Growth and surface structure analysis of a new SiON single layer on SiC(0001)

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Abstract

A new silicon oxynitride layer was **formed on a 6H-SiC(0001) surface by a nitrogen oxide treatment**. The atomic structure of this single layer on the SiC(0001) substrate was determined by means of low-energy electron diffraction (LEED) analysis. **The surface layer has a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity. Its LEED $I(E)$ spectra are different from those of the previously reported silicon oxynitride layer which has a $\text{Si}_4\text{O}_5\text{N}_3$ composition [Phys. Rev. Lett. 98 (2007) 136105].** The best-fit structure has a single layer of Si_2ON_3 composition terminated by O bridges. The Si–N layer of the determined structure has **the same structure as that in the $\text{Si}_4\text{O}_5\text{N}_3$ surface.** The obtained Si_2O_3 structure would be useful **for preparing an ideal SiC–insulator interfaces with a low interfacial density of states.**

Keywords: Low energy electron diffraction (LEED); SiC; silicon oxynitride layer

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1. Introduction

The silicon carbide (SiC) is a promising material for electronic devices because of its wide band gap, high dielectric strength, and high thermal conductivity [1]. These significant features are useful for the development of energy-saving power devices and miniaturization of devices. Silicate layers are able to grow on SiC substrate, and practical uses for Schottky barrier diodes and applications for metal-oxide-semiconductor field-effect transistors (MOSFET) have been successful. Nevertheless, the interface between the SiC substrate and silicate layer have a high interface state density [2,3], which can significantly weaken the electronic features [4-6]. Therefore, research of perfect interface growth remains an important subject.

Epitaxial growth of silicate layers on SiC(0001) by H₂ etching has been reported [7-9]. This method shows abrupt termination of the SiC(0001) substrate with a well-ordered single-layer silicate with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity [8-10]. Because there is one dangling bond in the unit cell, intrinsic interface states are inevitable. On the other hand, the epitaxial growth of the dangling-bond-free silicon oxynitride (SiON) layer on SiC(0001) has been reported by Shirasawa et al. [11]. This interface is not only abrupt but also has no dangling bond in the unit cell. It has a chemical composition of Si₄O₅N₃, and exhibits a substantial band gap of 9 eV at the surface [11-13]. The Si₄O₅N₃ layer was obtained by H₂ etching followed by N₂ treatment at 1360 °C at atmospheric pressure. Because the numbers of Si and C atoms are not controllable in this process, there exist residual Si and C atoms and those oxides [13]. These residual materials would significantly lower the electronic properties for the application toward MOSFET.

In this study, we tried to prepare the SiON layer by NO treatment of Si-adsorbed SiC(0001) surfaces in an ultra-high vacuum (UHV) to eliminate the residual materials. As a result, we obtained a new surface structure with a chemical composition of Si₂ON₃, which was determined by quantitative LEED analysis.

2. Experiment

A single-crystal 6H-SiC(0001) wafer with a size of 8 mm × 4 mm and a thickness of 0.5 mm was treated by H₂-gas etching at 1360 °C for 30 min in a cold-wall reactor of a quartz furnace under atmospheric pressure to remove scratches on the wafer surface [14]. The sample was then clamped by Ta plates for resistive heating. The experiments were performed in a UHV chamber equipped with LEED, Auger electron spectroscopy (AES) optics (SPECTALEED, Omicron) and magnetic shields, in which the base

pressure was better than 1×10^{-8} Pa. The temperature of the sample was measured by using an infrared thermometer (FTZ6, Japan Sensor Corp, Tokyo). The sample prepared in the cold-wall reactor showed a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern without any cleaning procedures in UHV. The intensity versus energy curves [$I(E)$ curves] showed the feature of the silicate layer on the sample. The silicate layer was removed by annealing the sample at 1200 °C for 2 min after degassing at 800 °C for 12 h in the UHV chamber. The sample was further cleaned by cycles of silicon deposition and annealing at 1200 K in UHV. Clear (3×3) or $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED patterns were obtained as previously reported [15-17]. The (3×3) surface, referred to here as the (3×3) -Si surface, had larger amount of Si adatoms than that of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface [$\sqrt{3}$ -Si surface]. The Si atoms were evaporated from a high-temperature Si wafer heated by direct resistive heating. Then, the sample surface was exposed to NO at various temperatures to obtain well-defined SiON layers.

The LEED spot intensities were measured by using a digital charge-coupled device camera with a computer-controlled data acquisition system [18]. For the structural analysis, the $I(E)$ curves of the LEED spots were measured within an incident energy range of 100–500 eV. The summation of energy ranges of inequivalent $I(E)$ curves, ΔE , was 3004 eV. A Barbieri–Van Hove symmetrized automated tensor LEED package was used to determine the atomic positions [19]. Thirteen phase shifts were used to represent atomic scattering. The dumping of incident electrons was represented by an imaginary part of the inner potential, V_{0i} , of -5.0 eV. Pendry’s reliability factor (R_P) was used to direct the automated search algorithm [19,20]. The best agreement between experimental and theoretical $I(E)$ curves involved minimizing the R_P . Errors in the structural parameters were estimated from the variance of the R_P , $\Delta R = R_P(8|V_{0i}|/\Delta E)^{1/2}$ [20].

3. Results and Discussion

First, we attempted the growth of the epitaxial silicate layer with the exposure to O or water during annealing the Si-adsorbed SiC(0001) surfaces under various conditions. Although an epitaxial silicate layer with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure was formed, the spots of LEED patterns were always broad with high background, which suggests a low quality of the ordering.

Next, we examined NO exposure on the Si-adsorbed SiC(0001) surfaces. On the $\sqrt{3}$ -Si surface, we obtained a different $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern by NO exposure at 950 °C. The $I(E)$ spectra of the new $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure are different from

those of the $\sqrt{3}$ -Si structure. The LEED pattern of the structure at 94 eV electron energy (Fig. 1(b)) was compared with that of the $\sqrt{3}$ -Si structure. Both structures had the same periodicity, although the intensities of their $(1/3\ 1/3)$ spots are significantly different. The LEED pattern in Fig. 1(b) is very sharp with low background, suggesting a well-ordered surface. The $I(E)$ curves of the NO treated structure are different from those of the other $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures: $\sqrt{3}$ -Si [16,17], epitaxial silicate [7] and $\text{Si}_4\text{O}_5\text{N}_3$ [11], indicating that the NO treated surface has a new structure.

We also examined NO treatment on a (3×3) -Si surface that had a larger number of Si adatoms on the surface than that of the $\sqrt{3}$ -Si structure. Only a broad $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern with high background was obtained, and its $I(E)$ spectra were similar to that of the newly obtained structure. The (3×3) -Si structure had 13 Si adatoms in the unit cell, which corresponded to 4.3 Si adatoms in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell, whereas the $\sqrt{3}$ -Si surface had a single Si adatom in the unit cell. This result indicates that the number of Si adatoms of the (3×3) -Si surface is too large to form the newly obtained structure.

Figure 2 shows N and O KLL AES peaks of the newly obtained structure (solid line). In order to estimate the N/O ratio, we also measured the AES of the NO physisorbed $\sqrt{3}$ -Si surface (dotted line), on which the N and O atoms would equally exist. The obtained N/O ratio of the new structure was approximately 3.

On the basis of these results, eight new structure models, shown in Fig. 3, were created and tested by LEED $I(E)$ analysis. The models 1 and 8 had a $p31m$ symmetry, whereas the models 2–7 had a pm symmetry. The atomic positions of the surface layer and three SiC bilayers were adjusted to minimize the R_p value for the models 1 and 8, in which the numbers of structural parameters were 27 and 26, respectively. On the other hand, the surface layer and two SiC bilayers were adjusted to minimize the R_p value for the models 2–7, in which the number of structural parameters was 31. We assumed S3 or S3* termination of SiC(0001) surface. It has been reported that the 6H-SiC(0001) surface is dominantly terminated by S3 and S3* terminations [21]. It was also confirmed that we could assume S3 and S3* terminations to obtain sufficiently small R_p value for the $\sqrt{3}$ -Si surface. The obtained R_p values for the newly obtained structure are listed in the parentheses in Fig. 3. The model 2 had the smallest R_p value of 0.22 among them, whereas other models had R_p values larger than 0.3. Therefore, we disregarded the other models. The detailed illustration and obtained structural parameters of the model 2 are shown in Fig. 4 and Table 1, respectively. A comparison of experimental and theoretical $I(E)$ curves of the best fit model is shown in Fig. 5. Because the structural parameters are reasonable and the experimental and theoretical $I(E)$ curves are

in good agreement, we conclude that model 2 is appropriate for the NO treated structure obtained in the present study.

The determined structure consists of a Si–N layer and terminating oxygen. Two Si atoms, one O atom, and three N atoms are included in the unit cell (Si_2ON_3). Because the Si atoms bond with the three N atoms and one O atom, the O atoms bond with two Si atoms, and the N atoms bond with three Si atoms, there are no intrinsic dangling bonds. The averaged values of the Si–O(N) bond length and Si–O(N)–Si bond angles are consistent with the epitaxial $\text{Si}_4\text{O}_5\text{N}_3$ surface and Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ crystals, as shown in Table 2 [11,22]. On the contrary, each Si–N bond has rather dispersed values of bond lengths in a range of 1.58–1.90 Å and bond angles of 106–134°. These differences from the averaged ones might be caused by the terminating O atom which bonded with Si(1) and Si(2) atoms. Consequently, the bond angles of Si(1) and Si(2) changes from the ideal conditions, and the Si–N layer is distorted.

The robustness of the obtained surface was verified by the exposure to the air for an hour. Although the LEED pattern was very faint after the exposure, a sharp LEED pattern appeared again after annealing at 850 °C in UHV. The obtained LEED pattern suggested that the Si–N layer was stable even in the air while the topmost surface was contaminated.

The determined structure in the present study has an Si–N layer similar to that in the $\text{Si}_4\text{O}_5\text{N}_3$ layer. Therefore, it is expected to produce a perfect SiON layer under the UHV conditions with proper procedures of Si deposition and following oxidation at certain temperatures.

4. Conclusion

We have found a new silicon SiON layer, Si_2ON_3 , on SiC(0001) surface with $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ periodicity by means of quantitative LEED $I(E)$ analysis. The determined structure consists of a Si–N layer and O termination. The Si–N layer is slightly distorted by the terminating O atoms. The previously observed $\text{Si}_4\text{O}_5\text{N}_3$ structure has the same Si–N layer. This experiment is a first step of the formation of the perfect SiON layer and may lead to the creation of the $\text{Si}_4\text{O}_5\text{N}_3$ structure and thick silicate layers in UHV with minimized interface state density.

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Figure captions

Fig. 1. LEED patterns of (a) SiC(0001)-Si-($\sqrt{3} \times \sqrt{3}$)R30° surface and (b) a newly obtained SiC(0001)-SiON-($\sqrt{3} \times \sqrt{3}$)R30° surface.

Fig. 2. AES spectra of an NO physisorbed (dotted line) and a newly obtained SiC(0001)-SiON-($\sqrt{3} \times \sqrt{3}$)R30° (solid line) surface.

Fig. 3. Top and side views of examined structure model. Pendry's r-factors are shown in parentheses.

Fig. 4. Top and side views of the best-fit structure model.

Fig. 5. Experimental (dotted lines) and the best-fit theoretical (solid lines) $I(E)$ curves of the best-fit model.

Table 1. Structural parameters obtained for the best-fit model.

Table 2. Summary of bond lengths and bond angles.

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Fig. 2. AES spectra of an NO physisorbed (dotted line) and a newly obtained SiC(0001)-SiON- $(\sqrt{3} \times \sqrt{3})R30^\circ$ (solid line) surface.

Fig. 3. Top and side views of examined structure model. Pendry's r-factors are shown in parentheses.

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Table 1. Structural parameters obtained for the best-fit model.

Atom (No.)	$[000\bar{1}]$ (Å)	$[11\bar{2}0]$ (Å)	$[\bar{1}110]$ (Å)
O(1)	0 ±0.07	0	2.65 ±0.11
Si(1)	0.36 ±0.02	-3.09 ±0.30	0.04 ±0.14
Si(2)	0.36 ±0.02	3.09 ±0.30	0.04 ±0.14
N(1)	0.86 ±0.09	0	2.31 ±0.10
N(2)	0.93 ±0.06	-1.93 ±0.25	-0.87 ±0.15
N(3)	0.93 ±0.06	1.93 ±0.25	-0.87 ±0.15
Si(3)	2.63 ±0.06	0	1.98 ±0.18
Si(4)	2.65 ±0.04	-1.53 ±0.21	-0.79 ±0.12
Si(5)	2.65 ±0.04	1.53 ±0.21	-0.79 ±0.12
C(1)	3.22 ±0.08	0	0.19 ±0.16
C(2)	3.37 ±0.05	-2.98 ±0.20	0.13 ±0.17
C(3)	3.37 ±0.05	2.98 ±0.20	0.13 ±0.17
Si(6)	5.13 ±0.03	0	0.04 ±0.18
Si(7)	5.22 ±0.03	-3.11 ±0.13	0.00 ±0.11
Si(8)	5.22 ±0.03	3.11 ±0.13	0.00 ±0.11
C(4)	5.80 ±0.08	-1.53 ±0.11	0.98 ±0.20
C(5)	5.80 ±0.08	1.53 ±0.11	0.98 ±0.20
C(6)	5.91 ±0.17	0	-1.53 ±0.20

Table 2. Summary of bond lengths and bond angles.

	This study	Si ₄ O ₅ N ₃	$\alpha(\beta)$ -Si ₃ N ₄	Si ₂ N ₂ O
Si(1)-O(1) (Å)	1.59	1.63		1.62
Si(1)-N(1) (Å)	1.68	1.74		
Si(1)-N(2) (Å)	1.90	1.74		
Si(2)-N(2) (Å)	1.58	1.74		
Si(3)-N(1) (Å)	1.80	1.75		
Si(4)-N(2) (Å)	1.77	1.75		
Si-N (average) (Å)	1.75	1.75	1.74 (1.73)	1.71
Si(1)-O(1)-Si(2) (°)	154	143		147
Si(1)-N(1)-Si(2) (°)	134	125		
Si(1)-N(2)-Si(2) (°)	124	125		
Si(1)-N(1)-Si(3) (°)	110	113		
Si(1)-N(2)-Si(4) (°)	106	113		
Si(2)-N(2)-Si(4) (°)	120	113		
Si-N-Si (average) (°)	119	119	119 (120)	120