Site-Specific Stereograph of SiC(0001) Surface by Inverse Matrix Method

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The 2π-steradian (full hemisphere) Si 2p and C 1s photoelectron intensity angular distributions (PIADs) of the 6H-SiC(0001) surface 4° off towards the [1100] direction were measured. In a bulk crystal, pairs of mirrored local atomic sites with respect to the [1100] planes exist. Thus, a sixfold symmetry is expected for PIADs from the bulk. However, all the measured PIADs showed a threefold symmetry owing to the preferential appearance of terraces with one type of local atomic site caused by anisotropic step bunching along the [1120] direction. Taking the finite inelastic mean free path of photoelectrons into account, PIADs for one kind of Si and C atomic sites were successfully derived by solving an inverse matrix. Three strong forward focusing peaks due to nearby Si and C atoms have been separated from those formed by farther atoms. They showed a circular dichroism of rotational shift around the incident-light axis, which corresponds to the parallax in stereo viewing.

KEYWORDS: SiC, forward focusing peak, photoelectron diffraction, stereo atomscope, crystal structure

A photoelectron from a localized core level is an excellent probe for element-specific atomic structure analysis.1,2) Atoms in different chemical environments can be distinguished using core level shifts.3) Furthermore, forward focusing peaks (FFPs) appearing in photoelectron intensity angular distribution (PIAD) indicate the directions of surrounding atoms seen from the photoelectron emitter atom.4,5) Therefore, FFPs from inequivalent sites appear in different directions. Consequently, the occupation site of a photoelectron emitter atom can be determined. Thus, FFP is a good probe for investigating the atomic properties of local atomic sites.6–9) This is also valid even in the case where no core level shift is present. For example, Kato et al. have revealed that a boron dopant in chemical-vapor-deposition grown superconducting diamond (111) films has a preferential occupation site on the base of their FFP intensity analysis.10)

Hexagonal SiC is composed of pairs of mirrored local atomic sites owing to periodic stacking faults. However, in the case of a vicinal surface tilted toward the (1100) direction, the anisotropic step bunching along (1120) direction occurs at the surface and leads to the preferential appearance of terraces with one type of local atomic site. Thus, a threefold symmetry is expected for PIADs from such surfaces.

We have measured 2π-steradian Si 2p and C 1s PIADs from the 6H-SiC(0001) surface. All the measured PIADs showed a threefold symmetry. Here, we report a new algorithm for separating site-specific PIADs without using chemical shifts of core levels. Taking the finite inelastic mean free path of photoelectrons into account, PIADs for one kind of Si and C atomic sites were successfully derived by solving an inverse matrix. Three strong FFPs due to nearby Si and C atoms have been separated from those formed by farther atoms.

Moreover, the three FFPs showed a circular dichroism of the rotational shift around the incident-light axis, which corresponds to the parallax in stereo viewing.10–12) We discuss the derived site-specific PIADs in conjunction with the atomic arrangement of the SiC(0001) surface.

The experiments were performed at the circularly polarized soft-X-ray beamline BL25SU of SPring-8, Japan.13) PIAD from the sample is most efficiently measured using a two-dimensional display-type spherical mirror analyzer (DIANA).14–16) which enables the measurement of a two-dimensional angular distribution snapshot of specific kinetic energy electrons.7–12) Light was incident from the direction 45° inclined from the analyzer center. Photoelectrons emitted from the sample are energy-analyzed and PIAD is projected onto a fluorescent screen with the emission angle preserved. The acceptance angle of the analyzer is ±60°.

The 6H-SiC(0001) surface covered with a thin SiON film was loaded into an ultrahigh-vacuum chamber and mounted on a five-axis manipulator.17) The surface was tilted toward the [1100] direction by 4°. No further treatment was applied. In the present case of normal incidence (θin = 0°), the emission angle (θout) dependence from 0 to 90° relative to the surface normal is measured simultaneously. A 2π-steradian PIAD was obtained by scanning the sample azimuth for 360°.18,19) The helicity (σ±) of monochromatized circularly polarized soft X-ray was reversed by switching the path of storage ring electrons in twin helical undulators at 0.1 Hz.20) The total acquisition time for a pair of 2π-steradian PIADs excited by σ+ and σ− helicity lights was 1 hr. All the data were measured at room temperature.

The [0001] direction at the center of PIAD matches the sample rotation axis. Whether the surface orientation is a Si face or a C face can be easily confirmed by comparing (0001) FFP profiles. However, the raw data were self-normalized by their polar angle intensity profile obtained by averaging their azimuthal intensity variations. The inhomogeneity of the detector can be removed in this normalization process but the information on both the [0001] peak and the diffraction rings around it is suppressed. Hereafter, [0001]-related photoelectron structures are not included in the following discussion.
Figures 1(a) and 1(b) show the set of $2\pi$-steradian Si 2p PIADs from the 6H-SiC(0001) surface with photoelectron kinetic energies of 800 and 600 eV, respectively. Figures 1(c) and 1(d) are the same as (a) and (b), respectively, but for the C 1s core level. PIADs obtained by both helicity excitations are summed.

In a bulk crystal, pairs of mirrored local atomic sites with respect to the {1100} planes exist. The chemical environments surrounding each site are equivalent. Hence, sixfold symmetric PIADs are expected for the bulk crystal. Kikuchi-band-like features in {1120} planes forming sixfold symmetric patterns were observed, however, together with threefold symmetric fine structures, as indicated by red and blue marks. This is due to the anisotropic step bunching along the [1120] direction and the preferential appearance of terraces with one type of local atomic site.\(^{21}\) Figure 2(a) shows the cross section of the 6H-SiC(0001) surface with steps along the [1120] direction. Stacking faults occur at the layers c and f. Figure 2(b) shows a top view of terraces close to steps. The anisotropic step bunching originates from the fact that the step energies are different between layers a–c and d–f.\(^{21,22}\)

Figure 2(c) shows the atomic arrangements around two different Si and C atom sites α (layers a, b, and c) and β (layers d, e, and f) within three nearest-neighbor layers. The observed PIAD $P_{\text{obs}}$ from the 6H-SiC(0001) surface is considered to be composed of the contributions of two types of PIADs, $P_{\alpha}$ and $P_{\beta}$, from these atomic sites. According to Shirasawa’s model, this is terminated by a SiO$_x$ overlayer with N atoms at the interface.\(^{15}\) The effect of Si within a SiO$_x$ layer on the following analysis is neglected since FFPs from the outermost Si atoms hardly disturb the PIAD patterns from the underlying Si atoms.

The inelastic mean free path lengths in SiC estimated by Tanuma et al.’s formula are 1.57 and 1.93 nm for 600 and 800 eV, respectively.\(^{23}\) Considering a finite inelastic mean free path $\lambda$ and the thickness of a triple bilayer ($d = 0.7545$ nm). Note that the $\beta$-site PIAD $P_{\beta}$ is equivalent to the $180^\circ$-rotated $\alpha$-site PIAD $P_{\alpha}$ multiplied by the intensity decay factor:

$$P_{\beta} = \frac{P_{\beta}}{1 - c_2(\theta)} = \frac{c_1(\theta)P_{\alpha}^\pi}{1 - c_2(\theta)} = c_1(\theta)P_{\alpha}^\pi.$$

The measured PIAD $P_{\text{obs}}$ as well as its $180^\circ$ rotation $P_{\text{obs}}$ has been decomposed into two PIADs $P_{\alpha}$ and $P_{\beta}$:

$$\begin{align*}
P_{\alpha}^\text{obs} &= \left( \frac{1}{c_1(\theta)} \right) P_{\alpha}^\pi, \\
P_{\beta}^\text{obs} &= \left( \frac{1}{c_1(\theta)} \right) P_{\beta}^\pi.
\end{align*}$$

The site-specific PIAD $P_{\alpha}$ is derived by solving an inverse matrix. α-Site-specific $2\pi$-steradian Si 2p and C 1s PIADs derived from the 6H-SiC(0001) surface are shown in Fig. 3. Threefold symmetry operation (C$_3$) is applied. Highly symmetric planes are indicated by dotted lines and arcs. Open circles indicate the directions of crystal axes. For convenience, Miller indices are also used to indicate local interatomic directions, as shown in Fig. 2(d).

Three kinds of bright FFPs were observed at {110} (Si$_1$), {001} (Si$_2$), and {112} (Si$_3$) in 2p PIADs. Less intense and broad FFPs were observed in the {131} (C$_1$–C$_3$) directions. Moreover, diffraction rings were observed around the {110} directions. The radii were about 27.0 for the first order and 42.9 for the second order at a kinetic energy of 800 eV.

On the other hand, three kinds of FFPs were observed in the {111} (Si$_1$), {001} (C$_3$), and {131} (Si$_3$) directions in C 1s PIADs. Diffraction rings were observed around the {001} directions. The radius was about 23.9. The radii of diffraction rings roughly coincide with calculated values, as in the case of the Si(001) surface.\(^{19}\)

As mentioned earlier, {1120} Kikuchi-band-like features were observed in the PIADs shown in Fig. 1. However, after the separation procedure into a single-site component, the overlapping FFPs have been resolved. It turned out that the Kikuchi-band-like features almost disappeared and are more likely due to the superposition of FFPs from mirrored atomic sites in this kinetic energy range.

Finally, we move on to the examination on circular dichroism. The FFP directions from the emitter to the scatterers in the PIADs obtained by different helicity lights rotate around the incident light axis. The rotation angle $\Delta\phi$ is well described by Daimon’s formula:

$$\Delta\phi = \tan^{-1} \left( \frac{m}{kR \sin^2 \theta_{\text{out}}} \right),$$

where $m$ and $k$ are the magnetic quantum number and the wave number of photoelectron, respectively. $R$ is the interatomic distance between the emitter and scatterer atoms, $\theta_{\text{out}}$ is the angle between the incident photon direction and the outgoing direction of the emitted photoelectrons. In general, the effective magnetic quantum number $m^*$ considering the contribution of the transition probability from different $m_{\text{core}}$ initial states at a particular angle is used.\(^{10}\) In the case of C 1s excitation, $m^*$ is 1;\(^{12}\) it depends on the polar angle in the case of Si 2p.\(^{19}\)
Figures 4(b) and 4(c) show the site-selective circular dichroism patterns for Si 2p and C 1s core levels, respectively. PIADs excited with $/C_27^+\text{/C}_0$ and $/C_27^-\text{/C}_0$ helicity lights are displayed as red and blue, respectively, and superimposed. Threefold symmetry operation ($/C_3$) is applied individually for each helicity excitation. PIADs with a photoelectron kinetic energy of 600 eV are shown here, which is the case where the rotational shifts are larger. The direction of the surrounding atoms shown in Fig. 4(a) is plotted using open circles. In the case of Si 2p PIAD, the rotational shifts of

Fig. 1. (Color) (a)–(d) 2π-steradian Si 2p and C 1s photoelectron intensity angular distributions (PIADs) of 6H-SiC(0001) surface tilted toward [1100] direction by $4^\circ$. They are displayed in stereo projection. Dotted lines in (a) indicate {1120} planes. Red and blue marks in (d) emphasize the three-fold symmetry.

Fig. 2. (Color) (a) (1120) cross section of 6H-SiC(0001) surface with steps along [1120] direction. (b) Close look at the vicinity of step indicated as a hatched region in (a). (c) Atomic arrangements around two different Si and C atom sites. (d) Miller indices are used together with Miller-Bravais indices for defining directions in the local structure.

Fig. 3. (Color) (a)–(d) Site-specific 2π-steradian Si 2p and C 1s PIADs from 6H-SiC(0001) surface. Dotted and dashed curves indicate the {110} and {001} planes. The open orange and blue circles indicate the directions of the observed Si and C forward focusing peaks, respectively.

Fig. 4. (Color) (a) Atomic configurations and corresponding directions of surrounding atoms. Site-selective stereographs of atomic arrangement around (b) Si and (c) C atoms. PIADs excited by $\sigma_+$ and $\sigma_-$ helicity light are indicated by red and blue, respectively.
FFPs for C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3} ($\Delta \varphi = 2.70^\circ$), and Si\textsubscript{1} (4.36$^\circ$) are well reproduced by simulation. Those of C\textsubscript{4}, Si\textsubscript{3}, and Si\textsubscript{2} FFPs differ from those reproduced by simulation owing to the effects of overlapping S\textsubscript{2} diffraction rings.\textsuperscript{10} On the other hand, the rotational shifts of FFPs for Si\textsubscript{1} (2.72$^\circ$) and C\textsubscript{5} (1.57$^\circ$) are well reproduced by simulation in the C 1s PIAD. \{011\} and \{111\} FFPs are good probes for detecting photoelectrons from Si atoms at site $\alpha$ while \{111\} FFPs are good probes in the case of C atoms.

The fact that FFPs in Si 2p and C 1s PIADs are different in the case of SiC and can be separated is important for determining the occupation ratio of emitter atoms at two different sites. Kato et al. have investigated the dopant site of B-doped diamond by photoelectron diffraction analysis.\textsuperscript{10} They have clarified that the B atoms are substitutionally doped into the diamond lattice based on the comparison of B 1s and C 1s PIADs. Furthermore, they have estimated the occupation ratio of B atoms at two different sites, i.e., (000) and (1/4, 1/4, 1/4) from the FFP intensity analysis. The present study supports the strategy of the dopant analysis by Kato et al. Furthermore, the atomic configurations around B dopants in SiC\textsuperscript{25} and N atoms at the interface\textsuperscript{17} may be determined on the basis of present substrate PIAD data.

In summary, we have measured the $2\pi$-steradian Si 2p and C 1s PIADs from the 6H-SiC(0001) surface with an off angle towards the [1100] direction. In a bulk crystal, pairs of mirrored local atomic sites with respect to the [1100] plane exist and the chemical environments surrounding each site are equivalent. However, all the measured patterns showed a threefold symmetry owing to the anisotropic step bunching along the [1120] direction resulting a preferential appearance of terraces with one type of local atomic site. Taking the finite inelastic mean free path of photoelectrons into account, photoelectron patterns for one kind of Si and C atom sites were successfully derived. After the separation procedure into a single-site component, the overlapping FFPs have been resolved. FFPs showed the circular dichroism of rotational shift around the incident-light axis corresponding to the parallax in stereo viewing. \{011\} and \{111\} FFPs are good probes for detecting photoelectrons from Si atoms at the $\alpha$-site, while \{111\} FFPs are good probes in the case of C atoms.

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