Novel Reconstruction Mechanism for Dangling-Bond Minimization: Combined Method Surface Structure Determination of SiC(111)-(3×3)

U. Starke, J. Schardt, J. Bernhardt, M. Franke, K. Reuter, H. Wedler, and K. Heinz
Lehrstuhl für Festkörperphysik, Universtät Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen, Germany

J. Furthmüller, P. Käckell, and F. Bechstedt
Institut für Festkörpertheorie und Theoretische Optik, Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany
(Received 22 August 1997)

The SiC(111)-(3×3) phase was analyzed by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) holography, density functional theory (DFT), and conventional LEED. A single adatom per unit cell found in STM acts as a beam splitter for the holographic inversion of discrete LEED spot intensities. The resulting 3D image guides the detailed analyses by LEED and DFT which find a Si tetramer on a *twisted* Si adlayer with cloverlike rings. This *twist* model with one dangling bond left per unit cell represents a novel $(n\times n)$-reconstruction mechanism of group-IV (111) surfaces. [S0031-9007(97)05084-9]

PACS numbers: 68.35.Bs, 61.14.Hg, 71.15.Mb, 71.20.Nr

The potential application of silicon carbide (SiC) for electronic devices has stimulated numerous research activities in recent years. Its large electric breakdown field and high electron mobility have made silicon carbide become a promising semiconductor material for high power and high frequency applications. Yet, a successful commercial production of devices is hampered by difficulties in growing wafers of sufficient electronic and crystalline quality. Besides, the polytypism of SiC [1] is also of fundamental interest. SiC exists in a variety of crystal modifications that exclusively differ by the stacking sequence of mutually rotated hexagonal bilayers. Although the corresponding polytypes are nearly degenerate as shown by total energy calculations [2–4], their electronic properties can be very different. In particular, the excitonic energy gap varies from 2.4 eV for a zincblende to 3.3 eV for a Wurtzite structure [5] opening the perspective of electronic heterostructures without lattice mismatch.

Recently, homoepitaxial growth of high quality SiC material has been achieved on hexagonal surfaces using chemical vapor deposition (CVD) [6] by establishing a step flow mechanism. Hereby, the polytype reproduction was mediated by diffusion of incoming particles to steps where the stacking sequence is exposed due to a polytype specific surface morphology [7–9]. In ultrahigh vacuum (UHV) experiments using molecular beam epitaxy (MBE) it was realized that such a growth mode is stabilized under silicon rich conditions when a (3×3) periodicity develops [10]. The atomic arrangement in this (3×3) structure is believed to be the key to understanding the step flow growth mechanism. However, the size and complexity of the (3×3) unit cell have hitherto prevented a structure analysis by a surface crystallography technique.

In this Letter we present a combined method approach solving this structure. Holographic low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) are used to determine partial but essential features of the surface unit cell. As a new development the holographic data inversion was applied using superstructure spot intensities rather than the originally proposed diffuse data [11]. The preinformation obtained allows one to drastically reduce the number of feasible models to be considered and guides the detailed analysis by two complementary methods, namely, total energy minimization by means of density functional theory (DFT) calculations and quantitative LEED. The atomic structure finally found for the (3×3) phase represents a novel reconstruction mechanism allowing for the saturation of all but one dangling bond per unit cell at the top of a tetrahedral Si adcluster. Because of a *twist* motion in the underlying Si adlayer five- and seven-membered rings are arranged in a cloverleaf pattern which provides the threefold bond saturation of the remaining two Si atoms, again resembling a clover arrangement.

The experiments were carried out using a stainless steel UHV chamber, which allows for an *in situ* sample transfer between LEED and STM together with facilities to cool, heat, and evaporate silicon on the sample. LEED-$I(V)$ spectra were acquired using an automated, video based data acquisition system [12]. The (3×3) phase was prepared by annealing to 800 °C under exposure to Si for 30 min. In contrast to hexagonal polytypes, on a cubic sample only one type of stacking sequence can be present at the surface [7,8]. Thus, the complication of stacking and domain mixtures is eliminated from the structure analyses. A comparison of experimental LEED intensities [13] obtained from a 4H and a 3C-SiC sample as well as DFT test calculations [4] indicate that the atomic structure of the (3×3) phase is rather independent of the sample polytype. Therefore we used a 3C-SiC(111) sample heteroepitaxially grown on Si(111) for the acquisition of a full set of LEED data [14]. For practical reasons, the

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STM images of the (3×3) phase were measured from a 4H-SiC(0001) sample where we could achieve a better image quality.

Auger electron spectroscopy (AES) and electron energy loss spectroscopy (ELS) measurements of the (3×3) phase [15] indicate the presence of a silicon adlayer on top of the SiC substrate. Consequently, a dimer adatom stacking fault (DAS) model containing two adatom clusters per unit cell with different stacking orientation was proposed in analogy to the (7×7) reconstruction on Si(111) [15]. In contrast, only a single protrusion per unit cell is found in STM studies [16–18]. This is shown in Fig. 1(a) in a topographic image with the (3×3) unit cell indicated in the zoomed area. A variant of the DAS model containing one adatom cluster on a silicon adlayer with two cornerholes per unit cell was therefore suggested by Kulakov *et al.* [16]. However, the STM data alone cannot reveal whether such an adatom cluster is bonded in a linear or faulted stacking geometry or if simple silicon tetramers are located directly on the SiC substrate [17].

Still a variety of models with a single adatom structure have to be considered in a structural analysis. A further reduction of models can be achieved using holographic LEED: The principle of LEED holography is based on the fact that such a prominent atom in the surface acts as a beam splitter on the incoming electron wave: electrons scattered back directly to the detector form a reference wave, electrons subjected to an additional scattering process in the substrate before reaching the LEED screen represent the object wave. The experimental diffraction pattern can thus be interpreted as a hologram [11] allowing one to extract crystallographic information on the atomic environment of the beam splitter by numerical inversion [19]. Well resolved three-dimensional atomic images have been obtained by inverting experimental LEED data created at different energies [20] and various angles of incidence [21]. Correcting numerically for the anisotropic scattering at the reference atom, a fully 3D image can be retrieved from just normal incidence data [22], the latter technique being applied in the present case.

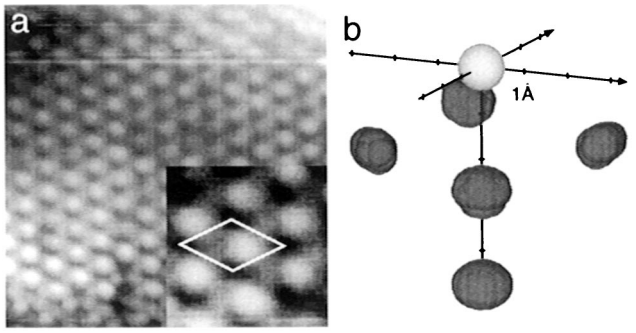

FIG. 1. (a) Topographic STM image (unprocessed data) of a 112 Å × 112 Å large section of the (3×3) SiC surface phase with the unit cell indicated in a 27 Å × 27 Å zoomed inset. (b) 3D image of the holographic reconstruction showing the local adcluster environment (dark spheres) of the topmost single adatom (light sphere) down to the fourth layer.

Yet, holographic LEED was never successfully applied to ordered superstructures with discrete diffraction spots although the theoretical concepts should be independent of the degree of order on the surface [23,24]. The important issue is the necessary sampling density required from the diffraction pattern. Of course, the larger the investigated superstructure mesh, the more fractional order LEED spots and thus the more angular data remain. Consequently, fewer aliasing effects are to be expected in the Fourier-like transform, increasing the lateral extension of real space visible in the reconstructed image [25]. For a primitive unit cell containing one adatom it has been shown that a (3×3) grid is sufficient to sample all scattering information available [26]. In this respect, the SiC(111)-(3×3) phase with one single beam splitter is the perfect candidate for a successful application of LEED holography to ordered superstructures.

The 3D real space image shown in Fig. 1(b) was obtained using fractional order spot LEED intensities acquired from the 3C-SiC sample for electron energies between 50 and 300 eV. The complete surrounding of the beam splitter is resolved free of artifacts, and atoms are depicted down to the fourth layer at an unprecedented low background noise as described elsewhere in detail [27]. The topmost adatom and beam splitter (light gray sphere) is surrounded by a trimer, thus constituting a tetrahedral adatom cluster. The adcluster is oriented opposite to the substrate orientation (local stacking fault) as determined by comparison with a previous LEED analysis of the (1×1) phase on the same sample [7,8,28]. Two atoms are visible underneath the adatom which can be attributed to the silicon adlayer and the topmost atom of the SiC bulk, respectively, in correspondence to the Kulakov model [16]. To the contrary, a tetrahedral adcluster located directly on the SiC substrate [17] is not consistent with the holographic reconstruction because it would contain only one atom underneath the beam splitter. The (3×3) DAS model with its two trimer orientations [15] can also be ruled out directly, as due to superposition six nearest-neighbor atoms would have to appear in the reconstructed image.

The only model remaining is the Kulakov model [16], yet with a stacking fault. However, a model with a full silicon adlayer should also be considered because cornerhole depressions as visible in STM images of Si(111)-(7×7) [29] are not supported by our STM images for the SiC-(3×3) surface [see Fig. 1(a)]. It should be noted that the atomic position at issue for this question is too far from the adatom to be resolved by the holographic reconstruction. So, based on the combined preinformation by AES, ELS, STM, and LEED holography the most promising model is a single adatom cluster arranged in a local stacking fault geometry on top of a silicon adlayer whose structure is yet to be determined.

The total energy minimization calculations were performed in the framework of DFT in the local density

approximation [30] using established programs [31,32] and parameters tested in detail [33]. The crystal truncation at the surface was modeled by repeated slab geometries of 3C-SiC(111) using a (3×3) surface unit cell. The slabs contained six Si-C bilayers and were separated by a vacuum region of about the same thickness shown to be sufficient for an accurate description of the SiC surface properties [33]. The atoms in the lower half of the slab were kept fixed in their ideal bulk positions. Additionally, this side of the slab was saturated with hydrogen in order to get rid of dangling bonds which could give rise to spurious interactions or charge transfer between the two slab surfaces. All other atomic coordinates were relaxed until the Hellmann-Feynman forces vanished.

Dynamical LEED intensity calculations were carried out using standard LEED programs [34] including tensor LEED for fine variation of the atomic geometry, stoichiometry, and vibrational amplitudes [35]. The Pendry R-factor [36] was used to guide an automated search algorithm [37] to determine the best-fit structure. Intensities were calculated in the energy range 50–230 eV providing a data base by far large enough for an unambiguous analysis of all parameters included in the structural search. Details of both calculational methods and analyses will be published elsewhere [33,38].

As expected from the preinformation, both the DAS model and simple silicon tetramers on SiC can be clearly ruled out by DFT and LEED. The most stable structure found in the total energy calculations and the LEED structure analysis represents a novel reconstruction model that consists of a complete Si adlayer on top of the uppermost bulklike SiC substrate layer. The adlayer containing no vacancies or cornerholes is covered by a tetrahedral adatom cluster with three basis atoms and one top atom per unit cell. Under Si-rich conditions this structure was found to be more stable by 0.14 eV per (1×1) surface unit cell than the Kulakov model which includes cornerholes. It yields a convincingly low Pendry R-factor of $R_P = 0.19$ in LEED. (For comparison, R-factors found after optimization are 0.78 and 0.80 for the Kulakov models with opposite stacking orientation, respectively, 0.68 for a single adatom with and without a Si adlayer, and 0.75 for a simple tetramer, well above the statistical error limit of the best-fit at $R_P + RR = 0.215$ [38].) In order to avoid the risk of being trapped in a local minimum of the total energy or the R-factor surface, respectively, in both methods different initial guesses were used for each model. In DFT input structures were designed to saturate as many dangling bonds as possible and to achieve a fourfold nearest neighbor coordination for most atoms while in LEED the starting geometries were based on SiC bulk positions. Convincingly, the same atomic displacements, in particular for the strongly restructured Si adlayer, were found by both methods (maximum deviation 0.07 Å [38]). As indicated by the arrows in Fig. 2(a) the adatom supporting trimer (dark shaded) is rotated by $9° \pm 2°$ and slightly expanded with respect to the adatom position [atom 1 in Fig. 2(a)] as compared to SiC bulk positions. (Because of the limited resolution this rotational displacement of 0.38 Å could not be found by STM or holographic LEED.) The neighboring six atoms (light shaded) in the Si-adlayer follow this *twist* reconstruction moving towards the two free atoms of the adlayer [atoms 2 and 3 in Fig. 2(a)] with lateral displacements of 0.81 Å (towards atom 2) and 0.74 Å (towards atom 3). Because of this relaxation these two atoms are now bonded in a cloverlike arrangement to three surrounding adatoms with bond angles close to 120° and bond lengths of 2.31 and 2.35 Å, respectively. The maximum displacement in the topmost SiC bilayer amounts to 0.16 Å.

The top view of the resulting structure in Fig. 2(b) shows that the model perfectly satisfies the requirement of fourfold coordination. The adatom cluster saturates nine of the 27 dangling bonds of the adlayer. The remaining dangling hybrids form a threefold coordination within the adlayer. Only one single dangling bond per unit cell remains at the topmost atom. All other atoms are fourfold coordinated, yet not always bonded tetrahedrally. For most of the Si atoms of the first adlayer the situation corresponds more to a "$sp^2 + p$" or "$sp + p + p$" bonding situation where the "sp^2" or "$sp + p$" orbitals form the bonds *within the first adlayer*, and the remaining "p" orbital forms a bond to the "substrate." The adatom itself appears to be unhybridized and bonded by p orbitals as judged from its bond angles of 90°. In effect, this allows an energetically favorable s-like dangling bond orbital. With this adlayer geometry the surface is largely passivated. This might be the reason for enhanced adatom diffusion in the presence of the (3×3) structure leading to better conditions for homoepitaxial SiC growth. Interestingly, the reconstruction found on the SiC(111)-(3×3) surface represents a markedly different and more efficient mechanism to saturate bonds than present in the DAS or Kulakov model which are derived from the well known Si(111)-(7×7) structure: There, cornerhole generation and dimerization are essential ingredients while absent in the true SiC(111)-(3×3). For SiC, instead, the *twist* motion and the sp^2 adlayer hybridization facilitate the reduction of dangling bonds, features that in turn are not present in the (7×7). The reason for this difference might be the difference in lattice constants of 20% for the two substrates.

The optimized *twist* model for the SiC(111)-(3×3) surface found by our combined method analysis is shown in Fig. 2(c) in a 3D view. The atoms revealed by the holographic reconstruction are whitened out for one of the clusters displayed. (Only the adatom is observed in STM.) The wave appearance of the Si adlayer resembles the *twist* motion around the adcluster allowing for the threefold cloverlike bonding of the remaining two atoms. We feel that without using the preinformation by STM and holographic LEED it would have been difficult if not impossible to solve this complex structure. The success

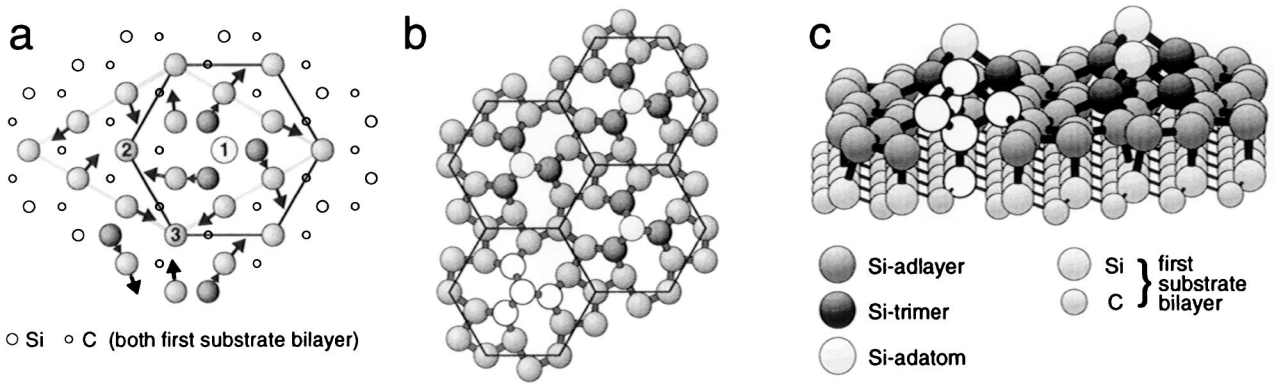

FIG. 2. The SiC(111)-(3×3) structure: (a) Lateral relaxations within the silicon adlayer and of the trimer supporting the adatom (numbered 1) indicated with respect to the ideal positions in the topmost SiC bilayer (white spheres) (b) Ball and stick model of the relaxed positions of silicon adlayer and adatom cluster (top view). (c) 3D view of the final structure. The whitened atoms represent the holographically reconstructed cluster.

of holographic LEED in this case is presumably possible due to the presence of a single prominent adatom per unit cell. We expect this method to be applicable to ordered structures under similar circumstances, although this yet awaits to be proven.

We thank A. Schöner and N. Nordell for providing SiC samples. This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through SFB 196 and SFB 292.

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