top view

S2

S1

buffer layer

SiC

Atomic structure of a bare buffer layer on SiC(0001) chemically resolved

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A chemical-specific photoelectron diffraction structure determination of the carbon rich buffer layer on SiC is reported. In addition to the long-range ripple of this surface, a local buckling in the hexagonal sublattice which breaks the local range order symmetry was unraveled.

The epitaxial growth of graphene on the surface of SiC(0001) has been shown to be one of the main routes for wafer-scale preparation of this material[1]. The direct growth of graphene on a semiconductor or isolating substrate is a first step for future technological applications on an industrial scale. On the surface of Si-terminated SiC, graphene-like layers grow epitaxially. The growth occurs by simple sublimation of Si atoms from the surface and reordering of the carbon atoms in a graphite-type structure[2]. By controlling the growth parameters, such as temperature and heating time, it is possible to prepare film thicknesses from submonolayer coverage to a few monolayers at the surface. The first layer, despite a structural similarity with graphene, does not present the same electronic characteristics of graphene and is commonly called the buffer layer (BL)[3]. For a better understanding of the influence of the BL on the electronic structure of graphene, it is of great importance to know the structure of the graphene-SiC interface, as well as that of the BL without an overlaying graphene layer. This particular system has been strongly debated in the literature for more than one decade without a definitive answer[2,4–6]. Early studies of the graphitization of the Si-face of SiC[2] proposed that the graphene layers were weakly bonded to the substrate, while more recent studies have suggested that the first carbon layer is covalently bonded to the substrate[4]. Also, an interface rich in Si has been proposed[5]. In general, a (6×6) reconstruction is observed in scanning tunneling microscopy (STM) images[7,8], which does not agree with the $(6\sqrt{3} \times 6\sqrt{3})R30°$ reconstruction usually observed in low energy electron diffraction (LEED)[2,5,9,10], a result of the differ-

ence between the lattice parameters of the honeycomb structure and SiC. It is now mostly accepted that the BL has a honeycomb structure of carbon atoms, which is demonstrated by the presence of the σ band in angle resolved photoemission spectroscopy (ARPES) results[11]. Also, these data show that the BL is covalently bonded to Si atoms on the SiC(0001) surface. A recent work, reported in a seminal article by Riedl *et al.*[12], converted a BL into a quasi-free-standing graphene monolayer after hydrogen intercalation. Further, atomically resolved STM revealed the honeycomb structure of the BL[6], but structural details seem still unclear.

In this paper, we report on x-ray photoelectron diffraction (XPD) results on the chemically resolved S1 and S2 surface components of the C 1s photoemission signal from a bare BL on SiC(0001). S1 and S2 originate from two different chemical environment inside of the corrugated unit cell of the BL, where S1 correspond to those C atoms that are more distant from the Si terminated layer of SiC(0001) substrate and S2 correspond to C atoms basically covalently bonded to this layer. Those components are indicated in Figure 1 as well as in the structure representation in Figure 3a. The unique advantage of the chemical sensitivity of synchrotron-based high-resolution photoelectron diffraction has allowed probing the local order of the carbon atoms in their different chemical environments of the BL. The comparison of the experimental diffraction patterns with simulations using a comprehensive multiple scattering calculation approach unambiguously reveals a buckling in the sublattice of the honeycomb structure in addition to the ripple attributable to the $(6\sqrt{3} \times 6\sqrt{3})R30°$ reconstruction. The S2 and S1 component indicate that the buckling is large and practically zero in the regions close to and far from the substrate, respectively.

The XPD experiments were carried out in an ultra-high vacuum (UHV) chamber at the U-55 PGM beamline at the DELTA Synchrotron in Dortmund, Germany. The base pressure was in the low 10^{-11} mbar range. The 6H-type SiC(0001) samples were cut out of a SiC wafer (n doped, N, $2-4 \times 10^{18}$ cm^{-3}) and etched in 1 atm hydrogen atmosphere for 10 minutes at 1100 °C, to remove polishing damage and to chemi-

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cally passivate the surface. In UHV, the sample was annealed at 1100 °C for 10 s and at 1150 °C for 20 s, producing the LEED pattern typical of the $(6\sqrt{3} \times 6\sqrt{3})R30°$ reconstruction[3]. It is important to note that flash annealing at 1150 °C is not leading to the formation of graphene at the surface[13], which is a crucial preparation detail since our focus is the bare BL. The photoelectron diffraction patterns were recorded over a polar angle range of $12° \leq \Theta \leq 75°$, and over a full 360° azimuthal range (Φ), in steps of 3° for both angles. Figure 1 shows one of the 2640 high-resolution spectra collected and which were used in the following for constructing the diffraction patterns. The photoemission data were processed by removing the inelastic scattered electrons[14] and three Voigt components were identified in the signal which are associated with each chemical species in the sample.
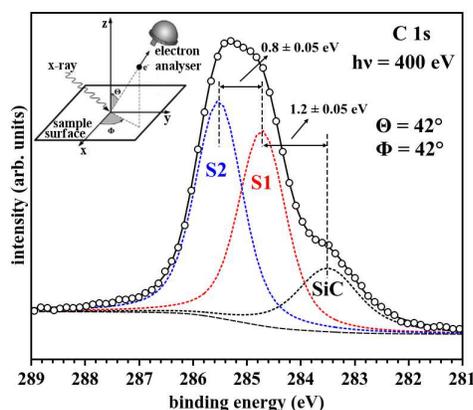
Fig. 1 C 1s core-level spectra recorded at a photon energy of $h\nu = 400$ eV and at polar and azimuth angles of $\Theta = 42°$ and $\Phi = 42°$, respectively. The continuous black line represents the fitting envelope consisting of the surface components S1, S2, and SiC. The inset shows the schematic for the XPD experiment.

The energy separation between the S1 and S2 components of $\Delta E = (0.8 \pm 0.05)$ eV agrees well with other results[11,15]. In general, the peak related to graphene is situated at about 1 eV higher binding energy relative to the C 1s peak of the SiC[11,16]. Figure 1 displays the S1 component at $\Delta E = (1.2 \pm 0.05)$ eV higher binding energy relative to the peak of the SiC, agreeing well with other results[15] and indicating that no substantial graphene is present. It is important to stress that due to the low kinetic energy of the photoelectrons, if even small areas would be covered by a graphene layer, the SiC component would appear much more damped. Moreover, in such a case a narrow and evident extra component would be necessary to fit higher polar emitting angles as demonstrated by Emery *et al.* in the Supplementary Information of ref.[17]. In addition, as we will show next, the distance between the lowest carbon layer adjacent to the top most Si-layer is too small for graphene[18].

Figures 2a and 2c show the experimental diffraction patterns obtained from the XPS component fitting procedure. In this work, we focus on the S1 and S2 components.
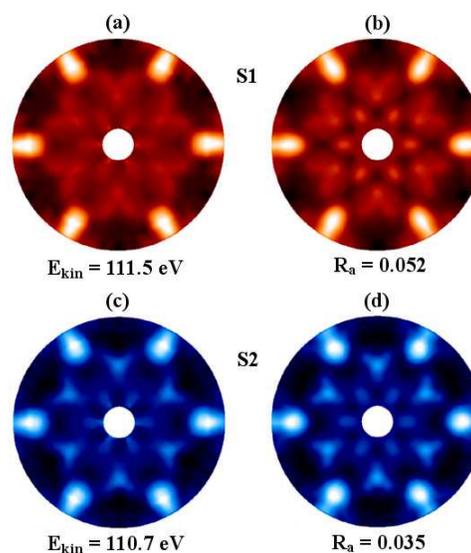
Fig. 2 Photoelectron diffraction patterns: (a) experiment and (b) theory for S1 component; (c) experiment and (d) theory for S2 component.

The diffraction patterns of Figure 2b and 2d were obtained from multiple scattering diffraction calculations with a maximum of 8 scatter events with a cluster of 453 atoms, using the MSCD package[19]. The structures were relaxed using an optimization process based on a genetic algorithm[20]. The structure is determined in a fitting procedure that searches for the set of parameters optimizing the agreement between theoretical and experimental diffraction patterns through minimization of the reliability factor (R_a), as described elsewhere[19,20]. The error bars were determined using the procedure reported in the literature[21,22].

Figure 3a shows a schematic illustration of the BL model in a side view. With the possibility of separating the S1 and S2 components within a spectrum, each region was simulated as a flat layer of carbon atoms with a honeycomb structure on the Si-face of a SiC cluster. The inset of Figure 3a shows a top view of the honeycomb structure, consisting of two hexagonal sublattices (A and B, green and red, respectively). Within the structure relaxation process during the simulations, sublattices A (green) and B (red), could be moved in the [0001]-direction, which results in a buckling of the surface layer. The vertical distance of the buckling is defined as $d1$ in Figure 3. The in-plane lattice parameters were fixed at 2.463 Å for the BL and 3.081 Å for the SiC.

Figure 3b shows the reliability factor (R-factor) as a function of $d1$ for S1 and S2. The best R-factor for the surface
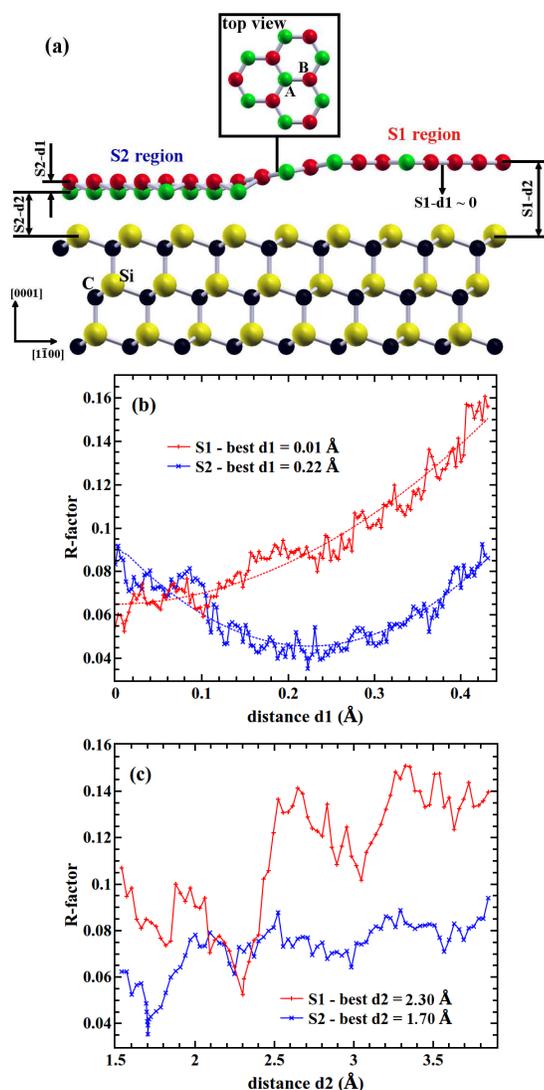
Fig. 3 (a) Schematic illustration of the BL model (side and top view). The buckling distance $d1$ is the vertical distance between the two hexagonal sublattices (A and B in detail, top view) and $d2$ is the distance between the BL and the Si layer of SiC (the reference is the closest hexagonal sublattice to the substrate). (b) R-factor as a function of the $d1$ distance for S1 and S2. (c) R-factor as a function of the $d2$ distance for S1 and S2 (dotted lines to guide the eye).

components S1 was obtained for $d1 = 0.01 \pm 0.02$ Å which is practically zero taking the experimental uncertainty into account. For the component S2 the lowest R-factor was $R_a = 0.035$ which corresponds to a distance of $d1 = 0.22 \pm 0.05$ Å. For the BL to SiC distance the best R-factor was obtained for $d2 = 2.30 \pm 0.05$ Å and $d2 = 1.70 \pm 0.06$ Å for the S1 and S2-component, respectively. The height difference between the S1 region and the highest hexagonal sublattice in the S2 region (1.70 Å + 0.22 Å = 1.92 Å) is 0.38 Å, which agrees

well with our results reported previously[18] of 0.4 Å, corresponding to the height of the Gaussian profile included in that BL model. This means that the S1 region is farther from the substrate and thus less bonded than the S2 region and does not have buckling. In fact, in terms of the binding energy for photoemission, S1 is more similar (structurally and electronically) to graphene than the S2 region, notwithstanding the fact that it is not pristine graphene. Within the BL, the largest vertical distance between atoms is 0.6 Å, which agrees well with theoretical results from density functional theory (DFT) calculations[23].

The quality of the presented results is expressed by nearly identical experimental and theoretical patterns of Figure 2 and indicated by the very low R-factors of $R_a = 0.052$ and $R_a = 0.035$ as displayed by Figure 2b and 2d, respectively.

The buckling for the BL has theoretically been predicted[23–25], however in a slightly different way from what is proposed in this work. In general, due to the different distances between the C atoms in the BL and the Si atoms in SiC, the relaxed structure has a height distribution for the C atoms at the local range. For the S2 region, the vertical parameter of $d2 = 1.92$ Å corresponds to the distance of a Si-atom within SiC to a C atom positioned above. Assuming the C atoms belonging to the S2 region are within a circle of radius 5 Å around the C atom's top as reported from STM measurements[6], the average distance between the Si atoms and the closest C atom in BL is 1.95 Å (13 Si atoms, standard deviation of 0.15 Å). This distance is very close to 1.90 Å, which is the C-Si distance of the SiC structure. This reflects the sp³ feature of the C atoms in the S2 region, already observed experimentally by Raman spectroscopy[26].

There are few works that depict the structural characteristics of the BL via a photoemission decomposition of the S1 and S2 components. Emery et al.[17] used x-ray standing wave-excited photoelectron spectroscopy (XSW) and x-ray reflectivity (XRR) experiments to determine the distance between the BL and the SiC substrate. They obtained a distance of S1-$d2 = 2.3 \pm 0.2$ Å for 0.5 layer of graphene on the BL, in perfect agreement with our result of S1-$d2 = 2.30 \pm 0.05$ Å. For the second interface parameter, they reported a distance of S2-$d2 = 2.0 \pm 0.1$ Å, a result that agrees well with our value of 1.92 ± 0.08 Å for the maximum height within the S2 region. In ref.[17] the global height distribution was indirectly obtained from a σ parameter in their XSW+XRR model. They find σ = 0.6 Å for S1 and σ = 0.18 Å for S2. In the present case, due the local-order sensitivity of the low-energy XPD, the buckling is directly obtained by minimizing a vertical displacement in the C sublattices into the cluster models that independently describe the regions related to S1 and S2 components. In opposition to ref.[17], we determine a higher $d1$ displacement for the C atoms in S2 and almost coplanar C atoms for S1. Such a find is intuitively expected since S2

reflect C atoms more covalently bonded to Si atoms of the Si-terminated layer of the substrate, while S1 represent C atoms with a graphene-like character. This findings are supported by previous theoretical predictions[23–25].

In conclusion, we presented the results of a photoelectron diffraction study with the S1 and S2 components of the buffer layer on SiC(0001) spectrally resolved. Our results show that region S1 reflects the honeycomb structure of graphene, basically flat and 2.3 Å distant from the Si layer on the SiC, with apparently an sp^2 character. The S2 region has the same honeycomb structure, but with an appreciable buckling of $d1 = 0.22$ Å between the two hexagonal sublattices that form the structure, supporting the idea of a pyramidalization of this structure, i. e., an sp^2-to-sp^3 rehybridization[25].

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