Surface core-level shift photoelectron diffraction study of β-SiC(001)-c(2×2) surface

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Abstract

Surface core-level shift energy scan photoelectron diffraction (PED) was used to distinguish the two structural models of the C-terminated β-SiC(001)-c(2×2) surface under debate. An experimental PED curve of the surface C 1s component is in good agreement only with the simulated curve of the unusual bridge dimer model denying the conventional dimer model. The optimized structural parameters of this bridge dimer model are 1.22, 1.84 and 2.7 Å for the C–M, C–Si and Si–M bond lengths, respectively, in agreement with recent theoretical calculations. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Because of its unique thermal and electronic properties, silicon carbide (SiC) is expected to be a device material which can overcome restriction of silicon (Si) devices in terms of high thermal stability and breakdown voltage. Especially β-SiC is remarkable since it can be grown on a Si(001) substrate by the chemical vapor deposition (CVD) technique which can produce large area crystalline SiC films. Several surface phases were reported for β-SiC(001), such as (2×3), (2×1) and c(2×2) depending on the coverage of silicon [1]. For the carbon-terminated phase of c(2×2), structural analyses were reported by both experimental [1–5] and theoretical [6–11] methods. By Auger and electron energy loss spectroscopies, low-energy electron diffraction (LEED) and electron-stimulated desorption of H+ Bermudez and Kaplan [2] proposed a surface structural model for the c(2×2) phase, which has staggered rows of carbon dimer units, where each surface carbon atom bonds to two Si atoms beneath (Fig. 1a, called the SD model hereafter). On the other hand, by tensor LEED, Powers et al. [3] proposed an unusual surface model terminated by a staggered array of carbon dimers in the silicon bridge site (Fig. 1b, called the BD model hereafter). Although several theoretical studies [6–11] were also performed for these two models, the c(2×2) surface structure is still controversial. Recently, a near edge X-ray adsorption fine structure (NEXAFS) study by Long et al. [4] supported the BD model, however, more direct structural information is necessary for the unambiguous determination of such an unusual surface structure.

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In this paper, we report surface core-level shift (SCLS) photoelectron diffraction (PED) study of a β-SiC(001)-(2×2) surface, where the experimental data of surface and bulk C 1s levels are compared with full multiple scattering simulations [12] for the two models.

2. Experimental

High-resolution SCLS-PED measurements were performed on the soft X-ray photoemission beamline 9.3.2 at Advanced Light Source synchrotron radiation facility in Berkeley, USA. The details of the instruments have been explained elsewhere [13]. The high-quality (2×2) LEED pattern was observed after annealing a CVD grown 3C-SiC thin film at 1180°C in ultra-high vacuum as described before [5]. The C 1s spectra were taken for normal emission and 45° off-normal emission (along the [110] direction, see Fig. 1) from the photoelectron wavenumber \( k (\text{Å}^{-1}) = 3.5 \) to 8.3 with a step of \( \Delta k = 0.1 \text{ Å}^{-1} \) by varying the incident photon energy. Typical spectra are shown in Fig. 2a and b. Each spectrum was decomposed through a standard curve fitting procedure to two major components: one bulk and one surface component as indicated by B and S, respectively, in Fig 2a and b. This decomposition and the energy separation between B and S of 1.1 eV are in good agreement with previous results [2-5]. The intensity of each component as a function of the photoelectron wavenumber \( k \) was converted to the so-called \( \gamma \) function \( \gamma = (I - I_0)/I_0 \), where \( I \) and \( I_0 \) are the intensity and its smooth background, respectively [12]. The experimental \( \gamma \) functions are then compared with the full multiple scattering simulations [12]. We assumed a cluster radius of 8.5 Å in the simulations, which includes over 200 atoms. \( R \)-factor analyses were done by the conventional method previously used in energy scan PED study [14].

3. Results and discussion

Before analyzing the PED of C 1s surface component, the experimental PED \( \gamma \) functions of the bulk component B were compared with those simulated using a cluster with the ideally bulk

In addition, the $\gamma$ function is sensitive to the structural parameters in this geometry because of strong backscattering from the Si atoms in the second layer.

Fig. 2c–e shows the $\gamma$ function of the S component for 45° off-normal emission. Simulated curves using the SD (Fig. 1a) model and the BD (Fig. 1b) model are shown as gray thick lines in Fig. 2c and d, respectively. Structural parameters predicted by ab initio total energy calculations [10] were used in these trial simulations. It is found that the simulated curve of the BD model (Fig. 2d) agrees with the experimental curve while that of the SD model (Fig. 2c) is substantially different from the experimental curve. For the normal emission (not shown here), the agreement between the experimental curve and the simulated curve of the BD model is also apparently better than that of the SD model. The $R$-factors ($R_m$) for the SD model and the BD model for 45° normal emission are 1.27 and 0.21 (1.44 and 0.44), respectively. The $R$-factors of the BD model are obviously smaller than those of the SD model, suggesting the unlikelihood of the SD model. Since further optimization of the structural parameters in the SD model in the top and second layers ($l_1$, $l_2$ as in Fig. 1) may affect the $\gamma$ functions, these parameters were varied within expectable ranges.

Fig. 2. Examples of typical photoemission spectra and their curve fittings (a, b). The experimental (dots with thin solid lines) and simulated (thick gray lines) $\gamma$ functions (c–e). The simulated curves c, d and e are for the SD model, the BD model and the BD model using optimized parameters, respectively. Therefore, it is unambiguous that the SD model is not appropriate as the structure of the $\text{c}(2 \times 2)$ surface. After optimizing variable parameters of the simulations besides structural parameters, the simulated curves are in good agreement with the experimental curves (not shown here, $R_m = 0.05$). These non-structural parameters, such as Debye and sample temperatures of 500 K and 300 K, respectively, are used in the following simulations for the surface components.

For the following two reasons, we used only 45° off-normal data for the detailed structural analyses. First, the intensities of the surface component for normal emission PES spectra are rather weak, making the experimental uncertainty in PED $\gamma$ functions quite large. For 45° off-normal emission, on the other hand, the intensities of the surface component were large enough to separate it from the bulk component precisely. In addition, the $\gamma$ function is sensitive to the structural parameters in this geometry because of strong backscattering from the Si atoms in the second layer.

The structural parameters of the BD model were then optimized using the 45° off-normal data. The value of $R_m$ as a function of bond length ($l_1$, $l_2$, see Fig. 1) is shown in Fig. 3. The lengths $l_1$, $l_2$ and $l_3$ give the minimum $R_m$ value at 1.22 ± 0.05 Å, 1.84 ± 0.02 Å and 2.7 ± 0.1 Å, respectively. These values are listed in Table 1 with the bond lengths in previous studies, i.e. tensor LEED study [3] and the ab initio calculation [10]. In our study, each uncertainty was estimated by the deviation of the $R$-factor value from the least square fitted curve shown in Fig. 3 and the curve shape at the minimum. The simulated curve using these optimized parameters is shown in Fig. 2e. The distinctive dip seen in the figure at $k = 4.5$–5.0
Table 1

Comparison of bond lengths (Å) optimized by the present PED and those in previous studies for the BD model. LEED(1) and LEED(2) are those for the samples with Si sublimation and \( \text{C}_2\text{H}_4 \) exposure, respectively.

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>This work</th>
<th>LEED(1)</th>
<th>LEED(2)</th>
<th>Ab initio calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l_1 )</td>
<td>1.22</td>
<td>1.31</td>
<td>1.25</td>
<td>1.22</td>
</tr>
<tr>
<td>( l_2 )</td>
<td>1.84</td>
<td>1.93</td>
<td>1.86</td>
<td>1.87</td>
</tr>
<tr>
<td>( l_3 )</td>
<td>2.7</td>
<td>2.71</td>
<td>3.09</td>
<td>2.40</td>
</tr>
</tbody>
</table>

The optimized value of \( l_1 \) is very close to the triply bonded C–C length, in contrast to the doubly bonded length suggested by tensor LEED [3] as listed in Table 1. This supports the result by NEXAFS in which two types of unoccupied \( \pi \) bonds have been observed [4] as well as the calculations [6,9,10]. In the paper of the tensor LEED study [3], two different procedures of sample preparation, i.e. Si sublimation as in this study and \( \text{C}_2\text{H}_4 \) exposure, cause different bond lengths. However, in a recent STM study of the \( c(2 \times 2) \) surface, it is found that both procedures give the same STM images [15]. This may suggest that the atomic arrangement was the same for the two samples. However, the surface condition, for instance amount of defects, was slightly different for samples with different procedures. This might have caused the different values for optimized geometries in the tensor LEED study [3]. The optimized values of \( l_1 \) by PED and LEED [3] indicate that Si–Si dimers of the \( c(2 \times 2) \) surface are much more elongated than the dimers on the Si(001) \( 2 \times 1 \) surface. A notable difference in \( l_3 \) among this work, LEED and the ab initio calculations is to be studied further.

4. Conclusions

The SCLS energy scan PED was used to determine the structure of C-terminated \( \beta\text{-SiC}(001) \) \( c(2 \times 2) \) surface. Photoemission spectra of the C 1s core level were decomposed into two major components: one from the bulk C and the other
from the surface C layer. The intensities of these components as a function of the kinetic energies of photoelectrons were measured and compared with full multiple scattering simulations for the two structure models under debate. The experimental energy scan PED curves are in good agreement only with simulated curves for the model with surface C atoms in an unusual bridge structure. Structural parameters of this bridge dimer model are optimized as $1.22 \pm 0.05$, $1.84 \pm 0.02$, and $2.7 \pm 0.1 \text{Å}$ for C—C, C—Si, and Si—Si bond lengths, respectively.

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References