A chemical-specific photoelectron diffraction structure determination of a 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. The direct growth of graphene on a semiconductor or an 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 via simple sublimation of Si atoms from the surface and reordering of the carbon atoms in a graphite-type structure. 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 bearing a structural similarity to graphene, does not present the same electronic characteristics of graphene and is commonly called the buffer layer (BL). 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. Early studies of the graphitization of the Si-face of SiC 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. Also, an interface rich in Si has been proposed. In general, a (6 × 6) reconstruction is observed in scanning tunneling microscopy (STM) images, which does not agree with the (6√3 × 6√3) R30° reconstruction usually observed in low energy electron diffraction (LEED), a result of the difference between the lattice parameters of the honeycomb structure and SiC. It has now been 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. 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., converted a BL into a quasi-free-standing graphene monolayer after hydrogen intercalation. Further, atomically resolved STM revealed the honeycomb structure of the BL, but structural details seem still unclear.

In this communication, we report on X-ray photoelectron diffraction (XPD) results of 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 environments inside of the corrugated unit cell of the BL, where S1 corresponds to those C atoms that are more distant from the Si terminated layer of SiC(0001) substrate and S2 corresponds to C atoms basically covalently bonded to this layer. Those components are indicated in Fig. 1 as well as in the structure representation in Fig. 3a. The unique advantage of the chemical sensitivity of synchrotron-based high-resolution photoelectron diffraction has allowed the probing of 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√3 × 6√3) R30° reconstruction. The S2 and S1 components 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 × 10¹⁸ cm⁻³) and etched in
higher binding energy relative to the C 1s peak of the SiC. In general, the peak related to graphene is situated at about 1 eV binding energy relative to the peak of the SiC, agreeing well with other results. \(^{11,15}\) In Fig. 1 displays the S1 component at \(E = (1.2 \pm 0.05)\) eV higher binding energy relative to the peak of the SiC, agreeing well with other results. \(^{15}\) The vertical distance of the buckling is \(0.05\) Å and \(d_{2}=0.02\) Å which is practically zero taking the experimental uncertainty into account. For the component S2 the lowest \(R\)-factor was \(R_{s} = 0.035\) which corresponds to a distance of \(d_{1} = 0.22 \pm 0.05\) Å. For the BL to SiC distance the best \(R\)-factor was obtained for \(d_{2} = 2.30 \pm 0.05\) Å and \(d_{2} = 1.70 \pm 0.06\) Å for the S1 and S2 components, 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 of 0.4 Å, corresponding to the height of the Gaussian profile included in the BL model. This means that the S1 region is farther from the substrate and thus less bonded than the S2 region and does not show buckling. In fact, in terms of 8 scattering 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 \((R_{s})\), as described elsewhere. \(^{19,20}\) The error bars were determined using the procedure reported in the literature. \(^{21,22}\)
has a height distribution for the C atoms at the local range. For the S2 region, the vertical parameter of $d_2 = 1.92$ 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 top of the C atom as reported by STM measurements, 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 $sp^3$ feature of the C atoms in the S2 region, already observed experimentally by Raman spectroscopy.

There are few studies that depict the structural characteristics of the BL via a photoemission decomposition of the S1 and S2 components. Emery et al. 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 $S1-d_2 = 2.3 \pm 0.2$ Å for 0.5 layer of graphene on the BL, in perfect agreement with our result of $S1-d_2 = 2.30 \pm 0.05$ Å. For the second interface parameter, they reported a distance of $S2-d_2 = 2.0 \pm 0.1$ 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 $\sigma$ parameter in their XSW + XRR model. They find $\sigma = 0.6$ Å for S1 and $\sigma = 0.18$ 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 contrast to ref. 17, we determine a higher $d_1$ displacement for the C atoms in S2 and almost coplanar C atoms for S1. Such a finding is intuitively expected since S2 reflects the C atoms more covalently bonded to Si atoms of the Si-terminated layer of the substrate, while S1 represents C atoms with a graphene-like character. This findings are supported by previous theoretical predictions.

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 $d_1 = 0.22$ 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.

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References