π Band Folding and Interlayer Band Filling of Graphene upon Interface Potassium Intercalation

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The structural and electronic properties of epitaxial monolayer graphene on SiC(0001) are examined upon potassium intercalation. Notably, the first real-space observation via scanning tunneling microscopy of the (2 × 2) superstructure in graphene-based thin films formed by the potassium atoms below the uppermost graphene layer is presented. Therein, additional signatures stemming from quasiparticle interference effects are found allowing investigations of the electronic bands of K-intercalated epitaxial monolayer graphene on a local scale. Those data are compared to area-averaged results obtained from photoelectron spectroscopy. In particular, backfolding of the graphene π bands are found as a consequence of the (2 × 2) superstructure of the K atoms with respect to the graphene lattice. This is accompanied by a strong n-type doping effect that causes a rigid shift of the Dirac bands to higher binding energies and filling of two parabolic interlayer bands at the Γ point of the surface Brillouin zone of the graphene lattice as well. This electronic configuration is promoted by additional penetration of potassium atoms into the interspace between the SiC substrate and the buffer layer that is located between the substrate and the quasi-freestanding graphene sheet. Consequently, the epitaxial monolayer graphene sample transforms to n-doped epitaxial bilayer graphene upon K intercalation.

1. Introduction

Graphene is a unique material that exhibits a variety of properties resulting from the linear dispersion of the π bands at the Dirac points, for example, quasiparticles behave like massless Dirac carriers,[1,2] an anomalous half-integer quantum Hall effect,[3] and a high carrier mobility.[4] Even superconductivity occurs in graphene-based systems either by twisting the adjacent layers of bilayer graphene[5,6] or upon intercalation with alkali and earth alkaline metals. In the latter case, the reported critical temperatures strongly depend on the number of adjacent layers and the choice of the atomic species used for intercalation.[7–15]

As a result of K intercalation of epitaxial bilayer graphene (EBLG) on SiC(0001) at low temperatures, Bostwick et al. determined a continuous rigid shift of the Dirac point to higher binding energies that scales with the potassium content.[16,17] Besides n-doping caused by additional charges in the graphene π bands, some studies also report on filling of one parabolic interlayer (IL) band located at the Γ point of the surface Brillouin zone (SBZ), for example, for epitaxial graphene bilayers intercalated with Rb[18] and Ca[19] atoms.

Samples of epitaxial graphene also undergo structural transitions upon metal intercalation under certain conditions. In particular, the covalent bonds of the buffer layer (located between the quasi-freestanding graphene sheet(s) and SiC) to the Si atoms of the substrate can be broken as a result of the intercalation of the metal atoms below the buffer layer. Consequently, the buffer layer is effectively electronically decoupled from the SiC substrate and, thus, develops graphene-like π bands[20–22] similar to hydrogen intercalation,[23] but is strongly n-doped.

Experimentally, electronic structures can not only be investigated by area-averaging experimental techniques like angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), but also on a more local scale by scanning tunneling techniques. Besides spectroscopic methods, 2D contours within the Brillouin zone (BZ) at certain energies can be determined using Fourier-transform scanning tunneling microscopy (FT-STM) that probes interference patterns resulting from scattering events of the charge carriers.[24,25] Scattering events of the quasiparticles in graphene and the resulting interference patterns have already been reported for pristine epitaxial monolayer graphene (EMLG) and epitaxial bilayer graphene on SiC(0001).[26–29] In particular, these quasiparticle interference (QPI) effects originate from intravalley scattering within a single Dirac cone, but also from intervalley processes upon transitions between two inequivalent electron pockets.[26–29]

In this paper, we scrutinize samples of potassium-intercalated EMLG on SiC(0001) by means of local and area-averaging experimental methods at low temperatures. For the highest accessible K concentration we find a highly ordered (2 × 2) superstructure that the K atoms form below the uppermost...
graphene layer. Further, we observe that the K atoms also reside below the buffer layer of the EMLG that is located between the quasi-freestanding graphene sheet and the SiC substrate. This causes an effective decoupling of the buffer layer from the SiC substrate and a transition to K-intercalated EBLG. This configuration promotes strong n-doping of the graphene sheets, where besides a rigid shift of the Dirac bands to higher binding energies also a filling of two parabolic IL bands is observed. Further, we examine the structural stability of the produced samples at room temperature (RT).

In passing we note that Li-intercalation on graphene/SiC(0001) results in so-called Kekulé-ordered graphene, which was shown by Bao et al. to exhibit a \((\sqrt{3} \times \sqrt{3})R30^\circ\) superlattice period.\(^{[30,31]}\) By contrast, we performed our ARUPS and FT-STM measurements mainly on K-intercalated graphene forming a \((2 \times 2)\) superstructure, which differs in the size of its supercell, in the orientation with respect to graphene, and in the number of alkali metal atoms per unit area. Hence, the \((\sqrt{3} \times \sqrt{3})R30^\circ\) and \((2 \times 2)\) superstructures exhibit different constant energy contours (or different electronic structures in general) and should therefore not be confused.

2. Results and Discussion

2.1. Characterization of the Intercalation Process

The deposition of potassium atoms was monitored optically using differential reflectance spectroscopy (DRS),\(^{[32,33]}\) which allows the reproducible preparation of samples with similar K content. Details on this procedure are provided in Section S1, Supporting Information. Without K intercalation, the EMLG on SiC(0001) is characterized by low-energy electron diffraction (LEED) patterns exhibiting diamond-like spot groups (formed by blue circles in Figure 1a), which are commonly attributed to the \((6 \times 6)\) reconstruction of the buffer layer located between the SiC substrate and the quasi-freestanding graphene layer.\(^{[34,35]}\)

At a certain amount of K on the EMLG on SiC(0001) sample, which is the highest K concentration before the surface is covered with potassium clusters (as indicated in the DRS signal, see Figure S1, Supporting Information), the subsequently acquired LEED pattern (Figure 1a) exhibits an additional feature in the center of the diamond-like spot groups. The positions of the additional features are indicated by green circles.

Figure 1. a) Contrast-inverted, distortion-corrected LEED image of K-intercalated EMLG on SiC(0001). Lines depict the 2D reciprocal unit cell of the SiC (red) and the graphene lattice (blue) as well as the \((2 \times 2)\) superstructure (green). Open circles indicate spot positions of multiple scattering between the graphene and the SiC lattice (blue) and of the \((2 \times 2)\) superstructure (green). b) STM image of the sample surface. A structural model of the carbon atoms (yellow) and the \((2 \times 2)\) superstructure (green) is depicted in the lower left corner and in the purple-framed close-up view. We suppose that every second C atom is imaged (as highlighted in red), which gives the impression of small rhombuses. The gray-framed close-up view focuses on a sample area with individually resolved C atoms forming hexagons (lower part). c) FT-STM image of (b) with corresponding reciprocal unit cells. d) Height profiles along the blue and green lines in (b) (endpoints of the lines are marked with red crosses).
in the LEED pattern of the K-intercalated EMLG sample shown in Figure 1a and correspond to the already reported \((2 \times 2)\) superstructure formed by the K intercalants with respect to the graphene lattice.\(^{[36]}\) Figure 1b shows an STM image of the K-intercalated sample. The largest area of the image shows a contrast modulation where every fourth honeycomb of the graphene lattice appears brighter. For clarification, an illustration of the graphene lattice is provided in the lower left part of the STM image and in the purple-framed close-up view as well. Accordingly, the FT-STM image in Figure 1c exhibits features of the graphene lattice (simulation drawn in blue) and additional features that arise from the \((2 \times 2)\) superstructure formed by the intercalants (simulation drawn in green; half the periodicity in reciprocal space). However, a small area is visible in the STM image (Figure 1b left of center) that does not show the \((2 \times 2)\) superstructure. As one can see in the gray-framed close-up view, there are parts of the surface where the six carbon atoms of the graphene hexagons are individually resolved, though with varying brightness. This small sample area is most likely not affected by potassium intercalation, leading to a different contrast that does not exhibit the \((2 \times 2)\) superstructure. It is reminiscent of the STM contrast obtained for quasi-free-standing monolayer graphene by Mallet et al.\(^{[27]}\) Due to the existence of this small area, tip-induced imaging artifacts can be excluded since both lattices are resolved in the same lines in the fast (i.e., horizontal) scan direction. Note that this is the first real-space observation of the \((2 \times 2)\) superstructure formed by K atoms with respect to the graphene lattice for a finite number of graphene sheets. Quite noteworthy, STM measurements in the literature imaging the \((2 \times 2)\) superstructure of K-intercalated highly oriented pyrolytic graphite exhibit a completely different contrast.\(^{[36]}\)

Figure 1d displays the height profiles extracted along the lines depicted by the corresponding colors in the STM image in (b). The measured periodicity in the intercalated area (green) is clearly doubled compared to the pristine area (blue). The apparent corrugation amplitude of the pristine area is about 0.2 Å (blue curve; peak-to-peak values are given), which is significantly smaller than the average value of 0.4 Å reported for pristine EMLG\(^{[34,38]}\) and the amplitude of about 1 Å reported for the sole buffer layer on SiC(0001).\(^{[39]}\) Compared to the small pristine area, the corrugation amplitude of the intercalated area is higher and amounts to about 0.3 Å (green curve in Figure 1d). As we show later, there is a significant charge transfer from the K atoms to graphene. Nonetheless, the corrugation amplitude of the intercalated area is much lower than the diameter of potassium (2.76 Å),\(^{[40]}\) which suggests that the potassium atoms are located below the topmost graphene layer. Similar observations have been reported for STM images of Ca-intercalated EBLG (corrugation amplitude 0.1 Å,\(^{[41]}\) atomic diameter of Ca 2.00 Å\(^{[42]}\)) and also for Li intercalation.\(^{[36]}\) Our STM images of the same EMLG on SiC(0001) substrate but prepared with a higher K content (cf. Figure S2, Supporting Information) exhibit disordered features with a corrugation amplitude that corresponds roughly to the diameter of K ions. Those features can be identified as K atoms residing on top of the uppermost graphene layer, but without any structural order. In comparison to the lower corrugation amplitude of the \((2 \times 2)\) superstructure, this finding proves that the highly ordered structure is indeed formed by potassium below the topmost graphene layer, since for spatially well-separated K ions in a \((2 \times 2)\) superstructure on top of the uppermost layer a much larger corrugation would be expected.

In order to determine the chemical composition of our samples we performed X-ray photoelectron spectroscopy (XPS) measurements.

Figure 2a shows the C 1s and K 2p core levels for the K-intercalated sample in normal and grazing emission (0° and 70° with solid and dotted lines, respectively). The spectral deconvolution is discussed in the text. b) C 1s core level spectra, measured under normal emission, for the K-intercalated sample (black) in comparison to pristine EMLG (red). c) ARUPS near the K point of K-intercalated EMLG on SiC(0001) (\(T_{\text{sample}} \approx 35\)K, detector resolution: 2.56 meV, 0.05° correction) corresponding to \(\sim 0.0018\) Å\(^{-1}\). d) Energy distribution curve of (c) integrated over all \(k\) values. The red arrow highlights a weak feature of the energy distribution curve that originates from a faint nondispersive band slightly visible in (c). e) Scheme of the SBZ of the graphene lattice (gray) and of the \((2 \times 2)\) superstructure (red). The green line depicts the intersection where the data in (c) was recorded.

Figure 2a shows the C 1s and K 2p core levels for the K-intercalated sample with the \((2 \times 2)\) superstructure measured at normal emission (0°, solid line) and grazing emission (70°, dotted line). Remarkably, the K 2p\(_{1/2}\) and K 2p\(_{3/2}\) peaks are both asymmetric, which is an indication for the presence of potassium in different chemical conditions, that is, some K atoms form additional chemical bonds to Si atoms of the topmost SiC layer while other K atoms do not. In particular, a rather similar behavior has been reported for the intercalation with atomic Li\(^{[43]}\), Au\(^{[44]}\), or Yb\(^{[45]}\) when the intercalants also penetrate into the interspace between the buffer layer and the SiC substrate. By contrast, asymmetric peak shapes were neither observed for K-intercalated monolayer graphene on Au\(^{[46]}\) nor for K-intercalated graphite.\(^{[47]}\) This is consistent with only one chemical environment of the potassium atoms, that is, in the first case only between graphene and Au, and in the second
in the case only sandwiched between adjacent graphene sheets. Thus, judging from the asymmetry of the K 2p doublet observed in Figure 2a we conclude that the K atoms are located below the topmost graphene layer and below the buffer layer in our samples. In principle, shake-up processes could also contribute to the XPS signal causing satellites at higher binding energies and thus asymmetric peak shapes. However, we consider these shake-up satellites to be unlikely in graphene samples because they seem to be absent in similar measurements of K-intercalated graphite, for instance. The angular dependence of the core level spectra reveals that the intensity in the entire range of the K 2p doublet is smaller for grazing emission (dotted line) than in normal emission (solid line). This finding suggests that the K atoms are located predominantly below the topmost graphene layer. To a somewhat lesser extent the K atoms may also be located below the buffer layer. This is consistent with the shape of the K 2p peaks discussed above. Although potassium could in principle also adsorb on top of the sample surface as already discussed, this occurs only very rarely in the optimally K-intercalated samples (i.e., leading to the $2 \times 2$ superstructure), since their contribution to the area-averaged XPS spectrum is negligible.

The analysis of the C 1s core level is more difficult. Figure 2b depicts the corresponding XPS data of the pristine (red curve) and K-intercalated (black curve) EMLG sample in normal emission. Apart from a slight intensity decrease, the component originating from carbon atoms bound to Si atoms in the SiC crystal (at $283-284$ eV, not to be confused with the graphene buffer layer) does not change significantly. However, the second maximum at $\approx 284.7$ eV shifts by about $0.3$ eV toward higher binding energies upon K intercalation. This shift is accompanied by an asymmetric line shape of the black curve that is most likely mediated by the emergence of at least one new component. We show in Supporting Information that a spectral deconvolution of the data does not allow for an unequivocal assignment of the spectral components, because the asymmetric peak shape does not exhibit individually resolved peaks. While the separately resolved peak at $283-284$ eV was assigned above, the remaining components can be attributed to K-intercalated graphene, but their exact origin is unknown. Intriguingly, the components originating from carbon atoms located in the buffer layer (cf. ref. [47]) are no longer identifiable in the spectra of the K-intercalated sample. However, a comparable shift of about $0.8$ eV accompanied by an asymmetric line shape upon K deposition has also been reported for 1 ML graphene on Au, where no buffer layer is present. Consequently, one cannot conclude a change in the buffer layer from the C 1s peaks alone, but only in combination with the results of the K 2p peaks explained above.

Independent of the emission angle, no distinct features of the K 2p doublet emerge in the XPS spectra that would allow a reasonable deconvolution of different components contributing to the total signal. Therefore, the total intensity can only be estimated reliably by numerical integration over the entire K 2p doublet range. For the estimation of the integrated intensity in the case of the C 1s core level spectra, four Voigt profiles are fitted to the data. As already mentioned above, the buffer layer features can no longer be identified. Thus, only the origin of the C 1s (SiC) component of C atoms that are bound in the SiC substrate is known. The remaining contributions stem from the graphene layer(s) and/or the (former) buffer layer that are influenced upon K intercalation. Thus, these features highlighted by the blue shaded area are cumulated to “C 1s (rest)” with a similar asymmetric line shape as for Yb-intercalated zero-layer graphene (ZLG). From the integrated intensities of the K 2p doublet and the C 1s (rest) feature a K:C ratio of $0.9 \pm 0.3$ can be estimated. This ratio can be approximated as K:C $\approx 1:8$. Considering that C 1s (rest) also includes contributions from the buffer layer of the pristine sample, this ratio indicates that almost twice the amount of potassium atoms that would be necessary for the formation of the $2 \times 2$ superstructure solely with the uppermost graphene layer are situated in the sample. Since the amount of K atoms located on top of the sample is negligible, this finding strongly suggests that the K atoms also penetrate below the buffer layer. In most cases (e.g., Cs, Na, Al) this is accompanied by a significant shift of the C 1s (SiC) component to lower binding energies. However, Figure 2b reveals that this component does not shift upon K intercalation. The example of Rb intercalation (same lateral $2 \times 2$ structure) verifies that penetration below the buffer layer can, in fact, occur without an energetic shift of this component.

As a consequence of the $2 \times 2$ structure that the K atoms form with respect to the graphene lattice, the $\pi^*$ bands of graphene also emerge at the K point (cf. Figure 2e) due to folding. Figure 2e shows the ARUPS data acquired near the K point of the SBZ of the hexagonal ($2 \times 2$) structure along an intersection depicted by the green line in Figure 2e. Obviously, the $\pi^*$ bands are rigidly shifted to higher binding energies (Dirac point at $\approx 1.5$ eV) compared to pristine EMLG ($\approx 0.4$ eV). Thus, K intercalation of EMLG causes strong n-doping in those samples. The electronic structure will be analyzed and discussed in detail later. Based on the ARUPS data near the K point (Figure 2c) the momentum-integrated intensity in Figure 2d exhibits a weak maximum, highlighted by the red arrow, at $\approx 0.7$ eV originating from a faint nondispersive band that can be most likely assigned to the still (partially) populated K 4s level. Similar nondispersive bands have already been observed for metal-intercalated EMLG where the intercalants were assumed to penetrate below the buffer layer (e.g., Yb). In particular, such bands were also observed upon Yb intercalation of ZLG, which led Rosenzweig et al. to the conclusion that these features originate from metal atoms located in the interspace between the SiC substrate and the former buffer layer.

Having now established the possibility that decoupling of the buffer layer might occur upon K penetration below the buffer layer, the structural properties are refined in the following. STM images of pristine EMLG and EBLG samples usually exhibit a long-range contrast modulation that results in the observation of defined features in the corresponding FT-STM images assignable to a $(6 \times 6)$ superstructure originating from the surface reconstruction of the buffer layer with respect to the SiC lattice. However, there is no evidence of similar features in the FT-STM image of the K-intercalated sample (cf. Figure 1) that can be assigned to a $(6 \times 6)$ superstructure. Faint features surrounding the image center and the first-order features of the graphene lattice appear in a different
direction and ii) describe a smaller lattice in real space with a lattice constant reduced by a factor of 0.72 compared to the \((6 \times 6)\) superstructure. Those features are addressed later. In agreement with a study of Li-intercalated EMLG,\(^{[38]}\) the lack of a \((6 \times 6)\) contrast modulation in the STM image indicates that the buffer layer changes its surface reconstruction upon K intercalation, which provides additional evidence that the buffer layer is not covalently bound to the substrate anymore. Moreover, this behavior can only be achieved upon penetration of K atoms into the interspace between buffer layer and SiC substrate. As an important result, the K-intercalated EMLG sample behaves like K-intercalated quasi-freestanding EBLG.

However, the LEED pattern acquired of the K-intercalated sample (Figure 1a) still exhibits features that are commonly attributed to the surface reconstruction of the buffer layer. In several studies those features vanished upon metal intercalation (e.g., Li\(^{[38]}\)), especially, when the intercalants penetrate between the buffer layer and the SiC substrate. Nevertheless, in the case of Yb intercalation of ZLG, where the decoupling of the buffer layer has clearly been demonstrated, those features are still discernible but strongly weakened,\(^{[48]}\) similar to our observations upon K intercalation of EMLG. The observed features and their intensity distribution can be described as a consequence of multiple scattering up to the second order between graphene and the SiC lattice\(^{[50]}\), as depicted by the blue circles in Figure 1a. As expected, the spot intensities of the observed pattern decrease with increasing order of the multiple scattering processes. Thus, also faint features are describable by considering higher diffraction orders. Consequently, the assumption of a reconstructed buffer layer is not required to explain the observed (geometric) diffraction pattern. With the mean free path of electrons at \(E_{\text{kin}} = 70\) eV being up to 10 Å,\(^{[53]}\) LEED can probe even the lattice of the SiC substrate, and multiple scattering processes are indeed possible. On the contrary, STM only probes the electronic density of states (near the Fermi energy) at the surface with an expectedly smaller information depth compared to LEED, which confirms the experimental findings above.

Under the assumption that the \((2 \times 2)\) superstructure in relation to the graphene lattice is formed by metal atoms above the buffer layer without modifying it, the intact buffer layer should still exhibit the \((6 \times 6)\) surface reconstruction with respect to the SiC lattice. Accordingly, one should expect at least first-order multiple scattering features of the \((6 \times 6)\) reconstruction surrounding the features of the \((2 \times 2)\) superstructure in the LEED pattern. However, this is not the case for the K-intercalated EMLG sample (cf. Figure 1a). On the other hand, as shown in Section S3, Supporting Information, those features were actually detected for low K concentrations in a different EBLG sample alongside weak spots of the usual diamond-like pattern. Deposition of even more K atoms leads to the appearance of the very same LEED pattern as observed upon K intercalation of EMLG. Therefore, it can be concluded that K atoms initially intercalate between the topmost layers of EBLG. For higher concentrations, they also penetrate between the buffer layer and the uppermost SiC layer, thereby decoupling the former from the underlying substrate. In retrospect, this finding supports the conclusion of an electronic decoupling of the buffer layer from the substrate upon K intercalation of EMLG.

![Figure 3](image-url)

**Figure 3.** ARUPS acquired with the 2D detector at the K point of K-intercalated EMLG on SiC(0001) after the sample had been stored in ultrahigh vacuum at room temperature for several days (detector resolution: 8.36 meV, 0.1° corresponding to \(=0.0034\) Å\(^{-1}\)). The observed bands are a superposition of two separate \(\pi\) bands, one with its Dirac point located at low binding energies \((=0.4\) eV\) similar to pristine EMLG,\(^{[51]}\) and one at higher binding energies \((=1.2\) eV\).

As we elucidate by means of LEED in the Supporting Information, the \((2 \times 2)\) structure of the K-intercalated EMLG sample remains stable even after 20 days in the STM setup at \(T < 5\) K. However, at 300 K a new \((\sqrt{3} \times \sqrt{3})R30°\) superstructure forms with respect to the graphene lattice while the \((2 \times 2)\) phase vanishes. If this structural transition is different for the uppermost graphene layer and the (former) buffer layer, then it is intriguing to examine how the electronic structure behaves in comparison to the as-deposited K-intercalated EMLG on SiC(0001) depicted in Figure 2c. **Figure 3** displays ARUPS data acquired near the K point of the graphene SBZ after the structural transition. The observed bands can clearly be identified as the superposition of two separate \(\pi\) bands, one with its Dirac point located at low binding energies \((=0.4\) eV\) similar to pristine EMLG,\(^{[51]}\) and one at higher binding energies \((=1.2\) eV\).

This observation agrees qualitatively with experimental data in the literature obtained after the annealing of intercalated samples, although at temperatures significantly above RT (Rb\(^{[49]}\) Na,\(^{[22]}\) Eu,\(^{[54]}\) Al,\(^{[50]}\) Yb\(^{[20,55]}\)). Earlier studies attribute this observation to a laterally inhomogeneous sample consisting of intercalated and pristine graphene areas.\(^{[49]}\) However, recent calculations of Yb-intercalated EMLG, which also consider possible penetration of intercalants below the buffer layer, reveal that this observation can be attributed to a configuration in which intercalants are only located between the former buffer layer and the SiC substrate and no longer between both graphene sheets.\(^{[46]}\) From this comparison to literature reports, we conclude that in this configuration the upper graphene layer is just slightly doped (similar to pristine EMLG), but that the lower graphene layer is strongly doped. The latter effect can only occur if the chemical bonds with the SiC substrate are passivated upon K intercalation, because in the case of strong
covalent interaction a possible charge accumulation at the buffer layer would be reduced by charge delocalization toward the SiC. Due to the concluded weakening of bonds, the lower graphene layer no longer behaves like a buffer layer in the usual sense of the term.

For this stage of intercalation we determined a work function of 3.44 eV from the secondary electron cutoff in the UPS data (not shown here). This value is higher than the value of 2.64 ± 0.01 eV before the structural transition and lower than the work function of the pristine sample of 4.20 ± 0.02 eV. This finding further illustrates that there is a lower effective doping compared to the as-deposited sample before the structural transition, but still a higher doping effect compared to the pristine sample. Since the effective concentration of K atoms participating in the doping process is found to be lower after the structural transition, and desorption of the K atoms from the sample at RT is unlikely, the location and chemical bonding of the expelled potassium atoms is discussed in Section S4, Supporting Information. To summarize the discussion on the position of the potassium atoms, after the structural transition at RT the (former) buffer layer, which does not form π bands in the pristine sample, is effectively electronically decoupled from the SiC substrate due to the penetration of K atoms into the interspace, which can be concluded from the existence of additional π bands assignable to this layer.

Considering all previous findings of the highly n-doped case, the intercalants are located beneath the (former) buffer layer and also between the carbon layers, accompanied by an effective decoupling of the (former) buffer layer. Thereby, EMLG is transformed into K-intercalated quasi-freestanding EBLG. This configuration can also be referred to as the thinnest limit of a graphite intercalation compound.[41] While the intercalants form a highly ordered superstructure beneath the uppermost layer (revealed via STM), the lateral structure of the intercalants below the buffer layer is not known. Since no distinct additional features appear in the LEED pattern, they might also arrange in a (2 × 2) superstructure or do not show any structural order at all. A (1 × 1) registry with the graphene or SiC lattice is not expected due to i) the ionic diameter of K and ii) the too low K concentration on the sample. Therefore, the physical structure of potassium intercalants below the buffer layer remains an open question.

2.2. Detailed Analysis of the Electronic Structure

In the following the electronic structure of the highly n-doped, as-deposited, former EMLG sample that exhibits the (2 × 2) superstructure is scrutinized by means of i) area-averaging ARUPS and ii) local tunneling techniques. In particular, the comparability of the acquired data in terms of the employed experimental methods is discussed. To this end, Figure 4 shall provide a graphical guidance.

The constant energy contours (CEC) of strongly doped graphene are depicted in Figure 4a. As in this case the Fermi

Figure 4. Scheme of characteristic features in reciprocal space. a) Constant energy contours (CEC) of graphene with triangular electron pockets (black solid lines), which emerge at a sufficient energetic separation from the Dirac point. Intravalley and intervalley scattering processes with the respective scattering vectors \( q \) and \( q' \) are depicted. Interference contours caused by quasiparticle scattering at defects are geometrically constructed for both processes, where the touching points between an initial CEC (black) and a final CEC (gray) account for parallel segments of those contours. b) Photoelectron momentum map (PMM) expected from the CEC in (a), but with additional features (dashed lines) due to zone folding at the (2 × 2) superstructure. Furthermore, the circular features around the M points most likely arise from parabolic interlayer bands (IL1) of graphene that are occupied as a result of the potassium intercalation. c) Quasiparticle interference patterns expected for intervalley (triangular features) and intravalley (hexagonal features) scattering. The scale bars are identical in all panels. The field of view of the PMM data (Figure 5) and FT-STM data (Figure 6) is depicted in cyan. Adapted with permission.[57] Copyright 2017, American Physical Society.
energy $E_f$ differs considerably from the Dirac energy $E_D$, the CEC resembles a (rounded) triangle at the K and K’ points of the surface Brillouin zone of the primitive graphene unit cell, which we abbreviate as SBZ$_{1 \times 1}$ hereafter. Those contours with the triangles’ corners pointing outward are expected in the photoelectron momentum maps, as visualized using red solid lines in Figure 4b. Due to folding at the $(2 \times 2)$ superlattice, the same triangular features (pink dashed lines) are also replicated at the $\mathbf{K}$ points of the SBZ$_{2 \times 2}$, albeit mirrored and with a strongly reduced intensity, which is consistent with previous reports.$^{[38]}$ Furthermore, one parabolic interlayer band (IL$_1$) at the M points is drawn as a circular contour and replicated at the $\Gamma$ point. The second interlayer band (IL$_2$) is omitted in Figure 4b for the sake of lucidity; it shall be scrutinized below.

Quasiparticle interference is a term used for modulations of the local density of states that arise around defects, and such modulations are often observed by means of STM.$^{[39]}$ In graphene, QPI occurs between electrons in their respective pockets at the K points and the K’ points. An explanation has been provided, amongst others, by Dombrowski et al.$^{[57]}$ which we summarize in Figure 4a,c. To this end, intravalley and intervalley scattering processes at defects are considered.$^{[26]}$ Intervalley scattering is associated with the coupling between two symmetrically inequivalent electron pockets at a K point and a K’ point of the SBZ$_{2 \times 2}$. By contrast, intravalley scattering is the coupling between states of the same electron pocket at either K or K’. As one can infer from the lengths of the scattering vectors $\mathbf{q}$ and $\mathbf{q}'$ in Figure 4a,c, the corresponding length scales in the real space are noticeably different, that is, short-range scattering for intervalley and long-range scattering for intravalley processes, respectively. Both are different from the periodicities associated with the $(2 \times 2)$ superstructure, which is readily discernible in our FT-STM data as bright spots that coincide with the M points of the SBZ$_{2 \times 2}$ of graphene (cf. Figure 6) and likewise in the Fourier-transformed $dI/dV$ data of Dombrowski et al.$^{[37]}$ Nonetheless, the $(2 \times 2)$ superstructure itself was not invoked by Dombrowski et al. for the explanation of the QPI patterns, which fit nicely to their experimental data, and which also explain our FT-STM contours displayed in Figure 6.

Figure 5 shows photoelectron momentum maps of the K-intercalated EMLG sample at different binding energies, $E_B$. In the vicinity of the Fermi level (see the leftmost panel for $E_B = 0.01$ eV), triangular electron pockets appear near the K points (for example at $k_x \approx 1.7 \text{ Å}^{-1}$, $k_y \approx 0 \text{ Å}^{-1}$) with an extended size within the SBZ compared to pristine EMLG.$^{[60]}$ For higher binding energies, the width of the electron pockets decreases, reaching a minimum size at $E_B \approx 1.5$ eV. This is due to the rigid shift of the Dirac cone to higher binding energies (cf. Figure 2c) upon n-doping of the sample as already mentioned above. However, a second triangular but mirrored electron pocket, located halfway between $\Gamma$ and K point, is also present in the PMMs. Those features are a direct consequence of the presence of the $(2 \times 2)$ superstructure and emerge due to zone folding. Additionally, the PMM at the Fermi level (see the leftmost panel for $E_B = 0.01$ eV) shows circular features at the M points of the SBZ that are partially filled. For increasing binding energies the diameter of those features reduces, until they vanish at binding energies of about 0.8 eV. Even though very weak, those circular features at the M point are likewise present at the $\Gamma$ point of the SBZ, which is also a direct consequence of zone folding. Those features most likely arise from parabolic IL bands of graphene that are occupied as a result of the K intercalation.

Figure 6a shows the central part of the FT-STM image in Figure 1c of the K-intercalated EMLG sample with a color scheme specifically chosen for improved visibility of faint features.

Besides the already discussed high-intensity features that correspond to the reciprocal lattice of graphene and the $(2 \times 2)$ superstructure (cf. Figure 1c), faint triangular contours are discernible around the K point of the SBZ of the graphene lattice as also depicted in the scheme in Figure 6b for better visualization. The triangular contours can also be identified in second

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**Figure 5.** PMMs of K-intercalated EMLG on SiC(0001) at binding energies given in the upper left corners (energy integration range: ±22 meV, resolution: $\Delta \phi = 1^\circ$, $\Delta \theta = 2^\circ$). As a guide to the eye, solid lines depict the SBZ$_{1 \times 1}$ of graphene and dashed lines depict the SBZ$_{2 \times 2}$ of the $(2 \times 2)$ supercell.
order, but mirrored at the second-order features of the \( (2 \times 2) \) superstructure. Moreover, faint rounded hexagonal contours surround the first-order features of the reciprocal graphene lattice. Based on previously published results regarding pristine EMLG and EBLG on SiC(0001),\(^{26,27,29}\) all of these discussed contours most likely originate from QPI effects. Since this STM measurement was performed at very low bias (20 mV), the integration range contributing to the tunneling current is very small. From this point of view, the triangular features are caused by intervalley scattering processes between two inequivalent K points. Compared to the triangular electron pockets apparent in the PMMs at the K point in the vicinity of the Fermi level (cf. Figure 5), the triangles appear flipped in the FT-STM image and are wider in \( k \) space. However, this behavior qualitatively agrees with literature reports where an FT-STM image for freestanding graphene significantly above the Fermi level is calculated by considering the triangular constant-energy contours of the \( \pi^\pm \) bands.\(^{61-63}\) Accordingly, the rounded hexagonal features in our FT-STM image can be assigned to QPI upon intravalley scattering processes. Compared to spots originating from the graphene lattice as well as the second-order spots of the \( (2 \times 2) \) superstructure, the first-order features caused by the \( (2 \times 2) \) superstructure appear strongly broadened. This position coincides with the M point of the graphene SBZ. Since circular constant energy contours around the M point are observed in the PMMs, the broadening indicates additionally possible intervalley QPI effects due to scattering between inequivalent M points. However, the quality of those features is not sufficient to allow a clear assignment. A hexagonal feature, which would be expected around the center of the FT-STM image (\( \Gamma \) point) upon intravalley scattering for strongly doped graphene, can neither be proven nor excluded, owing to the limited size of the STM image and, obviously, due to noise in the data. Nevertheless, this feature should be duplicated at each \( (1 \times 1) \) replica of the \( \Gamma \) point in adjacent Brillouin zones, and there it indeed bears similarity to a (somewhat blurred and rounded) hexagon, as highlighted by a short black arrow in Figure 6. Contrary to the PMMs, the FT-STM image shows no evidence of contours originating from folded bands in the smaller SBZ\((2 \times 2)\), even though lattice features of the \( (2 \times 2) \) superstructure are clearly present.

From the extent of the triangular features surrounding the K points and the diameter of the rounded hexagonal features surrounding the first-order spots of the graphene lattice (see Figure 6) an average Fermi wave vector \( q_F = 2.621 \pm 0.003 \text{ nm}^{-1} \) is determined under consideration of the hexagonal lattice (\( q_F = 2.270 \pm 0.002 \text{ nm}^{-1} \) if hexagonal lattice not considered). This value is about four times as large as the value reported for pristine EMLG and EBLG of \( q_F = 0.61 \pm 0.07 \text{ nm}^{-1} \) \( (q_F = 0.53 \pm 0.06 \text{ nm}^{-1} \) if hexagonal lattice not considered).\(^{29}\) From \( q_F = 2.621 \pm 0.003 \text{ nm}^{-1} \) a charge carrier concentration of \( n = 1.642(3) \times 10^{14} \text{ cm}^{-2} \) can be estimated (valley degeneracy of K point, \( g_v = 2 \)). This implies that, compared to freestanding pristine graphene, 0.3444 \( \pm 0.0006 \) additional electrons are donated to the graphene layers per unit cell of the \( (2 \times 2) \) superstructure. However, this approach underestimates the total charge carrier concentration, as it neglects the circular features observed in the PMMs at the M and \( \Gamma \) point of the graphene SBZ. As we will demonstrate in the following, these circular features are the result of the filling of two parabolic interlayer bands, which shall be called \( \text{IL}_1 \) and \( \text{IL}_2 \). Given that they are not discernible in the FT-STM data, it is necessary to scrutinize the ARUPS measurements for an appropriate estimation of the total charge carrier concentration.

To determine a proper estimate of the total charge carrier concentration, ARUPS data are extracted from the PMM data stack (cf. Figure 5) along the high symmetry \( \Gamma M \) and \( \Gamma K \) directions as presented in Figure 7a. In \( \Gamma K \) direction, the \( \pi \) and \( \pi^\circ \) bands of the Dirac cone are clearly visible with an intersection at the K point of the graphene SBZ \( (k_{\parallel} = 1.7 \text{ Å}^{-1}) \). The apparent asymmetry between the left and the right branch of the \( \pi\circ \) band is a result of the triangular shape of the electron

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**Figure 6.** a) Section of the FT-STM image in Figure 1c with contrast-enhancing color scheme. The white hexagon represents the SBZ\((2 \times 2)\) of graphene. b) Schematic diagram reproduced to scale from Figure 4c. The triangular and hexagonal contours are caused by intervalley and intravalley QPI processes, respectively, as observed in the measurement. The arrows point at representative features in the measurement (a) and in the scheme (b). The filled red circles in (b) highlight the FFT spots stemming from the graphene lattice and from the \( (2 \times 2) \) superstructure. The diameters of those circles roughly correspond to the intensities of the features in (a) and only serve as a guide to the eye.
pockets observed in the PMMs. Further, the intensities of both branches are markedly different, which is a consequence of using p-polarized light for this experiment. The polarization dependence originates from the anisotropy caused by the two inequivalent carbon atoms in the graphene unit cell.\cite{21} However, the left branch is still visible, because the incident light is not perfectly polarized (degree of polarization $\approx 64\%$). Upon folding, the Dirac cone is also visible in the vicinity of the $K$ point ($k_\parallel = 0.85 \, \text{Å}^{-1}$) that corresponds to the $K$ point of the $(2 \times 2)$ superstructure SBZ, however, with mirrored asymmetry and intensity distribution.

In the $\Gamma M$ direction of the ARUPS data, two nearly parabolic bands centered at the $M$ point of the graphene SBZ are apparent, which are responsible for the circular contours in the PMMs (cf. Figure 5). Upon folding, those nearly free-electron-like bands are also present in the vicinity of the $\Gamma$ point, better visible in the contrast-enhanced image section in Figure 7d. In this region, however, the bands appear slightly different due to the presence of various bands in a smaller $k$-space volume for low $k_\parallel$ values. In particular, the folded $\pi^*$ band overlaps with the parabolic bands in $\Gamma K$ direction, but it is also responsible for the high-intensity feature close to the Fermi level in $\Gamma M$ direction (cf. Figure 5). In accordance with literature, electronic bands of graphene with a parabolic dispersion at the $\Gamma$ point exhibit interlayer character\cite{11} and are thus labeled as $IL_1$ and $IL_2$. Although filling of one interlayer state upon metal intercalation has already been determined experimentally (e.g., Rb-intercalated, H-passivated ZLG,\cite{58} Rb-intercalated,\cite{18} and Ca-intercalated EBLG),\cite{41} this is to our knowledge the first observation of two IL bands below the Fermi level of a metal-intercalated graphene-based material. Moreover, the ARUPS data centered at the $M$ and the $\Gamma$ point exhibit significantly increased intensity at higher binding energies, which is readily visible in the contrast-enhanced image sections in Figure 7b,c, respectively. Since it is present at both high-symmetry points, it can be excluded that this observation is merely an experimental artifact, and the presence of an additional parabolic band opening downward is assumed to be the cause. Since graphene does not exhibit electronic bands in the relevant energy region, those dispersive bands most likely originate from the metal intercalant layers.

In the previous section decoupling of the buffer layer and the formation of an effective $K$-intercalated bilayer was established. Accordingly, the observation of two Dirac cones is expected just like in the case of pristine EBLG.\cite{51} However, neither the ARUPS data in Figure 7a nor the PMMs in Figure 5 show any evidence of other energetically shifted $\pi$ or $\pi^*$ bands. In fact, two slightly separated $\pi$ bands were observed experimentally upon Li intercalation of EMLG,\cite{64} with both Dirac points located at higher binding energies compared to the pristine
sample. This observation was confirmed by calculations that consider the intercalants located beneath the (former) buffer layer and also between the carbon layers (Li\cite{64} and also Yb\cite{56}). Surprisingly, the separation of the \( \pi \) bands is also correctly predicted for Li intercalation by a different theoretical study that was carried out for freestanding bilayer graphene intercalated with various metals between both graphene layers solely.\cite{65} Indeed, this study predicted two \( \pi \) bands also in the case of K and Rb intercalation, albeit without energetic separation so that they overlap completely and appear as a single band. This prediction was confirmed experimentally in the case of Rb.\cite{49} Thus, the experimental finding of just one apparent Dirac cone in the ARUPS data in Figure 7 is strongly supported. While the highly doped as-deposited sample was found to be stable at low temperatures for several weeks, its stability at RT is limited to a few minutes. In particular, at RT the K atom concentration between the substrate and the former buffer layer increases while the potassium interlayer between both adjacent carbon layers is depopulated. Upon this transformation, the topmost layer behaves similarly to pristine EMLG, while the lower layer remains doped.

Our results represent a crucial foundation for the understanding of the mechanisms that possibly lead to superconductivity in this material class.

### 3. Conclusion

Upon K intercalation of EMLG on SiC(0001) we observed that the metal atoms form a \((2 \times 2)\) superstructure with respect to the graphene lattice, at the highest doping level achieved. This structure was imaged via STM, which is the first real-space observation of this structure in the thin film limit. Importantly, we present clear evidence that the K atoms not only penetrate below the graphene layer, but also below the buffer layer. As a result, the buffer layer decouples electronically from the underlying SiC substrate, and the sample behaves like K-intercalated bilayer graphene. The formation of this structure is accompanied by a rigid shift of the Dirac cones toward higher binding energies. Further, two occupied IL bands were identified at the \( \Gamma \) point of the SBZ. A total charge carrier density for the highly doped phase was estimated to \( \approx 50 \) times the value of pristine epitaxial graphene, resulting from a charge transfer of \( 0.93 \pm 0.08 \) electrons per unit cell of the \((2 \times 2)\) superstructure to the graphene-based system. Due to the emergence of a quasiparticle interference pattern in the FT-STM images, it was demonstrated that the same electronic structure is probed on a local (STM) and area-averaged (ARUPS) scale.

While the highly doped as-deposited sample was found to be stable at low temperatures for several weeks, its stability at RT is limited to a few minutes. In particular, at RT the K atom concentration between the substrate and the former buffer layer increases while the potassium interlayer between both adjacent carbon layers is depopulated. Upon this transformation, the topmost layer behaves similarly to pristine EMLG, while the lower layer remains doped.

### 4. Experimental Section

Graphene sheets were synthesized on 6H-SiC(0001) wafers with a similar procedure as described elsewhere.\cite{67} The wafers were etched in a hydrogen atmosphere at \( \approx 1600 \) °C for 20 min to remove surface polishing damages. Subsequently, the etched wafers were tempered in an Ar atmosphere also at \( \approx 1600 \) °C for 20 min.

All characterization experiments were performed in ultra-high vacuum (UHV) conditions (base pressure \( \approx 10^{-10} \) mbar). Prior to every new K intercalation the sample was annealed (with electron bombardment heating from the backside) at \( \approx 1200 \) °C in UHV to remove possible contaminations. Potassium was deposited from a dispenser (commercial products from SAES Getters and Alavec were used), while the sample located between the SiC substrate and the former buffer layer, donating their charge partially to the substrate and to the graphene system. For comparison, pristine EMLG and EBLG are slightly doped due to the presence of the SiC substrate yielding the donation of \( \approx 0.005 \) electrons per graphene unit cell\cite{66} (or 0.02 electrons per four graphene unit cells whose combined size is equivalent to a \((2 \times 2)\) supercell). Compared to the charge donation upon K intercalation estimated in Table 1, this value is indeed negligible. Thus, the substrate influence on the doping is so small that the properties of the K-intercalated sample can be considered as isolated K-intercalated bilayer graphene.

### Table 1. Estimation of the charge transfer to the graphene sheets based on the intersection of every band with the Fermi level from the ARUPS data in Figure 7. The twofold degeneracy of the \( \pi \) point is already accounted for.

| Band | \( \Delta k_\parallel \) [Å\(^{-1}\)] | \( q_\parallel \) [nm\(^{-1}\)] | \( n \) \([10^{14} \text{ cm}^{-2}]\) | \( e^-\text{ per UC}_{\text{IL2}}\) |
|------|------------------|-----------------|---------------------|---------------------|
| \( \pi^\ast \) | 0.52 ± 0.02 | 2.60 ± 0.09 | 1.6 ± 0.1 | 0.34 ± 0.03 |
| IL\(_1\) | 0.88 ± 0.01 | 4.44 ± 0.06 | 2.36 ± 0.06 | 0.49 ± 0.01 |
| IL\(_2\) | 0.40 ± 0.08 | 2.0 ± 0.4 | 0.5 ± 0.2 | 0.10 ± 0.04 |

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temperature was kept at RT. Instead of estimating the K content by controlling the flux, the changes of the optical properties of the sample were monitored via DRS to achieve comparable and reproducible doping stages of the sample. More information about the method and its results is presented in Section S1, Supporting Information. In particular, this procedure did not require the assumption of a constant material flux from the dispenser. According to Jolie et al.[68] a \( (2 \times 2) \) superstructure of alkali metal atoms with respect to the graphene lattice corresponds to \( 0.25 \) ML, or in other words, one alkali metal atom per primitive \( (1 \times 1) \) unit cell of monolayer graphene can be defined as \( 1 \) ML.

LEED measurements were performed at RT using a dual microchannel plate LEED (MCP-LEED) device purchased from OCI Vacuum Microengineering. The images were calibrated and corrected for distortions and systematic errors by the freely available program LEEDCal\(^{[69,70]}\) using the Si(111)-\((7 \times 7)\) superstructure as a reference sample.\(^{[71]}\) Structural analyses were carried out using LEEDLab\(^{[72]}\) as also described in refs. \([73, 74]\).

The presented STM measurements were performed with a JTEM/AFM system purchased from SPECS Surface Nano Analysis by using a cut PtIr tip at a temperature of \(1.1 \) K. Data analysis and the Fourier transform of the real-space images were carried out with the help of the software Gwyddion\(^{[75]}\) that scales the reciprocal-space images in terms of \(1/x\). To account for the hexagonal lattice, the FT-STM images were rescaled by the factor \(4\pi/\sqrt{3}\). For reasons of comparability to literature data that apply the commonly used mathematical \(2\pi/x\) scaling, the determined values had to be rescaled by the factor \(2/\sqrt{3}\).

For a quantitative analysis of distinct quasiparticle interference contours, line scans along particular directions were analyzed to determine the extension of the respective features. To account for possible distortions of the STM image, the determined values were calibrated with the help of a known length in the specific direction assuming the graphite lattice constant to be \(2.461 \) Å.\(^{[76]}\)

Photoelectron spectroscopy was performed with a surface analysis system purchased from SPECS Surface Nano Analysis equipped with a microwave-heated light source (UVLS) using the He(I) excitation (21.2182 eV) in combination with a toroidal mirror monochromator (TMM 304, line width \(< 21.2182 \) eV) in combination with a toroidal mirror monochromator (TMM 304, line width \(< 21.2182 \) eV) and the He(I) line (21.2182 eV) in combination with a toroidal mirror monochromator (TMM 304, line width \(< 21.2182 \) eV) and the He(I) line (21.2182 eV). The emitted photoelectrons were analyzed with a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150). PMMs were taken in the 2D mode of a hemispherical electron energy analyzer (PHOIBOS 150) equipped with a delay line detector (3D-DLD4040-150).

Photons were extracted from the data stack by cutting through data points at fixed binding energy with an integration range of 44 meV in steps of 12°. In the vicinity of the K point in ARUPS measurements,\(^{[51]}\) for the determination of the K-to-C ratio, the sensitivity factors\(^{[78]}\) or cross sections\(^{[79]}\) for each atomic species needed to be considered. The ratio provided in this study corresponded to the mean value of both methods.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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