

Structure and morphology of SiC surfaces studied by LEED, AES, HREELS and STM

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Abstract

Low energy electron diffraction, Auger electron spectroscopy, high resolution electron energy loss spectroscopy and scanning tunnelling microscopy investigations used for structure and morphology determinations of different hexagonal SiC surfaces are presented. The analyses include sample orientation, layer stacking, step morphology, layer spacings as well as the species and coordination of surface terminating adatoms. The samples were prepared ex situ and investigated without further treatment. Predominant ABCACB stacking is found for 6H-SiC(0001) corresponding to a triple step morphology. The surface is covered by hydroxyl species bound to the topmost Si atoms. The surface of a 3C-SiC(111) sample was found to be covered by oxygen on only 50% of the available Si sites. On both surfaces the first bilayer is slightly compressed on an otherwise bulk-like geometry. 6H-SiC(000 $\bar{1}$) exhibits a single step morphology in agreement with the mixed stacking found on the surface. All three possible surface stacking sequences are present in equal amounts. © 1997 Elsevier Science S.A.

Keywords: Low-energy electron diffraction; Morphology; Silicon carbide; Surface structure

1. Introduction

The physical properties of silicon carbide make it a promising semiconductor material for new applications such as high power and high frequency devices or electronics in high temperature environments. Still the difficulties in growing SiC material of sufficient crystalline and electronic quality have so far prevented a vast commercial development. It is apparent that the surface structure of the substrate plays an important role for the crystallization process. The natural growth plane of SiC is a hexagonal bilayer consisting of alternating Si and C atoms in tetrahedral bond coordination which is the (0001) plane in hexagonal SiC crystals and the (111) plane of the cubic modification. The different polytypes are distinguished by the sequence of linearly stacked and mutually rotated hexagonal bilayers. For a specific polytype surface, different termination domains are feasible distinguished by the topmost stacking sequence. In Fig. 1 the different stacking sequences for 6H and 3C polytypes and the termination possibilities for a 6H surface are shown. The analysis of the surface stacking is a major part of the present study. In addition we

address the distinction between the two possible crystal orientations as well as the determination of surface layer geometries and the identification of possible adatoms and their sites applying scanning tunnelling microscopy (STM), high resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES) and quantitative low energy electron diffraction (LEED). In a previous study of 6H-SiC(0001) we found large steps of multiple triple bilayer height, equivalent to odd or even numbers of half 6H unit cells, and the layer stacking sequence could be determined to be ABCACB [1,2]. In the present study we present a refined analysis of this 6H-SiC(0001) allowing for mixtures of domains with different surface termination. Additionally, new results of the hexagonal surfaces of other samples of different polytype and different polarity, that is, 6H-SiC(000 $\bar{1}$), 4H-SiC(0001) and 3C-SiC(111) are given.

2. Experimental

Samples of either bulk grown Lely material or CVD grown homoepitaxial films were prepared involving dry oxidation, chemical cleaning steps and HF treatment

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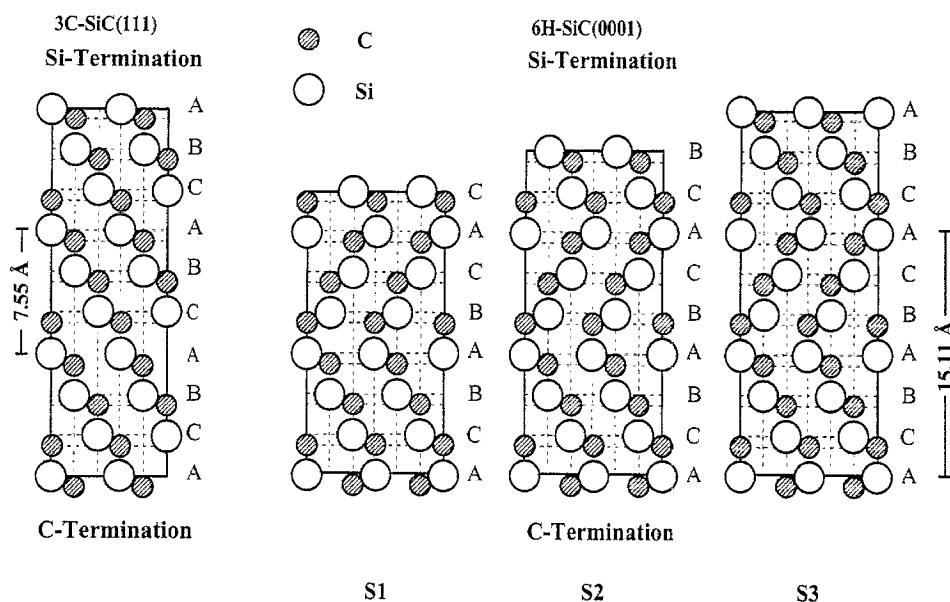


Fig. 1. Cross-sectional view of the linear stacking present in the cubic (3C) polytype (β -SiC) and three different stacking sequences possible at the surface of the 6H polytype. The different surface terminations are labelled according to the depth of the orientation change (S1, CACBABC; S2, BCACBAB; and S3, ABCACBA).

[3]. The 3C-SiC sample used was an epitaxial film grown in (111) orientation on Si(111). By a fast transfer into vacuum recontamination and oxidation of the sample surfaces could be kept to a minimum. In ultra-high vacuum we used different techniques to investigate the surface structure. AES was used to determine the stoichiometry of the surface as well as the presence of adatoms. The complete atomic surface structure was analysed using quantitative LEED. The lateral surface periodicity is immediately related to the periodicity of the diffraction pattern. Atomic positions can be accurately determined by analysing the spot intensities by means of fitting experimental intensity spectra to spectra obtained from model calculations [4,5]. The best-fit model was identified by minimizing the Pendry *R*-factor [6] calculated between the experimental and theoretical data. Additional information about the nature of dangling bond saturating ad-species was gathered using HREELS to detect their vibrational modes. Finally, STM was used to monitor the step morphology of the surfaces in real space.

3. Surface structure analysis

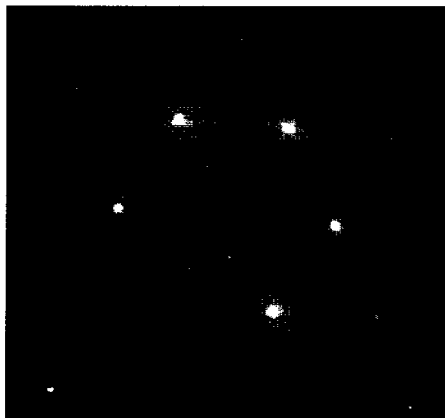
Immediately after the chemical treatment all samples showed a well ordered LEED pattern. This was found with and without oxidation included in the preparation treatment and was regardless whether 50% HF or buffered NH_4F (pH 7.8) was used. The surface periodicity as judged from the diffraction angles corresponds to the SiC bilayer structure for all polytypes and preparation procedures. Hexagonal and cubic samples can easily

be distinguished by the symmetry of their LEED pattern when the primary electron beam is aligned normal to the surface. A single domain of a specific layer stacking always exhibits three-fold surface symmetry. This gives rise to a three-fold diffraction pattern, where for example, within first order diffraction two groups of three spots, that is, the (10), ($\bar{1}1$) and ($0\bar{1}$) and the (01), ($\bar{1}0$) and ($1\bar{1}$) have different intensities. This is indeed the case for the cubic modification which contains only linearly stacked bilayers. However, on surfaces of hexagonal polytype we expect equally weighted domains rotated by 60° with respect to each other illuminated simultaneously by the electron beam. Their intensities add giving rise to the observed six-fold rotational symmetry. Fig. 2 demonstrates this symmetry difference between a 3C-SiC(111) and a 6H-SiC(0001) LEED pattern.

Information about the chemical composition of the surfaces was obtained from AES. We observe oxygen for all ex situ prepared samples. Unfortunately, the Si and C signal does not accurately reflect the SiC-stoichiometry due to contamination before the sample transfer. Therefore, the surface polarity, that is, whether (0001) or ($000\bar{1}$) orientation applies, cannot be determined by AES. Yet, LEED intensity versus energy spectra are very different for the two crystal sides as demonstrated in Fig. 3(a) and therefore can be used as an experimental fingerprint.

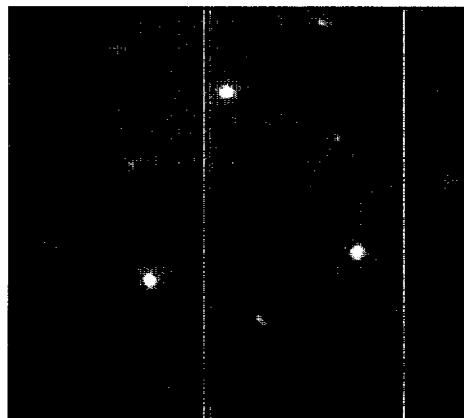
As mentioned above, the surface of a 6H-sample may be terminated by three different topmost layer stacking sequences (see Fig. 1), equivalent to different cuts in the ABCACBA... stacking of the crystal. From a new, detailed intensity analysis of LEED diffraction spots of

a) 6H-SiC(0001)



120 eV

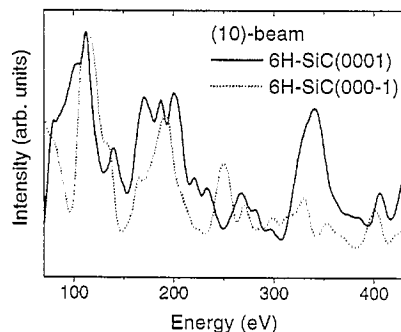
b) 3C-SiC(111)



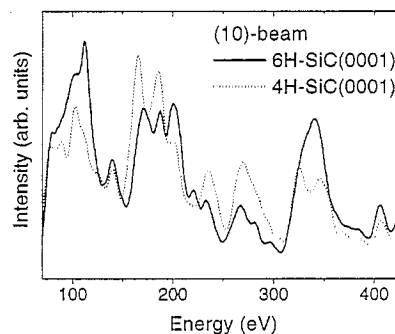
180 eV

Fig. 2. LEED pattern for a 3C-SiC(111) and a 6H-SiC(0001) sample acquired with normal electron incidence.

a) Polarity



b) Polytype

Fig. 3. Experimental LEED intensity spectra of the (10) beam of a silicon (0001) and carbon (000 $\bar{1}$) terminated 6H-SiC sample.

the 6H-SiC(0001) sample we identify the “A” layers to be the predominant (80%) surface layer (S3 stacking in Fig. 1), in agreement with the $n \times 3$ bilayer step heights found in STM [1,7]. An additional layer of oxygen on top of the topmost silicon atoms (the so-called T1 site) was also found in the LEED analysis (bondlength $d_{\text{Si-O}} = 1.66 \text{ \AA}$). This oxygen obviously represents the hydroxyl species that were detected by vibrational analysis using HREELS [1]. The presence of OH-groups is consistent with the pronounced electron beam sensitivity of the samples causing the LEED pattern to disappear after a few minutes of measurement. The topmost bilayer is compressed to $d_{11} = 0.55 \text{ \AA}$ due to the anisotropic bond coordination of the topmost silicon atom, accompanied by an expansion of the spacing between the first two bilayers ($D_{12} = 1.94 \text{ \AA}$). Other atomic distances were determined to be similar to the geometry in a bulk crystal ($d_{\text{nm}} = 0.63 \text{ \AA}$, $D_{\text{nm}} = 1.89 \text{ \AA}$). Further details of the LEED analysis can be found elsewhere [8]. Experimental intensity spectra of 6H- and 4H-SiC(0001) shown in Fig. 3(b) are not as different as observed for different surface polarities, cf Fig. 3(a). This holds in

particular when a mixture of surface terminating domains is present as shown in our previous theoretical study [2]. A structure analysis of the 4H-SiC(0001) sample has been published elsewhere [9].

On the 3C-SiC sample the linear stacking sequence of the bulk crystal structure is found to extend up to the surface. The three-fold symmetry of the LEED pattern indicates that the crystal contains exclusively a single stacking orientation which is quantitatively corroborated by the intensity analysis. The oxygen found in AES is again bonded in T1 geometry ($d_{\text{Si-O}} = 1.61 \text{ \AA}$), yet with the oxygen layer incomplete – only 50% of the available Si atoms are covered by adatoms. There is no compression of the topmost bilayer. As in the case of 6H all other layer spacings are unrelaxed.

On the 6H-SiC(0001) surface a predominant stacking sequence ABCACB was found in accordance with step bunching observed by STM. To the contrary, on the 6H-SiC(000 $\bar{1}$) surface all possible stacking sequences are present in equal amounts as determined by the LEED analysis. A model with a domain mixture yields a far better R -factor ($R_p = 0.20$) than any single domain

