Reactions of 6H-SiC(0001) $3 \times 3$ surfaces with oxygen molecules at high temperature

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Surface reactions of the 6H-SiC(0001) $3 \times 3$ with oxygen molecules (O$_2$) at high temperature were investigated using reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy (AES). The Si-terminated $3 \times 3$ surface transformed into the C-rich $1 \times 1$ surface by O$_2$ exposure of $1.2 \times 10^2$ L at 1000°C. Mass spectra measured during the experiment using a Quadrupole Mass Spectrometer (QMS) suggest that Si atoms and C atoms on the $3 \times 3$ surface were etched by the O$_2$ exposure. Morphologies of the $3 \times 3$ surfaces before and after the O$_2$ exposure were also observed using scanning electron microscopy (SEM). Many droplets were found on the $3 \times 3$ surface, which were determined to be Si droplets generated in the preparation process of the $3 \times 3$ phase. The Si droplets were removed from the surface by the O$_2$ exposure at high temperature.

Keywords: Reflection high-energy electron diffraction (RHEED), Scanning electron microscopy (SEM), Auger electron spectroscopy, Quadrupole mass spectrometer, Silicon carbide, Etching, Oxidation, Oxygen

I. INTRODUCTION

Silicon carbide (SiC), a semiconductor material with wide band gap, high saturation electron mobility and stability at high temperatures, is a candidate for fabricating high-power, high-temperature and high-frequency devices.[1] Furthermore, in the filed of surface science, SiC is an attractive material in the characterization of atomic structure on the surface. Periodic structures are obtained by annealing SiC in ultra high vacuum (UHV). Depending on the polytypes, the polarity and the sample preparation procedures, various surface structures have been reported.[2–7] For example, C-terminated structures are formed by annealing SiC in UHV, and Si-terminated structures are formed by annealing SiC in UHV under the Si rich environment. A $3 \times 3$ phase on SiC(0001) or SiC(111) is one of the most extensively discussed structures. The $3 \times 3$ phase is obtained by annealing SiC surfaces in UHV under the Si rich environment at the lowest temperature and has the largest Si coverage among the various periodic structures formed on the SiC surface. Atomic structures of the $3 \times 3$ phase have been explained by several structural models in many studies by various techniques[3, 8–10]. The structural model proposed by Starke et al. [10], consist of three Si adlayers on the SiC surfaces with an excess Si coverage of 1.44 monolayer, is considered to be the most probable structure for the $3 \times 3$ phase.

Initial reactions of the $3 \times 3$ phase with oxygen molecules have also been studied. It has been found that the 4H- and 6H-SiC(0001) $3 \times 3$ surfaces are highly reactive to oxygen and have higher oxidation rate than silicon surfaces.[11] According to the study using scanning tunneling microscopy (STM) and core-level photoemission spectroscopy, the oxygen molecule is readily dissociated at room temperature (RT) on the surfaces, and the oxygen atoms are found to bond to the Si adlayer located well below the surface.

Recently, temperature and oxygen exposure dependence of the initial oxidation processes of the SiC(0001) $3 \times 3$ surfaces at low oxygen pressure have been reported. Amy et al. reported that increasing the temperature from 25 to 500°C and the oxygen exposure from 1 L to 1000 L (1 L = 1 × 10$^{-6}$ Torr) improve the efficiency of the oxidation process with larger amount of oxidation products and higher oxidation states including SiO$_2$ with a more favorable situation for the 6H-SiC(0001) $3 \times 3$ surface than the 4H-SiC(0001) $3 \times 3$ surface.[12] They also showed that the $3 \times 3$ periodicity was maintained even after the exposure of oxygen at RT. Kubo et al. reported that the $3 \times 3$ periodicity on the initial 6H-SiC(0001) $3 \times 3$ surface was almost destroyed by exposing oxygen molecules of 10.5 L at 500°C, suggesting the insertion of the thermally activated oxygen into the deeper layers.[13] Furthermore, they reported that the surface Si atoms on the 6H-SiC(0001) $3 \times 3$ are etched by the oxygen molecules exposure of 2 L at 700°C, resulting in the formation of $2\sqrt{3} \times 2\sqrt{3}$ periodicity or the disordered surface.

In this paper, reactions of the 6H-SiC(0001) $3 \times 3$ surface with oxygen molecules at high temperature such as 1000°C are reported. The atomic structures of the surfaces before and after the exposure of the oxygen molecules were observed by using reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy (AES). Surface morphologies of the two surfaces were also observed by using scanning electron microscopy (SEM).

II. EXPERIMENTAL

Samples used were 6H-SiC(0001) wafers (Cree Research Inc.), nitrogen-doped n-type with a dopant concentration of $\sim 10^{18}$ cm$^{-3}$. Specimens were cut to the size of $3 \times 25 \times 0.26$ mm$^2$, cleaned in acetone by an ultrasonic cleaner for 5 min, dipped into concentrated HF (49%) for 5 min, rinsed in deionized water for 10 min and blown dry with N$_2$ gas. The specimen was set up in a UHV system equipped with a RHEED facility with a base pressure of $4 \times 10^{-10}$ Torr. After a pre-deposition of Si on the
surface of the specimen, the specimen was resistively annealed in a Si flux. The flux of Si vapor was obtained by resistively heating a Si platelet positioned at about 40 mm away from the surface of the specimen. The deposition rate of Si was estimated from the variation of the RHEED pattern when Si was deposited on the surface of the Si(111) 7×7. It is known that 0.7 BL of Si is deposited on the Si(111) 7×7 surface when the RHEED pattern shows the δ7×7 structure.[14] The deposition rate of Si was estimated to be about 0.7 BL/min, and the thickness of the pre-deposited Si was calculated to be about 5 nm. The 6H-SiC(0001) 3×3 surface was obtained by annealing the specimen in the Si flux for 5 minutes at 1000°C. The temperatures were measured by an optical pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H). Surface structure of the 3×3 pyrometer (Universal Pyrometer "Optix": PYRO-WERK G.M.B.H).

The glancing angles of the incident beam were also measured in the one beam condition to examine the surface structure. RHEED rocking curves served by RHEED with a primary beam energy of 10 keV were obtained. When Si was deposited on the surface of the specimen, the specimen was resistively annealed in a Si flux. The flux of Si vapor was obtained by a Quadrupole Mass Spectrometer (QMS) during the exposure. Furthermore, RHEED and RHEED rocking curves with the same condition were observed by RHEED and RHEED rocking curves with the same condition before the O2 exposure. Mass spectra were measured by a Quadrupole Mass Spectrometer (QMS) during the process to investigate the reactions. Ex-situ observations using SEM were also carried out to observe the surface morphologies of the both surfaces before and after the O2 exposure. Furthermore, the two surfaces were prepared with the same procedure in another UHV system equipped with RHEED and AES, to investigate the reaction considering the variation of the surface compositions by the O2 exposure.

III. RESULTS AND DISCUSSION

Figure 1 shows the RHEED pattern and the SEM image from the 6H-SiC(0001) 3×3 surface before the O2 exposure. Although the diffraction spots on the zeroth Laue zone are streaky, the RHEED pattern clearly shows the 3×3 periodicity on the SiC substrate. The SEM image, taken by the ex-situ observation for the surface prepared by another experiment under the same condition, shows that the surface has many droplets.

A detailed SEM image of the 3×3 surface shown in Fig. 2(a) reveals that diameters of the droplets are in the range of 0.1-1 μm. AES spectra for one of the droplets (point A) and an area with no droplet (point B) are shown in Fig. 2(b). The AES spectra show that the droplets contain Si, C, and O atoms, which is the same as in the droplet-free area. However, peak-to-peak ratios of Si(LVV)/C(KLL) for the two regions are quite different, 3.0 for the droplets and 1.3 for the droplet-free area. The results suggest that the droplets consist of only silicon atoms. The Si(LVV) peak energy of 83-84 eV shows that the Si atoms are oxidized by exposure to the ambient gas due to the ex-situ observation.

When the 3×3 surface was exposed to the O2 of 1.2×105 L at 1000°C, the RHEED pattern and the SEM image have drastically changed. Figure 3(a) shows the RHEED pattern from the surface after the O2 exposure. All the fractional spots observed in Fig. 1(a) have disappeared. The SEM image of the surface after the O2 exposure is shown in Fig. 3(b). The Si droplets on the surface observed in Fig. 1(b) have also disappeared. Figure 4 shows the comparison of the 00-rod RHEED rocking curves from the two surfaces. The peak located at 1° on the curve (b) indicated by arrow A is shifted to lower angle by 0.4° from that of the curve (a) indicated by arrow A’. The peak located at 2.7° on the curve (b) indicated by arrow B is not observed on the curve (a).

Figure 5 shows the QMS spectra, (a) before and (b) after the O2 exposure. The mass spectrum in Fig. 5(b) has a peak at 16, 28 and 44 a.m.u. The peak at 16 a.m.u. corresponds to the residual O2. The other peaks appeared at 28 and 44 a.m.u. are considered to be the reaction products between the SiC surface and oxygen, such as CO for 28, CO2 and/or SiO for 44.

In order to investigate the reaction of the 3×3 surface with O2 at 1000°C, AES spectra for each surface were obtained by using the RHEED/AES system. Figure 6 shows the AES spectra for each surface in the series of the exper-

![FIG. 1: RHEED pattern and SEM image from the 6H-SiC(0001) 3×3 surface. (a) RHEED pattern in the direction of [10¯10] with the glancing angle of 3.5°. (b) SEM image taken by ex-situ observation. The 3×3 surface has many droplets.](image-url)
FIG. 2: (a) A detailed SEM image of the 6H-SiC(0001) 3×3 surface. (b) AES spectra for one of the droplets (point A) and the droplet-free area (point B) with a primary beam energy of 10 keV. The observations were carried out by ex-situ observation using a FE-AES system. Diameters of the droplets are in the range of 0.1-1 µm. The Si(LVV)/C(KLL) peak-to-peak ratio of the point A is larger than that of the point B.

Now, we discuss about the surface after the O₂ exposure. In Fig. 6, the energy of the Si(LVV) peak of the spectrum (d) for the surface after the O₂ exposure is 87 eV, which is the same as that of the spectrum (a) for the HF treated surface. As the reported energy of the Si(LVV) peak for the SiC surface is in the range of 87-91 eV,[15–17] it is difficult to determine whether the surface after the exposure has Si-C bond or Si-O bond. Muehlhoff et al. reported that the Si(LVV) peak energy for the Ar⁺ sputtered SiC surface is 89.9 eV,[17] which was also confirmed in our other experiment. Based on the fact, it seems appropriate to conclude that the Si(LVV) peak energy of 87 eV corresponds to the Si-O bond. Therefore, we conclude that the Si (LVV) peak in the spectrum (a) originates from the native oxide, and that in the spectrum (d) originates from the adsorbed species on the surface such as SiO. The absence of the Si (LVV) peak originating from the Si-C bond in the spectrum (d), although the intensity may be too weak to be distinguished, means that the thickness of the carbon layers on the surface after the O₂ exposure is no less than the escape depth of the Si(LVV) Auger electron.

It has been discussed whether the conversion of the Si-terminated surface to the C-terminated surface by the O₂ exposure at high temperature occurs by a self-limiting mechanism,[18] or by competitive etching of both Si and C atoms.[19] In the self-limiting mechanism, only the Si atoms on the SiC surface are etched by the O₂ exposure, while C atoms remain to work as an oxidation-resistant layer. On the other hand, both the Si atoms and the C atoms are etched by the O₂ exposure in the case of the competitive etching. Recently, the pressure-temperature
phase diagram for the oxidation of SiC was presented by Song et al., and the dominant reactions depending on the pressure and the temperature were predicted.[20] According to their calculation of the Gibbs free-energy changes ΔG for the vapor phase products — Si(g), SiO(g), CO(g), CO２(g) — and the solid phase products — Si(s), SiO₂(s), C(s) —, the dominant reaction at high temperature and low O₂ pressure is predicted as follows:

\[
(2 + x)\text{SiC}(s) + O_2(g) \rightarrow (2 + x)\text{Si}(g) + 2\text{CO}(g) + x\text{C}(s).
\]

The formula explains the QMS spectrum shown in Fig. 5 (b). As the Si(g) is considered to be immediately oxidized in the presence of O₂ or stick to somewhere in the chamber in our experimental condition, the mass of 28 a.m.u. corresponds to CO. The mass of 44 a.m.u. corresponds to SiO(g) or CO₂(g), which are the oxidation products of Si(g) or CO(g), respectively. The existence of the reaction products between the O₂ and the SiC substrate means that the conversion of the Si-terminated surface to the C-terminated surface in this experiment occurs by the competitive etching of both Si and C atoms.

The results described above reveal the reaction of 6H-SiC(0001) 3×3 surface by the O₂ exposure of 1.2×10⁵ L at 1000°C as follows. The surface before the O₂ exposure has Si adatoms and Si droplets on the SiC substrate. The Si adatoms, Si droplets and also the SiC substrate are etched by the O₂ exposure. As a result, the Si-terminated surface transforms into the C-rich surface, and the reaction products such as CO, CO₂ and SiO adsorb the C-rich surface.

It is important to note that the 3×3 surface has many Si droplets as shown in Fig. 1(b) and Fig. 2. Since now, atomic structures of the 3×3 surface have been studied extensively. However, there is no report observing the morphology of the 3×3 surface. In this study, we found many Si droplets on the 3×3 surface by the SEM observation. We have also found that the \(\sqrt{3} \times \sqrt{3}\) surface has no droplet on the surface in our other experiment. The 3×3 and \(\sqrt{3} \times \sqrt{3}\) surfaces are prepared by annealing the SiC substrate in UHV under the Si rich environment to restrict the surface graphitization. Considering the result that the \(\sqrt{3} \times \sqrt{3}\) surface which is obtained at higher temperature than 3×3 surface has no droplet, the Si droplets on the 3×3 surface is caused by the excess Si atoms in the preparation process. As the control of the balance between the Si desorption and the deposition is difficult on the 3×3 surface, the excess Si atoms form droplets on the 3×3 surface. In the study to observe the surface structure and the oxidation process of the 3×3 surface, existence of the droplets on the initial surface is not desirable. One of the approach to remove the Si droplets from the 3×3 surface is to prepare the 3×3 surface in the cooling process under the Si flux after the formation of the \(\sqrt{3} \times \sqrt{3}\) surface. In our another experiment using the procedure, the density of the droplets was suppressed, however, it was impossible to obtain a droplet-free 3×3 surface.

A further important point is that the Si droplets on the 3×3 surface are removed by the O₂ exposure. It is known that the surface reaction of Si or SiC with O₂ depends on...
The surface at low O$_2$ pressure, the reaction leads to the growth of SiO sublimate at high temperature and the pressure. [20–22] At high temperatures, the reaction leads to the growth of a SiO$_2$ layer at high O$_2$ pressure (passive oxidation) and etching of the surface at low O$_2$ pressure (active oxidation). The phenomenon that CO, CO$_2$ and SiO sublimate at high temperature in UHV is generally used as a useful technique to remove the native oxide and contaminations from the Si and SiC surfaces. In the same way, exposing the O$_2$ to the SiC 3×3 surface at high temperature under the decreased pressure is effective to remove large amount of Si such as the Si droplets from the surface.

It is not well known what determines the terminating atoms, Si or C atoms, of the O$_2$ exposed SiC surface at high temperature and low O$_2$ pressure. In most cases, the O$_2$ exposed SiC surfaces are C-terminated. On the other hand, Pehrsson et al. reported that Si-terminated surface was partially obtained when the O$_2$ exposed SiC was cooled down under O$_2$ [19]. Growth of carbon layers on SiC is an important technique to produce carbon nanotubes on SiC, [23, 24] while the Si-terminated surface is preferable in the study on the oxidation process of SiC and the abruptness of the SiO$_2$/SiC interface. Control of the terminating atoms of SiC by the O$_2$ exposure will promote the study of surface science and nanotechnology using SiC. Further study is required to examine the pressure and temperature dependence of both the surface composition and the morphology for the SiC surfaces exposed to oxygen.

IV. CONCLUSION

The Si-terminated 6H-SiC(0001) 3×3 surface was exposed to 1.2×10$^5$ L of O$_2$ at 1000$^\circ$C. The 3×3 surface before the O$_2$ exposure was found to have many Si droplets, which were removed by the O$_2$ exposure. Reaction products such as CO, CO$_2$ and SiO were generated by the O$_2$ exposure. As a result, the initial 3×3 surface transformed into the C-rich 1×1 surface with the reaction products adsorbed on the surface. The results suggest that the reaction occurs by the competitive etching of both the Si and C atoms.

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