Surface Science 605 (2011) 328–332

Contents lists available at ScienceDirect

Surface Science

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

Atomic and valence-band electronic structures of the epitaxial SiON layer on the SiC(0001): X-ray diffraction and angle-resolved photoemission spectroscopy investigations

Tetsuroh Shirasawa [a,*], Kazuyuki Sakamoto [b], Toshio Takahashi [a], Hiroshi Tochihara [c,*]

[a] Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan
[b] Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan
[c] Faculty of Engineering Sciences, Kyushu University, Fukuoka, 816-8580, Japan

ARTICLE INFO

Article history:
Received 22 September 2010
Accepted 25 October 2010
Available online 30 October 2010

Keywords:
Silicon carbide
Silicon oxynitride
Ultrathin epitaxial layer
X-ray diffraction
Photoemission spectroscopy

ABSTRACT

Atomic and valence-band electronic structures of a recently discovered epitaxial silicon oxynitride (SiON) layer on a 6*H*-SiC(0001) surface were investigated with x-ray diffraction (XRD) and angle-resolved photoemission spectroscopy (ARPES). The atomic structure optimized by XRD analysis well agrees with a previous low-energy electron diffraction analysis and a first-principles calculation. Band dispersions of surface states observed by ARPES can be explained by the previous calculation. Interface states intrinsic to the SiON layer were not observed above the valence-band maximum of SiC, but a diffuse, non-dispersive state was found by ARPES. Its origin is suggested to be a by-product of graphite-like clusters formed on the SiON layer during heat treatment.

1. Introduction

Silicon carbide (SiC) has been regarded as a promising material for next-generation semiconductor electronics, because of its fundamental properties suited for high-power, high-frequency, and high-temperature electronics [1]. One of the great advantages making this semiconductor material more attractive is that the native oxide of SiC is SiO_2. The oxide can relatively easily be produced on SiC surfaces by dry or wet methods similar to those well established for Si processing technology. However, the density of interface states at the SiO_2/SiC interface is larger than that at the SiO_2/Si interface by one to two orders of magnitude [2]. Despite variety of pre- and post-oxidation treatments, substantial improvement of the interface has not yet been achieved [3,4]. Recently, as an alternative approach, we have realized the formation of an epitaxial silicon oxynitride (SiON) layer on 6*H*-SiC (0001) surface, which has a $(\sqrt{3}\times\sqrt{3})$R30° periodicity with respect to the substrate surface [5]. As a structure model, a hetero-double-layered structure consisting of a silicon oxide monolayer and a silicon nitride interfacial monolayer connected to the unreconstructed SiC substrate (Fig. 1) has been suggested based on a low-energy electron diffraction (LEED) analysis [5]. This model is free from dangling bonds in the unit cell and has an atomically abrupt interface.

After our first report [5], two first-principles calculation studies addressed the structural and electronic properties of this system [6–8]. Devynck et al. supported the structure model, and then derived energy band profiles across the SiON/SiC(0001) interface similar to those of a hypothetical abrupt SiO_2/SiC interface model [6,7]. We studied the band gap structures by using a combination of x-ray absorption/emission spectroscopy experiments and the first-principles calculations [9]. Krüger et al. also supported the structure model, and showed surface valence and conduction band structures of the SiON layer [8]. They showed derivations of the surface bands and found no mid-gap state between the substrate valence and conduction bands. Experiments on the band structure of the SiON layer have not been reported yet.

Since it is expected that the SiON layer might show great its potential as a passivation layer of the SiC surface in the SiC-based electronics, characterizing fundamental structural and electronic properties is an important starting step. In this article, the suggested structure model and valence-band electronic structure of the SiON/6*H*-SiC(0001) are investigated by using x-ray diffraction (XRD) and angle-resolved photoelectron spectroscopy (ARPES) experiments. In order to confirm the rather complex structure model (*cf.* Fig. 1) without ambiguity, we conducted the XRD structure analysis to which the simple single scattering theory can be applied. The atomic structure optimized by the XRD analysis well agrees with LEED analysis and the first-principles calculations. The ARPES experiments observed surface states very

* Corresponding authors. Shirasawa is to be contacted at Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan. Tel./fax: +81 4 7136 3371. Tochihara, Faculty of Engineering Sciences, Kyushu University, Fukuoka, 816-8580, Japan. Tel.: +81 92 583 7541; fax: +81 92 583 7039.
E-mail addresses: sirasawa@issp.u-tokyo.ac.jp (T. Shirasawa), tochihara.hiroshi.146@m.kyushu-u.ac.jp (H. Tochihara).

0039-6028/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2010.10.038

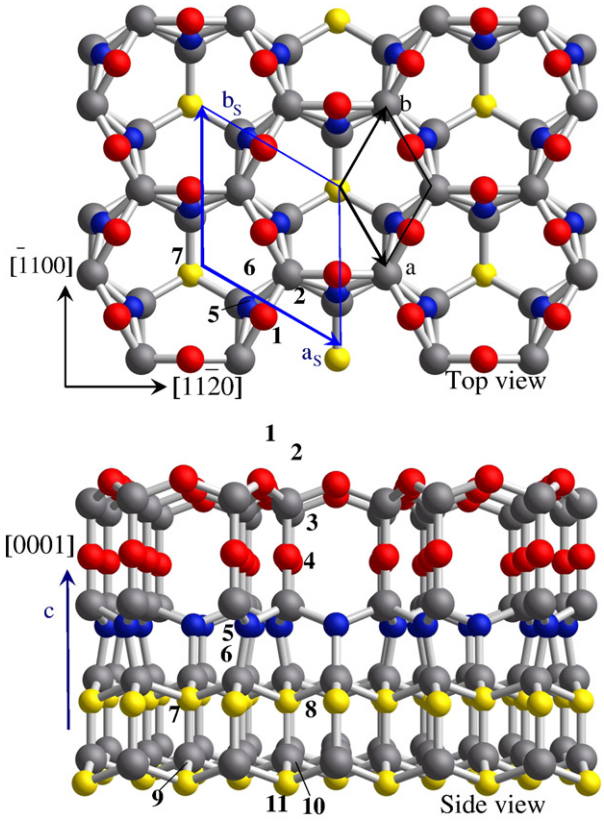

Fig. 1. Top and side views of the structure model of the SiON/SiC(0001). Basis vectors **a** and **b** for the (1×1) substrate surface, and $\mathbf{a}_s$ and $\mathbf{b}_s$ for the (√3×√3)R30° surface are indicated in the top view. Symmetrically inequivalent atoms in the (√3×√3)R30° unit cell are numbered.

similar to those obtained by the calculation. Mid-gap states intrinsic to the SiON layer were not observed, as predicted in the theories.

2. Experimental method

A nitrogen-doped off axis (4° off toward [11–20] direction) 6*H*-SiC (0001) wafer was used as the substrate of the SiON layer. The SiON layer was prepared with a hydrogen gas etching at 1350 °C for 15 min and a subsequent annealing in nitrogen atmosphere at the same temperature for 10 min. The off-axis substrate exhibits almost regular one-dimensional array of a basal (0001) plane (width of ~150 Å) and a bunch of steps after the treatment [10]. By using the off-axis substrate, almost the single domain SiON/SiC(0001)-(√3×√3)R30° structure was obtained. Details of the sample preparation are described elsewhere [5]. The quality of the sample was checked by LEED and scanning tunneling microscopy (STM) observations. Since the SiON layer is stable over a long time in air [5], the ex-situ prepared sample was used for XRD and PES measurements.

The XRD experiment was conducted at beamline 3A of the Photon Factory at KEK. The experiment was done in air. Since intensity and transverse width of the one-third order reflections from the SiON layer did not change during an experimental period of 5 days, crystallinity of the sample was not deteriorated during the experiment in air. The domain size of the SiON layer along the [1–100] direction, parallel to the steps, is ~1500 Å estimated from transverse profiles of the fractional order reflection spots. Along the [11–20] direction, perpendicular to the steps, the domain size falls to ~130 Å, due to the (0001) terrace width of ~150 Å limited by the bunched steps. We purposely used a relatively wide acceptance angle of the detector so as to fully receive the rather broad scattering distribution in the direction perpendicular to the steps, and measured integrated intensity with the sample rotation method. The intensity distribution along the [0001] direction was obtained for four symmetrically inequivalent fractional order reflection rods. The measured intensity was corrected by the Lorentz factor, reciprocal lattice rod intersection, and active sample area, after background subtraction.

The ARPES measurements were performed at beamline 18A of the Photon Factory at KEK. Core-level PES measurements were carried out at BL-27SU of the SPring-8. Both of the valence-band and core-level PES spectra were measured with a total energy resolution of ~100 meV and an angular resolution of ±1°. The scattering plane was parallel to the electric field of the linearly polarized incident photon beam. Fermi level (E_F) of the sample was determined by measuring the Fermi edges of metal sample holders. All the PES measurements were performed at room temperature under the pressure less than 10^{-8} Pa.

3. Results and discussion

3.1. Atomic structure investigation with XRD

The scattering amplitudes, square root of the measured intensities, of the fractional order rods along the [0001] direction are plotted in Fig. 2. The real space unit cell of the substrate, **a** = [1000], **b** = [0100], **c** = [0001] with **a** = **b** = 3.09 Å and **c** = 15.12 Å, is the criteria of the reflection indices *h*, *k*, and *l*. The scattering amplitude distribution in each rod shows broad main peaks separated from each other by Δ*l* ~ 4. Firstly, the scattering amplitudes were fitted with the structure factors calculated for a free-standing SiON layer, that is, substrate atoms were not displaced from the bulk positions to associate with the (√3×√3)R30° periodicity. Atomic positions and their isotropic Debye–Waller factors were used as the parameters in the least-squares fit. The fit was judged by the χ^2 value. The *p*31*m* symmetry was imposed on the atomic displacements. As the starting model, the atomic positions obtained by the LEED *I*–*V* analysis under the *p*31*m* symmetrical restriction were used (atomic coordinates in ref. [5] were the results under the *p*3 symmetry). The best-fit model gave the χ^2 value of 3.0. Resulting atomic positions show good agreement with those obtained by the LEED analysis within error ranges. The best-fit structure factors are plotted as dashed lines in Fig. 2. The calculated structure factors well reproduce the locations and heights of the main peaks of the experimental scattering distribution. Roughly speaking, the periodicity of the main peaks Δ*l* ~4 arises from the interference between the topmost O–Si layer and the interfacial Si–N layer. The height difference between the midpoints of each of these layers is 0.25 in the *c*-axis lattice unit.

Minor features seen in the measured curves, indicated by open circles in Fig. 2, could not be reproduced by the free-standing SiON layer. For further structural refinement, displacements of the substrate atoms were allowed in the fit. By taking two SiC bilayers into the fit, the minimum χ^2 value of 1.45 was achieved. The best-fit calculated structure factors plotted as solid lines in Fig. 3 reproduce the experimental data very well including the minor features. Displacing substrate atoms in further deep layers did not improve the fit. The fitted atomic coordinates in the SiON layer are the same as those obtained in the free-standing model within error ranges. Allowing displacement of atom positions under lower symmetries did not produce significant difference. The optimized atomic positions in the SiON layer are listed in Table 1, and the displacements of the substrate atoms from the bulk positions are in Table 2. In these tables, the atomic coordinates obtained by the LEED analysis and the first-principles calculations are given as well for comparison [8]. The results of the three different methods show good agreements, strongly supporting the structure model.

3.2. Valence-band electronic structure investigated with ARPES

ARPES spectra of the SiON/SiC(0001) taken at a photon energy of 50 eV and an incident angle of 45° are shown in Fig. 3. The spectra were recorded at emission angles from 0 to 43° along the $\overline{\Gamma M}$ direction in (b)