

Stable surface reconstructions on 6H–SiC(000 $\bar{1}$)

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Abstract

We used scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) to identify and investigate stable surface reconstructions on 6H–SiC(000 $\bar{1}$). Starting from ex situ prepared (1 × 1) ordered surfaces heating of the sample in ultra-high vacuum leads to (3 × 3), (2 × 2)_C and (1 × 1)_{graphitic} phases with increasing temperature. The stoichiometry of the phases was determined by AES by comparison to the initial, bulk like (1 × 1) phase: the (3 × 3) structure is carbon enriched, while the (2 × 2)_C structure reaches the bulk like stoichiometry again. The two superstructures were investigated in detail by STM revealing significant differences in structural complexity. Additional Si flux during heating produces a silicon enriched surface phase, which also exhibits (2 × 2) periodicity. However, this new phase, denoted as (2 × 2)_{Si}, has a different surface structure than the (2 × 2)_C phase obtained by mere heating. Apart from the different stoichiometry this is revealed by significantly different LEED intensities. © 1999 Elsevier Science S.A. All rights reserved.

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1. Motivation

The atomic structure of crystal surfaces influences many processes of technical interest, e.g. epitaxial growth or metallisation of semiconductor surfaces. As an example, it is evident that the incorporation of atoms during growth is affected by the geometric and electronic structure of adsorption sites on the surface. Therefore, some control of growth processes via preparation and stabilization of certain surface configurations appears to be possible. A certain structure might initiate a specific and intended growth behaviour. In order to get more insight in this technologically important step it is necessary to know which surface phases can be reproducibly prepared in situ by adjusting the stoichiometry of the topmost layers without distortion of the bulk structure beneath and by which atomic structure these phases are characterized. This demands detailed structural analyses. On SiC, a very promising semiconductor material [1], such investigations recently provided significant progress for surfaces of (0001) orientation most commonly used in growth experiments

(see e.g. [2,3] and refs. therein). However, for the reverse crystal orientation, namely (000 $\bar{1}$), only a few studies up to now have focussed on this issue [4–10]. As this orientation exhibits different properties with respect to e.g. growth and chemical reactivity, surface structures considerably different from those characteristic for (0001) orientation must be expected.

2. Experimental

Measurements were performed using an ultra high vacuum (UHV) system operated at a base pressure of 2×10^{-10} mbar which included a standard 4-grid reverse view low energy electron diffraction (LEED) optic, a 5 kV electron gun and hemispherical sector electron energy analyser for Auger electron spectroscopy (AES) and a beetle type scanning tunneling microscope (STM). Different samples cut from the same research grade CREE wafer were used. They were prepared by a sequence of ex situ and in situ procedures. Following the standard RCA cleaning [11] and taking care to avoid contamination, three different ex situ preparation methods were tested: (1) sacrificial oxidation and subsequent oxide removal in HF, (2) etching of the surface in a hydrogen flow at 1540°C and (3) heating the crystal to 800°C in hydrogen plasma. In

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situ treatment was performed by heating in (UHV) with or without additional Si flux provided by an electron beam evaporator. The samples were heated indirectly whereby the temperature was controlled by the respective power of the electron beam and calibrated using a retractable W/Re thermocouple. All measurements were performed after the sample had cooled down from the preparation to room temperature.

3. LEED and AES measurements

Immediately after introduction into vacuum the samples exhibited different LEED patterns depending on the ex situ preparation applied. For H₂ plasma treated or hydrogen etched samples we observed a low background LEED pattern with sharp, bright spots in $(\sqrt{3} \times \sqrt{3})R30^\circ$ symmetry while samples prepared by sacrificial oxidation exhibit a (1×1) pattern with slightly increased background intensity. The latter phase was already subject of a quantitative LEED analysis which identified a bulk truncated SiC crystal¹ [4]. AES of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase reveals the presence of oxygen which obviously is bonded to Si as indicated by an additional peak (see Fig. 1). A separate investigation of the structure of this $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase will be published elsewhere [12]. By heating the sample in situ with or without additional Si flux a series of different surface phases can be prepared. The se-

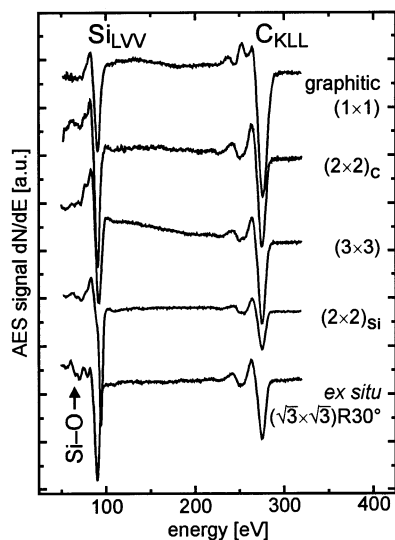


Fig. 1. Typical Auger electron spectra recorded for different surface phases ($E_p = 2.5$ kV).

¹ An adsorbate could not be confirmed directly with our LEED-analysis, i.e. in this particular case we were not able to distinguish, whether the surface is covered with hydrogen or oxygen in T1-position or is uncovered. However, the layer distances indicate that the bonds of the topmost layer are somehow saturated and XPS/UPS indirectly indicate hydrogen as adsorbate.

Table 1

AES peak-to-peak height ratios determined for the differentiated (dN/dE) Si_{L_{VV}}/C_{K_{LL}} signal and preparation temperatures required

Surface phase	Si/C ratio	Preparation
$(\sqrt{3} \times \sqrt{3})R30^\circ$ or (1×1)	1.4	ex situ
(3×3)	1.2	1050°C
$(2 \times 2)_C$	1.4	1075°C
$(1 \times 1)_{\text{graphitic}}$	0.7 or less	1150°C
$(2 \times 2)_{\text{Si}}$	≈ 2.9	Si-flux ~ 1 ml min ⁻¹ 1150°C

quence and structure of these phases appear to be independent from the ex situ preparation method used as outlined below. When heating the sample to temperatures up to 950°C the LEED pattern essentially remains unchanged. Also the amount of oxygen and the Si/C ratio is constant as indicated by AES (for exact values see Table 1) after initial degassing effects. Upon annealing to 1050°C for at least 15 min, the LEED pattern transforms to (3×3) periodicity with bright and sharp spots (Fig. 2a). At the same time, the AES oxygen signal vanishes and the Si/C peak ratio decreases (Table 1 and Fig. 1). These findings are in close analogy to XPS investigations published recently [5]. When heating at slightly higher temperatures, i.e. around 1075°C, a $(2 \times 2)_C$ phase² slowly evolves, exhibiting a slightly increased Si/C ratio (Fig. 2b–c and Table 1). The preparation of this $(2 \times 2)_C$ phase without residual contributions from the (3×3) phase is rather delicate as also indicated by previous investigations [6,7]. We achieved our best $(2 \times 2)_C$ structures in terms of LEED spot brightness, sharpness and low background only in coexistence with the (3×3) phase (Fig. 2b). Consequently, it is difficult to determine the correct surface stoichiometry quantitatively. However, it is clear that the $(2 \times 2)_C$ contains more Si than the (3×3) phase. The weight of the latter can be reduced by prolonged heating ($T = 1075^\circ\text{C}$). Though this is accompanied by a slight disordering of the $(2 \times 2)_C$ phase a quantitative LEED analysis is still possible. Finally, after about 60 min heating only the $(2 \times 2)_C$ phase remains (see Fig. 2c). Obviously, the two phases tend to coexist presumably due to nearly equal surface energies of the two structures. Elevated temperatures of 1150°C and above lead to a (1×1) LEED pattern with increased background intensity. Occasionally ring shaped intensity distributions appear, from whose position in reciprocal space a lattice parameter of 2.5 Å can be derived, which is close to the value of graphite, $a = 2.46$ Å. The shape of the C_{K_{LL}} peak in the Auger spectra changes to graphitic type and the Si/C ratio decreases

² In order to distinguish this structure from the Si-enriched $(2 \times 2)_{\text{Si}}$ introduced below we denote this structure $(2 \times 2)_C$.

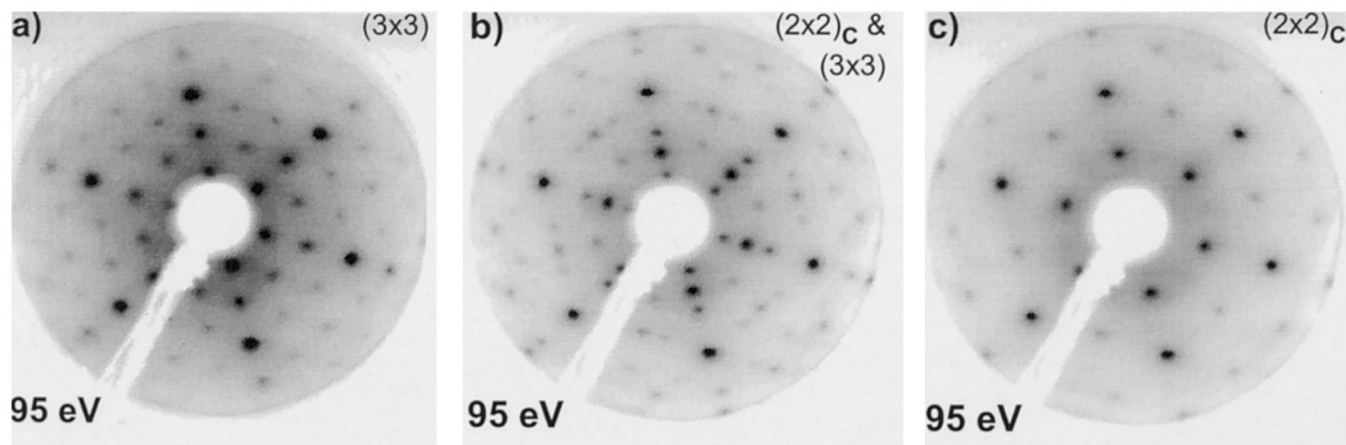


Fig. 2. LEED pattern recorded for selected surface structures at 95 eV electron energy: the pure (3×3) , (3×3) with already dominating $(2 \times 2)_C$, pure $(2 \times 2)_C$. (Black indicates high electron intensities).

further (see Fig. 1 and Table 1). This indicates the formation of graphite on the surface which is in close analogy to the XPS study of Johansson [5] and former AES/XPS investigations [6–8].

So far, phases considered were characterized by a depletion of Si as compared to a bulk truncated surface. Providing a Si flux during heating the depletion can be compensated or even reversed. Heating in a Si flux for 20 min ($\sim 1 \text{ ml min}^{-1}$, $T = 1150^\circ\text{C}$) results in another phase of (2×2) symmetry. This structure has a larger Si/C ratio than the $(2 \times 2)_C$ phase obtained by mere heating and is therefore denoted by $(2 \times 2)_{Si}$ (see Table 1). By comparison of LEED $I(E)$ spectra recorded for several half order beams it becomes evident, that the two (2×2) pattern originate from surface structures of significantly different geometry³. The Si_{LVV} peak in the Auger spectra broadens possibly due to a superposition of signals emerging from silicon in inequivalent bonding geometries. In order to estimate the influence of different preparation methods for Si enriched structures [9] we also covered the sample with a Si film ($d_{\text{film}} \geq 20 \text{ \AA}$) at room temperature and subsequently heated the sample for very short periods (less than 30 s) in order to avoid overshooting any structures. At temperatures above 700°C the Si film desorbes and a (1×1) LEED pattern with moderate background evolves. The Si/C ratios determined for this phase vary in a certain range which we attribute to the presence of a mixture of disordered and partially Si enriched surface areas. Annealing at 1150°C for about 45 s results in the $(2 \times 2)_{Si}$ structure. Yet, the quality of this structure is poor compared to the preparation by heating

with Si flux applied. Annealing the $(2 \times 2)_{Si}$ structure at 1050°C for several minutes restores the (3×3) structure described above. When this step is performed carefully (i.e. applying slightly lower temperatures for longer times) several intermediate structures with larger periodicities are visible with LEED. This indicates that the $(2 \times 2)_{Si}$ to (3×3) transition is accompanied by a severe restructuring of the surface.

4. STM measurements

For two of the phases prepared by in situ annealing, namely the (3×3) and the $(2 \times 2)_C$, atomically resolved STM images were obtained. A strongly different bias dependence for the two phases is found. While the appearance of the $(2 \times 2)_C$ structure is almost independent of the tunneling voltage used (see Fig. 3a), the corrugation of the (3×3) structure changes drastically with voltage: Empty state images of the (3×3) phase show a single well defined protrusion per unit cell while filled state images display a chain like structure with an additional protrusion between the chains in (3×3) periodicity (Fig. 3b–c). Under certain tunneling conditions, the structure even appears to have a lowered symmetry as the 3-fold rotational symmetry is barely visible (cf. Fig. 3c). Hoster et al. [9] obtained similar STM results although using a different preparation method. Previously published STM images by Li et al. [10] remarkably agree with our images and with those shown in [9]. However, Li et al. attribute a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ periodicity to this structure [10]. In Fig. 3b the upper and lower (3×3) reconstructed areas are shifted against each other by one additional substrate lattice unit vector \underline{a}_0 (see figure caption). This kind of domain boundary is frequently observed in the (3×3) phase and exhibits severe atomic distortions. This is in contrast to the $(2 \times 2)_C$ structure, where domain

³ It should be noted that we can a priori not exclude the possibility that this structure is of (2×1) periodicity and all three possible and equivalent domains superpose to the observed LEED pattern; the $(2 \times 2)_C$ is already imaged in STM and therefore confirmed to be of real (2×2) periodicity.

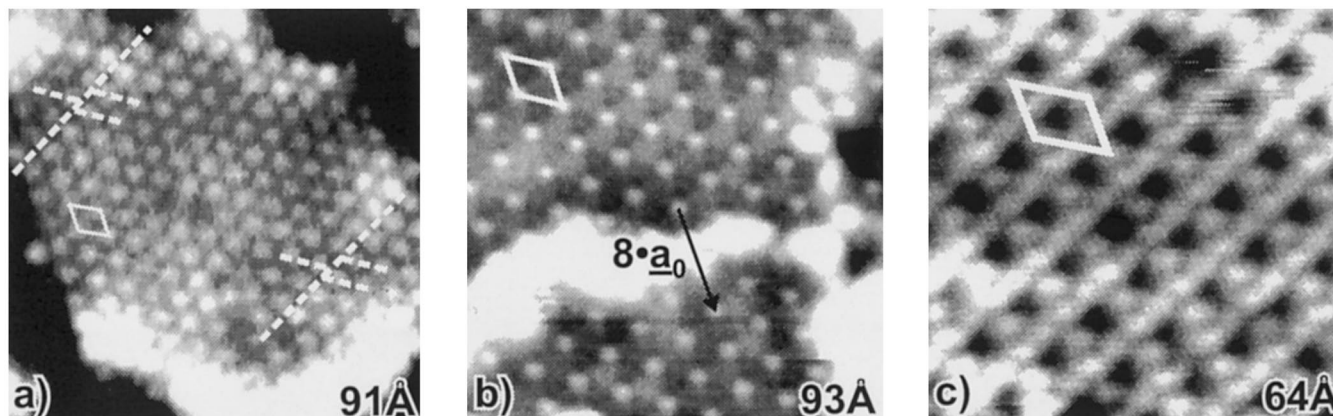


Fig. 3. STM images for selected surface structures. The length scale of the image and the unit mesh of the corresponding structures are indicated. All images recorded in constant current mode $I = 0.3$ nA, raw data displayed, only contrast enhancement applied for convenient printout: (a) Empty state image of $(2 \times 2)_C$, $V_{\text{tip}} = -2.75$ V. Indicated by the long dashed lines are the boundaries of domains shifted against each other by one substrate unit vector, short dashed lines denote the shift. (b) Empty state image of the (3×3) , $V_{\text{tip}} = -2.75$ V, upper and lower part of the image belong to two domains shifted against each other by one substrate unit vector (the arrow indicates the distance between two clearly resolved unit cells in the neighbouring domains; its length is one substrate unit vector less than three times the periodicity of the reconstruction), the boundary appears strongly distorted. (c) Filled state image of the (3×3) , $V_{\text{tip}} = +2.00$ V.

boundaries show an undisturbed corrugation even directly at the boundary. Vertical corrugations are in the range of 0.3 \AA for the empty state images of the $(2 \times 2)_C$, 0.3 \AA for filled state and 0.5 \AA for empty state images of the (3×3) structure. It should be noted that tunneling with negative tip bias, i.e. when probing empty states, always reached more stable conditions than positive tip biases.

5. Discussion

Previous XPS/AES analyses of the surface stoichiometry have already shown that SiC(000 $\bar{1}$) exhibits a more complex behaviour than the (0001) orientation in the temperature range up to about 1000°C : using XPS/AES Muehlhoff et al. determined a decreasing Si/C ratio when heating in the range $627\text{--}827^\circ\text{C}$ followed by a constant Si/C ratio up to 1027°C and afterwards again a steeply decreasing Si/C ratio [8]. Nakanishi observed also a decreasing Si/C ratio by means of AES for temperatures up to 800°C , then an increase to even higher ratios than the bulk structure with a maximum at 1000°C and again a decreasing ratio at higher temperatures [7]. Our observations are in good agreement with those earlier results (see Table 1). Moreover, we found that the changes in surface stoichiometry are practically coincident with changes of the surface structure as monitored by LEED, e.g. the transition from the (3×3) to the $(2 \times 2)_C$ structure. Consequently, one should investigate the structures of these surfaces in order to achieve an understanding of the segregation processes and their unusual temperature dependence.

Little is known about the structure of the (3×3) phase. However, by comparison of LEED $I(E)$ data we

are able to prove that the (3×3) structures emerging from the different preparations (i.e. heating a Si covered surface [9], heating an ex situ prepared (1×1) phase [5] or as additionally realised in the present work by heating the ex situ prepared $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase) are practically identical. By a detailed analysis of their XPS data Johansson et al. suggest the presence of two different carbon layers on top of bulk truncated SiC [5]. Based on their STM results, Hoster et al. proposed also a model for the (3×3) structure [9] which, however, to our opinion does not account for the reduced symmetry observed for certain imaging conditions both displayed in ref. [9] and in the present work (Fig. 3c). Considering the data of the present paper we agree with the model of a carbon enriched adlayer on SiC(000 $\bar{1}$) whereby, however, the geometric structure of the surface seems to be rather complex.

The $(2 \times 2)_C$ phase, on the other hand, is of bulk like stoichiometry (cf. Table 1) with a Si/C ratio slightly higher than that of the (3×3) structure and almost equal to the value of the (1×1) phase. Its structure seems to be rather simple for two reasons: (1) The tunneling images of the well ordered areas are almost independent of the applied voltage showing a single protrusion per unit cell even in the proximity of defects. (2) Antiphase domains meet without any noticeable distortion of the structure even at the very boundary (see Fig. 3a). This excludes complex reconstructions (e.g. based on dimerization, ring- or cluster-type adstructures) with broken bonds at the boundaries causing local electronic density distortions which should clearly show up in STM, as observed for the (3×3) structure (Fig. 3b).

Most interestingly, the two structures which are thought to be of completely different geometry, obvi-

ously have a very similar energetic stability as estimated from their strong tendency for coexistence under the same preparation conditions.

6. Conclusion

The stable surface structures with different surface stoichiometries on 6H–SiC(000 $\bar{1}$) were investigated by means of LEED, AES and STM. Starting either from ex situ prepared $(1 \times 1)/(\sqrt{3} \times \sqrt{3})R30^\circ$ or in situ prepared $(2 \times 2)_{\text{Si}}$ surface structures, a (3×3) phase is observed by heating the surface to about 1050°C accompanied by a silicon depletion of the surface. Careful annealing of this structure at 1075°C leads to the development of a $(2 \times 2)_{\text{C}}$ phase which, with the (3×3) phase gradually vanishing, finally dominates the surface whereby the Si/C-ratio slightly reincreases. Yet, we are not sure whether the latter is characteristic for the $(2 \times 2)_{\text{C}}$ phase or caused by contributions from disordered parts of the surface whose presence is indicated by some increased background in the LEED pattern. Using higher annealing temperatures ($T \geq 1150^\circ\text{C}$) leads to a strong carbon enrichment of the surface accompanied by the transition of the $(2 \times 2)_{\text{C}}$ pattern to (1×1) symmetry with, however, significant background intensity. The only stable silicon enriched surface phase found in the present experiments is the Si rich $(2 \times 2)_{\text{Si}}$ phase which can either be prepared through additional Si deposition while heating either surface phase at 1150°C (1 ml min^{-1} , 20 min) or by heating a surface covered with a Si film of thickness $d_{\text{Si}} \geq 20 \text{ \AA}$ (1150°C for 1 min). The comparison of LEED I(E) spectra reveals a considerable difference between the structures of the $(2 \times 2)_{\text{Si}}$ and $(2 \times 2)_{\text{C}}$ phases.

The (3×3) and $(2 \times 2)_{\text{C}}$ phases were investigated in more detail by STM. We found indications for a rather complex geometry of the (3×3) phase, while a more simple structure seems to apply for the $(2 \times 2)_{\text{C}}$ phase. Despite of their geometric differences the structures seem to have equal energetic stability in view of their tendency to coexist.

Acknowledgements

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