Surface Science 628 (2014) 148–152

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

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

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ARTICLE INFO

Article history:
Received 9 April 2014
Accepted 11 June 2014
Available online 19 June 2014

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

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° periodicity. Its LEED $I(E)$ spectra are different from those of the previously reported silicon oxynitride layer which has a $Si_4O_5N_3$ 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 $Si_4O_5N_3$ surface. The obtained Si_2O_3 structure would be useful for preparing an ideal SiC–insulator interfaces with a low interfacial density of states.

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 has 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 H_2 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° 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 $Si_4O_5N_3$, and exhibits a substantial band gap of 9 eV at the surface [11–13]. The $Si_4O_5N_3$ layer was obtained by H_2 etching followed by N_2 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 Si_2ON_3, 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 H_2-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° 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° 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° surface [$\sqrt{3}$-Si surface]. The Si atoms were evaporated from a high-temperature Si

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http://dx.doi.org/10.1016/j.susc.2014.06.007
0039-6028/

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°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° LEED pattern by NO exposure at 950 °C. The $I(E)$ spectra of the new ($\sqrt{3} \times \sqrt{3}$) R30° 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° structures: $\sqrt{3}$-Si [16,17], epitaxial silicate [7] and $Si_4O_5N_3$ [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° 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° 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.

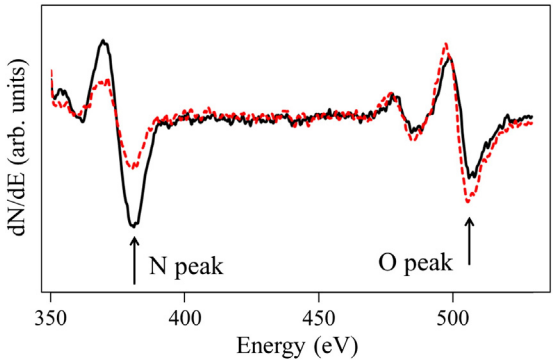

Fig. 2. AES spectra of an NO physisorbed (dotted line) and a newly obtained SiC(0001)-SiON-($\sqrt{3} \times \sqrt{3}$) R30° (solid line) surface.

Fig. 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

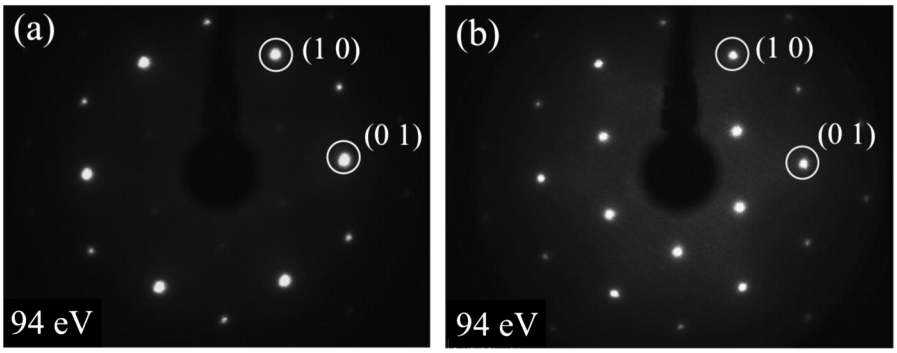

Fig. 1. LEED patterns of (a) SiC(0001)-Si-($\sqrt{3} \times \sqrt{3}$) R30° surface and (b) a newly obtained SiC(0001)-SiON-($\sqrt{3} \times \sqrt{3}$) R30° surface.