Mechanism of Low Temperature Oxidation of 4H-SiC by Nitric Acid Vapor Oxidation Method at 600°C

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Oxidation of 4H-SiC proceeds at 600°C by use of nitric acid vapor. The plots of the SiO2 thickness vs. the square root of the oxidation time are linear, indicating that diffusion of oxidizing species is the rate-determining step. The initial oxidation rate of the C-faced surfaces is 3 times higher than that of the Si-faced surfaces. It is found from cross-sectional transmission electron microscopy (TEM) measurements that the SiO2 thickness is uniform and steps originating from miss-orientation from the (0001) direction having 0.25 nm height are present before and after oxidation, showing that oxidation of SiC proceeds only from step-edges along the (−1100) direction for the C-face and the (1−100) direction for the Si-face.

Because of excellent physical properties such as high breakdown field of 3 MV/cm, high thermal conductivity of 4.9 W/cmK, and high electron mobility of 800 cm²/Vs, SiC is expected to apply to power devices and high frequency devices. On the other hand, SiC is much more chemically stable than Si, and consequently thermal oxidation of SiC for the formation of gate oxides in metal-oxide-semiconductor (MOS) devices requires more than 200°C higher temperature (i.e., ~1100°C) than that of Si.

For improvement of interfacial characteristics of SiO2/SiC structure, extensive studies have been performed so far, including heat treatments in N₂O and NH₃,5,6 formation of oxynitride by heating in N₂O or NO,7,8 oxidation in oxygen-containing trichloroethylene,9,10 hydrogen treatment at high temperatures in the range between 800 and 1000°C,11,12 etc. In spite of these studies, interface state densities at SiO2/SiC interfaces are more than one order of magnitude higher than those for SiO2/Si interfaces.13–15 It is also reported that in the case of thermal oxidation of SiC, the interface state density increases with the oxidation temperature.16,17

Oxidation of SiC with ozone also requires high temperatures above 900°C.18 Plasma oxidation of SiC can be performed at low temperatures,19,20 but damages introduced by plasma cannot be avoided.

We have developed methods of low temperature formation of an SiO2 layer on Si and use of nitric acid (HNO3), i.e., nitric acid oxidation of Si (or SiC) (NAOS) method, which simply involves immersion of Si (or SiC) in high concentration (e.g., 68 wt%) HNO3 aqueous solutions below 120°C.21–23 We have also developed the nitric acid vapor oxidation of Si (NAVOS) method.24,25 In the present study, the NAVOS method has been applied to form SiO2/4H-SiC structures at 600°C, and the NAVAOS oxidation mechanism is investigated using transmission electron micrograph (TEM) and X-ray photoelectron spectroscopy (XPS).

Experimental

SiO2/SiC structure was formed from nitrogen-doped n-type 4H-SiC(000−1) C-face and (0001) Si-face wafers with a miss-orientated by 4° and a 5.5 μm thick epitaxial layer of 1.0 × 1016 cm−2 dopant concentration. The wafers were cleaned using the RCA method and etched with dilute hydrofluoric acid (DHF) solutions. These wafers were oxidized in 68 wt% HNO3 vapor (i.e., vapor of azotropic mixture of HNO3 with water21) at 600°C. Heating was performed by irradiation with a halogen lamp placed outside a quartz reactor.

TEM measurements were carried out with a JEOL JEM-3000F apparatus at the incident electron energy of 300 keV. XPS measurements were performed using a VG Scientific ESCALAB 220i-XL spectrometer with a monochromatic Al Kα radiation source. Photoelectrons were collected in the surface-normal direction.

Figure 1 shows the XPS spectra in the Si 2p region for the SiO2/4H-SiC structure formed by use of the NAVAOS method at 600°C. The substrate Si 2p peak was used as the energy reference (101.0 eV). The Si 2p peak due to SiO2 was observed at 3.4 eV higher than the substrate peak for the SiC(000−1) C-face and 2.4 eV higher for the SiC(0001) Si-faced surfaces. From the ratio in the area intensity between the SiO2 and substrate peaks,26,27 the SiO2 thickness on the SiC(000−1) C-faced surfaces was estimated to be 2.8, 3.1, and 3.5 nm for oxidation time are linear, indicating that diffusion of oxidizing species is the rate-determining step.

The initial oxidation rate of the C-faced surfaces is 3 times higher than that of the Si-faced surfaces. It is found from cross-sectional transmission electron micrograph (TEM) measurements that the SiO2 thickness is uniform and steps originating from miss-orientation from the (0001) direction having 0.25 nm height are present before and after oxidation, showing that oxidation of SiC proceeds only from step-edges along the (−1100) direction for the C-face and the (1−100) direction for the Si-face.

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Figure 2. TEM micrographs for the SiO2/4H-SiC(000−1) C-face structure formed by the NAVOS method at 600°C for 4 h. High resolution TEM micrographs of the highlighted area in the figure (a) are shown in figures (b) and (c).

for 1, 2, and 4 h, respectively. On the other hand, the intensity of the SiO2 peak for the Si-faced surfaces was much weaker, and the SiO2 thickness was estimated to be 1.1, 1.2, and 1.7 nm for oxidation for 1, 2, and 4 h, respectively, i.e., much thinner than those on the C-faced surfaces. It is reported that in the case of thermal oxidation of SiC, the oxidation rate for the C-faced surfaces is higher by approximately ten times than that for the Si-faced surfaces.28,29 We often measured XPS spectra in the N1s region, but we have never observed an N 1s peak.

Figure 2 shows the TEM micrographs for the SiO2/4H-SiC(000−1) C-faced surfaces structure formed by the NAVOS method at 600°C for 4 h. The thickness of the SiO2 layer was 3.8 nm, in good agreement with the XPS result (Fig. 1c), and it was nearly uniform (Fig. 2a). The interlayer distance of the (000−1) faced surfaces of 1.008 nm was clearly observed. The SiO2/SiC interface was atomically flat as observed in Figs. 2b and 2c. Steps with the height of 0.25 nm originating from miss-orientation from the (000−1) direction by 4° were present at the SiO2/SiC(000−1) interface even after the NAVOS method as shown by the solid line.

Figures 3a and 3b show the enlarged XPS spectra in the O 1s region and the valence band spectra, respectively, for the SiO2/4H-SiC structures. In the O 1s spectra for both the C-faced and Si-faced surfaces, a broad structure was present, and the crossing point of the extrapolated line with the background line was located at 8.7 eV with respect to the substrate O 1s peak. This structure is attributable to the satellite which involves transition from the SiO2 valence band to the conduction band,31 and therefore, the SiO2 band-gap energy is determined to be 8.7 eV.

The valence band spectra for the bare 4H-SiC C-faced and Si-faced surfaces (top spectra in Figure 3b) possessed nearly the same structure, and the valence band maximum (VBM) was determined to be 2.2 eV below the Fermi level (of the spectrometer) for both the C-fased and Si-faced surfaces. The bottom spectra in Figure 3b were obtained by subtracting the SiC component from the spectra measured for the
SiO₂/SiC structures, and thus the spectra were for the SiO₂ layer. When an SiO₂ layer was formed on these surfaces, the valence band spectra considerably changed, and the SiO₂ VBM was determined to be 3.95 and 2.82 eV below the VBM of the SiC substrates for the C-faced and Si-faced surfaces, respectively. This result indicates that the valence band discontinuity energy at the SiO₂/SiC interfaces was 3.95 eV for the C-faced surfaces, and 2.82 eV for the Si-faced surfaces.

Discussion

Using the NAVOS method, oxidation of SiC proceeds at 600 °C, which is lower by more than 400 °C than the thermal oxidation temperature. Oxygen atoms generated by decomposition of HNO₃ molecules at the surface are the most probable oxidizing species:

\[
2\text{HNO}_3 \rightarrow \text{NO}_2 + \text{NO} + \text{H}_2\text{O} + 2\text{O.} \quad [1]
\]

For oxidation to proceed at the low temperature, activation energies both for the interfacial reaction and for diffusion through growing SiO₂ should be low.

Figure 4 plots the SiO₂ thickness vs. the square root of the oxidation time. The plots are almost linear for both the C-faced and Si-faced surfaces. The linear plots indicate that diffusion of oxidizing species (i.e., oxygen atoms) is the rate-determining step for oxidation longer than 5 min. From the slopes of the plots, the diffusion rate constant is estimated to be 0.53 nm²/h and 0.30 nm²/h for the C-faced and Si-faced surfaces, respectively. The lower diffusion rate constant for the Si-faced surfaces is probably due to the presence of the C-rich interfacial layer.

The SiO₂ thickness formed by oxidation for 5 min on the C-fased and Si-faced surfaces is 2.1 and 0.7 nm, respectively. For initial oxidation, interfacial reaction is the rate-determining step. The present result shows that oxidation reaction at the interfaces for the C-faced surfaces proceeds more easily than that for the Si-faced surfaces because of a lower activation energy. Assuming that oxidation up to 5 min is reaction-limited, the activation energy of the interfacial reaction for the C-faced surfaces is estimated to be 30 mV lower than that for the Si-faced surfaces. It is well known that in the case of thermal oxidation of SiC, the oxidation rate of C-faced SiC is much higher than that of Si-faced SiC. It is likely that C atoms in the second layer possess a lower reaction rate than that in the first layer due to the higher coordination number (cf. Fig. 5). Therefore, the first layer C atoms in the C-faced SiC surfaces are more easily oxidized than those in the second layer C atoms in the Si-faced SiC surface, leading to much higher oxidation rate of the C-faced SiC surfaces.

The strong dependence of the oxidation rate on the oxidation time is likely to result from low temperature oxidation with a low diffusion rate, i.e., without SiO₂ layer, the oxidation rate of SiC is high while after the formation of a thin SiO₂ layer, diffusion of oxidizing species through SiO₂ is greatly retarded. The band-gap energy of SiO₂ formed by the NAVOS method on the SiC C-fased and Si-faced surfaces is both 8.7 eV (Fig. 3a). On the other hand, the valence band discontinuity energy between SiO₂ and SiC is 2.8 eV for the Si-faced surfaces, which is ~1 eV lower than that for the C-faced surfaces of 3.9 eV (Fig. 3b). The difference may be due to a dipole layer present at the SiO₂/SiC Si-face interface.

Periodic bi-layer steps originating from miss-orientation from the (000−−) direction are preserved at the SiO₂/SiC interfaces even after NAVOS oxidation (Fig. 2), indicating formation of atomically flat interfaces. This result can be well explained assuming that the oxidation rate at step edges is much higher than that on terraces, and oxidation proceeds in the horizontal direction, i.e., (−1100) direction for the C-faced surfaces and (1−100) direction for the Si-faced surfaces (cf. Fig. 5). Oxidation hardly proceeds on terraces, and therefore the step edges move in the horizontal direction (Fig. 5a). The presence of steps after oxidation shows that oxidation of Si and C layers proceeds simultaneously, which can be achieved easily by the proposed step edge oxidation mechanism. For the NAVOS method, oxidizing species is oxygen atoms generated by decomposition of HNO₃ molecules (Eq. 1). It is very likely that oxygen atoms easily diffuse through SiO₂ and reach step edges where oxidation proceeds. When the step edge oxidation proceeds, step edges move in the surface-parallel direction (cf. Fig. 5a), but they are always present with the constant density.

This step edge oxidation mechanism is also supported by the different oxidation rates for the C-fased and Si-faced surfaces. It is very likely that the rate determining-step for the reaction is the removal process of C atoms. In the case of the C-faced surfaces, C atoms are present in the first layer and bound to Si atoms in the second layer (cf. Fig. 5b). Therefore, O atoms can easily attack the Si-C bonds, resulting in desorption as CO. In the case of the Si-faced surfaces, on the other hand, C atoms are present in the second layer and these C atoms are bound not only to Si atoms in the first layer but also to Si atoms in the third layer. These Si-C bonds are more difficult to rupture because of the structural reason.

Conclusions

SiO₂/4H-SiC(000−−1) C-face and SiO₂/4H-SiC(0001) Si-face structures are fabricated using the NAVOS method at 600 °C. Diffusion of oxygen atoms through growing SiO₂ is the rate determining step, and the diffusion constant at 600 °C is determined to be 0.53 nm²/h and 0.30 nm²/h for the C-faced and Si-faced surfaces, respectively. The reaction rate constant at the SiO₂/SiC C-face interface is 3 times higher than that at the SiO₂/SiC Si-face interface, and the
activation energy for the C-faced surfaces is lower by 30 mV than that for the Si-faced surfaces. The thickness of the SiO₂ layer is uniform, and steps originating from miss-orientation from the (000−1) direction are present even after the NAVOS oxidation, indicating that oxidation proceeds only from step edges along the (−1100) direction.

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