Tailoring the SiC subsurface stacking by the chemical potential

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Abstract: The stacking orientation of bilayers determines the polytype of SiC material. For the development of polytype heterojunctions a controlled switch from one stacking sequence to another is required. In the present paper it is demonstrated for 4H-SiC and 6H-SiC, that the chemical environment during preparation of the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction on SiC(0001) influences the bilayer stacking in the topmost surface region. A silicon rich growth environment results in three bilayers in identical orientation at the very surface, which in the case of 4H-SiC corresponds to breaking the bulk stacking sequence. Oxygen rich preparation conditions lead to a reduction to two identically oriented bilayers for both polytypes. The reconstruction geometry of the ($\sqrt{3} \times \sqrt{3}$)R30° phase is independent of the polytype and the terminating stacking sequence of the underlying material. In consequence, the surface stacking and as such the starting point of a polytype heterojunction can be tailored by the chemical potential.

Introduction

The potential of SiC for electronic devices with novel properties in areas such as high temperature, high power and high frequencies stems from the unique physical properties of SiC. An important step in the fabrication of SiC devices is the control of the crystal structure and in particular of the SiC polytype. Growth of high quality crystalline material has been achieved by homo-polytype epitaxy utilizing the step flow growth mode on off-axis samples. However, a polytype control on flat surfaces is still difficult. Yet, the band gap variation for the different SiC polytypes (from 2.4 eV for 3C-SiC to 3.3 eV for 2H-SiC) makes this an issue of major importance, since strain-free band gap engineered heterojunctions appear feasible.

Figure 1: T₄ Si adatom (black sphere) structure for the ($\sqrt{3} \times \sqrt{3}$)R30° phase on SiC(0001) displayed (a) in a side view projection along the [11̅2] direction. The main parameters are indicated. (b) Top view. The lateral displacement $\Delta r_1$ of substrate Si atoms bound to the adatom is indicated.

We have recently reported that the preparation method of the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction phase on SiC(0001) influences the stacking sequence of the topmost SiC bilayers underneath the atomic reconstruction pattern [1, 2], which promises a possibility to trigger the desired heteroepitaxial junction development. The ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction geometry has long been under debate as reviewed in [3], in part due to its particular electronic structure with a coulomb interaction of neighboring dangling bond orbitals of the Mott-Hubbard type [4]. The actual surface structure finally determined is relatively simple, characterized by a Si adatom placed in a so-called T₄ site, i.e. three-fold coordinated to the topmost Si atoms and on top of a C atom of the topmost SiC bilayer. Top and side view

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model of the \((\sqrt{3} \times \sqrt{3})R30^\circ\) phase are displayed in fig. 1 with the major reconstruction parameters indicated [1]. The SiC bilayer sequence underneath the reconstruction was found to be shifted towards cubic stacking by larger amounts of Si present during the preparation of this \((\sqrt{3} \times \sqrt{3})R30^\circ\) phase [1]. Using low-energy electron diffraction (LEED) we quantify this effect for different polytypes and show that a reversal effect can be achieved by oxygen treatment of the surface.

**Surface Preparation**

The \((\sqrt{3} \times \sqrt{3})R30^\circ\) reconstruction can be prepared using vastly different methods which also caused some debate in the literature with many different structure proposals. Several authors prepared it starting from a chemically pre-treated sample by simple annealing [5, 6]. Kaplan obtained it by annealing the Si-rich \((3 \times 3)\) phase [7], a third method proposed was annealing a SiC(0001) surface under Si flux [8]. All these methods yield the same reconstruction geometry [1]. However, the stacking sequence at the surface depends. For a quantitative analysis of this effect we have chosen four different preparation recipes, which are listed in table 1. Three of them (I-III) are derived from the above discussed publications. They can be characterized by the different amount of Si excess in the preparation environment, whereby method III includes oxygen from the ex situ treatment. We introduce a fourth recipe which represents a pronounced oxygen surplus combined with a low Si presence realized by cyclic adsorption of O\(_2\) with exposures of 3-6 Langmuir (L) and subsequent desorption – still maintaining the \((\sqrt{3} \times \sqrt{3})R30^\circ\) geometry.

**Table 1:** In situ preparation procedures for SiC(0001)-\((\sqrt{3} \times \sqrt{3})R30^\circ\) reconstruction with Si-T\(_4\)-adatom geometry.

<table>
<thead>
<tr>
<th>(T_{SiC})</th>
<th>Si-flux</th>
<th>time</th>
<th>initial surface condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) 950 – 1000 °C</td>
<td>–</td>
<td>30 min.</td>
<td>Si-rich ((3 \times 3)) reconstructed</td>
</tr>
<tr>
<td>(II) 1050 – 1100 °C</td>
<td>(\sim 1/4) ML/min.</td>
<td>30 min.</td>
<td>any clean surface phase</td>
</tr>
<tr>
<td>(III) 950 – 1000 °C</td>
<td>–</td>
<td>30 min.</td>
<td>ex situ prepared ((1 \times 1)) or silicate phase</td>
</tr>
<tr>
<td>(IV) RT (\rightarrow) 900 °C (ramped)</td>
<td>–</td>
<td>30 min.</td>
<td>((\sqrt{3} \times \sqrt{3})R30^\circ)-structure exposed to 3 – 6 L O(_2) at RT</td>
</tr>
</tbody>
</table>

**SiC Bilayer Stacking and LEED Analysis**

The stacking sequence of SiC bilayers along the c-axis characterizes the different SiC polytypes. Very briefly, in the cubic 3C-SiC all bilayers possess the same orientation, whilst in hexagonal polytypes consecutive slabs of identically oriented bilayers ("cubic stacking") are mutually rotated by 60° ("hexagonal stacking"). The unit cells of 4H-SiC and 6H-SiC, the polytypes which are discussed in the present paper, consist of 4 and 6 bilayers, respectively, arranged in two slabs of 2 (3) "cubic" bilayers each, with a 60° rotation in between. Each of these 4 (6) bilayers might be the terminating layer at the surface. Accordingly, slabs of 3, 2 or 1 bilayers in identical orientation might terminate the crystal, as indicated in fig. 2 by configurations S3, S2 and S1.

Note, that the polytype difference is only encountered at the second 60° rotation below the surface. Certainly, the corresponding difference of the atomic structure should be visible in a diffraction experiment such as LEED. However, the intensity differences are only subtle, as demonstrated in fig.3.

![Figure 2: Surface termination layer sequences on 6H-SiC(0001): Configurations S3, S2 and S1, differing by and denoted according to the number of identically oriented bilayers directly at the surface. The layer orientation and stacking sequence are indicated by the enhanced Si-C bond train parallel to the \((11\bar{2}0)\) projection plane.](image-url)
by the first order diffraction spots for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction on 4H- and 6H-SiC(0001) surfaces obtained from different preparation methods. The structures shown in panel a) are obtained by annealing ex situ pre-treated samples (method III in table 1), those in panel b) by annealing the Si rich $(3 \times 3)$ reconstruction (I in table 1). Quantitative LEED analyses prove that all four cases correspond to the T4 site reconstruction with the geometry shown in fig. 1. Nevertheless, spot intensity differences can be seen in the grey shaded energy ranges in fig. 3 which are due to different bilayer stacking sequences in the terminating layers. The LEED analysis successfully differentiates between domains of different stacking sequences. The results for the four surfaces are listed in table 2 (lines 1, 2 and 4, 5). For preparations from ex situ samples, the stacking sequence of the dominating domain reflects the polytype unit cell with the surface truncated where a $60^\circ$ rotation would continue the crystal. Notably, for preparation from the Si-rich $(3 \times 3)$ phase, the analysis finds 3 bilayers in cubic stacking independent of the polytype, which in the case of 4H-SiC corresponds to breaking the bulk symmetry (fig. 3b, dashed line). The preparation method II, i.e. annealing in Si flux still leads to an enhancement of S3 stacking domains on 4H-SiC(0001) where it should not be expected, but less pronounced then for method I. A correlation with the Si amount present during the preparation is obvious.

Surface Bilayer Stacking Determined by the Chemical Potential

Using consecutive oxygen adsorption/desorption cycles (method IV) the influence of the chemical environment can be studied in detail. The starting point of the experiments on a 4H-SiC(0001) sample is the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface prepared from a $(3 \times 3)$ phase, i.e. under Si rich conditions, when the surface is dominated by S3 stacking domains (80%, cf. table 1). In fig. 4(a) the intensity features significant for this situation can be seen in the grey shaded areas: in the energy range 140-190 eV the larger peak is at lower energy, whereas in the range between 300 eV and 360 eV the double peak structure is more intense on the high energy side. Oxygen exposure and subsequent annealing changes these features (curve b). At low energies the $165 \text{ eV}$ peak rises at the expense of the $150 \text{ eV}$ shoulder. In the high energy range the $320 \text{ eV}$ shoulder increases while $340 \text{ eV}$ intensities are reduced. This effect continues upon further cycles (curves c,d), until a saturation is reached around $10-18 \text{ L}$ of $O_2$. After $18 \text{ L}$ (curve d) the spectra are practically identical to those obtained from preparation III from an ex situ pre-treated sample (curve e and fig. 3a), which in turn was characterized by mostly S2 terminated domains [1]. Obviously, these features can be used as fingerprint.

Table 2: Domain ratios of different surface termination for the four datasets shown in Fig. 3 and Fig. 4(f).

<table>
<thead>
<tr>
<th>sample</th>
<th>preparation</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>R_{pe}</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H-SiC(0001)</td>
<td>from $(3 \times 3)$ (I)</td>
<td>10%</td>
<td>0%</td>
<td>90%</td>
<td>0.14</td>
</tr>
<tr>
<td>4H-SiC(0001)</td>
<td>from $(3 \times 3)$ (I)</td>
<td>10%</td>
<td>10%</td>
<td>80%</td>
<td>0.13</td>
</tr>
<tr>
<td>4H-SiC(0001)</td>
<td>annealed in Si-flux (II)</td>
<td>15%</td>
<td>50%</td>
<td>35%</td>
<td>0.13</td>
</tr>
<tr>
<td>6H-SiC(0001)</td>
<td>from ex situ (III)</td>
<td>10%</td>
<td>30%</td>
<td>60%</td>
<td>0.17</td>
</tr>
<tr>
<td>6H-SiC(0001)</td>
<td>Fig. 4(f) (IV)</td>
<td>20%</td>
<td>70%</td>
<td>10%</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Figure 3: LEED IV-curves for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase from 4H-SiC(0001) and 6H-SiC(0001). (a) $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase prepared from fresh ex situ pre-treated samples, the spectra reflect the different bilayer stacking at the surface in the grey shades areas. (b) $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase prepared from Si rich $(3 \times 3)$ phase, spectra indicate identical (S3) stacking for both polytypes.
for the surface bilayer stacking, however, only for identical substrates. For different polytypes that becomes more difficult. A 6H-SiC(0001) surface treated according to preparation IV with 6 L of O$_2$ yields intensities (curve f) where the low energy feature is close to the S2 situation on 4H-SiC (curve d,e), whilst the high energy range seems to contradict. However, it should be kept in mind that the position of the second 60° rotation differs between the two polytypes. A LEED structure analysis of the full data set for this oxygen treated 6H-SiC sample indeed resolves the stacking to be predominantly S2 (70%, cf. table 1, line 6). Interestingly, including S4 domains into the parameter space of the analysis did not change the picture. In both polytypes investigated, i.e. 4H- and 6H-SiC, Si rich preparation leads to a termination by three “cubic” layers (S3), oxygen rich environment (adsorption/desorption cycles) leads to a reduction to two "cubic" layers (S2). S4 domains never exceed 10% coverage (the error margin is just ±10%), even on 6H-SiC. The oxygen treatment induced reduction of the cubic slab saturates with S2. A switch to S1 is somehow impeded, i.e. the effect is not related to a simple etching mechanism. These experiments show a clear influence of the chemical potential on the SiC bilayer stacking sequence, controlled by Si or oxygen excess during the ($\sqrt{3} \times \sqrt{3}$)R30° preparation. Recent theoretical investigations predicted a general preference of cubic stacking at the SiC(0001) surface [9, 10].

Summary

The SiC bilayer stacking sequence can be influenced by the chemical environment during the preparation of the ($\sqrt{3} \times \sqrt{3}$)R30°-SiC(0001) reconstruction. Si rich conditions lead to a “cubic” surface termination with three bilayers in identical orientation. Oxygen treatment restricts the "cubic" slab to two layers. The stacking sequence is independent of the substrate polytype but only determined by the chemical potential.

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References