Real Time Observation of SiC Oxidation Using an In-situ Ellipsometer

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Abstract. Real time observation of SiC oxidation was performed using an *in-situ* ellipsometer over the temperature range from 900°C to 1150°C. The relations between oxide thickness and oxidation time were obtained precisely by virtue of the real time measurements. We analyzed the relations between oxide thickness and oxidation time by applying the Deal and Grove model to obtain the linear and parabolic rate constants. Taking advantage of *in-situ* measurements, we successfully obtained the oxidation rate constants with high accuracy.

Introduction

Silicon carbide with its wide band gap, high thermal conductivity and high breakdown electric field is an attractive material for electronic device applications including high-power and high-frequency devices whose specifications cannot be obtained using Si and GaAs. In addition, SiC surfaces can be thermally oxidized to form SiO_2 layers as the gate insulator for metal-oxide-semiconductor applications in a manner similar to Si [1]. SiC-metal-oxide-semiconductor field-effect-transistors (MOS-FETs) are expected to have an on-resistance two orders of magnitude lower than those of Si-MOSFETs at the same breakdown voltage [2].

However, SiC MOSFETs have some problems to be solved before practical use, such as their higher on-resistance than those predicted from bulk properties. These poor electrical characteristics have been attributed to high interface state density at the SiC-oxide interface. In order to elucidate the origin of the interface states, it is important to know the mechanism of SiC oxidation, especially at the initial stage of oxidation. Many studies have been performed on the oxidation rate of SiC [3-8] by use of, e.g., Nomarski polarized interferometer for 6H-SiC [3], and RBS and spectroscopic ellipsometer for 4H-SiC [4]. In these studies, however, measurements were carried out after the SiC oxidation, i.e. *ex-situ* measurements. In the *ex-situ* measurements, the relations between oxide thickness and oxidation time are inaccurate because the oxidation proceeds during rising and dropping in substrate temperature. Especially in the initial stage of oxidation, this inaccuracy prevents *ex-situ* measurements from the precise study on the oxidation process. Therefore, real-time observation techniques are desired in order to study in more detail the mechanism of SiC oxidation. We have developed a lamp-heated furnace combined with a spectroscopic ellipsometer (SOPRA GESP5), i.e. an *in-situ* ellipsometer system, to observe the SiC oxidation in real time.

In this study, SiC oxidation processes have been observed in real time using the *in-situ* ellipsometer. Taking advantage of the accurate relations between oxide thickness and oxidation time, we have obtained the values of oxidation rate of SiC accurately by adopting the Deal and Grove model [9]. We have also derived the activation energies from the temperature dependence of the oxidation rates and discuss the mechanism of SiC oxidation.

Experiments

Epitaxial wafers of 4H-SiC (9mm × 9mm) with 8° off-oriented (000-1) C-face, *n*-type were used in this study. After RCA cleaning, an epi-wafer was put into the *in-situ* ellipsometer and heated at temperatures between 893 and 1154°C. First, to determine the optical constants of SiC at oxidation temperatures, ellipsometric parameters (Ψ, Δ) were measured in the argon atmosphere. (Ψ, Δ) are defined by $r_p / r_s = \tan\Psi \exp(i\Delta)$, where r_p and r_s are the reflected amplitudes for *p* and *s*-polarized light, respectively. Then, (Ψ, Δ) were measured during dry oxidation in atmospheric pressure with oxygen flow rate of 1 slm. Oxidation time dependences of (Ψ, Δ) were measured at wavelength $\lambda = 400$ nm, at an angle of incidence of 75.8°. The oxidation was performed up to the oxide thickness around 80 nm. The oxidation time was 1.5h at 1154°C and 11h at 893°C

Fig. 1: The change of (Ψ,Δ) at $\lambda = 400$nm, oxidized at 972°C.

Figure 1 shows an example of the observed values of (Ψ, Δ) over the oxidation time range from 5 min to 6 h in the case of the oxidation temperature 972°C. Ψ and Δ are shown by the radius and angle in this pole figure, respectively. The experimental points (Ψ, Δ) move clockwise with oxidation time. In the analysis, we used a model of the three-layer structure, a SiO_2 layer, an interface layer and SiC substrate. The SiO_2 thickness (X) was evaluated as the only free parameter from the ellipsometric parameters (Ψ, Δ) measured. We assumed that the optical constant of the interface layer does not evolve during SiC oxidation in this study.

In our previous report by spectroscopic ellipsometry, we have reported that an interface layer of 1 nm in thickness with high refractive index $n \sim 3$ and extinction coefficient $k \neq 0$ exists at SiC/SiO_2 interfaces [10, 11]. Therefore, the interface layer should be taken into account in the derivation of oxide thickness. We assumed the interface layer of 1 nm in thickness with the refractive index $n = 3$ and extinction coefficient $k = 0.5$ at $\lambda = 400$ nm for the analysis model [10]. As we have confirmed that the optical constants of SiO_2 change little with temperature in the range between room temperature and 1154°C, we used the values of *n* and *k* for SiO_2 at $\lambda = 400$ nm, as 1.47 and 0, respectively, referred from the literature values at room temperature [12]. We have examined surface roughness of oxide films on SiC as well as that of SiC epilayers before oxidation [13]. The AFM study suggested that the surface roughnesses of oxide films and epilayers were well below 1 nm. The influence of surface and interface roughness in the evaluation of oxide thickness from the optical measurements at $\lambda = 400$ nm is negligibly small in our experiment. Therefore, the effects of surface and interface roughness were neglected in the model. We have also evaluated SiO_2 thickness with and without taking account of the influence of the anisotropy, and found that the difference in the SiO_2 thickness was less than 0.1 %. Thus, the influence of the anisotropy was neglected.
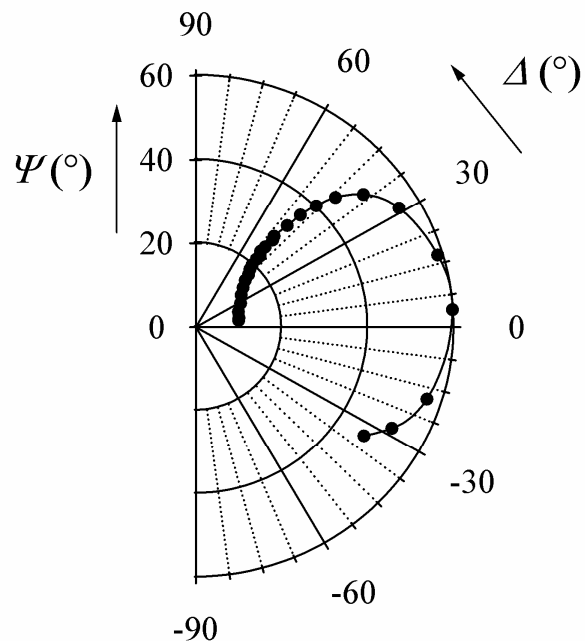
Results and Discussion

Figure 2 shows the oxide thickness as a function of oxidation time at various oxidation temperatures. The figure indicates that the data at the initial stage of oxidation could be successfully obtained. Compared with the previous reports [4, 5], we could obtain data during the initial oxidation stage much improved in detail and with much smaller spread.

The relation between the oxide thickness X and the oxidation time t of the thermal oxidation of silicon has been explained by use of the Deal and Grove equation [9],

$$X^2 + AX = B(t + \tau), \qquad (1)$$

where B/A and B, and τ are denoted as the linear and parabolic rate constants of oxidation, and a quantity related to the presence of
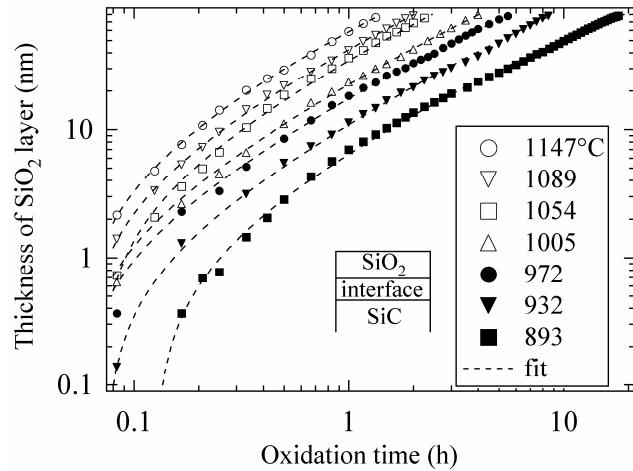

Fig.2: Oxidation time dependence of oxide thickness at various oxidation temperatures. The dashed lines show the fitted curves derived from the Deal and Grove equation.

the initial oxide layer, respectively. This model is based on the reaction processes at the interface (B/A) and the process of oxygen diffusion through the oxide layer (B). It has been reported that the Deal and Grove model can be applied to SiC oxidation [4]. We also applied the Deal and Grove model to the relations between X and t obtained from *in-situ* measurements. The dashed lines in Fig. 2 are the fitted curves derived from Eq. (1). The fits using the Deal and Grove model are excellent at all of the oxidation temperatures. Thus, we found that the Deal and Grove model can be applied to the relation between X and t obtained accurately from *in-situ* measurements.

Figure 3 shows the temperature dependences of log B/A and log B obtained from *in-situ* real time measurements. The oxidation rate constants obtained in this study are different from the values re-
ported previously on the 4H-SiC C-face [4], i.e., around half for B/A and 2 times for B compared with the reported values. The dashed lines in Fig. 3 are the fitted lines derived from Arrhenius equation. The values of B/A and B obtained are almost on the straight lines. Therefore, it is found that the rate-controlling-reactions corresponding to B/A and B do not change within the temperature range measured. The activation energies of B/A and B were determined from the slope of the straight lines in Fig. 3. The activation energies of B/A and B for the SiC C-face were estimated as 28.9 and 44.9 kcal/mol, respectively.

As mentioned above, there is a discrepancy between the values of B/A and B obtained in this study and those reported by Song *et al.* [4]. It is noted that in this study, the relations between oxide thickness X and oxidation time t
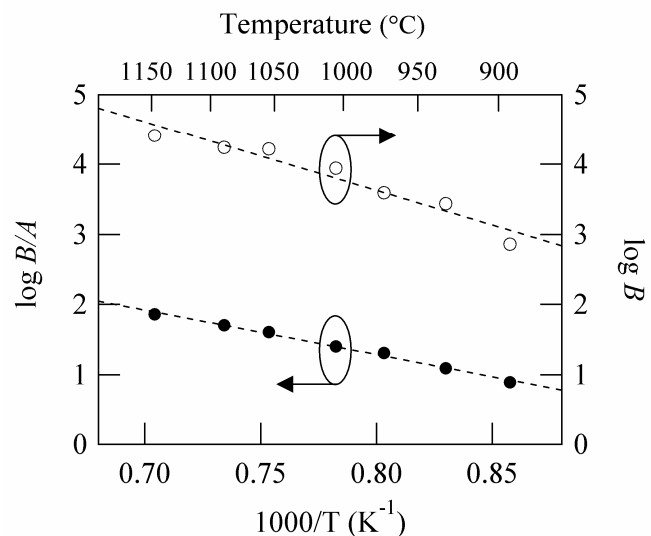

Fig.3: Temperature dependence of the linear and the parabolic rate constants.

were precisely obtained because of the *in-situ* measurements and the use of an analysis model taking into account the interlayers, which results in obtaining the rate constants with high accuracy. In the case of *ex-situ* measurements performed by Song *et al*. and Suzuki *et al*. [4,5], it is very difficult to obtain the data precisely in the short oxidation time region because the oxidation proceeds during the rise and drop of the substrate temperature. In particular, the values of *B/A* from *ex-situ* measurements lead to inadequate values because *B/A* corresponds to the gradient of the tangential line at $X \to 0$. Therefore, we can say that the rate constants can be determined accurately only by the *in-situ* and real-time measurements.

In this study, the real time measurements of (Ψ, Δ) were performed at the single wavelength $\lambda = 400$ nm. We have undertaken the spectroscopic observation of SiC oxidation by using a CCD detector in order to elucidate the interface layer.

In conclusion, we have observed in real time the oxidation of SiC using an *in-situ* ellipsometer. Accurate oxidation rate constants could be obtained taking advantage of the real-time measurement.

References

[1] S. Yoshida: *Electric Refractory Materials, ed*. Y. Kumashiro (Marcel Dekker, New York, 2000) p. 437.

[2] V. V. Afanas'ev, M. Bassler, G. Pensl and M. Schultz: Phys. Status Solidi A **162** (1997), p. 312.

[3] R. C. A. Harris: J. Am. Ceram. Soc. **58** (1975), p. 7.

[4] Y. Song, S. Dhar, L. C. Feldman, G. Chung and J. R. Williams: J. Appl. Phys. **95** (2004), p. 4953.

[5] A. Suzuki, H. Ashida, N. Furui, K. Mameno and H. Matsunami: Jpn. J. Appl. Phys. **21** (1982), p. 579.

[6] T. Narushima, T. Goto and T. Hirai: J. Am. Ceram. Soc. **72** (1989), p. 1386.

[7] J. A. Costello and R. E. Tressler: J. Am. Ceram. Soc. **69** (1986), p. 674.

[8] Z. Zheng, R. E. Tressler and K. E. Spear: J. Electrochem. Soc. **137** (1990), p. 854.

[9] B. E. Deal and A. S. Grove: J. Appl. Phys. **36** (1965), p. 3770.

[10] T. Iida, Y. Tomioka, M. Midorikawa, H. Tsukada, M. Orihara, Y. Hijikata, H. Yaguchi, M. Yoshikawa, H. Itoh, Y. Ishida and S. Yoshida: Jpn. J. Appl. Phys. **41** (2002), p. 800.

[11] Y. Tomioka, T. Iida, M. Midorikawa, H. Tsukada, K. Yoshimoto, Y. Hijikata, H. Yaguchi, M. Yoshikawa, Y. Ishida, R. Kosugi and S. Yoshida: Mater. Sci. Forum **389** (2002), p. 1029.

[12] G. E. Jellison, Jr: Optical Materials **1** (1992), p. 151.

[13] T. Iida, Y. Tomioka, Y. Hijikata, H. Yaguchi, M. Yoshikawa, Y. Ishida, H. Okumura and S. Yoshida: Jpn. J. Appl. Phys. **39** (2000), p. 1054.