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Positron diffraction study of SiC(0 0 0 1) surface

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Abstract

Surface structures of 6H SiC(0 0 0 1) after heat treatment in a UHV has been studied using reflection high-energy positron diffraction (RHEPD). After heat treatment at 900 °C, a typical interference effect of positron waves due to Si adatoms appears in the total reflection region of the rocking curve. The further heat treatment at 1100 °C results in surface graphitization. The rocking curve is well reproduced by theoretical calculation assuming the graphite monolayer on SiC substrate. The interlayer distance is fairly large (2.5–3.2 Å), which is comparable to that in the graphite monocrystal suggesting that the weak binding of the graphite monolayer to the SiC surface by the van der Waals force.

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Keywords: Reflection high-energy positron diffraction; RHEPD; SiC(0 0 0 1); Total reflection

1. Introduction

Silicon carbide (SiC) is a promising wide band gap semiconductor for high power and high temperature devices. For growing high quality epitaxial layers and fabricating flat SiC–SiO_2 interfaces, it is important to prepare well-defined atomically flat surfaces. So far, high temperature hydrogen (H_2)- and hydrochloride (HCl)-etching techniques were established to obtain the atomically flat SiC surfaces [1,2].

Recent times, phase transitions of SiC(0 0 0 1) surface due to heating are extensively studied [3]. Either after high temperature H_2-etching or sacrificial oxidation plus HF dipping, SiC(0 0 0 1) surfaces exhibit a 1×1 periodicity. Upon heating at 900–1000 °C with and without in situ Si deposition, a $\sqrt{3} \times \sqrt{3}$-R30° periodicity appears [4]. This is explained in terms of Si adatoms at T_4 site with 1/3 ML coverage. By the further heating above 1000 °C, a $6\sqrt{3} \times 6\sqrt{3}$-R30°-like surface appears accompanying graphitization [5]. When this periodicity is observed by low-energy electron diffraction (LEED), the scanning tunneling microscopy (STM) image exhibits a 6×6 periodicity [6]. This discrepancy is explained

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as follows: The diffraction pattern looking like the $6\sqrt{3} \times 6\sqrt{3}$-R30° at first sight is not due to the reconstructed surface with such a periodicity and caused by the double diffraction from graphite monolayer on top of a SiC(0 0 0 1)–1 × 1 surface [7]. The STM 6 × 6 image is just a Moiré-pattern caused by the graphite monolayer and below it [8]. However, a recent STM study claims that the $6\sqrt{3} \times 6\sqrt{3}$-R30° periodicity can be observed when the tip bias voltage is low enough [3]. Thus, it is still in debates if the $6\sqrt{3} \times 6\sqrt{3}$-R30° periodicity originates from real reconstructed surface or just from graphite monolayer.

Reflection high-energy positron diffraction (RHEPD) has emerged as a powerful tool to investigate atomic structures and vibrational states associated with solid surfaces [9]. Total reflection of positrons at solid surfaces is very useful to analyze the topmost surface structures without any influence from the bulk using RHEPD [10]. In this research, we studied a series of irreversible change of 6H SiC (0 0 0 1) surface from 1 × 1, $\sqrt{3} \times \sqrt{3}$-R30° to $6\sqrt{3} \times 6\sqrt{3}$-R30° introduced by UHV heating.

2. Experiment

The samples used in this study were cut from a n-type modified-Lely grown 6H SiC(0 0 0 1) wafer doped with nitrogen. After the sacrificial oxidation at 1200 °C in a dry oxygen ambient for 4 h and dipping in HF (50%) for 20 min, a high temperature H_2-etching was carried out at 1450 °C in a chemical-vapor-deposition reactor. A well-flatten surface was obtained by this procedure. Subsequently, samples were transferred into a UHV chamber evacuated to a base pressure of 6×10^{-10} Torr. Surface flashing was conducted at 900 °C and 1100 °C for 10 min with an infrared lamp. From preliminarily reflection high-energy electron diffraction observations, a 1 × 1 and weak $\sqrt{3} \times \sqrt{3}$-R30° periodicities were found after H_2-etching and 900 °C annealing, respectively. After annealing at 1100 °C, graphitic patterns were observed and no clear $\sqrt{3} \times 6\sqrt{3}$-R30° periodicity. Using a 20 keV well-collimated positron beam, RHEPD experiments were carried out. Rocking curves were recorded below 4.0° with an angle step of 0.1° in a so-called one-beam condition (7.5°-off oriented from the $[1\,\bar{1}\,0\,0]$ direction) [11,12]. Based on the dynamical diffraction theory [13], the rocking curves were analyzed. To reveal the surface composition, the Auger electron spectroscopy (AES) measurements were also carried out using a PHI 10-155A cylindrical mirror analyzer system.

3. Results and discussion

Fig. 1(a–c) shows the experimental rocking curves obtained after H_2-etching and subsequent heating at 900 °C and 1100 °C. The rocking curves in the total reflection region dramatically change upon heating. After H_2-etching a small plateau is seen in the total reflection region. This vanishes due to heating at 900 °C and a distinct absorptive peak appears at around 1.3°. After heating at 1100 °C, a broad and complex peak structures appears. The series of transition of rocking curve indicates the change of surface structure upon heating.

As seen from AES spectra in Fig. 2, after H_2-etching, the O_{KLL} peak is identified in addition to Si_{LMM} and C_{KLL} peaks. After heating at 900 °C, the

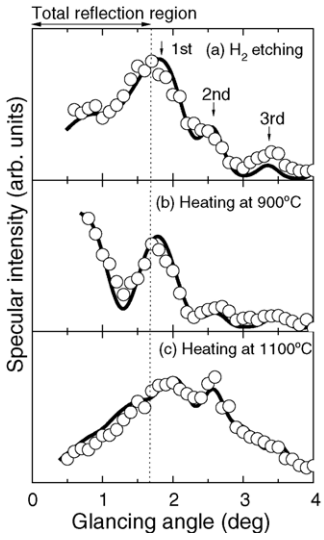

Fig. 1. Open circles denote the experimental RHEPD rocking curve (specular intensity vs. glancing angle plot) from 6H SiC(0 0 0 1) surfaces after (a) high temperature H_2-etching and subsequent heating at (b) 900 °C and (c) 1100 °C in one-beam condition. Solid lines represent the theoretical rocking curves simulated based on the dynamical diffraction theory using structural models in Fig. 3. Positions for the first to third Bragg peaks are also shown by arrows.

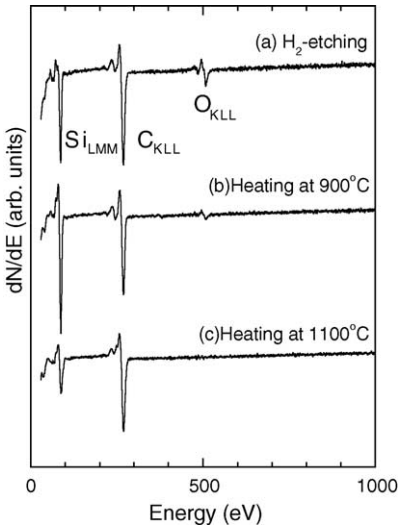

Fig. 2. AES spectra obtained after (a) high temperature H_2-etching and subsequent heating at (b) 900 °C and (c) 1100 °C.

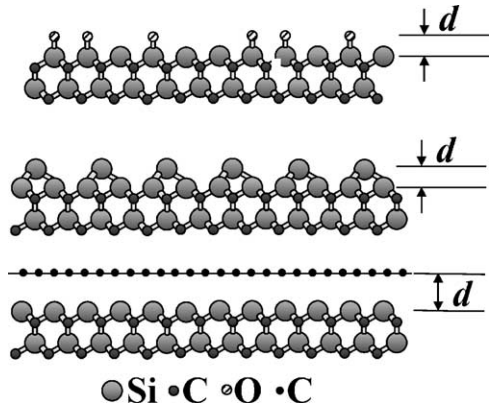

Fig. 3. Possible structural models of 6H SiC(0 0 0 1) surfaces formed after the high temperature H_2-etching and subsequent heating at 900 °C and 1100 °C; *d* denotes the interlayer distance between the topmost surface and the substrate.

O_{KLL} peak diminishes while the Si_{LMM} peak intensity increases. This phenomenon is commonly observed in the previous studies. Probably, a part of carbon atoms and/or hydrocarbon species are removed accompanying the sublimation of oxygen. Above 1000 °C, the Si_{LMM} peak intensity sufficiently decreases and the chemical shift of C_{KLL} peak due to graphitization appears. These results show the sublimation of Si atoms from the surface and subsequent graphitization.

After the high temperature H_2-etching the root mean square roughness was less than a few Å [1]. An ideally atomically flat surface should result in a monotonic increase of the specular intensity up to the first Bragg peak and no plateau structure in the total reflection region like in Fig. 1(a). Considering the oxygen adsorption shown from the AES measurements, the plateau is explained as the simple oxygen attachment on the surface [14].

The absorptive peak in the RHEPD rocking curve (Fig. 1b) observed after 900 °C heating is explicitly explained as the interference effect among positron waves diffracted from an adlayer and substrate below it. Previous STM study shows the formation of $\sqrt{3} \times \sqrt{3}$-R30°-ordered protrusions probably due to Si adatoms at T_4 site with coverage of 1/3 ML [4]. Thus, the absorptive peak in the rocking curve is most likely to originate from Si adatoms. To confirm this we examined the rocking curve based on the dynamical diffraction theory. The atomic positions below the second layers were assumed to be the same as those of the bulk here. The coverage of Si adatoms and the distance from the first layer are varied in the calculation so as to minimize the reliability factor *R*, which is defined as $R = \sqrt{\sum_\theta (I_\theta^{\mathrm{cal}} - I_\theta^{\mathrm{exp}})^2}$, where *I* denotes the normalized specular intensity. The solid line in Fig. 1 denotes the calculated rocking curve. The experimental rocking curve is well reproduced by calculation with the above model. The coverage of Si adatoms and the distance from the first layer are 0.2–0.3 ML and 1.7–1.9 Å, respectively. These are in good agreement with those obtained in the previous studies [3] (Fig. 3).

Considering the surface graphitization above 1000 °C, the dramatic change of the rocking curve shown in Fig. 1(c) is explained as the formation of a graphite layer. Indeed, as shown in Fig. 4, the calculated rocking curve systematically changes with graphite coverage and approaches the experiment. Minimizing the *R*-factor, the experimental rocking curve is well reproduced assuming 3 ML graphite monolayer and the interlayer distance from the substrate to be 2.5–3.2 Å. Probably, the previously proposed mechanism of graphitization, i.e., the collapse of three Si–C bilayers because of the sublimation of Si atoms, may be right. The above interlayer distance is close to that for the graphite

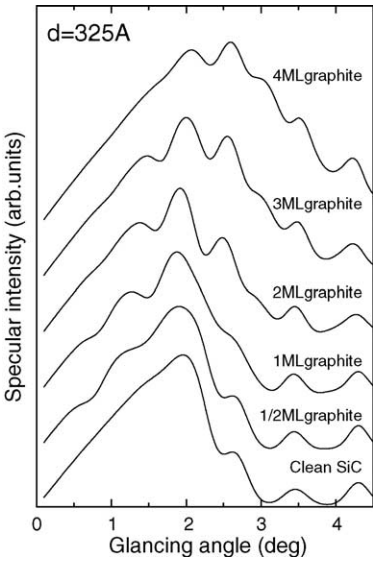

Fig. 4. RHEPD rocking curves from graphite layer plus 6H SiC(0 0 0 1) system at different graphite coverage in one-beam condition simulated based on the dynamical diffraction theory. The interlayer distance of the graphite layer from the substrate is fixed at 3.25 Å.

crystal. It is suggested that the graphite layer formed on the SiC(0 0 0 1) is weakly bound on it by the van der Waals force. The $6\sqrt{3} \times 6\sqrt{3}$-R30°-like periodicity is observed by LEED [5] when graphitization may be caused by the double diffraction from graphite monolayer on top of a SiC(0 0 0 1)–1 × 1 surface. The STM image with a 6 × 6 periodicity is explained as a Moiré-pattern caused by the graphite monolayer and below it [6]. The present RHEPD result is consistent with such an explanation.

4. Summary

We studied the phase transition of 6H SiC(0 0 0 1) surface upon UHV heating using RHEPD technique. The experimental rocking curves were analyzed based on the dynamical diffraction theory. The surface structure formed due to heating at 900 °C is described in terms of 1/3 ML Si adatoms. The further heating above 1000 °C generated a graphite monolayer on the surface with an interlayer distance from the substrate of approximately 3 Å.

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