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Growth Rate Enhancement of ($000\bar{1}$)-Face Silicon–Carbide Oxidation in Thin Oxide Regime

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The thermal oxidation of silicon carbide (SiC) has been studied by performing *in-situ* ellipsometry. We have found that the oxidation rates at the oxidation thickness of approximately less than around 20 nm are much larger than those given using the Deal–Grove (D–G) model, suggesting that the oxidation time dependence of the oxide thickness cannot be explained using the D–G model, i.e., a simple linear-parabolic model, in the initial oxidation stage. By using the empirical relation, which has been proposed for Si oxidation, i.e., adding an exponential term to the D–G equation, the origin of the growth rate enhancement in SiC oxidation has been discussed. [DOI: 10.1143/JJAP.46.L770]

KEYWORDS: silicon carbide (SiC), ($000\bar{1}$) C-face, oxidation, *in-situ* ellipsometry, Deal–Grove model, Massoud empirical equation

Among wide band-gap semiconducting materials, only silicon carbide (SiC) can be thermally oxidized, and insulating SiO_2 layers, known as superior dielectric films for metal–oxide–semiconductor (MOS) applications, can be grown on it, similarly to Si.[1] In addition, its physical properties, such as high-breakdown electric field and high thermal conductivity, compared with Si, are good for high-speed switching and low-power-loss electronic devices. For these reasons, SiC MOS field-effect transistors (MOSFETs) are expected to have superior specifications that cannot be obtained using Si. However, the electrical characteristics of SiC MOSFETs, such as on-resistance, are seriously poorer than those predicted from SiC bulk properties.[2] It has been considered that these poor characteristics result from a high interface state density.[3] Therefore, the clarification of the structure of SiC–oxide interfaces and the formation mechanism of the interface layer is one of the most important subjects to be studied to improve the electrical characteristics of SiC MOS devices.

In a previous work, we have performed real-time observation of SiC thermal oxidation using an *in-situ* ellipsometer.[4] The results show that the oxidation-time dependence of oxide thickness can be represented using the Deal–Grove (D–G) model,[5] which has been originally proposed for the explanation of Si oxidation. Song *et al.*[6] have modified the D–G model for application to SiC oxidation taking into account the presence of carbon. They have concluded that a linear-parabolic formula can also be applicable to SiC oxidation, although the parabolic term includes the contribution from the diffusion of CO or CO_2 molecules from the SiC–oxide interface to the surface as well as that of oxygen from the surface to the interface. Because it is well known that the oxidation behavior of Si cannot be explained using the D–G model, i.e., a simple linear-parabolic model, particularly at the initial oxidation stage, several models have been proposed for the explanation of Si oxidation.[7–12]

In this work, we have studied ($000\bar{1}$)-face SiC oxidation at the initial stage in more detail by performing *in-situ* ellipsometry and discussed the mechanism of SiC oxidation by comparing it with that of Si oxidation.

To obtain data over a wide oxide thickness range even at low oxidation temperatures, we adopted SiC($000\bar{1}$) C-face in this study. 4H-SiC($000\bar{1}$) C-face epitaxial layers with 8° off-angles (n-type, $N_d - N_a = 7 \times 10^{15}\,\mathrm{cm}^{-3}$) were used in this study. After Radio Corporation of America (RCA) cleaning was executed, an epiwafer was placed into the *in-situ* ellipsometer and was heated at temperatures between 893 and 1147 °C. First, to determine the optical constants of SiC at the oxidation temperature, ellipsometric parameters (Ψ, Δ) were measured in the argon atmosphere. Then, the oxidation time dependence of (Ψ, Δ) was monitored during dry oxidation in atmospheric pressure with an oxygen flow rate of 1 slm. Ellipsometric measurements were carried out at a wavelength $\lambda = 400$ nm, and at an angle of incidence of 75.8°.

In the evaluation of oxide thickness from the ellipsometric measurements, we assumed three-layer structures, i.e., the sample is composed of a SiO_2 layer, an interface layer, and a SiC substrate. We have evaluated the thickness of SiO_2 layers under the assumption that the interface layer of 1 nm thickness has the refractive index $n = 3$ and the extinction coefficient $k = 0.5$ at $\lambda = 400$ nm following the results reported.[13] The details of the ellipsometric measurements and the evaluation of oxide thickness have been described elsewhere.[4]

We have applied the D–G model to the relations between oxide thickness, X, and oxidation time, t, observed, and have obtained the values of the parameters B/A and B in the D–G equation[5] by fitting the calculated curve to the observed values in the entire thickness range. The fits are in general good at all of the oxidation temperatures, as reported previously.[4] However, we found that, in the thickness range of less than approximately 20 nm, there is a tendency for the observed values to be slightly larger than the calculated ones. To investigate these discrepancies in more detail, we have derived the oxidation rates dX/dt as a function of oxide thickness. Figure 1 shows the values of dX/dt as a function of oxide thickness at various oxidation temperatures. We have successfully obtained the values of the oxidation rate even in the thin oxide thickness range of less than 10 nm by real-time *in-situ* observation.

We have failed to fit the dX/dt against the X curves calculated using the D–G equation to the observed ones over the entire oxide thickness range measured at any oxidation temperature. However, as shown by the solid lines in Fig. 1, we can fit well the calculated curves to the observed ones

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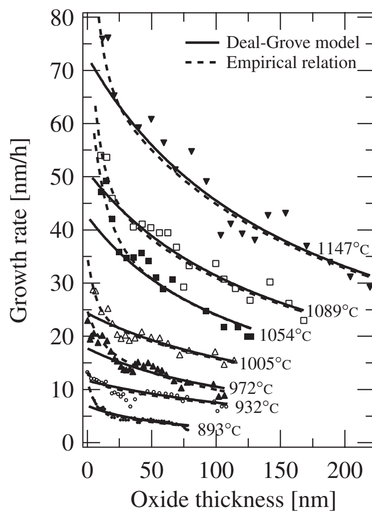

Fig. 1. Oxide thickness dependences of oxidation rate at various oxidation temperatures. The solid and dashed lines denote the values derived from the Deal–Grove model eq. (1)[5] and those from the empirical relation eq. (2),[8,9] respectively.

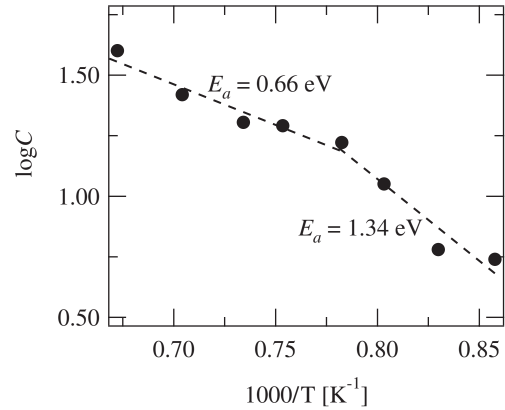

Fig. 2. Arrhenius plots of C, pre-exponential constant in exponential term in eq. (2).

when the thickness range of curve fitting is limited in the range thicker than approximately 20 nm. In this case, the figure shows clearly that the values of dX/dt in the thin thickness region are larger than the values given using the D–G equation at all the oxidation temperatures measured. These results suggest the existence of oxidation having a larger growth rate than that predicted by the D–G model.

It is well known that the oxidation rate of Si in the thin oxide thickness range cannot be reproduced by the equation given by Deal and Grove as[5]

$$\frac{dX}{dt} = \frac{B}{A + 2X}, \tag{1}$$

and several models have been proposed.[7–12] Among them, Massoud *et al.*[8,9] have proposed an empirical relation for the oxide thickness dependence of oxidation rate, that is, the addition of an exponential term to the D–G equation, i.e.,

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

where B/A and B are denoted as the linear and parabolic rate constants of oxidation, and C and L are the pre-exponential constant and the characteristic length, respectively. We have found that it is possible to fit the calculated values to the observed ones using eq. (2) much better than using eq. (1) in any oxidation temperature, as shown by the dashed and solid lines, respectively, in Fig. 1.

We have derived the values of C and L as well as B/A and B by curve fitting of the calculated values using eq. (2) to the observed ones. The L derived is approximately 7 nm, which is almost the same as that for Si oxidation,[8] and does not depend on the oxidation temperature as in the case of Si oxidation.[8] This result suggests that oxidation enhancement is predominant when oxide thickness is less than 7 nm. C changes with temperature. Figure 2 shows the Arrhenius plots of C. The figure shows the existence of two activation energies, i.e., 0.66 eV, at the temperatures equal to or higher than 1000 °C and 1.34 eV at the temperatures lower than 1000 °C, and the break point in the activation energy is approximately 1000 °C. Each of these activation energies is smaller than that for Si oxidation,[8] as in the case of the linear rate constant B/A.[4]

According to Kageshima *et al.*,[10] in their proposed theory for Si oxidation based on the interfacial Si emission model, L is explained by the diffusion length of the emitted Si atoms from the Si–oxide interface. Therefore, it is reasonable that L is the same between SiC and Si, because the thermal oxide layer is SiO_2 regardless of SiC and Si. Uematsu *et al.*[14] also pointed out that the emission rate of a Si atom from the interface exhibits a break point in its activation energy at approximately 1000 °C, which is attributed to the change in the viscoelastic property of SiO_2 at approximately 960 °C. Since C in the case of Si oxidation is closely related to the emission rate of Si, the similarity in the break points in the activation energy suggests that the growth enhancement mechanism of SiC oxidation is similar to that of Si oxidation.

In the evaluation of oxide thickness from the ellipsometric measurements, we took into account the presence of the interface layers between the SiC and SiO_2 layers, and assumed that the optical constants of the interface layer do not change with oxidation time, i.e., there exist interface layers having the same structures regardless of oxidation time or oxide thickness. However, as the practical interface structure plausibly changes with oxidation time, the oxide thickness obtained might include some uncertainty because of the assumption on the interface. To clarify the effect of the assumption on the oxide structure model to the evaluation of oxide thickness, we have also evaluated oxide thickness under the assumption of two extreme cases, i.e., with the interface layer having the optical constants of crystalline Si, and without the interface layer. As the interface layers are considered to be composed of Si, C, and O atoms, and the material having the highest refractive index and extinction coefficient among the compounds composed of Si, C, and O atoms may be Si ($n = 5.5$ and $k = 0.5$ at $\lambda = 400$ nm),[15] and that having the lowest refractive index may be SiO_2, the optical constants of the practical interface layer are considered to lie between those of Si and SiO_2. In the case that the interface is SiO_2, the oxide structure is identical to that without the interface. Figure 3 shows the values of dX/dt as a function of X at 893 °C estimated using these two

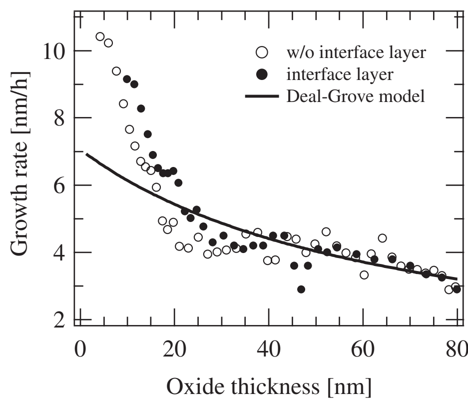

Fig. 3. Oxidation rates as function of oxide thickness at 893° derived using structural models with and without interface layer (closed and open circles, respectively). The solid line denotes the values derived from the Deal–Grove model.[5)]

analysis models and the fitted curve derived from the D–G model. The figure confirms the existence of growth enhancement in the thin oxide regime for any oxide thickness evaluation method used. Therefore, even though the analysis model for the evaluation of oxide thickness is not fully accurate, the existence of growth enhancement compared with the D–G model is surely evidenced in SiC oxidation.

Recently, some Si oxidation models[11,12)] in addition to the Si emission model[10,14)] have been reported. The common view of these models is that the stress near/at the oxide–Si interface is closely related to the growth enhancement in the initial stage of oxidation. Since the density of Si atoms in SiC ($4.80 \times 10^{22}\,\mathrm{cm}^{-3}$)[16)] is almost the same as that in Si ($5 \times 10^{22}\,\mathrm{cm}^{-3}$)[17)] and the residual carbon is unlikely to exist at the oxide–SiC interface in the early stage of SiC oxidation, the stress near/at the interface is considered to be almost identical to the case of Si oxidation. Therefore, it is probable that the interfacial stress also accounts for the growth enhancement in SiC oxidation.[10,14)] However, since there are some differences between SiC and Si oxidation, such as a difference in Si–C and Si–Si binding energy, and the out-diffusion process of carbon in SiC oxidation, such an effect of carbon should be taken into account to clarify the mechanism of growth enhancement in SiC oxidation as well as the mechanism of SiC oxidation.

In conclusion, we have, for the first time, observed the growth enhancement in oxidation rate at the initial stage of SiC oxidation, which means that the D–G model is not suitable for SiC oxidation in the whole thickness regime, as in the case of Si oxidation. Using the empirical relation, taking into account the exponential term for the D–G model, we have found that the thickness range where the growth enhancement occurs is up to approximately 7 nm, which is independent of temperature and almost the same as that of Si oxidation. From the temperature dependence of pre-exponential constants C, we found that there exist two activation energies and their break point is approximately 1000 °C. The similarity between the temperature dependences of C in SiC oxidation and the Si emission rate in Si oxidation suggests the similarity in the growth enhancement mechanism between Si and SiC.

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