the studied temperature range. On the other hand, those for C-face are less than 1. These results suggest that the growth rate enhancement phenomenon is more marked for Si-face than for C-face. The temperature dependences of the values of C and L for Si-face, as well as those for C-face, are shown in Fig. 4. Figure 4 shows that the values of C for Si-face are smaller than those for C-face and almost independent of temperature, which is in contrast to the result for C-face. Figure 4 also shows that the values of L for the Si-face, around 3 nm at 1100°C , are smaller than those for C-face, around 6 nm at the same temperature, and increase with temperature, which is also in contrast to the result for C-face, i.e., almost independent of temperature. It should be noted that the temperature dependences of C and L for Si-face are in contrast to those for C-face. In the case of Si oxidation,¹⁰⁾ in comparison with SiC, the values of L are around 7 nm and almost independent of temperature, and the values of C increase with temperature. Therefore, it can be considered that the values of L and the temperature dependences of C and L for SiC C-face are almost the same as those for Si, but different from those for SiC Si-face. As seen in the oxide thickness dependence of the growth rate, the surface reaction-limiting-step regime, in which the growth rate is constant against the oxide thickness X , does not appear in the temperature range studied for SiC C-face,^{8,9)} as in the case for Si.¹⁰⁾ This means that the oxidation mechanism of SiC C-face is in some sense

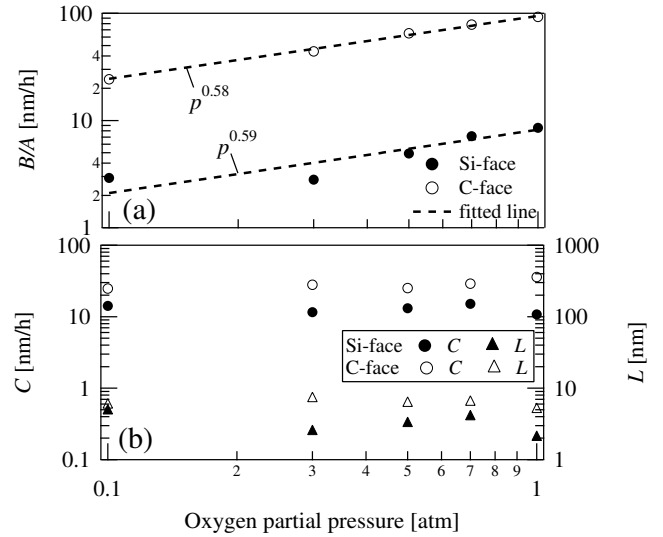


Fig. 5. Oxygen-partial-pressure dependences of B/A , C , and L for Si- and C-faces.

similar to that of Si, but that of SiC Si-face is very different from that of Si. For SiC Si-face, the surface reaction rate is much smaller than the rate limited by oxygen diffusion, compared with the cases of SiC C-face and Si, which may cause the characteristics of the SiC Si-face oxidation to differ from those for SiC C-face and Si.

Figure 5 shows the oxygen-partial-pressure (p) dependence of the values of the linear rate constant B/A and the enhancement parameters C and L for Si-face, as well as for C-face reported in the previous work.⁹⁾ Figure 5(a) indicates that these polar faces have similar pressure dependences of B/A , i.e., $\propto p^{0.6}$. In accordance with the D-G model,⁴⁾ B/A and B are predicted to be proportional to p . Hence, our results are contradictory to this prediction, which is similar to the case of Si oxidation, i.e., $\propto p^{0.7-0.8}$.¹⁰⁾ We have already reported that B for both Si- and C-faces is proportional to p .⁹⁾ Therefore, the pressure dependences of B for SiC Si- and C-faces can be explained by considering that in the parabolic rate region, the growth rate is limited by the quantity of oxidant in-diffusion inside the oxide, as suggested for the oxidation of Si.⁴⁾ Figure 5(b) shows that the variations in C and L with oxygen pressure for both Si- and C-faces are similar, i.e., the values of C and L are almost constant with respect to pressure. These results for the pressure dependences of C and L , compared with those of B/A and B , suggest that the existence of an oxidation-rate-limiting mechanism, which is independent of the quantity of oxygen supplied, in addition to the interface reaction of oxygen with SiC and the diffusion of oxygen through SiO_2 layers, should be introduced to explain the SiC oxidation.

In the case of Si, many models have been proposed to explain thermal oxidation.¹²⁻¹⁵⁾ Kageshima *et al.*¹³⁾ and Uematsu *et al.*^{14,15)} have attempted to explain Si oxidation by introducing the Si atom emission at the oxidation interface, accompanied by the Si atom oxidation. Si atoms are emitted into the oxide layers caused

by the strain due to the expansion of Si lattices by oxidation. In accordance with their model, the oxidation rate at the interface is primarily large and is suppressed by the accumulation of Si atoms emitted with an increase in oxide thickness, i.e., the oxidation rate does not increase in the small thickness regime but rapidly decreases with thickness. They have calculated the oxidation time dependence of oxide thickness numerically and showed that the experimental results are well explained in the entire thickness range including a very small thickness regime. They have suggested that the model can derive a growth rate equation similar to eq. (2) in the small thickness limit and discussed the nature of the four parameters B/A , B , C , and L .¹³⁾ For example, they have showed the $p^{0.7}$ dependence of B/A .¹⁴⁾ Therefore, an analogous model might account for the SiC oxidation. In our recent work,¹⁶⁾ we have shown that the growth rate of SiC C-face can be represented in the entire oxide thickness regime using this Si-emission model, even though the oxidation process of carbon is ignored in the model. However, there exist some issues in the physical viewpoints in the explanation of SiC oxidation by the Si-emission model, such as an oxygen diffusivity value in SiO₂ that is different from that of Si oxidation is required to explain SiC oxidation.¹⁶⁾ An oxygen diffusivity value that is almost the same as that of Si oxidation has been obtained for SiC oxidation when taking into account the production of CO or CO₂ in the oxidation process.^{6,17)} Therefore, to explain the oxide growth rate of SiC, we should consider the presence of C in the Si-emission model, which may be necessary for the explanation of the difference in oxidation mechanism between SiC Si- and C-faces.

4. Summary

By *in-situ* spectroscopic ellipsometry, we have observed the occurrence of the oxide growth rate enhancement in the thin oxide regime for the oxidation of SiC Si-face at any oxidation temperature and oxygen partial pressure, which reveals that oxidation enhancement is not peculiar to C-face but occurs also for Si-face. We

have also observed that the growth rate of SiC for both polar faces can be well represented by the empirical equation proposed by Massoud *et al.* using the four adjusting parameters B/A , B , C , and L , and that the values of B/A , C , and L , and the temperature dependences of C and L for Si-face are different from those for C-face. In contrast, both polar faces have similar pressure dependences of the four parameters. Finally, we have discussed the SiC oxidation mechanisms in comparison with those of Si oxidation.

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