Surface reconstructions of 3C-SiC(001) studied by high-resolution core-level photoemission

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Abstract

The different surface reconstructions of the 3C-SiC(001) surface have been systematically studied by high-resolution core-level photoemission spectroscopy. For the Si-rich 3×2 surface, three different Si 2p surface components are clearly identified supporting the structure model with 1 ML of Si ad-dimers. It is confirmed that the c(2×2) and 2×1 surfaces are respectively C- and Si-terminated by observing a single dominant surface component in the C 1s or Si 2p spectra with binding energy shifts of 1.04 eV and ~0.50 eV respectively relative to the bulk component. The atomic origins of these surface core levels are assigned and the core-level shifts are compared with previous measurements and recent theoretical calculations. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Low index single crystal surface; Silicon carbide; Soft X-ray photoelectron spectroscopy (using synchrotron radiation); Surface relaxation and reconstruction

Our recent high-resolution core-level study on the 3×2 surface has revealed three surface Si 2p components with an intensity ratio of ~2:2:1.

Owing mainly to its technological potential in high temperature, high power, high voltage and high frequency device applications, much attention has been paid to the surface properties of SiC crystals grown by chemical-vapor-deposition. SiC surfaces also have interesting properties as the surfaces of a unique group IV–IV compound semiconductor, which exhibit a polar character and intriguing surface reconstructions. Among various polytypes of SiC, the cubic 3C-SiC(001) surface has been one of the most extensively studied surfaces. This surface exhibits three major surface phases, c(2×2), 2×1 [or c(4×2)] and n×2, for a review, see Ref. [1]. The c(2×2) and 2×1 surfaces are known to be terminated by 1 ML of C and Si atoms respectively. On the other hand, the Si-rich surface shows the n×2 (n=3, 5, 8, 9) reconstructions, whose structural building blocks are believed to be identical [1-4]. However, the detailed structures of these surface reconstructions are under debate [1]; for a review of the theoretical considerations of the different surface reconstructions, see Ref. [2].

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which unambiguously confirms the structure model with 3 ML of Si ad-dimers [5]. In this report, we present a systematic high-resolution Si 2p and C 1s photoelectron spectroscopy investigation of the 3 × 2, 2 × 1 and c(2 × 2) surfaces at ~120 K at a photon energy $h\nu$ of 130 eV (dots) and 118 eV (solid lines). The electron emission angles $\theta_e$ from the surface normal are 50° (dots) and 0° (solid lines). Si 2p\(_{3/2}\) peak positions are indicated for the different components assigned (see text).

Fig. 1 shows the Si 2p spectra taken at 120 K for the 3 × 2, 2 × 1 and c(2 × 2) surfaces with a photon energy $h\nu$ of 130 eV at an emission angle $\theta_e$ of 50° for the highly surface-sensitive measurements and with $h\nu$ = 118 eV at normal emission for bulk-sensitive measurements [5]. These spectra are aligned by the peak position of the bulk component B in order to compensate the overall shifts due to the different band bendings of the different surface phases and due to the surface photovoltage effect.

As reported previously, for the 3 × 2 surface three different surface components (S1, S2 and S3) are identified at lower binding energy than the bulk component (surface core-level shifts) are −0.58 eV, −0.92 eV and −1.27 eV respectively [5]. By annealing at ~1150 °C, a series of clear low-energy electron-diffraction (LEED) patterns were obtained.

Fig. 1. Si 2p photoelectron spectra for the 3C-SiC(001) 3 × 2, 2 × 1 and c(2 × 2) surfaces at ~120 K at a photon energy $h\nu$ of 130 (dots) and 118 eV (solid lines). The electron emission angles $\theta_e$ from the surface normal are 50° (dots) and 0° (solid lines). Si 2p\(_{3/2}\) peak positions are indicated for the different components assigned (see text).

Fig. 2. Decompositions of the Si 2p photoelectron spectra for the 3C-SiC(001) (a) 3 × 2, (b) and (c) c(2 × 2), and (d)–(f) 2 × 1 surfaces. Each surface component is indicated with different hatching. The results of fitting overlap the experimental data.

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The $2 \times 1$ surface is formed by sublimating the Si ad-dimer layer at $\sim 1150 \, ^\circ C$ from the $3 \times 2$ surface [1]. The Si 2p spectra for the $2 \times 1$ surface exhibit a rather broad structure at a lower binding energy than B (Fig. 1). Decompositions of these spectra (Fig. 2d-f) show a dominant surface component $S$ with an energy shift of $-0.50 \, eV$. $S$ has a Gaussian width (GW) of 0.60 eV (full width at half maximum), which is significantly larger than for the surface components of the $3 \times 2$ surface (0.38 eV [5]). The $S$ component is obviously due to the Si atoms of the termination layer, which are believed to form symmetric dimers. The core-level shift of $S$ is very similar to that of $S1$ of the $3 \times 2$ surface. This is naturally explained by the similar chemical environments of the Si surface atoms of the $2 \times 1$ surface and the second-layer Si atoms of the $3 \times 2$ surface represented by $S1$: two bonds with C atoms beneath, one bond with other Si atoms and one dangling bond. The broadening of $S$ could be due to the increased number of defects, as discussed below, and/or the local fluctuation of the Si dimer height [6].

In addition to $S$, two other minor structures are observed in the broad tail on the low binding energy side, denoted $S'$ and $D'$, with surface core-level shifts of $-0.96$ and $-1.50 \, eV$, respectively. From the binding energy and intensity, $D'$ may be related to the similar component $D$ of the $3 \times 2$ surface, which has been assigned to surface defects [5]. The intensity of $S'$ is $7-20\%$ of that of the $S$ component and its core-level shift coincides with that of the Si ad-dimer component $S2$ of the $3 \times 2$ surface. This leads us to assign $S'$ as due to Si ad-dimers remaining on the $2 \times 1$ surface. The presence of Si ad-dimers on the $2 \times 1$ surface can be expected from the fact that the sublimation of the Si ad-dimer layer is not a self-limited process.

The previous Si 2p studies [7,8] on the $2 \times 1$ surface observed two different surface components with core-level shifts of $-0.5$ and $-1.4 \, eV$. From the shifts and line shapes, these components are unambiguously related to $S$ and $D'$. The $S'$ component was not observed in the previous studies probably due to the limited resolutions. Although these studies agree in the assignment of the major component ($S$) as being due to the surface Si atoms of the $2 \times 1$ lattice, the interpretation of the other components $D'$ has been uncertain. One of the previous studies observed an intriguing behavior of the $D'$ component for the surfaces prepared in different ways [7]. This behavior may be understood from the defect origin of $D'$ as being due to the different defect densities for different preparation methods. However, the conclusive assignment of the atomic origin of $D'$ must await a more detailed study including that of the well-ordered $c(4 \times 2)$ surface. Such a study is also expected to help in the understanding of the structural relationship between the $2 \times 2$ and the $c(4 \times 2)$ surfaces. A recent ab initio calculation of the Si 2p surface core-level shifts of the $2 \times 1$ surface has reported surface core-level shifts of $-0.9$ and $-1.4 \, eV$ for the Si atoms in the termination layer and for the Si ad-dimers respectively [9]. Although this trend of shifts is qualitatively consistent with the present results, the calculation apparently overestimates the shifts by 0.4-0.5 eV for both components.

The Si 2p spectra for the $c(2 \times 2)$ surface (Figs. 1 and 2b and 2c) exhibit a bulk component and two very small components $SS$ and $SS'$ with shifts of $-0.50 \, eV$ and $0.40 \, eV$ respectively. From the binding energy, it is reasonable to assign $SS$ to the remaining Si atoms on top of the C termination layer as being due to incomplete sublimation. $SS'$ shows less surface sensitivity than $SS$ and its origin is unclear at this stage. However, it is evident that there are no surface Si atoms intrinsic to the $c(2 \times 2)$ phase, since the observed surface components have only negligible intensities.

Similar high-resolution measurements were also performed for the C 1s core levels at photon energies of 330 and 500 eV for the $2 \times 1$ and $c(2 \times 2)$ phases respectively. As previously discussed, the C 1s spectra for the $3 \times 2$ surface have essentially a single bulk component [5]. The C 1s spectra of $2 \times 1$ and $c(2 \times 2)$ phases are shown in Fig. 3 together with their decompositions. For the $c(2 \times 2)$ surface (Fig. 3a), we find an intense surface component $c$ and two very weak components $c$ and $d$. These two minor components $c$ and $d$ can hardly be due to the intrinsic building blocks of the $c(2 \times 2)$ reconstruction owing to their small intensities. They may stem from surface defects or the subtle asymmetry of the C 1s spectra observed for the $3 \times 2$ surface. A recent scanning tunneling microscopy (STM) study on the $c(2 \times 2)$
The C 1s spectra of the 2 × 1 surface (Fig. 3b) show a small surface component \( s \), which has the same core-level shift as \( s \) of the c(2 × 2) surface. This suggests that the 2 × 1 surface prepared in the present study has some local areas with the c(2 × 2) structure. We have shown above that this 2 × 1 surface also has an excess of Si atoms. The coexistence of extra Si atoms and the c(2 × 2) areas, together with the major 2 × 1 domains, may be intrinsic to the Si sublimation process from the Si-rich surface. This may partly explain the broad Si 2p surface component and the relatively diffuse LEED pattern of the 2 × 1 surface. It has been noted that a well-ordered Si-terminated surface is formed only with the additional Si dose, which leads to a c(4 × 2) surface instead of 2 × 1 [1,6,7].

Fig. 3. C 1s photoelectron spectra and their decompositions for the 3C-SiC(001) (a) c(2 × 2) and (b) 2 × 1 surfaces at \( \sim 120 \) K at photon energies \( h\nu \) of 330 eV for surface-sensitive (top) and 500 eV for bulk-sensitive (bottom) measurements. Spectra were collected in normal emission. The results of fitting overlap the experimental data.

The dominant surface component \( s \) with a core level shift of 1.04 eV is naturally attributed to the surface C dimers. This assignment and the core-level shift is in good agreement with a previous report on the c(2 × 2) surface prepared by \( \text{C}_2\text{H}_4 \) exposure [1]. This seems to exclude the presence of two different c(2 × 2) structures for the surfaces prepared by annealing or \( \text{C}_2\text{H}_4 \) exposure [1,12]. A recent STM study corroborates this conclusion [10,11]. From these C 1s spectra, we also rule out the possibility of the significant graphitization of the surface by the high temperature annealing used. At present there exist two contradictory structure models of the c(2 × 2) reconstruction that have 1 ML of C dimers in common [1]. Since both models have a unique site of C surface atoms, the present C 1s core-level result cannot distinguish these two models. A photoelectron diffraction study is underway to extract quantitative structural information from the surface component \( s \). In quantitative discrepancy to the present result, an ab initio calculation reported surface core-level shifts of 0.44–0.48 eV for the c(2 × 2) surface [12].

The C 1s spectra of the 2 × 1 surface (Fig. 3b) show a small surface component \( s \), which has the same core-level shift as \( s \) of the c(2 × 2) surface. This suggests that the 2 × 1 surface prepared in the present study has some local areas with the c(2 × 2) structure. We have shown above that this 2 × 1 surface also has an excess of Si atoms. The coexistence of extra Si atoms and the c(2 × 2) areas, together with the major 2 × 1 domains, may be intrinsic to the Si sublimation process from the Si-rich surface. This may partly explain the broad Si 2p surface component and the relatively diffuse LEED pattern of the 2 × 1 surface. It has been noted that a well-ordered Si-terminated surface is formed only with the additional Si dose, which leads to a c(4 × 2) surface instead of 2 × 1 [1,6,7]. The additional C 1s component \( \alpha \) is thought to be due to the asymmetry of the bulk component, as discussed for the 3 × 2 surface [5].

In summary, high-resolution Si 2p and C 1s photoemission studies were performed for the 3 × 2, 2 × 1 and c(2 × 2) phases of the 3C-SiC(001) surface. The Si-rich 3 × 2 surface shows three Si 2p surface components, which are attributed to the three different surface Si atoms of the 3 × 2 surface reconstruction with 1/2 ML of Si ad-dimers. This assignment is also corroborated by the changes of the Si 2p line shape due to formation of the H-adsorption-induced 3 × 1 phase [13]. One relatively broad Si 2p surface component is observed for the Si-terminated 2 × 1 surface, which originates from the surface Si dimers. The C 1s and Si 2p spectra for the 2 × 1 surface suggest that this surface has both extra Si and the c(2 × 2) areas locally. The c(2 × 2) surface exhibits Si 2p spectra with essentially a single bulk component and the C 1s spectra with a dominant surface component representing the surface C dimers. The Si 2p and C 1s spectra for the c(2 × 2) and 2 × 1 surfaces do not provide crucial information for clarifying their surface structures. The available surface core-level shift calculations have large quantitative discrepancies with the present measurements.

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References