Intercalation of Graphene on SiC(0001): Ultra-high Doping Levels and New 2D materials

Interkalation von Graphene auf SiC(0001): Ultrahohe Dotierung und Neue 2D-Materialien

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Introduction

The discovery of graphene sets in a sense a singularity in solid state research and thus has drawn a lot of attention in the last decade. While living in a three-dimensional world, a system was discovered, that acts strictly two-dimensional, as it is one atom thick. And indeed, it can stand as an autonomous system, which was meant to be impossible before. While being the first realization of this materials class, graphene is considered a model 2D crystal. Although very simple in its structure, as carbon arranged in a honeycomb, it is rich in physics unimaginable before. One of its most famous properties lies in the linear parts of its band structure, the so-called Dirac cones, which yield several implications. The low energy excitations mimic the behavior of ultra-relativistic particles, and therefore certain scattering mechanisms are forbidden. This effect, also known as Klein tunneling [1], together with the very high optical phonon frequencies in graphene can lead to a very high charge carrier mobility up to room temperature [2]. Consequently, many applications were put to prospect and are also on the brink of commercialization especially in electronics [1–18]. One key to graphene’s popularity is its stability in rough conditions, e.g. chemically, thermally and mechanically. On the other hand, it is very sensitive to its environment due to its two-dimensional nature. In this sense, its properties are widely tunable to achieve certain functionalities. By binding certain molecules onto the graphene, a detection of specific substances in the environment is possible, which might lead to the use in sensor technology [19, 20]. The presented thesis is dedicated to this material, more precisely to its controlled modification. The technique of modification aims on graphene’s electronic prop-
properties and builds up directly on the fact that graphene is usually supported by a substrate. It is possible to introduce foreign atom species between the graphene and its substrate, which is called intercalation [21]. The then called intercalant functionalizes the graphene in a specific way. On one hand, this method is relatively simple in terms of processing. On the other hand, the resulting sandwich configuration itself is beneficial in many aspects. The intercalant is protected by the graphene layer, which makes this configuration chemically very stable. Furthermore, the intercalant is forced into a two-dimensional configuration, providing high thermal stability. Intercalation is further extremely versatile and thereby powerful. It was shown by Riedl et al. [22] that the intercalation of hydrogen can effectively decouple the graphitic layers from the substrate, yielding high quality quasi-free standing graphene. By the intercalation of germanium, graphene’s doping level could be manipulated on a nanometer scale [23]. Together with lithographic patterning, this could be combined to produce nanostructures [24]. The intercalation of copper could introduce a superpotential onto the graphene, which led to the reconstruction of the electronic spectrum to form so-called mini-cones [25]. The intercalation of gold drastically enhanced spin splitting of the \( \pi \) band structure in graphene [26]. In this manner, exploiting intercalation is interesting on a basic research level and also in the scope of applications prospected.

Based upon epitaxial graphene on SiC(0001), a system of extremely high quality [27] was utilized within this thesis. The semiconducting nature of the SiC exhibits an ideal playground for basic research. Yet, especially this configuration represents a very promising candidate for commercial applications.

The presented work was firstly aimed towards producing graphene with ultra-high doping levels, utilizing the technique intercalation. Especially reaching the regime of the Van Hove singularity at the Fermi level is interesting in the viewpoint of effects driven by many-body physics [90, 91]. Due to the difficulty of reaching this regime and the accompanied instability of the system, a deeper characterization of graphene in this regard was missing up to this point. Therefore, creating such a system with the stability of the intercalation configuration is a formidable challenge. There, classical surface science techniques like photoelectron spectroscopy of valence and core level states and electron diffraction methods were essential. Yet, also techniques regarding the electronic transport characteristics were employed. Going beyond this, also the role of the intercalant was further examined as a general aspect to the technique intercalation itself.
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Graphene as the thinnest limit of graphite was first isolated in the mid 2000s. Although theoretically studied before [28], it was thought to be unstable [29] and thus not able to be produced. The unique properties manifested in graphene also promised great potential in technical applications. Among them, the configuration of epitaxial graphene on SiC, especially on the (0001) surface, holds a special place. It provides high quality graphene on a semiconducting substrate which can be produced on a wafer size scale [27]. The work done within this thesis builds on this system, therefore the following paragraphs provide basic information on graphene, SiC and epitaxial graphene on SiC(0001). Also, the concept of the electronic spectral function is elucidated, as it is one cornerstone of understanding the physics behind the technique most extensively used within this thesis, namely photoelectron spectroscopy. Finally, a collection of spectral features will be elaborated, which is often observed especially in graphene.
1.1 Introduction to graphene & graphene on SiC

1.1.1 Basics of monolayer & bilayer graphene

Crystal structure

Within graphite, single atomic layers are arranged in a honeycomb, i.e. a triangular lattice with two equivalent sublattices [30] (see Fig. 1.1 (a)). The orbital configuration is $sp^2$, where the three in-plane orbitals build $\sigma$-bonds with neighboring atoms and the out of plane $p_z$ orbitals form $\pi$-bonds. The carbon-carbon bond length is 1.42 Å. Consequently, the length of the usually chosen primitive unit vec-

![Fig. 1.1: (a) Ball and stick model of a single graphitic layer, whereas the unit cell vectors are indicated. (b) Graphene’s reciprocal space. The first BZ and the high symmetry points are indicated. (c) Sketch of bilayer graphene in AB configuration.](image)

tors, $a_1 = a/2 (1, \sqrt{3})$ and $a_2 = a/2 (1, -\sqrt{3})$, is $a = 2.46$ Å. This corresponds to an atom density of $3.82 \times 10^{15}$ cm$^{-2}$. The Brillouin zone (BZ, see Fig. 1.1 (b)) is hexagonal and the reciprocal lattice vectors are given by $b_1 = 2\pi/a (1, 1/\sqrt{3})$ and $b_2 = 2\pi/a (1, -1/\sqrt{3})$ with a length of 2.95 Å$^{-1}$. The length of the vectors connecting $\Gamma$ with $\overline{M}$ and with the $K/K'$ points as high symmetry points is 1.474 Å$^{-1}$ and 1.702 Å$^{-1}$, respectively. When introducing a second graphitic layer, bonding is given mainly by van der Waals forces [31]. Generally, the two layers can be stacked with different rotational and translational degrees of freedom. Here we focus on the so-called AB stacking (see Fig. 1.1 (c)), as it will be of importance for this thesis. In this case, the unit vectors in real space as well as in reciprocal space coincide with the sole monolayer case, whereas the primitive basis then contains 4 atoms. One layer is shifted such that only atoms of one sublattice within a layer have a direct neighbor in the other layer. This bilayer configuration exhibits reduced symmetry compared to the monolayer case, as the sublattices within the layers are distinguishable.
Electronic band structure

To understand graphene’s electronic structure in a most basic way, a tight binding description is very successful [32]. As this model is based on a single particle picture, it will be extended with many body concepts in later chapters. Graphene is often referred to as the prototype of Dirac materials [31]. The perfect symmetry of the sublattices in monolayer graphene is a key ingredient for its most renowned property. The low-energy bands, also called \( \pi \)-bands, as they are built up by the \( p_z \) orbitals, exhibit a characteristic double conical structure, where valence and conduction bands touch [30] (sketched in Fig. 1.2 (a) and described by Eq. 1.1).

\[
E(q) = \pm \hbar v_F |q|, \tag{1.1}
\]

where \( q \) is the crystal momentum relative to \( \overline{K}/\overline{K}' \) and \( v_F \simeq 10^6 \text{ m/s} \) the Fermi velocity. This means that near the high symmetry points \( \overline{K} \) and \( \overline{K}' \) the dispersion is linear. It resembles that of relativistic massless fermions and the physics can be described by the Dirac equation with zero mass rather than the Schrödinger equation [30]. The touching point of valence and conduction band is thus usually referred to as the Dirac point at the energy \( E_D \). As a consequence, an anomaly in the density of states (DOS) is present. Instead of being constant, as for two-dimensional materials with parabolic bands, the DOS follows a linear dependence. It vanishes at the energy at which conduction and valence band touch, thus graphene is often referred to as zero bandgap semiconductor [30].

Away from the Dirac point, the bands lose their linearity (see Fig. 1.2 (c)) and can be described within the tight binding formalism in the nearest neighbor ap-
In introduction to graphene & graphene on SiC approximation [31]:

$$E(k) = \pm \gamma_0 \sqrt{3 + f(k)},$$  \hspace{1cm} (1.2)

with

$$f(k) = 2 \cos (ak_x) + 4 \cos \left(\frac{a}{2}k_x\right) \cos \left(\frac{\sqrt{3}}{2}ak_y\right),$$

with $\gamma_0$ being the nearest neighbor hopping parameter with an empirical value of about 2.8 eV and $a = 2.46$ Å being graphene’s lattice parameter. In the picture of tight binding, $\gamma_0$ is the orbital overlap of two neighboring C atoms’ $p_z$ orbitals. This variable is connected to the band velocity near the $K$ point by $v_F = \sqrt{3} \gamma_0 a/(2 \hbar)$. While the constant energy contours around $E_D$ at $K$ and $K'$ show circular symmetry, they get warped into a triangular shape away from this energy, until they merge at the $M$ points (see Fig. 1.2 (b)). This behavior is steered by the presence of a saddle point at the $M$ points. The constant energy contours undergo a so-called Lifshitz transition at this energy, and the resulting pocket is then centered around $\Gamma$ [34]. The point of transition is also conjoint with a divergence in the DOS, also called a Van Hove-singularity (VHs) (see Fig. 1.2 (d)).

In the AB bilayer case, drastic differences in the dispersion near $K$ and $K'$ are present. Bands from tight binding in nearest neighbor in- and out-of-plane approximation near $K$ and $K'$ are given by Eq. 1.3 [35, 36]:

$$E_\alpha(q) = \pm \sqrt{\frac{\gamma_1^2}{2} + \frac{u^2}{4} + v_F^2 q^2 + (-1)^\alpha \sqrt{\Gamma(q)}},$$  \hspace{1cm} (1.3)

$$\Gamma(q) = \frac{1}{4} \gamma_1^4 + v_F^2 q^2 (\gamma_1^2 + u^2)$$

where the initial $\pm$ defines the conduction and valence bands respectively. $\alpha = 1, 2$ defines the so-called low (1) and high (2) energy bands as two different branches of the conduction and valence band, respectively. The low and high energy branches can be seen as additional bonding and antibonding pairs produced by interlayer orbital overlap. The nearest neighbor intra layer hopping parameter $\gamma_0$ is involved in the relation $v_F = \sqrt{3} \gamma_0 a/(2 \hbar) \simeq 10^6$ m/s and is defined analogously to the monolayer case. $\gamma_1$ is the interlayer hopping parameter between the atoms with a direct neighbor in the neighboring layer. The model already involves the possibility of applying an asymmetry potential $U$, which introduces an asymmetric charge carrier distribution for the two layers. This can be realized by apply-
ing an electric field perpendicular to the plane [30], which was shown in various experiments [7, 37]. The π band topology as a whole shows similarities to the sole monolayer case as both systems are built up on a triangular lattice [30] (see Fig. 1.3 (a)). The most striking difference to the monolayer case is that the bands near the $\overline{K}$ points are no longer linear but parabolic (see Fig. 1.3 (b)), thus the electrons can be assigned a mass $m = \gamma_1/(2v_F^2)$. Yet, as the two layers are indistinguishable in the unbiased case, the low energy branches of the valence and conduction band touch at $\overline{K}$ and $\overline{K}'$ [30, 35]. The respective high energy branches are split by $2\gamma_1$. When including the layer asymmetry in the form of the asymmetry potential $U$, the degeneracy is lifted, thus the electronic spectrum gets gapped (see Fig. 1.3 (c)). For values of $U << \gamma_1$ the energy gap $\Delta$ corresponds to about $U$, whereas for large $U$, $\Delta$ saturates to $\gamma_1$ [30].

**Phononic band structure**

One of graphene’s exceptional properties is the very high energy of its lattice vibrational modes, especially the optical modes. This directly results from the fact that the carbon-carbon bonding in the $sp^2$ configuration is the stiffest among all known materials [31]. Besides the peculiar electronic band structure, this is a key ingredient for the fact that graphene can show extremely high charge carrier mobilities up to temperatures even beyond room temperature [31]. The occupancy of optical phonon modes is low at room temperature.
The phononic band structure is very similar for all graphitic allotropes. In Fig. 1.4 calculated phonon dispersions for the monolayer and bilayer are shown [38]. The

Fig. 1.4: Phonon dispersion of graphene: (a) In the reduced scheme for monolayer graphene. (b) Zoom-in to the phonon dispersion around $\Gamma$ in $\Gamma K$ direction of AB-bilayer graphene. Both figures were adapted from ref. [38].

high energy optical branches are in the range of about 1200-1600 cm$^{-1}$ (150-200 meV) (see Fig. 1.4 (a)). For monolayer graphene these are single branches. For bilayer graphene, the number of branches are doubled, as again the number of atoms per unit cell is doubled. Due to the relatively low interlayer coupling compared to the intralayer coupling, there is only a minor splitting of the branches compared to their total energy (see Fig. 1.4 (b)).

1.1.2 Basics of silicon carbide

SiC is a wide band gap semiconductor [39, 40]. It has a strong thermal and chemical robustness compared to Si and thus it is exploited in commercial electronics. Especially the niche application of high-power, high-frequency and high-temperature electronics is wide spread. It is a compound system of carbon and silicon, both in sp$^3$ configuration, where every Si atom has 4 neighboring C atoms and vice versa (see Fig. 1.5 (a)). Although SiC cannot be viewed as a layered material, a double layer can be seen as a basic brick stone (see Fig. 1.5 (b)). This layer consists of one C and one Si layer where one C atom has three bondings to neighboring Si atoms and vice versa. The brick resembles a triangular lattice with a two-atom base and a lattice constant of 3.08 Å. Atoms within the double layer exhibit one covalent bond to a neighboring double layer’s atom. These layers can
be stacked in two different orientations. As sketched in Fig. 1.5 (c), the three in-plane bondings of one layer can be aligned with the bondings in the neighboring layer or they can be rotated by 60° with respect to each other. This gives the possibility to build up a SiC crystal in manifold stacking sequences, the so-called polytypes [42]. Two prominent polytypes are sketched in Fig. 1.5 (d) & (e). The so-called 4H-SiC has a sequence length of four double layers, 6H-SiC of six, both being hexagonal crystal structures in total. The properties of the different polytypes can vary significantly. This can also be seen in the range of band gaps, for example 2.35 eV for 3C-SiC and 3.08 eV for 6H-SiC. Due to the bonding situation, it is energetically more favorable for the system to leave the double layers intact, when cleaving the crystal along the layer plane. This means, one side will be terminated with Si and the other with C. Using the Miller-Bravais nomenclature with four unit vectors, the C-side is denoted as the (0001) and the Si-side as the (0001) surface. The polytype used in this thesis was 6H-SiC and graphene was grown by thermal decomposition on the (0001) side (see paragraph 2.6).
1.1.3
Graphene on SiC(0001)

While the properties of graphene and SiC were handled within the previous paragraphs, these systems are now combined. Here, graphene on SiC(0001), produced by thermal decomposition, will be treated, the basic system used in this thesis.

Growth mechanism and method

The most common way of producing graphene on SiC(0001) is by thermal decomposition [43, 44]. In UHV conditions the crystal is heated to temperatures higher than 1300 °C. At these temperatures, Si sublimes. C on the other hand is left behind to rearrange in the stable graphitic configuration (see Fig. 1.6 (a) & (b)). The first graphitic layer arranges such that a (13×13)-graphene cell is aligned
d to a \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\)-SiC(0001) cell, thus it is called epitaxial graphene. These respective supercells differ in size by only about 0.1 % (see Fig. 1.6 (c)) [46]. One third of the first graphitic layer’s atoms is covalently bound to the substrate in saturating the free Si bonds on its surface, as indicated in Fig. 1.6 (b) [44]. The resulting configuration is often referred to as the carbon rich \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) reconstruction of SiC(0001). This stage is also called zerolayer graphene (ZLG), as some of graphene’s characteristic properties are strongly distorted due to the

![Fig. 1.6: SiC graphitization illustrated with ball and stick models: (a) Si sublimating from a heated SiC crystal. (b) & (c) ZLG on SiC(0001) in side and top view, respectively. The surface unit cell of SiC(0001) is marked by the orange and the unit cell of graphene is marked by the black diamond. (d) MLG on SiC(0001). The figures were partially adapted from ref. [45]](image-url)
partial covalent bonding, yet the crystal structure is very similar to graphene. Graphitizing further decouples the initial bound layer, as a new layer is formed beneath (see Fig. 1.6 (d)). When decoupled, the layer keeps its fixed orientation. This is also the case for further graphitization stages [47]. The variety of graphitization, used for this thesis, was with an atmospheric Ar back pressure [27]. At these conditions, strongly increased graphitization temperatures between 1450 °C and 1650 °C are necessary. At these temperatures, a controlled and uniform growth process takes place, which results in homogeneous samples on a macroscopic wafer scale. Ref. [27] can be viewed for further details in this regard and more details about the sample preparation can be found in paragraph 2.6.

**Basic physical properties of epitaxial graphene**

At this point a collection of experimental results will be given in the scope of core level spectroscopy (CLS), low energy electron diffraction (LEED) and angle resolved photoelectron spectroscopy (ARPES), as they mark the techniques used most extensively in this thesis. Details to the techniques can be found in chapter 2 and details to the system can be found in refs. [27, 41, 44, 46–48]. A key to understanding some basic peculiarities of this system lies in the first graphitic layer, which is still partially covalently bound to the top Si layer of the substrate [44]. This partial bonding manifests itself in several interesting experimental observations. One such observation can be made in CLS of the C 1s. Due to the partial bonding, different C atoms within the graphitic layer can be distinguished by their chemical environment and thus in the respective core level binding energies. In Fig. 1.7 (a) a representative C 1s spectrum is plotted. Two components, labeled S1 and S2, can clearly be distinguished, besides the SiC’s carbon component [49]. Another consequence of this partial bonding manifests itself in the imposed buckling of the graphitic layer. In diffraction experiments, like LEED, this shows in a fingerprint diffraction pattern. Fig. 1.7 (b) shows one such characteristic pattern. Besides the expected (1×1)-graphene and (1×1)-SiC(0001), a manifold of diffraction spots is visible. These spots are on a (13×13)-graphene or (6√3×6√3)R30°-SiC(0001) pattern. Due to similar structural elements within this large unit cell, a part of the diffraction spots are suppressed, thus one often refers to a quasi (6×6)-SiC(0001) structure. Due to the partial bonding, ½ of the C atoms within the layer is given in a $sp^3$ configuration, thus a strongly distorted π band system is built up [44]. In this view, the classical linear band structure
Fig. 1.7: CLS, ARPES and LEED on graphene on SiC(0001): (a) C 1s CLS from ZLG (adapted from ref. [49]). (b) LEED pattern obtained with 67.5 eV initial electron energy of the ZLG. The non-marked spots are related to the \((6\sqrt{3}\times6\sqrt{3})R30^\circ\)-SiC(0001) reconstruction. (c) ARPES of the ZLG in the region around the \(\bar{K}\) point (from ref. [21]). (d) ARPES around \(\bar{K}\) of MLG on SiC(0001) (from ref. [50]). (e) ARPES around \(\bar{K}\) of BLG on SiC(0001) (from ref. [51]). The orientation of the ARPES measurements is given by the sketched BZ.

is missing, which is made visible by ARPES in Fig. 1.7 (c). At the \(\bar{K}\) point near the Fermi level, only two localized states are present as flat distributions, instead of a double cone structure. The conjoined localization also leads to the fact that this layer cannot carry current and is thus referred to as electronically nonactive. An important aspect to the first graphitic layer is that it acts as a buffer layer between the additional graphene layers on top and the SiC on the bottom. With a single graphitic layer on top, this additional layer shows strong resemblance to classical monolayer graphene properties [44]. ARPES shows the characteristic double cone structure (see Fig. 1.7 (d)), thus this system is usually referred to as monolayer graphene on SiC(0001) (MLG). Fig. 1.7 (d) gives also evidence that the graphene layer is n-type doped with the Dirac point shifted by about 0.4 eV below the Fermi level. This is driven by the interfacial partially bound carbon layer. The localized states within this buffer layer act as charge traps, thus introducing electrons into the layer above [52]. Moderate n-type doping is thus also present in the case of a graphene double layer system on top of the buffer layer, which is then called bilayer graphene on SiC(0001) (BLG). In this case, ARPES measurements also reveal a classical AB stacking configuration (see Fig. 1.7 (e)).
Due to the substrate-induced asymmetric doping of the two graphene layers, a band gap of about 150 meV is present at the Dirac point [7]. This corresponds to an asymmetry potential of 160 meV (see also paragraph 1.1.1).

1.2 Spectral function

In this section, light will be shed on a very important concept to interpret angle-resolve photoelectron spectroscopy (ARPES) measurements of the valence band, the technique used most extensively in this thesis. Yet, this concept goes beyond ARPES, as also the photoelectron spectra of atomic core levels can be understood in a similar way. This is the concept of the electronic spectral function. As it is here an entity which summons up particularly the electron dynamics of a solid, this is of utmost importance for understanding the physics behind many phenomena. In this manner, a general description will be given first. Then basic spectral features associated with different phenomena will be summarized. This paragraph is based on refs. [53–55].

1.2.1 General description

Starting from an electronic band model for solids, harsh simplifications are implemented. It is a picture simplifying the physics to the point of a static, non-interacting system [56]. Single electron states within a periodic potential are described, whereas dynamical interactions are neglected. This means, the electrons’ states are not altered with time by any correlations like electron-electron interaction, electron-phonon coupling et cetera. Many models exist to tackle this problem. Most basic examples are perturbational approaches to free electron states or tight binding approaches [34]. The concept of the spectral function $A(\vec{k}, E)$ can be seen somewhat as an extension to the electronic band model, as it per se gives the probability density of finding an electron in a given Bloch state with momentum $k$ and energy $E$. A general background for obtaining this is the Green’s function formalism. There, the propagation of a single electron or hole in a many-body system is described. One starts with the time ordered one electron Green’s function $G(\vec{k}, t - t')$. This basically gives the probability amplitude that an electron added to the system in a certain state at a certain time can be found
in this state at a time \( t - t' \) when interacting with the many-body system. Complementary in this sense is the removal of an electron from a state and finding this state empty at a time \( t - t' \). By transcribing this into the energy domain, the Green’s function can be simplified to the following form:

\[
G(\vec{k}, E) = \frac{1}{E - \epsilon^b_{\vec{k}} - \Sigma(\vec{k}, E)}, \tag{1.4}
\]

where \( \epsilon^b_{\vec{k}} \) is the bare non-interacting band in a single particle picture. In this concept, the entity \( \Sigma(\vec{k}, E) = \Sigma'(\vec{k}, E) + i\Sigma''(\vec{k}, E) \) is introduced as the complex self energy. Its real and imaginary parts contain the information on the renormalization of the energy levels and the lifetime of an electronic state with band energy \( \epsilon^b_{\vec{k}} \) and momentum \( \vec{k} \), respectively. The connection to the spectral function is given by \( A(\vec{k}, E) = -\frac{1}{\pi} \text{Im} G(\vec{k}, E) \), thus it takes the following form:

\[
A(\vec{k}, E) = -\frac{1}{\pi} \frac{\Sigma''(\vec{k}, E)}{\left[E - \epsilon^b_{\vec{k}} - \Sigma'(\vec{k}, E)\right]^2 + \left[\Sigma''(\vec{k}, E)\right]^2} \tag{1.5}
\]

Since the spectral function can per constructionem be seen as a linear response function, as it describes the damping of a Bloch state, certain properties are inherent. Firstly, if certain conditions are fulfilled, it shows a resonance near the non-interacting bare band \( \epsilon^b_{\vec{k}} \). Furthermore, the real and imaginary parts of \( A(\vec{k}, E) \) and \( \Sigma(\vec{k}, E) \) are connected by causality, thus they are related by a Kramers-Kronig transformation. Also, the spectral weight as a whole as well as the total number of electrons has to be preserved:

\[
\int_{-\infty}^{\infty} dE A(\vec{k}, E) = 1, \tag{1.6}
\]

\[
\int_{-\infty}^{\infty} dE f(E) A(\vec{k}, E) = 1,
\]

where \( f(E) \) is the Fermi distribution. In the limit of a non-interacting system, the self energy goes to zero. The spectral function then collapses to the bare band \( \epsilon^b_{\vec{k}} \), as \( A(\vec{k}, E) = \delta(E - \epsilon(\vec{k}, E)) \). Complementarily, as the self energy goes to zero, the energy levels do not get renormalized and the lifetime is infinite. In a basic physical picture, transition matrix elements vanish and electrons will not be scattered into other states.
Although the described framework is a successful tool for understanding different phenomena, it is worth noting that many-body problems can be tackled within different approaches depending on the interaction type and strength. For example, electron-electron and electron-phonon interaction can be described in a static mean-field formalism. This means, the electrons do not only see the bare potential of the atoms, but additional potential distortions (e.g. by the other electrons, or lattice vibrations) are added in the Hamiltonian. Within Hartree-Fock theory, this gets reduced to an effective Hamiltonian [34] and thus to an effective one particle problem. With this method, similar energy renormalizations can be found, especially for moderate electron-phonon coupling strengths [34]. Yet, since no temporal evolution is considered, this fails to describe the system’s dynamics.

1.2.2

Quasiparticle picture

The quasiparticle picture can be seen as a different point of view to the more abstract description in the Green’s function formalism, depicted in the previous paragraph. Although the term quasiparticle is also used in different contexts, here the electrons are seen as particles, which are dressed as a consequence of interactions, like for instance electron-electron [56]. In this sense, the physical picture changes from the behavior of single electrons in certain states to the one of the electronic system as a collective. This collective has certain excitations and the properties of these excitations will be similar to that of non-interacting electrons. Yet, the effective mass of these excitations, thus the energy levels, will be renormalized and the lifetime of the quasiparticle will be finite. In this description, one speaks of a Fermi liquid, which is a generalization of a Fermi gas [34]. One constriction to this picture is that the lifetime has to be defined in the sense that the spectral function $A(k, E)$ has to show a defined resonance in a Lorentzian shape. Mathematically, the condition $Z_k \equiv (1 - \frac{\partial \Sigma'(k, E)}{\partial E})^{-1} > 0$ has to be fulfilled, with $Z_k$ being the pole strength and $\Sigma'(k, E)$ being the real part of the self energy (see previous paragraph). This picture is strictly only valid near the Fermi level. Yet, the mentioned condition for $Z_k$ does not have to apply for the spectral function as a whole. In a generalization, one can divide the spectral function into a sharp quasiparticle resonance (also called coherent part) and a
broader distribution (incoherent part) [54]:

\[ A(\vec{k}, E) = Z_{\vec{k}} \frac{\Gamma_{\vec{k}} / \pi}{(E - \epsilon_{\vec{k}}^q)^2 + \Gamma_{\vec{k}}^2} + A_{\text{incoher}}, \]  

with \( \epsilon_{\vec{k}}^q = Z_{\vec{k}} (\epsilon_{\vec{k}}^b + \Sigma') \) and \( \Gamma_{\vec{k}} = Z_{\vec{k}} |\Sigma''| \), whereas the self energy is evaluated at \( E = \epsilon_{\vec{k}}^q \). The incoherent part itself does not have to be smooth and featureless. It can show similar resonance-like features than the coherent part. This can for instance be achieved by coupling of electrons with bosonic modes like phonons. The lifetime is then defined as the lifetime of the composite of electrons with the phonons. Thus one speaks of another type of quasiparticle, a polaron. It can again be argued in this polaron picture that there is a correspondence to the elementary excitations of a non-interacting system. Spin, charge and momentum will not be altered, yet other quantities like mass will.

1.2.3 Selected spectral features

The shape of the spectral function can be very diverse, as it depends on the exact shape of the bare non-interacting band, as well as on the strength and nature of the interaction to a vast of different excitations. It is not unambiguous to assign different spectral features to certain coupling mechanisms. However, it is possible to determine general features produced by certain mechanisms. In the case of graphene, specific many-body features can be found within ARPES measurements. In Fig. 1.8 (a) a typical spectrum of the \( \pi \) bands is shown [57]. The system is doped such that the Dirac point is located at about 1 eV binding energy and due to transition matrix element effects in the photoemission process (see paragraph 2.1.2), only one branch of the Dirac cone is visible [59, 60]. The bare band as such is linear in graphene, but strong deviations from linearity are evident. These deviations are caused by a superposition of different mechanisms. In Fig. 1.8 (b), the accompanying band broadening in terms of momentum distribution curve (MDC) width is plotted. Three main mechanisms were assigned to contribute to the picture by Bostwick et al. [57]. Electron-plasmon coupling gives strongest renormalizations in the vicinity of the Dirac point and electron-phonon coupling gives a step-like broadening away from the Fermi level. Electron-electron
interaction in the picture of electron-hole pair creation, i.e. Auger processes, are most pronounced away from the Dirac point. The peculiar shape is a consequence of graphene’s linear band structure and accompanied DOS, governing binding energy dependent transition matrix elements in the temporal evolution of the system. Depending on the environment, i.e. substrate in this case, electron-plasmon coupling can be so strong in graphene systems that polarons are formed, the so-called plasmarons [50, 58]. This shows as a splitting of the branches around the Dirac point, where a diamond-like shape is formed (see Fig. 1.8 (c) [58]).

The energy renormalization for electron-phonon coupling at moderate strength shows in the typical kink structure near the Fermi level, as it is generally the case for metals [61–65]. This kink is located approximately at the energy of the phonon involved, which can be seen in Fig. 1.9 (a) [66] for graphene’s $\pi$ bands, as produced by coupling to optical phonon modes [67, 68]. In an intermediate to strong coupling regime a splitting of the bands is observed, similarly to the previously described plasmon case in graphene. This can be seen exemplarily in Fig. 1.9 (b) [69], which shows the SrTiO$_3$(001) surface state at a certain doping level. Resembling Eq. 1.7, the splitting is such that a series of bands is observed. A sharp coherent part near the Fermi level is accompanied by incoherent replicas at higher binding energy [63, 70, 71]. The separation corresponds to about the
Fig. 1.9: Example spectral function features produced by electron-phonon coupling: (a) ARPES on potassium intercalated graphene on Ir(111) taken parallel to the ΓK direction (adapted from ref. [66]). (b) ARPES spectral cut through Γ of the 2D electron liquid at the SrTiO₃(001) surface. (c) EDC through Γ of the spectrum from (b). (b) & (c) were adapted from ref. [69].

phonon energy involved, respectively. For the SrTiO₃ case, this is about 100 meV (see Fig. 1.9 (c)).
CHAPTER 2

Overview of experimental techniques

This chapter is dedicated to give an overview over the experimental methods utilized in the scope of this thesis. As the main focus was put on the creation and characterization of new systems based on epitaxial graphene on SiC(0001), classical surface science techniques were most important. In this manner, core level spectroscopy (CLS) and low energy electron diffraction (LEED) were used to gain insight in the chemistry and ordering of the systems. As complementary microscopic probes, low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM) measurements were conducted. The core of this work was to modify graphene's electronic properties, thus angle resolved photoelectron spectroscopy (ARPES) was utilized to acquire information on the electronic band structure. X-ray magnetic dicroism (XMCD) measurements were conducted to gain information of the magnetism in these systems and magnetotransport (MT) measurements were made to get information of the electronic transport properties.

2.1 Photoelectron spectroscopy

Photoelectron spectroscopy (PES) is a general term for a plurality of techniques [55]. They all rely on the photoelectric effect, i.e. the photon-induced excitation of electrons from a material into vacuum. Depending on the binding energy of these electrons, a spectrum of different kinetic energy can be detected. In this manner, the spectrum gives information on many material properties and in turn,
depending on the photon energy used and the kinetic energy of the electrons to be investigated, a manifold of information can be acquired [55].

2.1.1 Experimental details

For all PES techniques, the measurement principle is similar. The sample is illuminated by monochromatic light with photon energy $E_{\text{phot}}$. The emitted electrons then are guided in an electron analyzer (see Fig. 2.1 (a)). State-of-the-art analyzers are built in a hemispherical geometry. There, the electron trajectories separate them by incidence angle and kinetic energy. The electrons eventually hit the detector, which is usually built up by an array of independent detectors, as a series of channeltrons or a channel plate. Every individual detector corresponds to a certain kinetic energy value and, depending on the measurement mode, incidence angle into the analyzer. From the electrons’ kinetic energy $E_{\text{kin}}$, one has to extract their binding energy $E_B$ within the sample. $E_{\text{kin}}$, however, is the energy exceeding the vacuum level $E_{\text{vac}}$. As the electrons are detected within the analyzer, $E_{\text{vac}}$ is defined with respect to the analyzer’s work function $\phi_A$ (see Fig. 2.1 (b)). Thus, the following relation has to be considered [55]:

$$E_{\text{kin}} = E_{\text{phot}} - E_{\text{vac}} = E_{\text{phot}} - \phi_A - E_B,$$

(2.1)
As already mentioned, in the photoemission process, a photon has to be absorbed, an electron has to be removed from the material and has to be detected. This can be viewed as a single coherent process within the so-called one-step model. The theoretical description, however, can be challenging, as the system as a whole will react to the external disturbance by the photon [53]. In this manner, one has to make further assumptions and simplifications. The first consideration is the timescale in which different processes take place. In other words, will the system adjust slowly or quickly compared to the disturbance produced by the photon. This will depend on the system itself and on the photon energy. In this sense, one can distinguish different regimes. If the system adjusts quickly, then the photoemission process is carried out in the so-called adiabatic limit [55]. In this case, interaction effects have to be considered even for the process itself. In the other limit one has to make do with the sudden approximation [55]. There, the system is too slow to adjust instantly, thus the excitation is considered sudden. A formally correct way to describe this in first order perturbation theory is Fermi’s golden rule [54]. There, the transition probability \( w_{fi} \) from an initial N-electron state \( \Psi_i^N \) with energy \( E_i^N \) and a possible final state \( \Psi_f^N \) with energy \( E_f^N \) is given by:

\[
w_{fi} = \frac{2\pi}{\hbar} \left| \langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle \right|^2 \delta(E_f^N - E_i^N - E_{\text{phot}}).
\]  

The interaction with the photon is treated as a perturbation with \( H_{\text{int}} = \frac{e}{2mc} \vec{A} \vec{p} \), where \( \vec{A} \) is the electromagnetic field. Within the simplest approximation, the N-particle state \( \Psi_i^N \) can be written as the product of the initial one-electron orbital \( \phi_i^\vec{k} \) with momentum \( \vec{k} \) and the state of the remaining (N-1) system \( \Psi_i^{N-1} \). Note that \( \Psi_i^{N-1} \) is not an Eigenstate of the (N-1) electron system, but just the remaining electrons in their initial orbitals after having pulled out one electron in the orbital \( \phi_i^\vec{k} \). Also, we can write \( \Psi_i^N \) in the representation of the initial orbital states \( \Psi_i^{N-1} \) and the expelled electron’s final state \( \phi_f^\vec{k} \) as \( \left| \Psi_f^N \right\rangle = \sum_m \left| \phi_f^\vec{k} \right\rangle \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle = \sum_m \left| \phi_f^\vec{k} \right\rangle c_{m,i} \). \( \Psi_m^{N-1} \) themselves represent the (N-1) electrons in the excited state after one electron was expelled. In the sudden ap-
proximation $H_{\text{int}}$ only acts on the orbital state $\phi_{i/f}^{\vec{k}}$, thus we can write:

$$w_{fi} = \sum_{m} \left| \langle \phi_{f}^{\vec{k}} | H_{\text{int}} | \phi_{i}^{\vec{k}} \rangle \right|^2 |c_{m,i}|^2 \delta(E_{\text{kin}} - E_{N}^{m-1} - E_{N}^{i} - E_{\text{photon}}),$$  \hspace{1cm} (2.3)

with $E_{\text{kin}}$ being the kinetic energy of the photoelectron. One can interpret $\langle \phi_{f}^{p} | H_{\text{int}} | \phi_{i}^{p} \rangle = M_{f,i}$ as the optical transition matrix elements. The photoemission intensity at a certain kinetic energy will then be proportional to the sum of $w_{fi}$ over the initial and possible final states of the system:

$$I \propto \sum_{f,i} w_{fi} = \sum_{f,i} |M_{f,i}|^2 \sum_{m} |c_{m,i}|^2 \delta(E_{\text{kin}} - E_{N}^{m-1} - E_{N}^{i} - E_{\text{photon}}),$$  \hspace{1cm} (2.4)

This relation has strong formal similarities to the spectral function representation in the Green’s function formalism (see paragraph 1.2). The spectral intensity can thus be seen as the spectral function weighted with the optical transition probability $|M_{f,i}|^2$. Effects that can be associated with these transition matrix elements are straightforwardly called matrix element effects. These can alter the relative intensity of certain features in PES and depend in general on the photon energy and polarization [53]. An example for graphene can be depicted in the so-called dark corridor (see also paragraph 1.2.3). Depending on the photon energy and polarization, parts of the $\pi$ band branches’ intensity can be suppressed completely [60].

Although the picture of the one step model is initially the most accurate, its mathematical representation has to be made with several simplifications. Especially, relaxation as interaction processes during the photoemission have to be treated with great effort. In this sense, one can introduce a different point of view in the phenomenological three step model. There, the process is artificially divided into three independent steps as following [53]:

(i) Optical excitation into a final state within the bulk of the material.
(ii) Travel of the excited electron to the surface.
(iii) Escape of the photoelectron into vacuum.

Step (i) can formally be treated like the one step model in the presented way (see above). In step (ii), the excited electron can lose energy due to interac-
tion/scattering with different excitations. In step (iii), the electrons can further change momentum and energy as they have to overcome the surface potential. The success of this model lies in its intuitiveness, thus easier understanding of different features in the PES that cannot be attributed to the intrinsic spectral function.

\subsection*{2.1.3 Core level spectroscopy}

One important regime of PES lies in the spectroscopy of core level electrons. Due to the large binding energy, the photon energies employed are commonly in the extreme ultraviolet to soft x-ray regime. This radiation is usually supplied by synchrotron facilities or x-ray sources producing Mg K\(\alpha\) (1254eV) or Al K\(\alpha\) (1487eV) lines. The obtained spectra can give valuable information about the chemical composition, as different elements have a fingerprint core level spectrum [55]. However, one has to be aware that binding energies can vary significantly within one chemical species. Especially in the scope of semiconductors, the location of the conduction and valence bands with respect to the Fermi level can strongly be altered by doping, in particular on the surface. In the scope of this thesis, the according surface band bending of the SiC rigidly shifts the location of the core levels. Yet, if a charge transfer between different atoms becomes significant, a reverse process comes into play. Let’s consider a simple case here, where two different atoms form a chemical bonding of an arbitrary kind. Both atoms will exchange charge, so that one will be negatively and one positively charged, respectively. The additional negative charge in one atom will additionally screen the respective core’s potential and lower the binding energy of the other electrons in this atom and vice versa for the other atom [55]. Depending on the case, such binding energy shifts can easily be on the order of a few electron volts and thereby different chemical states within one chemical species can be distinguished.

Another aspect to CLS are energy loss processes during photoemission and many-body considerations (see paragraphs 1.2 & 2.1.2). This can have influence on the spectral intensity distribution, thus CLS can also provide valuable information on different excitations within the system, like plasmonic degrees of freedom [72].

One major aspect to CLS is the inelastic mean free path (IMFP) of a photoelectron within the material, which defines the surface sensitivity of a probe. This
is limited by scattering processes and strongly depends on the photoelectrons’ energy. The IMFP itself is rather insensitive to the material itself, thus it is often referred to as the ‘universal curve’. It follows the phenomenological relation $\lambda = \frac{143}{E^2} + 0.054 \times \sqrt{E}$ [73], plotted in Fig. 2.2 (a). The most surface sensitive

![Diagram](image)

**Fig. 2.2:** (a) Inelastic mean free path as a function of the electron energy (reproduced from ref. [73]). (b) Sketch for the length, electrons have to pass to reach the material's surface for different escape angles.

regime lies at electron energies between 40 eV and 70 eV with an IMFP of about 4 Å. This corresponds to about one monolayer for a majority of materials. At about 200 eV the IMFP is doubled. In some cases, however, it is beneficial to not alter the electrons’ kinetic energy, as transition matrix elements and features relying on many-body physics can in general be photon energy dependent. For this, electrons, emitted from different angles can be examined in order to take influence on a probe’s surface sensitivity. For geometrical reasons, a signal produced from below the surface is damped away from normal emission (see Fig. 2.2 (b)). Combining these considerations brings the possibility for chemical depth profiling. This is commonly also used in samples of mixed composition. There, a quantitative analysis can be made by comparing the relative intensities of different spectral features with probes of different surface sensitivity.

CL spectra are usually accompanied by a step-like background from inelastic scattering of the photoelectrons. It has to be subtracted in order to evaluate the peak position, intensity and shape. Most commonly this is done by fitting a Shirley function to the spectra [74].
2.1.4 Angle-resolved photoelectron spectroscopy

ARPES is a technique probing the band structure of a crystalline solid. There, not only the energy of the photoelectron is determined, but also its emission angle and thereby momentum. A sketch of the measurement geometry is given in Fig. 2.3. In this coordinate system, the components of a photoelectron’s momentum are given by:

\[ K_x = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \vartheta \cos \varphi, \]
\[ K_y = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \vartheta \sin \varphi, \]
\[ K_z = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cos \vartheta, \]

with \( m \) being the bare electron mass and \( E_{\text{kin}} \) its kinetic energy. An aspect not considered in CLS (see previous paragraph) is that not only the energetics has to obey certain conservation laws (see Eq. 2.1), but also the momentum of the electrons during photoemission:

\[ \vec{k}_f^N - \vec{k}_i^N = \vec{k}_{\text{photon}}, \]

for the initial and final momentum of the N-electron system \( \vec{k}_i^N \) and the photon momentum \( \vec{k}_{\text{photon}} \). Generally, \( \vec{k}_{\text{photon}} \) can be neglected in the usual parameter window: As the typical photon energies are a few electronvolts to 100 eV, \( \vec{k}_{\text{photon}} \) is small compared to the typical momenta of the electrons involved, i.e. the
size of the Brillouin zone [54]. The difference between CLS and valence band spectroscopy lies in the fact that valence bands are delocalized states in contrast to the core levels, thus assigning an initial momentum to core levels is not reasonable in this sense [55]. In this manner, the emission angle gives direct access to the initial electron’s crystal momentum for valence electrons. During photoemission, the momentum component parallel to the surface \( k_{\parallel} \) is preserved, as translational symmetry in \( x \) and \( y \) is still given. Accordingly, one can write [53]:

\[
k_{\parallel} = |\vec{K}_{\parallel}| = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \vartheta. \tag{2.7}
\]

Due to the abrupt potential change, the momentum perpendicular to the surface \( k_{\perp} \) is not conserved. It is not a good quantum number and cannot be determined exactly. Yet, if some \textit{a priori} assumptions are made for the electron’s final states, one can assign a \( k_{\perp} \). In particular, one can adopt a nearly free electron dispersion for the final bulk Bloch state within the three step model:

\[
E_f(\vec{k}) = \frac{\hbar^2 k_{\parallel}^2}{2m} - |E_0| = \frac{\hbar^2 (k_{\parallel}^2 + k_{\perp}^2)}{2m} - |E_0|, \tag{2.8}
\]

where the electron momenta are defined in the extended zone scheme, i.e. periodic in multiples of reciprocal lattice vectors. \( E_0 \) is the bottom of the band with respect to the Fermi level. Then \( k_{\perp} \) can be rewritten accordingly [53]:

\[
k_{\perp} = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2 \vartheta + V_0)}, \tag{2.9}
\]

where \( V_0 = |E_0| + \phi \) is the so-called inner potential, i.e. the bottom of the band with respect to the vacuum level, as \( \phi \) is the work function.

As \( k_{\perp} \) is not a good quantum number, an additional complexity is added to ARPES. When investigating materials with a three-dimensional band structure, the resulting spectrum will be a weighted average over a certain range of \( k_{\perp} \) [53]. The spectrum will be broadened artificially and does not represent the actual spectral function. On the other hand, if the material has a negligible dispersion in one direction (e.g. certain layered materials [54]) or even a purely two-dimensional dispersion (e.g. graphene) direct access to the spectral function weighted with transition matrix elements is given (see paragraphs 1.2 & 2.1.2).
2.2 X-ray magnetic circular dicroism

XMCD is a technique based on the evaluation of a material’s absorption spectrum. It gives direct access to its magnetic properties. Due to the spectroscopic nature, this can be done chemically resolved [75–78]. The regime lies in the photon energy range, where excitations from core levels to valence states are possible. Different methods are used to obtain this absorption spectrum. The most convenient and commonly used way is collecting the so-called total electron yield (TEY) as the total number of electrons leaving the material at a fixed photon energy $E_{\text{phot}}$. Besides direct photoemission processes, electrons are mainly emitted by Auger processes. This means, as core level electrons are excited into the valence band, empty core states are left behind. During relaxation, lower energy electrons are emitted from the sample [76]. Apart from a background signal, the photocurrent is - in good approximation - proportional to the absorption coefficient $\sigma(E_{\text{phot}})$ [79].

Mathematically, an absorption process can be described by Fermi’s golden rule, similarly to the photoemission process (see paragraph 2.1). If one assumes a non-interacting system in the sense used in paragraph 1.2 & 2.1, one can describe the excitation process as following:

$$\sigma(E_{\text{phot}}) \propto |\langle f | H_{\text{int}} | i \rangle|^2 \rho_f,$$

where $|\langle f | H_{\text{int}} | i \rangle|$ is the transition matrix element from an initial $i$ to a final state $f$ with a perturbation Hamiltonian $H_{\text{int}}$ defined analogous to paragraph 2.1.2. $\rho_f$ is the density of final states. In XMCD, one utilizes these transition matrix elements in the form of optical selection rules for right and left circularly polarized light. Considering the orbital and spin degrees of freedom of the core level states, only transitions to states with certain spin above the Fermi level can be made for a given light polarization. In a non-magnetic sample, the density of states above the Fermi level is spin degenerate [34] and spectra obtained with the two polarizations are indistinguishable. Considering a magnetic or magnetically polarized system, the DOS above the Fermi level is not fully spin degenerate [34]. This introduces an asymmetry for the two light polarizations. By evaluating and comparing different parts of the absorption spectrum, an averaged spin and orbital momentum of a certain atom species can be extracted by applying the so-called sum rules [80].
2.3 Low-energy electron diffraction

LEED is a widely used technique in surface science, as it gives direct access to ordering of a crystal’s surface [76]. As already indicated by the name, electrons are accelerated by a voltage $U$ in an electron gun to a defined energy and guided to a material’s surface (see Fig. 2.4 (a, left). They then get reflected at the surface and hit a screen, where their impact can be made visible by fluorescence. The electrons’ energy is typically in the range of a few to a few hundred electron volts. Following the argumentation in paragraph 2.1.3, these energies make LEED very surface sensitive [81]. However, electrons hitting the surface will be scattered elastically at different atomic sites, thus their respective wave functions will interfere. As the scattering potential at the surface is periodic, only scattering to certain directions will be possible and a characteristic diffraction pattern will be visible on the screen. At normal incidence, the diffraction criterion is given by the Laue condition in two dimensions for the component parallel to the surface [76]:

$$\vec{k}_\parallel = \vec{g}_{hk},$$

(2.11)

where $\vec{k}_\parallel$ is the component parallel to the surface of the outgoing electron’s momentum and $\vec{g}_{hk}$ a reciprocal lattice vector of the periodic surface. To obtain the possible complete $\vec{k}$-vectors and therefore the direction electrons are scattered to, the Ewald construction is a valuable tool (see Fig. 2.4 (a, right). The reciprocal space of the surface is represented by rods that are spaced according to $\vec{g}_{hk}$. As

![Fig. 2.4: (a) Sketch of the LEED setup (left) and the Ewald construction (right). (b) Sketch of single scattering events and multiple scattering events. (c) Sketch of a simple triangular lattice with a ($\sqrt{3}\times\sqrt{3}$)R30° superstructure.](image-url)
the scattering process is elastic, the absolute value of the wave vector has to be preserved. In this manner, one can draw a circle (Ewald sphere), like shown in Fig. 2.4 (a), with the radius being the absolute value of the incident electron’s momentum $\vec{k}_0$. The intersects of the rods and the circle then define the possible $\vec{k}$-vectors.

Considering that a material surface’s primitive unit cell can be made up by an arrangement of different atoms, which can have different scattering cross sections, the picture gains complexity. Also, besides single scattering, multiple scattering events can occur (see Fig. 2.4 (b)). As a consequence, the intensity of the diffraction spots is in general strongly dependent on the initial electron energy and can show an oscillation-like behavior [81].

It is also necessary to introduce a useful nomenclature here, the Wood notation [76]. In simple cases, this can give the relation between the reciprocal lattice of a crystal, to a different ordering on its surface, which could for instance be produced by adsorbed molecules. The nomenclature is $(p \times q)\text{Ra}-MS$ [76]. $MS$ specifies the surface, the superstructure is referring to, for example SiC(0001). $p$ and $q$ give the length of the supercell unit vectors with respect to the $MS$ unit vectors and $\alpha$ denotes to a possible angle between surface and superstructure unit vectors. For illustration, a simple triangular lattice is sketched in Fig. 2.4 (c) with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure. There, $\sqrt{3}$ is the relation between the respective unit vectors, where the two sets of unit vectors are rotated by $30^\circ$.

### 2.4 LEEM & PEEM

LEEM and PEEM can be seen as the complementary microscopic method of LEED and PES, respectively [82]. Due to their similar experimental requirements, the two techniques are often combined in the same experimental setup. Although the energy resolution to date is not comparable to the standard PES, the possibility to connect electronic and chemical properties with structural properties in a microscopic way is unique [83]. A sketch of such a setup is given in Fig. 2.5. For the LEEM part, electrons are accelerated to about 15 keV and focused by lenses. The electrons are then guided towards the sample by a magnetic field. In a very short distance from the sample, they are decelerated in the objective lens to the required energy. On the sample, these electrons are diffracted, like in normal LEED (see paragraph 2.3). The diffracted electrons then again gain
the initial energy and are guided into the analyzing system by the magnetic field. The analyzing system consists of a series of lenses and a hemispherical electron analyzer. In this section, the electrons can be selected by energy and momentum. Finally, they are guided to a channel plate, where they are detected. The lens system can be adjusted such that the channel plate is set into the image plane or the focal plane, representing the real or reciprocal space, respectively. Standard modes for LEEM are LEED on a μm spot size (μ-LEED) and electron energy dependent real space microscopy. For the PEEM part, the sample is not bombarded by electrons, but with UV or X-ray photons. Detecting the photoelectrons is then analogous to the LEEM case. Standard modes for PEEM are CLS on a μm spot size (μ-XPS) and real space photoelectron imaging. Adjusting the lens such that the channel plate is in the focal plane gives also the opportunity to map constant energy surfaces of the valence states’ band structure [82–84].

### 2.5 Magnetotransport

Magnetotransport measurements belong to the most basic techniques to probe certain electronic properties of a solid. Basic concepts in terms of a Hall bar measurement geometry will be elucidated here. Generally, a current is imposed onto the sample (see Fig. 2.6). The resistance is measured by a longitudinal voltage drop $U_{xx}$ across a defined length $L$. The resistivity is then given by $R_{xx} = \frac{W U_{xx}}{L}$, where $W$ is the width of the sample. The Hall resistance is then given by $R_{xy} = \frac{U_{xy}}{LB}$, with $U_{xy}$ being the transversal voltage driven by a magnetic field $B$ (see Fig. 2.6).

We consider now the motion of point-like massive electrons in the two-dimensional sample in an external electric field $\vec{E}$ in $x$ direction (see Fig. 2.6) based on the
Drude model [34]. These electrons will be accelerated by this field and scattered after a mean time $\tau$. One can then define a mean drift velocity of the electrons $\vec{v}$ and with that a current density $\vec{j}$. The relation is given by [34]:

$$\vec{j} = \frac{ne^2\tau}{m^*} \vec{E} = \sigma_0 \vec{E},$$  \hfill (2.12)$$

where $n$ is the two-dimensional charge carrier density, $e$ the electron charge and $m^*$ the effective mass of the electrons in the sample. $\sigma_0 = \frac{ne^2\tau}{m^*}$ is the conductivity, giving the voltage drop $U_{xx}$ over a sample (see Fig. 2.6). One can further define a new quantity as the charge carrier mobility $\mu = \frac{e\tau}{m^*} = \frac{\sigma_0}{ne}$. When introducing a magnetic field $\vec{B}$ in $z$ direction as $\vec{B} \varepsilon_z$, the Lorentz force will bend the electrons’ path. Assuming $\tau$ is not affected, their absolute velocity will not be altered and the $x$ component of $\vec{v}$ will decrease, as well as $\sigma(B)$. One can then obtain [56]:

$$\sigma(B) = \sigma_0/(1 - \left(\frac{e\tau}{m^*}\right)^2 B^2) = \sigma_0/(1 - \mu^2 B^2).$$  \hfill (2.13)$$

This means a sample’s resistivity, as inverse of the conductivity, will increase with $B^2$. Since the Lorentz force bends the path of the charge carriers in the $y$ direction, current flows accordingly. For a finite sample, an electric field $E_y$ in $y$ direction will be built up to counteract the Lorentz force, which is measured as the Hall voltage $U_{xy}$ across the sample (see Fig. 2.6). $E_y$ is then given by [34]:

$$E_y = -\frac{B}{ne} j_x = BR_H j_x,$$  \hfill (2.14)$$

$j_x$ is the current density initially imposed onto the sample. $R_H = -\frac{1}{ne}$ is the Hall coefficient. One can directly extract the carrier density and carrier type by the size and sign of $R_H$. 

**Fig. 2.6:** Sketch of the magnetotransport setup.
At sufficiently high field and charge carrier mobility, another effect sets in, as
the electrons' orbit can form closed loops. Consequently further quantization
conditions have to be fulfilled, which lead to discretization of the allowed energy
spectrum to the Landau levels in the DOS [56]. For a parabolic dispersion the
sequence of Landau levels is described by

$$E_n = \left(n + \frac{1}{2}\right) \frac{\hbar e}{m^*} B,$$

with $n$ being the level index as an integer. For graphene on the other hand, the sequence changes
due to its linear dispersion to [31]:

$$E_n = \text{sgn}(n) \sqrt{2e\hbar v_F^2 |n| B},$$

where $v_F$ is graphene’s Fermi velocity. When changing $B$, the chemical potential
will cross the Landau levels and the conductivity will oscillate [56]. These osc-
cillations are called Shubnikov-de Haas oscillations and are periodic with inverse
magnetic field. The periodicity $\Delta \left(\frac{1}{B}\right)$ is directly connected to the area $S$ that is
enclosed by the Fermi surface, independent on its shape, by [56]:

$$\Delta \left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar S}$$

The ratio of $S$ and the size of the whole BZ, on the other hand, is proportional
to the filling of the band, i.e. the charge carrier density. This directly follows
from Pauli’s principle in a single particle picture, but is also valid for many-body
systems, which is known as Luttinger’s theorem [85]. Due to scattering of the
charge carriers by defects or phonons, the Landau levels are broadened in energy.
Scattering, however, defines $\mu$ in the presented picture. Thus in general, the
condition $\mu B > 1$ has to be met in order to observe these oscillations [56] and $\mu$
can be estimated by the onset field of oscillations $B_{\text{onset}}$.

### 2.6 Sample preparation

For the work presented in this thesis, single crystals of the 6H-SiC polytype were
used, obtained from SiCrystal GmbH. These wafers were initially mechanically
polished and showed a typical miscut of less than 0.1° with respect to the (0001)
direction. The wafers were initially n-type doped by the incorporation of a con-
trolled density of nitrogen atoms within the lattice [39]. Typical for semicon-
ductors, the impurities create midgap states which can be thermally activated
at certain temperatures [86]. The resulting free charge carrier density led to a typical specific resistivity of about 13 mΩm at room temperature\(^1\). It is worth noting, that the resistivity at room temperature was low enough that PES and LEED experiments could be conducted without extra experimental measures. On the other hand, due to the semiconducting nature, the charge carriers could not be thermally activated at temperatures beneath 50 K. With this it was possible to conduct transport measurements below these temperatures on the produced graphene samples without the influence of conduction channels in the substrate. Prior to further processing, the wafers were cut usually into 10 mm×5 mm-pieces by the crystal preparation group in our institute.

### 2.6.1 Wet chemical cleaning

Before the actual growth process, the samples had to be cleaned in a wet chemical cleaning procedure in order to remove oxide and metallic contamination, following Emtsev [48]. The different steps are summarized in table 2.1. Every one of these steps was followed by rinsing in deionized water. After these steps, the surface was clean and further preparation steps could be done.

<table>
<thead>
<tr>
<th>Step</th>
<th>Solution</th>
<th>t (min)</th>
<th>T (°C)</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>10</td>
<td>RT</td>
<td>Remove grease</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)SO(_4):H(_2)O(_2) (4:1)</td>
<td>10</td>
<td>180</td>
<td>Remove organic cont.</td>
</tr>
<tr>
<td>3</td>
<td>HF 5%</td>
<td>5</td>
<td>RT</td>
<td>Remove oxide</td>
</tr>
<tr>
<td>5</td>
<td>HF 5%</td>
<td>5</td>
<td>RT</td>
<td>Remove oxide</td>
</tr>
</tbody>
</table>

Table 2.1: Steps of the wet chemical cleaning procedure for the SiC samples.

### 2.6.2 Hydrogen etching and graphene growth

Since the wafers were initially mechanically polished, the surface was covered with polishing scratches. In order to flatten the surface, which is necessary for

\(^1\)This value was obtained by resistive measurements in the scope of this thesis.
homogeneous graphene growth, the samples were annealed in a 800 mbar hydrogen atmosphere at about 1500 °C (following refs. [48, 87]). After this step, the surface showed parallel terraces with unit cell step height, which was always controlled by means of atomic force microscope (AFM) measurements. This process was carried out in a home built cold wall quartz reactor, similar to refs. [27, 48] and described in ref. [33]. Samples were graphitized in the same reactor in an Ar atmosphere to the required stage, i.e. ZLG or MLG on SiC(0001) (see paragraph 1.1.3). After the graphitization stage all of these samples were characterized by AFM, XPS and ARPES to approve their quality. Also, the growth parameters were constantly optimized to get a consistent result. This was of great importance, as these samples were the basis for all further preparation steps, done in the course of this thesis. A high emphasis was set on the production and use of the highest quality samples as this was crucial for a major part of conclusions drawn from the experimental results. The intercalation treatments were done in situ either in our home vacuum facilities or in the vacuum facilities supplied at different synchrotrons (see following paragraphs).

2.7 Experimental setups & data evaluation

2.7.1 Facilities in Stuttgart

The main part of the experimental work was done in the home laboratories at the MPI FKF in Stuttgart and there in the group’s vacuum facilities (details can for instance be found in ref. [33]). The system is designed for maximum versatility, such that sample preparation and characterization with multiple surface science techniques can be combined without exposing the samples to air. A distribution chamber connected a load lock, a magazine for sample storage, a preparation chamber and an analysis chamber. The preparation chamber was equipped with ports, where multiple evaporators or other machinery could be mounted. Also, a LEED system (ERLEED from Specs GmbH) was readily available. The sample position could be adjusted with a 5 axis manipulator (3 translational and 2 rotational degrees of freedom). The analysis chamber was equipped with a He discharge lamp with a monochromator, providing HeI (21.2 eV) or HeII (40.82 eV) light, and an X-ray source delivering Mg Ka light (1253.6 eV). Furthermore, the
analysis chamber was equipped with a 5 axis manipulator, whereby the control of the angular degrees of freedom were automated. Photoelectrons were analyzed in a SPECS Phoibos 150 hemispheric analyzer equipped with a micro-channel plate, which allowed APRES measurements at a range of angles at once. The samples themselves were mounted on sample holders that allowed resistive heating to temperatures higher than 1400 °C, which was controlled using pyrometers. Besides the mentioned machinery, the group also had access to a Bruker Dimension Icon AFM, which was mainly used to control the sample growth process here, prior to intercalation.

2.7.2 Equipment at synchrotrons

Many of the measurements, shown in this work, were made at different synchrotrons, as the instrumentation there has advantages compared to the equipment at the MPI FKF in Stuttgart. The provided light can be 1 to 2 orders of magnitude brighter than what is provided by the sources in the home laboratory. Also, the photon energy could be altered. As already mentioned in chapter 2.1, this gives the possibility to get more information on the origin of certain spectral features. Furthermore, as the beam could be focused onto the sample to a smaller spot, a better resolution in both energy and emission angle of the photoelectrons could be achieved. ARPES measurements were done either at the MAX-Lab synchrotron in Lund at beamline I4, at the ANTARES beamline at the Soleil synchrotron near Paris or at the 1² end-station at BESSY in Berlin. The machineries at these beamlines were equipped with a preparation chamber, where different evaporators could be mounted besides a LEED optics, respectively. The analysis chambers were equipped with 6-axis manipulators, while the samples could be cooled with liquid nitrogen at MaxLab and Soleil and with helium at BESSY. At I4 the electron analyzer was a Specs Phoibos 100, at ANTARES it was a Scienta R4000 and at 1² it was a Scienta R8000. The available photon energies were 14 eV-200 eV at I4, 12 eV-1000 eV at ANTARES and 4 eV-250 eV at 1².

LEEM, PEEM and CLS experiments were done at beamline I311 at MAX-Lab, which provided photon energies in the range of 30-1500 eV. CLS measurements were conducted using a hemispherical Scienta-SES200 electron energy analyzer with the samples mounted on a 4-axis manipulator. LEEM/PEEM experiments
were done with a LEEM III from Elmitec. The presented XMCD measurements were conducted at beamline I06 at Diamond light source near Oxford. The chamber was equipped with a total electron yield and fluorescence detection system, where partial and total photocurrents could be measured. During measurement, the samples were embedded in a cryogenic system for temperatures down to 1.5 K. Superconducting magnets supplied a magnetic field of up to 6 T. More details can be found on the respective websites [84, 88, 89].

2.7.3 Magnetotransport equipment and procedure

Magnetotransport measurements were conducted in collaboration with Jurgen Smet’s group, in particular Johannes Geurs and Federico Paolucci, from the MPI FKF in Stuttgart. Part of the experiments were conducted in a top load $^4$He cryostat with a variable temperature insert (sample rod), where temperatures from room temperature down to 1.5 K could be achieved. In this setup, magnetic fields of up to 15 T could be applied. To get to lower temperatures, a different technique was used. In a dilution fridge, temperatures down to about 20 mK could be reached by utilizing mixtures of $^4$He and $^3$He. Magnetic fields of up to 21.5 T could be applied. As the samples would degenerate in air, a procedure was developed to incorporate them into the cryogenic facilities in inert gas atmosphere. The samples were not exposed to air at any step. The procedure can be followed in the work flow diagram in Fig. 2.7. First the samples were prepared in our group’s vacuum facilities and characterized by means of LEED.

![Fig. 2.7: Illustration of the different steps that were conducted in order to perform transport measurements. The respective environments, where the samples are kept in, are specified within the chart.](image-url)
CLS and ARPES. They were then transferred into a vacuum suitcase in which they were brought to a glove box in static vacuum. The samples were glued onto a chip carrier and bonded inside the glove box under Ar atmosphere. Bonding was done with Indium or gold wires, that were pressed or glued onto the sample with silver epoxy, respectively. The samples were not treated with lithographic patterning procedures. The contacts were placed on the sample edge to obtain a Hall bar geometry. The chip carrier was then inserted into the respective sample rod, where they could be kept in Ar atmosphere until insertion into the cryostat. After conducting the transport measurements, the sample rod was inserted into the glove box, where the sample was removed and again inserted into the suitcase. At this stage it was possible to insert the samples into our vacuum facilities. This was done to perform control measurements for every sample by means of ARPES. There, we could assure that the samples did not degenerate during the cycle.

2.7.4 Software

Most of the CLS and ARPES data were acquired using the SpecsLab2 and CCD Acquire softwares, respectively, provided by SPECS GmbH. At ANTARES in Soleil and at 1² at BESSY it was the SES software from Scienta. The XMCD data were acquired with a software supplied by the beamline. Magnetotransport data was acquired with a software written by Jurgen Smet’s group. LEEM/PEEM data was acquired with a software supplied by Elmitec. The data evaluation was conducted using the Wavemetrix Igor 6 software. There, procedures were either developed in the scope of this thesis, by former group members or the scientific community. The LEED data shown was acquired and evaluated with the EE2010 software.
2.7 Experimental setups & data evaluation
Motivation & Outline

A major aspect to graphene is its chemical, thermal and mechanical stability. Yet, at the same time it holds great sensitivity to its environment and therefore its properties are widely tunable. This, together with the fact that graphene is commonly supported by a substrate is utilized by the technique intercalation [21]. The inserted atom species takes influence on the graphene and is at the same time protected by the graphene. The work done here aims towards utilizing these natural advantages of the technique intercalation and modifying graphene’s properties in a controlled way. Building upon graphene on SiC(0001), maximum versatility is given by the high quality and the semiconducting nature of the substrate on a useful wafer scale [27]. Within this thesis, the focus was not directly put on possible applications, but rather to explore graphene’s properties on a basic research level.

One main aspect to intercalation is the charge carrier density introduced by the intercalant in the graphene. In this manner, one aim was to n-type dope graphene to the extreme and explore its properties in this regime. In particular, the saddle point at the $\overline{M}$ point should be reached at the Fermi level. At this point the DOS diverges, which means a Van Hove singularity (VHs) is present. The focus in this Van Hove scenario has to be put on effects driven by correlations, which are predicted to be drastically enhanced compared to the case at low doping. Interesting states of matter could occur there, like unconventional chiral superconductivity driven by repulsive electron-electron interaction [90, 91]. The possibility of reach-
ing the VHs in graphene was shown by McChesney et al. [92] by the combination of intercalation and adsorption of calcium and potassium in/on standard MLG on SiC(0001). Yet, the introduction of dopants on the blank samples led to a drastically reduced chemical and thermal stability. For this reason, no measurements existed in this regime, going beyond in situ characterization with ARPES. In this sense, the VHs should be reached by only intercalation. No adsorption of dopants should be involved to assure the necessary stability for further exploring this regime. This topic will be treated in chapter 4.

Going beyond this, also highly doped bilayer graphene should be produced and explored. There, the differences with the monolayer graphene case are especially interesting. Besides the relation to the monolayer, bilayer graphene exhibits substantially different properties in many aspects, especially with regard to many-body physics [30, 31, 93, 94]. Chapter 5 is dedicated to this topic.

A further point in the scope of intercalation was to take the focus away from the graphene and examine the role of the intercalant, which was done here in the case of Au intercalation. The intercalant is commonly arranged in a densely packed two-dimensional way. Thus the question arose, whether it can be neglected as a passive layer, especially electronically. Focusing on this should bring additional insight in the technique intercalation, which is of importance for basic understanding and applications. This facet will be exploited in chapter 6.

In chapter 7, the work done in this thesis will be connected and put into a wider context. There, also further possibilities for graphene and the technique intercalation will be highlighted.
As the goal was to produce graphene doped to the VHs by intercalation, a suitable intercalant had to be determined. Simulations based on density functional theory (DFT) showed that lanthanides are supposed to dope strongly when adsorbed on graphene [95, 96]. Previous work on intercalation of europium [97] and ytterbium [98] produced strongly doped graphene, yet the VHs was not reached. Within the lanthanides, Gd is supposed to have an especially strong doping efficiency [95, 96], which was already proven when adsorbed on graphene [99]. Although intercalation and adsorption are not completely complementary, as it was shown for example by the intercalation of gold [100, 101], Gd was chosen here.

4.1 General characterization

To intercalate ZLG on SiC(0001) with a solid material, generally a combination of evaporation onto and subsequent annealing of the sample leads to success [23, 25, 97, 98, 100]. This approach however, was not sufficient in the Gd case. A more advanced procedure had to be developed here, which consisted of a combination of evaporation on a heated sample (800 °C), followed by a short heating procedure to higher temperatures (1250 °C). Details can be found in appendix B. In this chapter, a general characterization of these samples will be given.
4.1.1 Reaching the Van Hove singularity

In Fig. 4.1 ARPES measurements of Gd intercalated ZLG are shown, containing the most prominent spectral features. The spectral cut trough $\overline{K}$ taken perpendicular to the $\overline{Gamma}$ direction in Fig. 4.1 (a) displays strongly n-doped graphene. The Dirac point is shifted by about 1.6 eV below the Fermi level. In the band course from $\overline{K}$ towards $\overline{M}$ in Fig. 4.1 (b), it is evident that there is spectral weight at $\overline{M}$ at the Fermi level. Only part of the branches are visible in this measurement due to matrix element effects [60]. The data shows unambiguously that the VHs was reached in graphene by the intercalation of Gd. This is also verified by the Fermi surface (FS) as plotted in Fig. 4.1 (c). A change in topology can be seen compared to lightly doped graphene. The FS no longer consist of two electron pockets around the $\overline{K}$ points but rather one hole pocket around the $\overline{Gamma}$ point, which can be nicely followed by the fit in the first BZ in Fig. 4.1 (c). These changes in the FS are usually referred to as Lifshitz transitions [102].

Following Luttinger’s theorem, which states that the filling of a band is proportional to the area enclosed by the Fermi surface [85], one can state that the number

\[ \int_{Fermi} \rho(E) \mathrm{d}E \propto A_{FS} \]

\( \rho(E) \) is the spectral density and \( A_{FS} \) the area enclosed by the Fermi surface. The spectral weight is a measure of the number of states available at a given energy, and it is directly related to the density of states. The Dirac point is shifted by about 1.6 eV below the Fermi level. In the band structure, the spectral weight is concentrated around the Fermi level, with a significant decrease for energies below and above this level.
of electrons in this band corresponds to about $4.5 \times 10^{14} \text{ cm}^{-2}$. In the view of nearest neighbor tight binding, the VHs should be at a filling of $\frac{1}{4}$ of the $\pi^*$ band, which corresponds to $9.5 \times 10^{14} \text{ cm}^{-2}$ [90]. The fact that the VHs was nevertheless reached is caused by severe renormalizations of the band structure near the Fermi level. The band course around $\overline{M}$ towards $\overline{K}$ is completely flat in a window of about $1 \text{ Å}^{-1}$ (see Fig. 4.1 (b)). This will be further examined in paragraph 4.2. As it is of utmost importance, a detailed characterization by means of chemistry, structure and magnetism for this system will be given in the following paragraphs.

4.1.2

Proof for intercalation, stability & homogeneity

While the appearance of the characteristic $\pi$ bands is an indication for intercalation, it is no proof and also provides no further information of other aspects like homogeneity and stability per se. For this, CLS is an appropriate tool. In Fig. 4.2 (a) core level spectra are plotted of an intercalated sample, taken with Al K$\alpha$ radiation at two different emission angles. The spectra are normalized such that the Gd 3d$_{5/2}$ peak has the same area for both emission angles. In the Si 2p, one notices a component that is shifted by about 1.1 eV from the pristine ZLG to lower binding energies. Such shifts are comparable to the intercalation of hydrogen [103] and are a good sign for decoupling of the graphitic layer. The bonds to the first graphitic layer are likely to be broken, thus the surface band bending in the SiC is altered. The C 1s on the other hand shows two distinct features. One is more and one is less pronounced when varying the angle, thus surface sensitivity. The component at about 282.7 eV has to be located within the SiC. The shift from the pristine ZLG is compatible with the shift observed in the Si 2p component. An assignment of the component at about 285 eV binding energy to the graphene is reasonable in view of surface sensitivity and binding energy shift. Neutral graphene exhibits a peak at a binding energy of about 284 eV. n-type doping then leads to a shift to higher binding energies. In the Gd 3d$_{5/2}$ different components cannot be distinguished when varying the surface sensitivity. Considering the simplicity of the initial pristine ZLG system, consisting of one graphitic layer on top of the SiC, the core level measurements point towards a sandwich configuration with Gd being between the graphene and the SiC. Furthermore, we could not find any trace of oxygen on our samples, even when
4.1 General characterization

Fig. 4.2: CLS and LEEM measurements on Gd intercalated ZLG: (a) CLS on the declared regions obtained with Al Kα radiation for two different emission angles. The spectra are normalized on the Gd 3d<sub>5/2</sub> intensity for both angles, respectively. The O 1s region is normalized to the C 1s peak at 0° emission angle. (b) LEEM-micrograph of an intercalated sample at electron energy 1.6 eV and 25 µm field of view. (c) LEEM reflectivity of the ZLG and Gd intercalated stage for comparison. The spectra were taken at the orange marked spot in (b).

keeping them in moderate vacuum conditions of about 2 × 10<sup>-9</sup> mbar for months (see Fig. 4.2 (a)). Tests, where Gd was only evaporated onto the samples, showed a pronounced O 1s component even within minutes of exposure to these conditions (not shown). This is due to the fact that Gd is a very reactive material, which binds remaining oxygen or water in the chamber. Consistent with the CLS measurements, also no degeneration in ARPES could be determined for the intercalated samples. This means firstly, that the Gd is protected by the graphene in the sandwich configuration, as intended. Secondly, clusterization of Gd on the blank surface could be excluded. An issue with usual intercalation procedures is clusterization on the surface, hindering the intercalation process. This could be avoided by the intercalation procedure described in appendix B. The lack of clusterization as well as the homogeneity of the system could be verified by LEEM measurements. In Fig. 4.2 (b) a LEEM micrograph is shown with 25 µm field of
Gadolinium intercalated ZLG

view, which shows a clean surface. The only contrast distinguishable are small initial MLG contributions at step edges in the SiC substrate, as the outcome of the advanced fabrication of graphene on SiC(0001) in Ar atmosphere [27]. The contribution of MLG on the pristine samples was less than 2%, which was set as standard for the samples. Apart from these edges, no reasonable contrast on the terraces can be seen, which is a clear sign for homogeneity on this mesoscopic scale. To prove consistency, also µXPS measurements were performed on this area (not shown), which resemble that of the "macro"-XPS measurements (see Fig. 4.2 (a)). A clear sign for intercalation can also be seen in LEEM reflectivity measurements, plotted in Fig. 4.2 (c). The non-intercalated sample shows a structure, typical for ZLG on SiC(0001) with no strongly pronounced dips or peaks [49]. After intercalation, a dip structure forms at 2-3 eV electron energy. This is again consistent with hydrogen intercalation [49] and standard monolayer graphene on SiC(0001) [104] and is a distinct sign for the formation of a monolayer of graphene on SiC(0001).

In conclusion, it can be stated that the system is thus far well defined. It is homogeneous, clean and stable in UHV, as the graphene layer acts as a protection layer, which was intended initially. It has to be noted that these samples do not withstand direct exposure to air (see paragraph 7). Yet, they could be well kept in UHV or inert gas atmosphere, which was essential to acquire a big part of the following experimental results.

4.1.3 Chemistry determined by CLS

Although the CLS measurements taken at different emission angle in Fig. 4.2 give good information about the depth distribution of the respective atomic species, it is not possible to obtain the highest energy resolution at this high photon energy. Consequently, a detailed analysis of the chemical bonding situation was out of reach. In this manner, measurements at lower photon energies were made. In Fig. 4.3 (a) Si 2p core level spectra are plotted, obtained with 210 eV and 330 eV which means more and less surface sensitivity for the Si 2p. These measurements are evidence that silicon is present with two different chemical environments. The spectrum taken with 210 eV photon energy was fitted by a pair of doublet Voigt functions. Standard constraints were set for this fit, such as spin splitting of
4.1 General characterization

Fig. 4.3: High resolution CLS measurements: (a) Si 2p spectra of the Gd intercalated sample for two different photon energies, together with a fit (see text). (b) C 1s of Gd intercalated ZLG together with the C 1s of H intercalated ZLG for comparison. The spectrum of H intercalated graphene is set of by 450 meV to higher binding energy for comparison. (c) C 1s spectral function calculations for differently doped graphene (adapted from ref. [105]).

0.63 eV and branching ratio of 0.5 for the 2p\(_{1/2}\)-2p\(_{3/2}\) doublet. The fitting results are given in table 4.1. First to notice is the value of the Lorentzian width \(\omega_L\), which is well comparable to literature for graphene on SiC systems [48]. This value gives the lifetime of the photohole, thus it is an intrinsic property. The Gaussian width, which is mainly given by experimental resolution, is also very low. Together with the overall good fit, this gives a good indication that no more significant components have to be involved. The more intense component at 100.27 eV (2p\(_{1/2}\)) can be assigned to bulk SiC. The relative intensity \(A\), i.e. the ratio of the bulk Si component to the total Si 2p intensity, goes down with increased surface sen-

<table>
<thead>
<tr>
<th></th>
<th>(E_B) (eV)</th>
<th>(\omega_L) (eV)</th>
<th>(\omega_G) (eV)</th>
<th>(A_{210}) eV (%)</th>
<th>(A_{330}) eV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC bulk</td>
<td>100.27</td>
<td>0.12</td>
<td>0.28</td>
<td>90.5</td>
<td>95</td>
</tr>
<tr>
<td>Si-Gd</td>
<td>99.16</td>
<td>0.12</td>
<td>0.31</td>
<td>9.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.1: Fit parameters of the Si 2p\(_{1/2}\) components of the Gd intercalated ZLG.
sitivity (see table 4.1). The assignment of the shift in binding energy compared to pristine ZLG to an altered surface band bending is very reasonable [22]. The second component has a binding energy of 99.16 eV. This value is consistent with the formation of gadolinium silicide on the surface of the crystal, when comparing to literature for gadolinium silicide [106]. Also, similar binding energies are found for Yb bound to Si in Yb intercalated MLG on SiC(0001) [107]. Taking the ratio of the two areas at $h\nu = 330$ eV of 5:95, the value seems rather low, compared to other systems. In the case of hydrogen intercalation, where every free Si bond at the surface of the crystal is passivated, the ratio of the total intensities of the Si-H to Si-C peaks is about 1:2 with $h\nu = 330$ eV [41]. In a simple estimation based on comparing the Gd to the H case (see for instance ref [55]), one can suggest that only $\frac{3}{20}$ of the topmost Si atoms are bound to Gd atoms. Assuming that one Si atom binds to only one Gd atom, respectively, and considering the amount of Gd intercalated of 0.75 Gd-monolayer (see appendix B), this means that about $\frac{7}{25}$ of the Gd atoms are bound to silicon. Verifying this thesis by analyzing the Gd core levels brings some difficulties. Firstly, the Gd core level spectra only shows shifts on the order of 0.1 eV in binding energy, when bonding to silicon [106]. Also, the core levels giving a reasonable photoemission intensity have a large intrinsic width due to multiplet splitting and many body features [108] (see also Fig. 4.2 (a)). Because of this, a reasonable analysis of these core levels in the precision needed is beyond reach here. Nevertheless, even considering the errors made in the estimation, the statement can be made that only a portion of the Gd binds to the silicon on the surface of the SiC.

Taking a closer look at the C 1s, the two components assigned to SiC bulk and graphene in the previous paragraph 4.1.2 are very distinct (see Fig. 4.3 (b)). The SiC part can well be fitted with a single Lorentzian function with a center at 282.7 eV. Again, the fit is reasonable considering the Lorentzian width of 0.11 eV and the Gaussian of 0.31 eV. This is not possible for the graphitic part. The spectral distribution is very broad. At first glance this appears to consist of multiple components. The components then should be produced by partial bonding to Gd. On the other hand, carbon bound to Gd could show components at 281 eV and 282.9 eV [109], far from the graphitic components observed. Furthermore, it is remarkable that the lower binding energy flank is very steep but the high energy flank very shallow and smooth with only a light shoulder at 285.6 eV. Attempts to fit this distribution in a reasonable way with a sum of Lorentzians
(not shown) fail for these reasons. This indicates, that the key to understanding the shape is not in chemical shifts. It is known for metals and also for graphene, that core level spectra can be asymmetric due to the coupling of the photoelectron to excitations near the Fermi level, like plasmons or electron-hole pairs [110]. A representative asymmetric spectrum of H intercalated ZLG is also plotted in Fig. 4.3 (b). The spectrum was shifted by 450 meV to higher binding energy in order to simplify the following comparison. The distribution can be well fitted by a Doniach–Sunjić function [22], which is generally used for low doped graphene. H intercalated graphene shows a low doping level \(2.3 \times 10^{12} \text{ cm}^{-2}\) compared to the Gd case \(4.5 \times 10^{14} \text{ cm}^{-2}\). For this reason, it is initially questionable, if the Doniach–Sunjić line shape is still valid for the Gd case. The size of the Fermi surface is increased, thus the phase space for creating excitations should also be increased. Sernelius [105] made C 1s spectral function calculations for this highly doped case. His results for doping levels comparable to the hydrogen and the Gd case are plotted in Fig. 4.1 (c). The blue dotted curve then corresponds to the hydrogen case. The green curve can be compared to the Gd case. The similarities are remarkable in the strong asymmetry, but also in the shoulder at about \(-0.8\text{eV}\) energy. This shoulder is produced by coupling to plasmonic degrees of freedom, which was realistically taken into account by Sernelius [105]. One has to note here, that similar features were also found in spectral function simulations by Despoja et al. [111]. Very similar features are seen in the C 1s spectra of other graphene systems [68, 112], which points towards a general characteristics of highly doped graphene. There, not only the line shape but also the binding energy for doping levels close to that of Gd intercalated ZLG is reproduced. It cannot be fully excluded here, that carbon atoms within the graphitic layer are exposed to different chemical environment, thus producing distinguishable C 1s spectral signal, yet a strong part of the spectral distribution must be associated with energy loss effects.

4.1.4 Structure determined by LEED

In the previous paragraph, insight was gained in the chemical bonding situation of this system. Yet, CLS is limited in terms of gathering information about the ordering and the structure. LEED is an excellent tool to widen the picture, but
especially the combination of these two techniques is valuable. In this sense, LEED measurements were performed on these samples. In Fig. 4.4 (a) diffraction patterns taken with two different electron energies of a pristine ZLG and an intercalated sample are shown. The first and most obvious observation is the complete vanishing of superstructure spots, that are characteristic for the ZLG, after intercalation. This can best be noticed in the spots, indicated by the diamond in the 30 eV pattern in Fig. 4.4 (a). These pronounced spots are produced by reconstruction, thus buckling, caused by the partial covalent bonding of the graphitic layer to the substrate [41]. Also noticeable after intercalation is the
emergence of very sharp and intense $(1\times1)$-graphene spots in the 67.5 eV pattern. These are, also due to the reconstruction, almost absent in the ZLG case at this electron energy [41]. Therefore we conclude, that the produced graphene layer is well ordered. The appearance/disappearance of the mentioned $(1\times1)$-graphene/reconstruction spots is an excellent indication for intercalation, as they show that the bonding between the initial ZLG and SiC is lifted. The complete vanishing of the diamond at 30 eV indicates the transformation of the whole ZLG layer to graphene, which is consistent with the CLS measurements.

Besides the changes mentioned before, a new superstructure appears, which contains complicated structural aspects. A clear $(\sqrt{3}\times\sqrt{3})R30^\circ$-graphene periodicity is evident in the $(\frac{1}{3},\frac{1}{3})$-spots, as indicated by the orange circle in the 30 eV pattern in Fig. 4.4 (a). However, additional features in LEED indicate a more complicated situation here. Firstly, a clear threefold symmetry is observed, as 3 spots are brighter than the others, whereas a simple $(\sqrt{3}\times\sqrt{3})R30^\circ$-graphene structure should be 6-fold symmetric. Also, these spots are surrounded by satellites in a threefold symmetry, respectively. The satellite structure itself consists of two spots, that are very close. They are marked by the green and blue hexagons around the $(\sqrt{3}\times\sqrt{3})R30^\circ$-graphene spots and are better visible in the closeup in Fig. 4.4 (b). Besides that, persistent satellites are visible surrounding the $(1\times1)$-graphene spots (see green hexagon in Fig. 4.4 (a) at 67.5 eV). In the ZLG case, a similar pattern around the $(1\times1)$-graphene spots can be observed as caused by the $(6\sqrt{3}\times6\sqrt{3})R30^\circ$-SiC(0001) superstructure. Due to kinematic suppression, a majority of the expected spots are not visible and one speaks of a quasi-$(6\times6)$-SiC periodicity [47, 113]. Furthermore, the vectors connecting the $(1\times1)$-graphene spots and their satellites are reproduced by the vectors connecting the $(\frac{1}{3},\frac{1}{3})$-graphene spots and one set of their satellites (both marked by the green hexagons in Fig. 4.4 (a)).

Resolving the real structure of this system is extremely challenging and beyond the scope of this thesis. Nevertheless, one can assign different structural aspects. For a start, it is known that the graphene initially adjusts to SiC(0001) such that the total periodicity is a $(13\times13)$-graphene [47, 113]. The observed $(\frac{1}{3},\frac{1}{3})$ spots and their satellites, on the other hand cannot be produced by a $(13\times13)$-graphene structure. Assuming the Gd atoms are arranged as a simple $(\sqrt{3}\times\sqrt{3})R30^\circ$-graphene structure this can easily be seen in a structural model for the whole system (see Fig. 4.4 (c)). Different sites connected by a $(13\times13)$-
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graphene supercell vector are not equivalent (orange diamond in Fig. 4.4 (c)). In this case, the total periodicity of the SiC(0001)/Gd/graphene system would be a \((\sqrt{3}\times\sqrt{3})R30^\circ\) on the \((13\times13)\)-graphene supercell. In terms of Wood notation this corresponds to \((13\sqrt{3}\times13\sqrt{3})R30^\circ\)-graphene (green diamond in Fig. 4.4 (c)). In fact, all the observed diffraction spots can be described by this superstructure. The \((1\times1)\)-graphene, \((\sqrt{3}\times\sqrt{3})R30^\circ\)-graphene, \((1\times1)\)-SiC(0001) as well as the spots marked by the green and blue hexagons are part of the reciprocal lattice of this structure. Also, the apparent 3-fold symmetry can be understood. The SiC(0001) surface shows a threefold symmetry, as caused by the stacking sequence of the Si-C double layers in 6H-SiC [114]. Note here, that corresponding threefold symmetric LEED patterns can also be obtained in the ZLG stage [115].

Considering information, gained with other characterization techniques, it is reasonable to assume the following scenario. The Gd arranges as \((\sqrt{3}\times\sqrt{3})R30^\circ\)-graphene in first approximation. The strength of the satellites around the \((\frac{1}{3},\frac{1}{3})\)-spots as well as the pronounced threefold symmetry suggests, that the structure of the Gd is reconstructed. The reconstruction itself would be produced by at least partial bonding to the Si beneath. As shown in paragraph 4.1.3 by CLS, a fraction of about \(\frac{7}{25}\) of the Gd atoms is bound to the topmost silicon atoms of the SiC(0001). The Gd atoms thus arrange with both, the graphene and SiC(0001) surface. It is important to note that the total amount of Gd evaporated onto the samples of about 0.75-0.8 monolayer (see appendix B) is consistent with the amount needed to form a simple \((\sqrt{3}\times\sqrt{3})R30^\circ\)-graphene structure (0.73 monolayer), as it is assumed in the structural model. Although this has to be kept in mind, when further interpreting the results shown in later chapters, it is beneficial to break this down to a simplified scenario. It is reasonable to suggest that the Gd arranges to the graphene, like sketched in Fig. 4.4 (d). The favored adsorption site of the Gd according to DFT calculations in the literature [96] is within graphene’s hexagons, also called hollow site.

4.1.5
Magnetism determined by XMCD

The VHs regime in the graphene being reached in the Gd intercalated samples (see paragraphs 4.1) pushes the system towards possible ordered ground states, such as spin/charge density waves or ordering, unconventional superconductivity
4.1 General characterization

or other exotic phases [90, 91, 116–120]. However, Gd is an atom species with a large magnetic moment with its half filled $f$ shell in atomic configuration. As coherently coupled magnetic momenta near by the graphene could destroy, enhance or even trigger all of the mentioned collective phenomena [90, 91, 116, 121], it is important to investigate the magnetic properties of this system. In this manner, XMCD measurements were performed on the Gd M-edge, i.e. transitions from the Gd 3$d_{3/2}$ and 3$d_{5/2}$ to the empty 4$f$ orbitals. Measurements on the C absorption edge could not be performed, as many technical parts within the beamline were contaminated with organic materials and thus the beam intensity got strongly damped. However, since the Gd is in direct vicinity, XMCD on its absorption edge should be sensitive to any magnetic ordering of the system.

Fig. 4.5 (a) shows the absorption spectra taken with left and right circular polarizations at a magnetic field of 6 T and after turning the field down to 0.05 T. The nominal sample temperature was 2 K. The lack of remanence gives a clear indication that no ferromagnetic ground state is built up at these conditions. The lack of hysteresis is also evident in the field dependent dicroism measurements (see Fig. 4.5 (b)). There, the difference in absorption at maximum dicroism signal (photon energy 1181 eV) for the two polarizations is plotted. The magnetization curves for different incidence angles almost overlap, which shows that there is no significant anisotropy. In order to extract the magnetization at 6 T, a standard evaluation procedure was performed [97, 122, 123]. The XMCD signal has to be normalized, which is done with the zero field spectrum, also called white line. From this spectrum, the background was subtracted in the form of a double step function (Fig. 4.5 (c)). The integral over the resulting spectrum shows pronounced plateaus with a height ratio of 2:1, due to different transition paths for absorption. The complete integral over the XMCD signal (also Fig. 4.5 (c)) becomes zero, which one expects for the half filled Gd $f^7$ configuration. Also, the spectra at zero field are indistinguishable from those of bulk Gd metal in the $f^7$ configuration, whereas $f^6$ and $f^8$ would show distinct deviations [124]. However, the orbital ($m_L$) and spin ($m_S$) magnetic momenta can be extracted by applying the following sum rules [97, 122, 123]:

$$m_L = \frac{q}{nh\mu_B},$$

(4.1)

$$m_S \approx \frac{5p - 3q}{2r},$$

(4.2)
where $n_h$ is the number of holes in the $f$-shell (i.e. 7) and $\mu_B$ is the Bohr magneton. $q$ and $p$ are the integrals of the XMCD signal over the $M_5$-edge and both edges, respectively. $r$ is the integral over the background subtracted white line. The formulas yield a vanishing $m_L$, again expected for an $f^7$ configuration, and a $m_S$ of 5.3 $\mu_B$/atom. With this value, the XMCD curve in Fig. 4.5 (b) was rescaled to the magnetization curve in Fig. 4.5 (d). One can extract a low zero-field susceptibility of 1.18 $\mu_B$/atom/T. Without further assumptions, one can first of all apply a theory based on paramagnetism, i.e. independent magnetic atoms in a magnetic field. The field dependent magnetization $M(B)$ per atom for a

**Fig. 4.5:** XMCD study: (a) XAS and XMCD spectra at the Gd M-edges taken with the two different circular light polarizations at two different magnetic fields alongside. The spectra were taken in normal incidence at a nominal temperature of 2 K. (b) Magnetic field dependent dicroism at the photon energy of maximal XMCD signal 1181 eV for different incidence angles. (c) White line spectrum with the applied background and the integral of the background subtracted white line and the XMCD. (d) Extracted symmetrized magnetization alongside with the fit of a Brillouin function and the Brillouin function for a temperature of 2 K.
paramagnet at a temperature $T$ is given by the Brillouin function [97]:

$$M(B) = g\mu_B J \left[ \frac{2J+1}{2J} \coth \left( \frac{2J+1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right) \right]$$  \hspace{1cm} (4.3)$$

with

$$x = \frac{g\mu_B J B}{k_B T}.$$ 

$k_B$ is the Boltzmann constant. $g$ is the Landé factor, which is 2 for Gd, and $J$ is the total magnetic moment of the half filled $f$ shell. $g = 2$, $J = 7/2$ and the nominal sample temperature of 2 K yields the blue curve in Fig. 4.5 (d). This curve is not sufficient to describe the magnetization. To reproduce the data, the sample temperature has to be increased to 13.8 K (see red curve in Fig. 4.5 (d)). Considering the experimental conditions, this discrepancy can be questioned. The nominal temperature was measured with a thermocouple near the sample. The sample itself was well shielded from external heat sources and radiation. Also, the sample was connected well to the cooling bath, mechanically and electrically. Comparing the Gd intercalated system to related materials, one could expect coupling of the Gd magnetic momenta due to Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and thus deviations from paramagnetism. A closely related material can be seen in Eu intercalated graphene on Ir(111) [97]. The Eu can build up a $(\sqrt{3} \times \sqrt{3})$R30°-graphene structure, comparable to the Gd case here, where Eu is also in the $f^7$-configuration. XMCD measurements at 10 K exhibit significant deviations from paramagnetism as a strong evidence for ferromagnetic coupling. Considering the differing substrate (Ir and SiC), coupling could even be enhanced in the case of a semiconductor compared to a metal. The interaction of magnetic momenta with conduction electrons in a metal can lead to severe destabilization, as additional relaxation paths are provided [125–128]. Furthermore, it was shown that utilizing insulating substrates can lead to very stable magnetic states, even for single atoms [129]. The comparison to certain graphite intercalation compounds, also yields interesting conclusions. EuC$_6$, where Eu is also arranged in a $(\sqrt{3} \times \sqrt{3})$R30°-graphene-like fashion, shows strong ferromagnetic coupling between the Eu atoms [130]. At a transition temperature of about 40 K, which is accompanied by a discontinuity in the material’s specific heat [131], different frustrated magnetic phases emerge [130, 132–134]. The low field susceptibility is very low and comparable to our Gd case, thus a complete magnetization at a temperature of 4.2 K is reached not until fields of about 20 T. Such measurements were not published to my knowledge for the Gd-GIC, where the Gd is
arranged similarly to the Eu case [135]. However, Mori et al. [136] report pronounced drops in the susceptibility at a temperature of 60 K and 4 K, indicating phase transitions to ordered ground states similar to the Eu case [137].

Putting these results and considerations together, (anti)ferromagnetic coupling between the Gd atoms can be expected and prototypical paramagnetism is rather unlikely. This is also supported by DFT calculations discussed in the following paragraph 4.2.1. The reduced susceptibility compared to theoretical predictions could be evidence for this. It is important to note in the context of superconductivity, that there is no long range ferromagnetic ordering present. Ferromagnetic exchange interactions are generally in strong competition with superconducting pairing mechanisms [138]. Antiferromagnetic correlations on the other hand can be beneficial for the formation of a superconducting ground state, as it is presumably the case in certain unconventional superconductors like members of the cuprate family [139, 140].

\section*{4.2 Detailed analysis of the electronic band structure}

As already indicated in paragraph 4.1.1, the band structure of the Gd intercalated ZLG is strongly modified compared to lower doped graphene. In this section a detailed analysis of the different spectral features will be given.

\subsection*{4.2.1 Extended Van Hove singularity}

The most striking spectral feature observed is the flat band connecting the pockets at $\textbf{K}$ and $\textbf{K}'$ (see paragraph 4.1.1 and Fig. 4.6 (a)). To quantify deviations from the expected shape, one can first of all compare this to a tight binding model in nearest neighbor approximation (see paragraph 1.1.1), which generally reproduces graphene’s band structure well [31, 32]. However, since tight binding is based on a single particle picture [34], whereas ARPES measures the spectral function [53, 54, 142], they are best not compared directly. As already pointed out in paragraph 1.2, the spectral function can be expressed by the bare non-interacting band $\epsilon_{\textbf{k}}^b$ and the complex self energy $\Sigma(\textbf{k}, E)$. Consequently, $\epsilon_{\textbf{k}}^b$ has to be extracted and compared to tight binding. This was done following a procedure developed by Pletikosić et al. [66] (described in appendix C) for the $\pi$ band.
4.2 Detailed analysis of the electronic band structure

Fig. 4.6: Band modeling of Gd intercalated ZLG: (a) Conglomerate ARPES spectra along KMK’ from three different measurements using different photon energies as indicated. The extracted bare band as well as the fitted tight binding bands are also plotted. (b) Unfolded DFT band structure of Gd adsorbed on graphene in the \((√3 \times √3)R30°\) structure described in paragraph 4.1.4 for spin projection in both z-directions (gray scale) together with tight binding bands (red). In the gray scale, the black lines correspond to an enhanced carbon \(p_z\) weight and the lighter lines roughly to an enhanced hybridization between carbon and Gd orbitals. (c) Spectral function simulated within the fluctuating exchange approximation theory. For comparison, tight binding bands at VH filling (green) and with its Dirac point adjusted to the Dirac point of the spectral function are superimposed. See text and ref. [141] for details about the simulations in (b) and (c).
branch going from $\overline{K}$ to $\overline{\Gamma}$. The procedure is generally only applicable if the bands cross the Fermi level and if renormalizations are weak, thus it fails for the $\overline{KM}$ direction. The branch in $\overline{K}\overline{\Gamma}$ direction is very sharp, indicating relatively small many-body renormalizations. A further evaluation of the extracted $\Sigma(k, E)$ will be given in paragraph 4.2.2. In Fig. 4.6 (a) the extracted bare band is plotted with a fitted $\pi$ band in nearest neighbor tight binding. The tight binding parameters were 3.1 eV for nearest neighbor hopping, which is a reasonable value for graphene [31], and 1.65 eV for the energy shift, i.e. the position of the Dirac point. Considering the rather narrow spectral width in $\overline{K}\overline{\Gamma}$ direction and the accompanied minor energy renormalizations of a few ten meV, the spectral distribution in $\overline{KM}$ direction is very broad and the energy renormalizations are extremely strong. Compared to tight binding, renormalizations of up to 1.5 eV are present, which lead to a flat band around $\overline{M}$ close to the Fermi level. Furthermore, also away from the flat section, strong deviations can be distinguished in this branch.

A first consideration are deviations produced by hybridization with the Gd states, as an ordered layer is in close vicinity to the graphene. In order to address this, our collaborators Tim Wehling and Malte Rösner from the University of Bremen performed DFT calculations. The simulations are based on the simplified $(\sqrt{3} \times \sqrt{3})R30^\circ$-graphene structural model described in paragraph 4.1.4. The more realistic $(13\sqrt{3} \times 13\sqrt{3})R30^\circ$-graphene structure cannot be dealt with in this model due to the extremely enhanced computational costs in this large unit cell. Correlation effects like electron-electron interaction and electron-phonon coupling are also not taken into account. The obtained bands, unfolded onto graphene’s Brillouin zone, are plotted in Fig. 4.6 (b). Severe hybridizations of graphene’s $\pi$ bands with the Gd 5d states and also a strong charge transfer were found. Yet, the graphene Dirac point is essentially intact. The simulations yield strong splitting of spin up and down states for the $z$-direction indicating the possibility of ferromagnetism in this system. Note, that ferromagnetism could not be verified by XMCD experiments at 2 K discussed in paragraph 4.1.5. An apparent splitting of the flat band at $\overline{M}$ is also present in the ARPES measurements (see Fig. 4.6 (a)). However, as will be discussed in paragraph 4.2.2, this band doubling can be assigned with high certainty to electron-phonon coupling rather than hybridization. Apart from this, relatively flat hybrid bands near the $\overline{M}$ point form for both spin up and down in the simulations. These, however, are located more than 0.5 eV below the Fermi level. Considering the experimental data, the
flat band seems to be pinned to the Fermi level over a wide momentum range of about $1 \, \text{Å}^{-1}$. Such a strict band course and furthermore, the accompanied topological transition in the Fermi surface to a single hole pocket centered around $\Gamma$ (see paragraph 4.1.1) cannot be reproduced by these simulations. Overall, the hybridizations in the simulation are not seen in the experiment. The only features that can directly be connected to the Gd are localized states at a higher binding energy. Flat spectral intensity at -5 eV and -9 eV can be associated with Gd 5d and Gd 4f states, respectively (see Fig. 4.7 (a) & (b)). The position and shape of the Gd 4f is consistent with a $f^7$ configuration [108], which was also verified by XAS measurements (see paragraph 4.1.5). Spectral features associated with Gd 5d are also consistent with the observations in the Gd-GIC [109, 135]. The missing dispersion of the 5d states might partially be explained by the fraction of Gd atoms bound to the topmost Si layer of the substrate, which was concluded from CLS and LEED measurements (see paragraphs 4.1.3 & 4.1.4). Similarly, the graphitic layer in the ZLG case is partially bound to the substrate and only localized states, related to the $\pi$ band structure, are found in ARPES near the Fermi level [44].

As already indicated by the increased band width, the band course between $\overline{K}$ and $\overline{M}$ as well as the flat band at $\overline{M}$, cannot be treated within a non-interacting theory. Especially the apparent pinning to the Fermi level is a hallmark of dynamical electron correlations, which are beyond DFT-based mean field theories. To investigate this, our collaborators at the Universities of Hamburg and Nijmegen, namely Daniel Hirschmeier, Alexander Lichtenstein and Mikhail I. Katsnelson, conducted simulations taking into account correlations, particularly in the form

![Fig. 4.7: Wide energy range valence band structure: (a) ARPES cut along $\overline{\Gamma KM}$ showing non-dispersive states connected to the Gd 5d & 4f levels in the text. (b) EDC taken at the $\overline{M}$ point.](image-url)
of spin fluctuations. Their calculations were based on the Hubbard model, which they solved in the so-called fluctuating exchange (FLEX) approximation. Within the FLEX approximation, the self energy is modeled by taking into account spin fluctuations as interaction channels. The results are further elaborated in ref. [141] and further details about the method can be found in refs. [143–145]. For the model, the bands are $\frac{1}{4}$ filled, which corresponds to the VH filling in the $\pi^*$ band in nearest neighbor tight binding [32]. The resulting spectral function is plotted in Fig. 4.6 (c). Superimposed in green are tight binding bands at VH-filling. This basically corresponds to the same model with electron-electron interactions, i.e. the Hubbard $U$ [56], set to zero. It is clearly visible that the Dirac point is shifted towards the Fermi level, whereas the position of the saddle point remains unchanged. The compression is, on the other hand, not uniform. A severe flattening near $\overline{M}$ occurs, while no severe renormalizations are present in $\overline{K}\Gamma$ direction. To directly compare the plots in Fig. 4.6 (a) & (c), tight binding bands are superimposed in (c), where its Dirac point was fitted to the FLEX spectral function’s Dirac point. The simulations capture the main features of the experiment, which speaks for the fact that the eVHs is indeed driven by spin fluctuations.

It is worth noting here, that graphene is not the only material exhibiting such band flattening near a VH filling. Prime examples for this effect are members of the cuprate [146] and ruthenate [147] family. Especially in the high-temperature superconducting cuprates, this effect is being connected again and again to their many-body ground states and rich phase diagram [148]. There, it is referred to as the extended VHs (eVHs). Further, it must be mentioned in this context, that also many of the interesting phenomena observed in the cuprates are connected to electronic correlations in the form of spin fluctuations [140, 142]. Yet, one has to be careful in directly comparing graphene with these strongly correlated materials, as strong differences are obvious in the differing lattice symmetry and chemical composition. Nevertheless, these considerations make further explorations of the Gd intercalated ZLG even more desirable.

4.2.2 Electron-phonon coupling

Since we gained greater insight in the remarkably strong effects driven by electronic correlations in Gd intercalated ZLG in the previous paragraph, we now go
on with further many-body renormalizations in this system. Especially the strong features in a very narrow energy window of about 200 meV around the Fermi-level are examined here, as this energy window is restricted by the energy of certain excitations (especially phonons) involved (see also paragraph 1.2). This chapter is divided into two parts, where the two extreme cases in $\vec{K}_\Gamma$ and $\vec{K}_M$ direction are treated separately.

$\vec{K}_\Gamma$ direction

Starting with the $\vec{K}_\Gamma$ direction, standard evaluation procedures can be applied, as renormalizations due to electron-electron correlations are less pronounced. As already applied in the last paragraph and further specified in the appendix C, MDCs were fitted with Lorentzian functions and the bare band $\epsilon_b^{\vec{k}}$ and the self energy $\Sigma(\vec{k}, E)$ were extracted from the binding energy dependent width and position. The assumption that $\Sigma(\vec{k}, E) \simeq \Sigma(E)$ in the small momentum range examined, has to be adopted for this. An ARPES spectral cut of the branch mentioned before near $E_F$ is plotted in Fig. 4.8 (a, left). The fitted positions and the extracted $\epsilon_b^{\vec{k}}$ are superimposed. The extracted real and imaginary parts of $\Sigma(E)$ are plotted in Fig. 4.8 (b). The real part shows pronounced peaks at about 170 meV and 40 meV. Accordingly, the imaginary part builds steps at these energies, as the real and imaginary parts are connected by Kramers-Kronig relations. The mentioned energy values directly correspond to the energies of the involved bosonic modes, presumably phonons.

A quantification to the total electron-phonon coupling strength is usually given by the dimensionless coupling constant $\lambda$ [61]. In a first attempt, one can express $\lambda$ in terms of mass enhancement $\lambda = -\frac{d}{dE} \Re \Sigma(E) \big|_{E=E_F}$ [66, 149], as $\Re \Sigma(E)$ gives the band’s energy renormalization (see paragraph 1.2). This yields a value of 0.56 for $\lambda$, which is more than twice the value mostly observed for highly n-doped graphene [66, 68, 150, 151]. Graphene doped with Ca, for example, has a comparable doping level, yet $\lambda$ is about 0.17 in the examined band branch [68]. However, to extract the responsible phonon modes, one has to apply a more sophisticated treatment. As $\lambda$ is not yet in the strong coupling regime and the Fermi energy is much larger than the phonon energies involved, we restrict ourselves in the following to the Eliashberg theory in the Migdal limit [64]. The real and imaginary parts were modeled self consistently by applying the following equations [149, 152, 153]
Fig. 4.8: ARPES evaluation in terms of electron-phonon coupling in \( K \Gamma \) direction: (a) Left: ARPES on the \( K \Gamma \) branch together with band fits and the extracted bare band. Middle: Self consistent model spectral function, calculated from the extracted bare band \( \epsilon_b^{\vec{k}} \) and modeled self energy \( \Sigma(E) \). Right: Self consistent model spectral function with experimental broadening taken into account. (b) Extracted imaginary and real part of \( \Sigma(\vec{k},E) \) together with their modeled functions. Model (A) also includes lower energy phonons, model (B) only includes higher energy phonons. (c) Eliashberg function \( \alpha^2F(\omega) \) and electron-phonon coupling constant \( \lambda(\omega) = 2 \int \omega \alpha^2F(\omega)/\omega \).

(see Fig. 4.8 (b)):

\[
\Re \Sigma(E) = \sum_n -\frac{1}{4} \lambda_n \Omega_n \ln \left| \frac{E + \Omega_n}{E - \Omega_n} \right|
\]

\[
\Im \Sigma(E) = \sum_n \pi \lambda_n \Omega_n \Theta(|E| - \Omega_n).
\]

The sum is over the involved phonon modes \( n \) with energy \( \Omega_n \). The respective weighting is given by \( \lambda_n \). A thermal and resolution driven broadening of 15 meV was taken into account for both the real and imaginary part. For binding energies lower than 250 meV, both the real and imaginary parts are modeled excellently.
The deviations at higher binding energies are most probably remnants of the formation of polaronic quasi-particles [63, 70, 71], going beyond the low coupling strength regime (see paragraphs 1.2.2 & 1.2.3). Nevertheless, we proceed with the modeled self energy in the low binding energy regime. Firstly, to prove consistency, the model spectral function was calculated with the modeled $\Sigma(E)$ and the extracted bare band $\epsilon^b_{\vec{k}}$ by applying Eq. 1.5. The resulting spectral functions are plotted in Fig. 4.8 (a, middle & right). The middle spectrum shows the result without taking into account experimental broadening, impurity scattering and a finite temperature. The superimposed peak positions from the fit of the experimental spectrum reproduces the course of the spectrum well, indicating a successful extraction of $\epsilon^b_{\vec{k}}$ and $\Sigma(E)$. In the right spectrum the mentioned broadening mechanisms and the Fermi statistics with a sample temperature of 100 K was taken into account. The experimental spectrum is very well reproduced by the simulations. To further quantify the contributions of the different phonon modes, one can extract the Eliashberg function from $\Im \Sigma(E)$ by utilizing the following relation [64, 154]:

$$\Im \Sigma(E, \vec{k}, k_B T) = \pi \int_0^{\infty} \alpha^2 F(\omega)(1 - f(E - \omega) + f(E + \omega) + 2n(\omega))d\omega \quad (4.5)$$

$$\simeq_{T=0} \pi \int_0^{E} \alpha^2 F(\omega)d\omega.$$

The Eliashberg function $\alpha^2 F(\omega)$ represents the phonon density of states weighted with the respective electron-phonon scattering cross section dependent of the frequency $\omega$. $f$ and $n$ are the Fermi and Bose distribution, respectively. As already indicated here, the expression can be simplified to a simple integral at $T = 0$ K. This is the simplification utilized here, as one can write $\alpha^2 F(\omega) \simeq \frac{d}{dE} \Im \Sigma(E)$. Including a finite temperature requires more sophisticated methods by integral inversion [155], which is beyond the scope of this thesis. The extracted $\alpha^2 F(\omega)$ and the total coupling constant $\lambda(\omega) = 2 \int d\omega \alpha^2 F(\omega)/\omega$ [64] are plotted in Fig. 4.8 (c). This procedure yields a $\lambda$ of 0.54, which is in agreement with our first estimation. The Eliashberg function yields 5 peaks (182 meV, 162 meV, 128 meV, 60 meV, 28 meV) according to the number of phonon modes used for modeling. Especially coupling to lower energy phonons significantly enhances the total electron-phonon coupling, as the respective contribution scales with $1/\omega$ [64]. Hence, this promotes

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1 The sample was cooled with liquid nitrogen during the measurement.
Gadolinium intercalated ZLG

the instability towards ordered ground states like superconductivity. These lower energy phonons mark the difference to usual graphene-based systems and their involvement is already obvious, when trying to model $\Re \Sigma(E)$ by only higher energy phonons (see Fig. 4.8 (b)). Graphene doped by different alkaline and earth alkaline adatoms usually shows significant coupling to phonons with energy close to 170 meV in the examined band branch [66, 68, 150, 151].

Comparing these results to literature, neither the eVHS state of the Gd intercalated samples nor the high doping level gives an explanation. Graphene on SiC(0001), doped into the eVHS regime by intercalated and adsorbed alkaline/earth alkaline atoms [92, 152], as well as the already mentioned highly doped graphene on metal substrate [68] show a significantly lower $\lambda$. It was stated for both systems, that the dopants are not ordered. Contrary to this, Li adsorbed on graphene in a $(\sqrt{3} \times \sqrt{3})R30^\circ$-graphene structure shows a significant enhancement of $\lambda$ [156].

Another related system can be found in GICs like CaC$_6$, where the Ca is also arranged in a $(\sqrt{3} \times \sqrt{3})R30^\circ$-graphene fashion, yet in a stacked way. There, also a significant increase in coupling constant was observed, which is presumably responsible for the emergent superconductivity in this system [157]. In fact, the Gd in our samples is ordered similar to a $(\sqrt{3} \times \sqrt{3})R30^\circ$-graphene structure (see paragraph 4.1.4). Theory supports the idea that the strong enhancement of $\lambda$ in the Li adsorbed graphene and the CaC$_6$ is associated with the occupation of the so-called interlayer band, which opens up additional electron-phonon scattering channels [158–160]. The interlayer band itself is a hybrid band of intercalant-related states presumably with graphene’s so-called image potential states [158, 160–162]. We find no indication for such a band in our ARPES data (see Fig. 4.1 (c)), examining spectra taken with photon energies ranging form 30 eV to 100 eV (not shown).

One can straightforwardly ask the question: Is the enhancement in $\lambda$ directly associated with the $(\sqrt{3} \times \sqrt{3})R30^\circ$-superstructure imposed onto the graphene? Suppose the superstructure imposes a significant superpotential onto the graphene, resulting in a spatially non-evenly distributed carrier density. The electrons can then be additionally scattered at this potential and Bloch reflections at the superstructure’s BZ boundaries take place. Effectively, this reflects a new band structure, where the bands are shifted by multiples of the superstructure’s reciprocal lattice vectors $k_{SC}$. One such shift is sketched in the duplicated FS of Gd intercalated ZLG on SiC(0001) in Fig. 4.9 (a). From the shape of the Fermi surface, one
can see that the flank around the $K\Gamma$ direction is very straight (marked by the blue dotted lines in Fig. 4.9 (a)). The mirroring of the FS leads to the condition that the marked straight areas can be connected by the same vector $k_{nest}$ to a non-equivalent part of the Fermi surface. Such a condition is generally called Fermi surface nesting and is a key ingredient for strongly enhanced electron-phonon coupling in many systems [142, 164-166]. This is easily understood, as electronic transitions between the mentioned branches mediated by scattering with particular phonons with momentum $k_{nest}$ show a enhanced resonance, thus stronger coupling. Due to the ($\sqrt{3}\times\sqrt{3}$)R30° superstructure, a multitude of scattering paths is added compared to the (1×1) structure. The phonon modes fitting the mentioned $k_{nest}$ are marked in the phonon dispersion in Fig. 4.9 (b) [163]. The energies fit the peak positions in the Eliashberg function of Gd intercalated samples, thus the involved phonon modes, very well (see Fig. 4.9 (d)). Slight deviations can
be explained by phonon softening due to the electron-phonon coupling, producing the well known Kohn anomalies as dips in the phonon dispersion [34, 56, 167]. As the effective coupling to these phonons is rather strong, energy renormalizations in the 20 meV range can be expected [163, 167–169].

This argumentation is also in agreement with Li decorated graphene [156]. The respective Eliashber function is plotted in Fig. 4.9 (c). In this case, also strong peaks emerge at phonon energies in agreement to the Gd case, which are responsible for the strong enhancement of $\lambda$. Furthermore, the energy of the phonon modes enhancing the coupling constant in CaC$_6$ are very similar to those in our Gd samples and Li decorated graphene [157]. Also in line with this argumentation, Einenkel et al. [170] pointed out, that due to the even distribution of charge carriers in graphene, electron-phonon coupling, mediated by Coulomb interaction between charge carriers and the lattice, is rather weak. Dietel et al. [171] on the other hand argue, that by introducing an electrical superpotential onto the graphene, this can be drastically changed, opening up the possibility for superconductivity at elevated temperatures mediated by electron-phonon coupling.

**KM direction**

Having analyzed the band branch in $\overline{K}\Gamma$ direction in terms of electron-phonon coupling, a closer look at the $\overline{K}\overline{M}$ branch will be taken here. As shown in paragraph 4.2.1, in this direction severe renormalizations are built up due to electron-electron interaction. Although the interplay of electron-electron and electron-phonon interaction is not trivial here, we can nevertheless identify specific spectral features associated with electron-phonon coupling as well. In Fig. 4.10 (a, left) an ARPES cut of the $\overline{K}\overline{M}$ branch is shown. At about 200 meV binding energy, the band seems to split into two separate branches. To guide the eye, a fit is superimposed in this plot, indicating the course of the splitting. Taking ARPES cuts through the BZ perpendicular to this direction (see Fig. 4.10 (b)), it is evident that the splitted structure evolves from the kink structure present in the $\overline{K}\Gamma$ direction (see previous paragraph). At about $k_y = 2.05 \, \text{Å}^{-1}$, the kink structure becomes a structure where a flat parabola is accompanied by a broader incoherent distribution.

To stress the difference between the simple electron-phonon coupling model in the Migdal limit, the spectral function was modeled. Analogous to the simulations in the previous paragraph, the self energy $\Sigma(E)$ was modeled using Eq. 4.5 with a
Fig. 4.10: (a) Left: ARPES spectrum along the \(\overline{KM}\) direction \((k_x)\) reaching into the repeated BZ, alongside with a fit of the band course. Middle and Right: Spectral function simulations, considering a coupling constant of 0.2 and 1 to a phonon mode with 185 meV, respectively. (b) ARPES cuts, taken at different representative \(k_x\)-values perpendicular to the cut in (a). (c) EDC from the \(\overline{M}\) point alongside with spectra, simulated with different electron-phonon coupling parameters. (d) The EDC from the \(\overline{M}\) point with a fit consisting of three Lorentzian functions. (e) Fermi surface near the \(\overline{M}\) point. The blue dashed lines indicate nesting. The measurements in (a) & (b) were taken with 35 eV and (c) & (d) with 100 eV photon energy.

A single phonon mode with an energy of 185 meV. Utilizing a parabolic bare band \(\epsilon^b(\vec{k}) = -6\text{eV} \vec{A}^2 k^2 - 0.06\text{eV}\), the spectral function was calculated with Eq. 1.5. The offset of -60 meV was chosen from the offset of the saddle point at \(\overline{M}\) (see last panel in Fig. 4.10 (b)). In Fig. 4.10 (a, middle & right) two such simulations are shown together with the bare band \(\epsilon^b(\vec{k})\) at two different coupling constants \(\lambda\). This model produces further band flattening above 185 meV binding energy. Yet below, only broad spectral intensity without contour can be found, in stark contrast to the measurements (marked yellow in Fig. 4.10 (a, left)). A comparison can best be made when taking EDCs at \(\overline{M}\) from the measurement and at the maximum of the bare band parabola from the simulations (see Fig. 4.10 (c)).
pronounced dip and hump at 190 meV binding energy and below cannot be reproduced by the model, as only an incoherent tail is present and the picture thus has to be refined. Generally, the observed spectral features are a sign for the formation of new quasiparticles, i.e. polarons [172]. There, new composites of electrons and in this case certain phonon modes with a defined lifetime are formed. The spectral distribution then shows a coherent band, which is accompanied by a series of replica bands with increased band width $w$ (see paragraph 1.2.3). These bands are separated by about the energy of the phonon mode involved $E_{ph}$. The EDC at $\bar{M}$ can be fitted by a series of Lorentzian functions $L_{0,1,2}$ as:

$$f(E) = \left( c + \sum_{n=0,1,2} L_n(E; E_0 + nE_{ph}, w_n) \right) f(E, T), \quad (4.6)$$

with $f(E, T)$ being the Fermi distribution, $c$ being a constant background and $E_0$ being a total energy offset. The resulting fit is plotted in Fig. 4.10 (d). Although one cannot state here that only one phonon mode is involved, the fit yields a satisfying accuracy with only a single phonon mode with energy 190 meV. Taking the relative intensity of the coherent part $Z_0$, one can estimate a coupling constant $\alpha$ to this single phonon mode. This entity is distinct from the total electron-phonon coupling constant $\lambda$, extracted for the $\overline{K\Gamma}$ branch in the last paragraph, as it describes coherent coupling to a single phonon mode. The fraction $Z_0 = 0.6$, gives a value of $\alpha \approx 1$, when comparing to diagrammatic quantum Monte Carlo simulations in the Fröhlich polaron picture [173]. Considering the overall state of the system, especially in context with the eVHs, this value has to be interpreted carefully, as the strong electronic correlations might strongly interfere. Nevertheless, it indeed gives a good indication for an anomaly increased electron-phonon coupling to a certain mode.

Following the argumentation of graphene being a non-ionic crystal [170], this is remarkable, as these effects are generally more pronounced in ionic crystals [174–183]. Lattice vibrations can then be accompanied by charge vibrations, which enhances coupling deduced from Coulomb forces [183]. However, when considering the shape of the Fermi surface, two long and parallel sections are present near $\bar{M}$ (see blue markings in Fig. 4.10 (e)). These sections are thus nested with their counterparts in the repeated BZ, modulo multiples of graphene’s reciprocal lattice vector. At these conditions, the argumentation is analogous to the previous
paragraph for the $\bar{K}\bar{\Gamma}$ direction, as transitions between the two sections mediated by the same phonon are strongly resonant. The phonons involved in this case are characterized by low momentum, i.e., they are located at $\bar{\Gamma}$ in the BZ. The involved energy of 190 meV points towards graphene’s higher energy LO/TO phonon branch. Raman measurements on low doped H intercalated graphene on SiC(0001) yielded an energy of 196 meV for these modes [184]. The slight phonon softening observed in our measurements can be associated with energy renormalization due to coupling to the electronic system [163, 167–169].

The mechanisms producing the observed polaronic spectral features could have strong influence to the possible formation of an ordered ground state like superconductivity. As it was shown in the case of FeSe on SrTiO$_3$ by Lee et al. [182], this can strongly enhance superconducting transition temperatures. Layered FeSe, as an example of the iron based superconductors, exhibits a superconducting transition temperature of 8 K in its bulk 3D structure [185], presumably driven by antiferromagnetic correlations in the electronic system. When placing a monolayer of FeSe on SrTiO$_3$, signs of superconductivity can be found up to 65 K [186], presumably by additional coupling to the SrTiO$_3$ substrate phonons [182]. However, as the graphene here is in the eVHs regime (see paragraph 4.2.1), the complexity of the system does not allow a priori statements.

### 4.3 Magnetotransport measurements

Building up on the characterization made in the previous paragraphs, magnetotransport measurements were conducted at low temperatures on the Gd intercalated ZLG samples. This was possible due to the combination of a semiconducting substrate with the strong stability and homogeneity of this system (see characterization in previous paragraphs). The measurement procedure is described in paragraphs 2.5 & 2.7.3. In Fig. 4.11 (a) a representative longitudinal resistance measurement taken at 50 mK is shown. The data does not show a sign of a superconducting phase at this temperature. Also, no hysteresis can be observed, after sweeping the fields through two subsequent field sweep cycles. This points to the absence of ferromagnetism, which is in agreement with results obtained by XMCD measurements in paragraph 2.2. However, the magnetoresistance is negative up to 18 T, whereas one would expect a positive $B^2$ relation (see paragraph 2.5). Apparently, three different regimes can be distinguished here. One, at absolute fields
lower than 1.7 T, shows a strongly peaked magnetoresistance of about 20 %. The intermediate regime between 1.7 T and 6.2 T has a bell-like parabolic shape with a MR of about 10 %. The regime at high field almost shows a linear behavior with a MR of 5 % up to 18 T. Interestingly, also Shubnikov-de Haas (SdH) oscillations set in at these fields. As visible in Fig. 4.11 (b), the low field regime does not show any dependence on the direction of the magnetic field, whereas strongest changes for the high field regime are found when the field is put parallel to the graphene plane. In this manner, the different regimes show substantially different behavior. Transversal MR measurements (see Fig. 4.11 (c)) show a linear course, indicating a constant Hall coefficient $R_H$ of about -1.36 $\Omega$/T. This corresponds to a charge carrier density of $4.6 \times 10^{14}$ cm$^{-2}$ (see paragraph 2.5), which is in agreement with the value obtained from the Fermi surface measurements by ARPES (see paragraph 4.1.1). Interestingly, the Hall coefficient is negative, which is indicative for electron transport here. This, however, is in disagreement with the observations made by ARPES. As $\overline{K}$ and $\overline{K}'$ are connected in the eVHs regime, the Fermi
surface consists of one hole pocket centered at $\Gamma$ instead of two electron pockets centered at $\bar{K}$ and $\bar{K}'$. From the resistivity at zero field and the charge carrier density, one can extract a mobility $\mu = \frac{\sigma e}{n}$ of 14 cm$^2$/Vs. This value is very low compared to other graphene systems. At carrier densities of about $1 \times 10^{11}$ cm$^{-2}$, mobilities higher than $200000$ cm$^2$/Vs could be measured [2]. The mobility, however, strongly depends on the carrier density, such that hydrogen intercalated ZLG on SiC(0001) shows a mobility of about $3000$ cm$^2$/Vs at a charge carrier density of about $5 \times 10^{12}$ cm$^{-2}$ [184]. Increasing the carrier density by about two orders of magnitude in the Gd intercalated ZLG might produce these very low mobilities.

The different regimes of negative MR could be caused by a mixture of mechanisms. The low field regime has similarities to weak localization, often observed in graphene [187–189]. However, weak localization generally shows a strong dependence on the field direction with respect to the graphene plane [190], which is in strong contrast to our observations. Another possibility could lie with the magnetic momenta of the Gd atoms. The XMCD measurements in paragraph 4.1.5 show, that no ferromagnetism is built up, yet the Gd atoms are in a $f^7$ configuration. Applying an external field aligns the magnetic moments, reducing magnetic inhomogeneity and thus scattering. Similarly to the case of the GIC C$_6$Eu, a decrease of the resistance with increasing external magnetic field can be expected [130].

To date, the intermediate and high field behavior is not understood. Ongoing experimental and theoretical effort will be provided in order to find a coherent picture.

The SdH oscillations are periodic in inverse magnetic field (see Fig. 4.11 (d)). As usual, one can assign a Landau level index to the observed resistance maxima, which is then plotted over the respective inverse field value (see Fig. 4.11 (d, inset)). The data points lie on a straight line and the intercept at zero inverse field gives direct information about the phase shift, the electronic wave function acquires when rotated by $2\pi$ (i.e. Berry’s phase). The extracted intercept of $1/2$ is indicative for a Berry’s phase of $\pi$. This is an indication, that the oscillations are related to a pocket, which envelops an odd number of Dirac cones of monolayer graphene here [31]. The distance between the resistance maxima is $1/120$ T, which directly gives the area enclosed by the Fermi surface (see paragraph 2.5). This area is about $1/650$ of graphene’s Brillouin zone. When assuming, that these oscillations are produced by graphene, one can make the following considerations. Consider-
ing two pockets (around $\overline{K}$ and $\overline{K}'$), the spin degeneracy of 2 and the number of bands ($\pi$ and $\pi^*$), the charge carrier density can be extracted by $n = 2n_C/650$, according to Luttinger’s theorem [85]. With $n_C$ being the density of C atoms in graphene ($3.82 \times 10^{15}$ cm$^{-2}$), one obtains $n = 1.2 \times 10^{13}$ cm$^{-2}$, which is two orders of magnitude below the value extracted from the Hall voltage. Also, utilizing the condition $\mu_B > 1$ (see paragraph 2.5), one can estimate a charge carrier mobility on the order of 2000 cm$^2$/Vs. It is reasonable to assume, that these oscillations are produced by small residues of MLG of about 2% on the sample produced during graphitization. The charge carrier density of this MLG is about $1 \times 10^{13}$ cm$^{-2}$ with a mobility of about 2000 cm$^2$/Vs [27, 184]. The sheet resistance is about 1 kΩ, which is comparable to the Gd intercalated ZLG. It grows preferably along the step edges of the SiC(0001) during graphitization [27], thus the magnitude of the observed oscillations is reasonable.

4.4 Conclusion for Gd intercalated ZLG

It was shown here, that monolayer graphene on SiC(0001) can be produced by the intercalation of Gd, which is doped into the eVHs regime. This system was thoroughly characterized in terms of surface science techniques (see paragraph 4.1). LEED, CLS and XMCD gave insight in the structure, chemistry and magnetism in this system. Having brought graphene in this state by utilizing only intercalation produces samples, which are comparatively stable and homogeneous (shown by LEEM/CLS/ARPES). This brought the possibility to characterize graphene in the eVHs regime with techniques not compatible with UHV conditions like magnetotransport measurements at mK temperatures (see paragraph 4.3). Reaching the eVHs regime was accompanied with strong renormalizations of the electronic energy spectrum, such that a flat band at the Fermi level was built up, as determined by ARPES. These observations further motivated the need for an advanced theoretical description of the origin of and the physics accompanied with the eVHs in terms of electron-electron interaction in the form of spin fluctuations (see paragraph 4.2.1). Graphene research can thus give further insight in correlation effects, due to the analogies to extensively investigated materials like members of the cuprate [146] or ruthenate [147] family, where the presence of the eVHs is meant to be strongly connected to their many body ground states [148].
An important aspect to the Gd intercalated samples is the strongly enhanced electron-phonon coupling compared to other graphene-based systems (see paragraph 4.2.2). The spectral function determined by ARPES shows signs of polaron formation in certain regions of the BZ, which appeared to be connected to the eVHs state as an intrinsic effect. On the other hand, resonant coupling to additional phonon modes was observed, which appeared to be connected to the ordered Gd adlayer as an extrinsic effect.
CHAPTER 5

Gadolinium intercalated monolayer graphene on SiC(0001)

As it was shown in the previous chapter, highly doped monolayer graphene can be produced by the intercalation of Gd in ZLG on SiC(0001) and many of its interesting properties were understood in this scope. Yet, the question rose, if the MLG system on SiC(0001) can also be intercalated with Gd. As it was shown for instance with hydrogen intercalation, one can obtain bilayer graphene building up on the MLG system [22]. So, in particular the goal was to produce highly doped bilayer graphene and compare to the highly doped monolayer graphene case, as substantial differences could be expected [30, 31, 93, 94]. In this chapter a detailed characterization of this system will be given, where also the differences to the ZLG case are worked out. In particular, it will also be demonstrated that the intercalation process indeed yields a bilayer system with no Gd incorporation between the carbon layers.

5.1 General considerations: Band structure, intercalation & homogeneity

The procedure of intercalating Gd in the MLG system on SiC(0001) was built up on the knowledge gained for the ZLG case. Owing to the altered starting point, it had to be slightly refined. Details to this procedure can be found in appendix B.
**Band structure determined by ARPES** We first take a brief overview of the band structure determined by ARPES on this system. A more detailed analysis will be given in the following paragraphs. In Fig. 5.1 (a) & (b), ARPES spectral cuts through the \( \bar{K} \) point are shown, taken perpendicular and parallel to the \( \Gamma \bar{K} \) direction. When comparing to expectations from the tight binding model described in paragraph 1.1.1, the picture does not resemble bilayer graphene at first glance (see Fig. 1.3). It rather seems to show a mixture of lower (\( E_{D1} \approx 0.5 \text{ eV} \)) and higher doped (\( E_{D2} \approx 1.6 \text{ eV} \)) monolayer graphene bands\(^1\) (see paragraph 1.1.1). One could thus jump to the interpretation by an inhomogeneous/non-complete intercalation, as it was done previously for many related intercalation systems on SiC(0001) [98, 107, 191–193]. These systems will be discussed later. The respective spectral features would then be produced by non-intercalated standard MLG.

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\(^1\)The nomenclature lower and higher doped bands for the apparent two band species is kept throughout this work.
\( (E_D \approx 0.45 \text{ eV} \ [57]) \) and Gd intercalated ZLG \( (E_D \approx 1.65 \text{ eV} \ (\text{see chapter 4})), \) supposing the sample was inhomogeneously prepared previous to intercalation. For such a scenario, the two branches should be independent in the spectral recognition. This picture, however, must be excluded for numerous reasons:

If the higher doped bands were to be produced by intercalated ZLG, one would expect the eVHs scenario to occur (see paragraphs 4.1.1 & 4.2.1). This can be excluded by considering the ARPES cut in Fig. 5.1 (b) in \( \overline{KM} \) direction and the FS in Fig. 5.1 (d). The higher doped bands seem to show a tendency to form the mentioned eVHs, as spectral weight is smeared towards the \( \overline{KM} \) direction, yet there is no obvious spectral weight at the Fermi level at the \( \overline{M} \) point. The lower doped band also shows features distinct from standard MLG. Firstly, this band species shows pronounced renormalizations at about 1 eV binding energy, which are absent in the MLG case [57] (marked by the blue arrows in Fig. 5.1 (a) & (b)). Complementary to this, also strong renormalizations appear in the higher doped bands at the same binding energy (marked by the blue arrow in Fig. 5.1 (c)). It comes naturally to mind, to assign these features to avoided crossing, and thus hybridization, of the lower and higher doped bands, which would be impossible for lateral inhomogeneity. Furthermore, severe deviations from a linear band course are also evident at the Dirac point of the lower doped bands at binding energy -0.5 eV in Fig. 5.1 (a) & (b). This is reflected in EDCs taken at the \( \overline{K} \) point of pristine and the Gd intercalated MLG in Fig. 5.1 (e). Two humps are present in the intercalated case, which are indicative for the formation of a bandgap on the order of 100 - 200 meV. These humps are absent in the pristine MLG case, as it does not exhibit a bandgap [57, 194].

**Homogeneity from LEED** The claim of a non-complete intercalation in the sense defined above can also be ruled out by considering results from LEED measurements. After intercalation, the spots characteristic for the initially bound first graphitic layer, i.e. the \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\text{-SiC}(0001)\) reconstruction, vanish completely. Exemplary, LEED patterns for two different electron energies before and after intercalation are shown in Fig. 5.2. Just like in the ZLG case (see paragraph 4.1.4), the vanishing of these reconstruction spots is strong evidence for decoupling of the buffer layer and therefore intercalation, on the complete investigated area. A remaining pristine MLG region should lead to the presence of reconstruction spots as shown in Fig. 5.2. Also, an increase in intensity of gra-
5.2 Proof for bilayer graphene

The information gathered up to this point strongly suggests the insertion of Gd in between the SiC and the graphitic layers above. However, as the system was well defined prior to intercalation in terms of two graphitic layers on top of the SiC, two configurations might be responsible for the observed spectral picture in ARPES. Firstly, the system could consist of a configuration sketched in Fig. 5.3 (a). There, the Gd is sandwiched by SiC on one side and bilayer graphene on the other. The second possibility is Gd being also between the two graphitic layers (see Fig. 5.3 (b)). To identify the correct model, potential differences will be worked out below for these two cases. For the argumentation we make the assumption,
that the bilayer configuration sketched in Fig. 5.3 (a) is the case here. Thus, characteristics of the system in terms of bilayer graphene will be carved out, which are incompatible with Gd being also between the graphitic sheets.

5.2.1 Band modeling

Despite the fact that the spectral picture could naively be interpreted otherwise, strong similarities to the expected picture for bilayer graphene based on tight binding \([30, 35]\) can be found. In Fig. 5.4 (a) the previously shown ARPES cut through \(\overline{K}\) taken parallel to \(\overline{\Gamma K}\) is plotted with tight binding bands superimposed. The parameters for this model are discussed later in this paragraph. The gap at the Dirac point of the lower doped bands in the measurements is reflected by the model. Also, at the energy of the renormalizations (1 eV), a band gap is present in the model.

However, obvious deviations at 1 eV binding energy cannot be neglected. These deviations have to be divided into two aspects. Firstly, there are bands connecting the valence and conduction band, called midgap bands in the following. Similar states are present in a majority of intercalation systems based on MLG on SiC(0001), which will be further discussed in paragraph 5.5. Generally spoken, such states can be produced by different mechanisms in real systems. It was claimed by Xu et al. [195], that strong electron-electron interaction can close this gap in biased bilayer graphene. Although counterintuitive, as one expects a Mott insulating state with a bandgap at sufficiently strong correlations, this is meant to be possible for such systems [196–198]. On the other hand, structural defects can produce such midgap states, as it was claimed by Kim et al. [199]. They assign their findings in a related bilayer graphene system on SiC to rotational disorder within the two graphitic layers. The second and more intriguing aspect is that the size of the gap around 1 eV binding energy itself appears to be smaller in
Fig. 5.4: Tight binding modeling of the band structure: (a)-(c) ARPES cuts at K of Gd intercalated MLG. (a) & (b) were taken perpendicular and (c) parallel to K. Tight binding bands are superimposed with different interlayer coupling parameters γ₁. (d) Momentum integrated spectral intensity of (a) (continuous black) with a sketch of a step-like function (dashed black) and a fit (continuous green) specified in the text. (e) ARPES cut through K taken perpendicular to K of Au intercalated MLG on SiC(0001) with tight binding bands superimposed. (f) Momentum integrated spectral intensity of (e) with a fit specified in the text. (a)-(d) were taken with 65 eV and (e)-(f) with 40 eV photon energy. The respective tight binding parameters are specified in the legend and tab. 5.1. The extracted energies are defined in the legend.

the experiment. Apart from the fainter midgap bands, the intense main bands strongly deviate from the tight binding model, as it is marked by the green arrows in Fig. 5.4 (a).

In order to extract deviations from the generally observed picture for bilayer graphene for the case of the Gd intercalated system, one has to quantify the characteristics of the spectral picture. For this, the following ansatz is pursued. Characteristic energies and energy differences, defined in the legend of Fig. 5.4, are extracted, which are then compared to a tight binding model. In this scope it turned out, that angular or in other words momentum resolution and broadening have a strong influence on the extracted values. This problem was circumvented by evaluating the momentum integrated spectral intensity distribution. The integrated spectrum corresponding to the spectrum in Fig. 5.4 (a) is plotted in
Fig. 5.4 (d). Two dips are present at energies, which correspond to $E_{D1}$ and $E_{D2}$ in our nomenclature. This spectrum was subsequently fitted by a function, which was constructed as a sum of four arctangent functions, rendering the four edges around $E_{D1}$ and $E_{D2}$:

$$f(E) = I_0 - \sum_{i=1}^{4} (-1)^i I_i \left[ \frac{1}{\pi} \arctan \left( \frac{E - E_i}{w_i} \right) + \frac{1}{2} \right],$$  \hspace{1cm} (5.1)$$

where the $E_i$ give the energies, that are compared to the tight binding model. $w_i$ denote the respective spectral width and $I_i$ are the respective weighting. $I_0$ is introduced as an intensity offset in order to take into account for background intensity.

This function is motivated as following. Firstly, one has to recall, that ARPES probes the spectral function \cite{53}. In first approximation this leads to a Lorentzian lifetime broadening in energy compared to bands in a single particle picture \cite{53}. If the lifetime broadening was energy independent, the momentum integrated spectral function can then be seen as the convolution of a DOS in a single particle picture with a Lorentzian. Such a DOS cannot be considered here, as the experimental spectrum in Fig. 5.4 (d) is only integrated in one dimension instead of the whole BZ. This entity is, however, approximated here by a sum of four step functions. The steps define the edges around $E_{D1}$ and $E_{D2}$, like sketched in Fig. 5.4 (d). The convolution of a Lorentzian with a step function, on the other hand, gives its primitive integral as an arctangent function. The different widths $w_i$ are then introduced to approximate binding energy dependent lifetime variations.

The tight binding model, to which the experimental values are compared to is calculated in nearest neighbor approximation. Therein, general relations can be found between the $E_i$ and the asymmetry potential $U$, the gap values $E_{G1/2}$ and the midgap energies $E_{D1/2}$ (see legend in Fig. 5.4) as:

$$U = |2((E_3 + E_4)/2 - E_2)|$$  \hspace{1cm} (5.2)$$

$$E_{G1} = |E_1 - E_2|$$

$$E_{G2} = |E_3 - E_4|$$

$$E_{D1} = (E_1 + E_2)/2$$

$$E_{D2} = (E_3 + E_4)/2.$$
As many approximations were made for this procedure, it’s validity was first tested on a system, simpler than the Gd intercalated MLG. Here, the system Au intercalated MLG was chosen. Similar to the ZLG case (see chapter 6, appendix A and ref. [100]), slightly n-doped bilayer graphene can be produced by Au intercalation in MLG on SiC(0001). A representative ARPES cut through \( \overline{\Gamma K} \) taken perpendicular to the \( \overline{\Gamma K} \) direction is shown in Fig. 5.4 (e). The momentum integrated spectrum can be fitted excellently by the function in Eq. 5.1 (see Fig. 5.4 (f)). The extracted values for \( U, E_{G1/2} \) and \( E_{D1/2} \) are tabulated in table 5.1. Taking the extracted value for \( U \), the gap values can be reproduced well by the tight binding model with a reasonable \( \gamma_1 = 0.405 \) eV [7] (see table 5.1). Using also the extracted \( E_{D2} \) as total binding energy shift of the bands and \( v_F = 5.8 \) ÅeV/\( \hbar \), the bands deduced from the tight binding model fit the experimental angle resolved spectrum excellently (see Fig. 5.4 (e)). This proves self-consistency of the procedure, as all parameters plugged into the tight binding model, besides \( v_F \) and \( \gamma_1 \), are extracted from the experiment. \( v_F \) is the value defining the band slope, which can be viewed irrelevant for the argumentation. \( \gamma_1 \), on the other hand, is the value to be extracted and discussed. Note here, that also in the Au case midgap bands are present (see Fig. 5.4 (e)). These midgap bands do not lead to severe disruptions for the presented procedure. In this manner, one can consider this procedure as credible.

Applying Eq. 5.1 to the Gd case again yields an excellent fit (see Fig. 5.4 (d)). The respective extracted parameters are also tabulated in table 5.1. Taking again the extracted \( U \), then \( E_{G1} \) can be reproduced with \( \gamma_1 = 0.42 \) eV (see parameter set TB #1 in table 5.1), which is again a value in agreement with bilayer graphene [7].

<table>
<thead>
<tr>
<th>( P ) (eV)</th>
<th>Au, fit</th>
<th>Au, TB</th>
<th>Gd, fit</th>
<th>Gd, TB #1</th>
<th>Gd, TB #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_1 )</td>
<td>0.405*</td>
<td>0.438 ± 0.001</td>
<td>0.42*</td>
<td>0.3*</td>
<td></td>
</tr>
<tr>
<td>( E_{D1} )</td>
<td>0.286 ± 0.001</td>
<td>0.592*</td>
<td>1.021 ± 0.002</td>
<td>1.021*</td>
<td>1.021*</td>
</tr>
<tr>
<td>( E_{D2} )</td>
<td>0.592 ± 0.003</td>
<td>0.269*</td>
<td>0.153 ± 0.001</td>
<td>0.152</td>
<td>0.082</td>
</tr>
<tr>
<td>( E_{G1} )</td>
<td>0.270 ± 0.001</td>
<td>0.262*</td>
<td>0.290 ± 0.002</td>
<td>0.388</td>
<td>0.288</td>
</tr>
<tr>
<td>( E_{G2} )</td>
<td>0.254 ± 0.003</td>
<td>0.262*</td>
<td>0.290 ± 0.002</td>
<td>0.388</td>
<td>0.288</td>
</tr>
<tr>
<td>( U )</td>
<td>0.342 ± 0.004</td>
<td>0.342*</td>
<td>1.011 ± 0.002</td>
<td>1.011*</td>
<td>1.011*</td>
</tr>
</tbody>
</table>

Table 5.1: Tabulation of the fit parameters \( P \) resulting from the spectral fit of Au and Gd intercalated MLG on SiC(0001) and the accompanied tight binding (TB) parameter. The values marked with (*) were used as input for the TB model in order to extract the gap values. Also, these values were used to calculate the tight binding bands in Fig. 5.4 (a, b, c, e).
However, the gap $E_{G2}$ cannot be reproduced by this parameter set, as it is off by about 25%. To reproduce $E_{G2}$, $\gamma_1$ has to be reduced to about 0.3 eV (see parameter set TB #2 in table 5.1), yet then $E_{G1}$ is off by a factor of 2. Again to prove consistency, the tight binding bands with $v_F = 5.8 \text{ ÅeV}/\hbar$ and $\gamma_1 = 0.42 \text{ eV}$ fit the bands around $E_{D1}$ best, which are the bands we initially compared to in Fig. 5.4 (a). On the other hand, a value of 0.3 eV fits the region around $E_{D2}$ much better (see Fig. 5.4 (b)). The direct comparison to the Au case, where the extracted values are in agreement with tight binding, leads to the insight, that the significant differences cannot be connected to the mentioned midgap bands connecting the valence and conduction band, which are also present in the Au case.

Considering the course of the higher doped bands in $\overline{KM}$ direction (see Fig. 5.4 (c)), also deviations are present, as the band is flatter than tight binding predicts. Similar features were also observed in the Gd intercalated ZLG system (see paragraph 4.2.1), although an eVHs is not build up here. One can speculate, that electron-electron interaction also plays an important role in Gd intercalated MLG, leading to analogies in this respect to Gd intercalated ZLG.

Summing this up, the presented data evaluation shows that the spectral picture in the Gd intercalated MLG indeed shows strong similarities to bilayer graphene, as it is generally produced on SiC(0001) with strong layer asymmetry $U$. The general band topology resembles that of bilayer graphene and certain characteristic binding energies ($E_{G1}$) match the expected values from tight binding. Yet, strong deviations are also found. $E_{G2}$ cannot be connected to this simple picture and it can also not be connected to the midgap bands, generally observed in bilayer graphene systems on SiC(0001). The band course of the higher doped bands in $\overline{KM}$ direction is much flatter than expected. This might be connected to electron-electron interaction in analogy to the Gd intercalated ZLG case. As a consequence of these deviations, the presented evaluation does not allow an unambiguous assignment to bilayer graphene yet. One can still argue, that Gd between the sheets might produce the observations. This will be excluded in the following.
Varying the doping level/asymmetry potential

A key to unambiguously prove the bilayer graphene scenario lies in the controlled modification of the system and with this, finding characteristic changes in the spectral picture in ARPES. This is done here by varying the doping level and as a result the asymmetry potential \( U \) between the graphitic layers [7]. The shape of the bands is then supposed to change in a very distinct fashion.

Description of the experiment

Assuming the Gd is sandwiched by the SiC and the bilayer graphene, one side of the graphene sheet sits blank on the surface. By depositing dopants like it is sketched in Fig. 5.5, one should be able to introduce additional charge carriers in the system. As an inherent property of bilayer graphene, these additional charge carriers will accumulate on the upper graphitic layer [7], which alters the asymmetry potential \( U \). Rb was chosen as dopant here, as it has shown strong doping efficiency when adsorbed on graphene earlier [68, 200]. It was consequently deposited in UHV conditions and ARPES was measured afterwards. It turned out during these measurements, that the doping induced changes in the band structure are strongly time dependent. The effective doping efficiency of the deposited Rb declined with time, such that the picture converged to the picture of the pure Gd intercalated samples. Such effects can generally be expected for an unstable system like dopants adsorbed on graphene. This can be caused by oxidization by remaining oxygen or water in the vacuum chamber. Also, diffusion and clusterization of the Rb on top of the graphene reduces the doping efficiency of the individual dopant atoms [201]. Due to these degeneration effects it was not possible to take steady measurements exceeding certain time scales. On the other hand, this effect brought the opportunity to track the doping induced changes...
continuously. A typical time scale for degeneration was in the 20 min range, thus a series of single measurements could be taken with respective measurement times of about 10 s. Without altering other parameters, the time dependent measurements translate to doping dependent measurements. In this manner, single ARPES cuts through the \( \overline{K} \) point perpendicular to \( \overline{\Gamma K} \) were taken. After one such deposition and measurement cycle, the Rb could be removed completely by annealing to temperatures higher than 600 °C, like it was shown in ref. [200], and the procedure could be repeated.

**Characteristic spectral changes**

Three exemplary ARPES cuts, obtained by the time dependent measurements described above, are shown in Fig. 5.6 (Top), where distinct changes are evident. \( E_{D1} \) as well as \( E_{D2} \) are shifted towards higher binding energy, indicating further n-type doping by the Rb. Also, the momentum splitting \( \Delta k \) of the two branches at \( E_{D2} \) is reduced as the asymmetry potential \( U \) is reduced. These changes in \( \Delta k \) are in agreement with the behavior expected from tight binding for bilayer graphene. Three representative sets of tight binding bands are sketched in Fig. 5.6 (Bottom), which correspond to the ARPES cuts in Fig. 5.6 (Top). This trend in \( \Delta k \) is very distinct for bilayer graphene and must be expected. On the other hand, such a
distinct behavior would be unlikely, if Gd was between the sheets.

**Characteristic binding energy shifts**

Evaluating the doping dependent measurements, we now turn to a detailed analysis of doping dependent binding energy shifts of the characteristic spectral features. This can give a core argument against Gd being between the two graphitic layers and for the status as bilayer graphene. As an inherent property of bilayer graphene, one would expect a correlated shift of certain spectral features with doping. This means, that the amount of shift in certain spectral features are connected very specifically, which is not given if Gd was in between the sheets.

In the view of standard bilayer graphene, one can firstly assume here that the higher doped band branches are not being shifted significantly in binding energy compared to the lower doped bands upon Rb deposition. This is reasonable, as on the one hand, the introduced additional charge carriers are accumulated on the upper graphitic layer (the layer nearest to the Rb, see Fig. 5.5). This reduces in first approximation the asymmetry potential and thereby shifting mainly the lower doped bands. On the other hand, due to the general shape of graphene’s π band system (see paragraph 1.1.1), the quantum capacitance $C_Q = e^2 \frac{d^2 n}{d \mu}$, which gives the connection between the introduced charge carriers $n$ and the shift of the chemical potential $\mu$, is much higher in the higher doped than in the lower doped branches [202]. This means, in order to shift the higher and lower doped bands rigidly, a much greater amount of charge carriers has to be filled in the higher doped compared to the lower doped branch. Considering the tight binding model used throughout this chapter (described in paragraph 1.1.1), these assumptions yield the mentioned relation in energy shift, which is illustrated by the sketched tight binding bands in Fig. 5.7. For simplicity, we turn off the interlayer coupling $\gamma_1$ first. The spectral picture then corresponds to two monolayer graphene bands, that are shifted with respect to each other due to a finite asymmetry potential $U$.

Including the previously made assumptions, that only the lower doped bands get shifted when changing $U$, then the crossing of the two band species moves exactly half as much as the Dirac point of the lower doped band species. When turning on $\gamma_1$, the characteristic gaps are built up. Yet, the characteristic energies marked with $E_{D2}$ and $E_2$ do not shift. For this reason, the shift in $E_{D2}$ must be exactly half the shift of $E_2$.

The single ARPES cuts, taken time dependently after Rb deposition, were an-
analyzed by the procedure described in paragraph 5.2.1 in order to extract the characteristic binding energies defined in Fig. 5.8 (a). This means, the intensity distribution in the different ARPES cuts (e.g. Fig. 5.8 (b)) were momentum (angle) integrated to obtain a spectrum such as plotted in Fig. 5.8 (c). These spectra were then fitted with the function from Eq. 5.1 and the mentioned characteristic energies were extracted. The temporal, thus doping dependent changes in the momentum integrated spectra are visualized in Fig. 5.8 (d), where the respective values for $E_{D1}$ and $E_{D2}$ are superimposed. It is obvious in this plot, that $E_{D1}$ and $E_{D2}$ are not being shifted rigidly.

In Fig. 5.8 (e), $E_{D2}$ is plotted versus $E_2$ for different Rb-deposition and measurement cycles together with a line denoting the mentioned $1/2$-relation for comparison. The error bars were extracted from the standard deviation of the fits by error propagation. Although the single measurement cycles deviate slightly from this relation, the combination of all cycles gives an excellent agreement. The deviations within the single cycles can be explained by systematic errors, made within the respective cycles. An inherent error is made, as time dependently single cuts perpendicular to the $\Gamma K$ direction were taken. As the angle, which corresponds to $K$ is binding/kinetic energy dependent (see Eq. 2.7), these straight cuts at certain angles translate to curved cuts through the dispersion. Therefore, it was not possible to take measurements exactly at $K$ for all binding energies. As the examined spectral features change in binding energy, an effective drift in momentum could not be avoided.

Fig. 5.7: Illustration of the $1/2$-relation: Sketch of three different tight binding bands for AB-bilayer graphene with different band parameters $\gamma$ and $U$ (see text for details).
To conclude, the $\frac{1}{2}$-relation proves that the binding energy shifts of the mentioned spectral features are connected, the way they should be for bilayer graphene. The spectral pictures at $E_{D1}$ and $E_{D2}$ therefore have to be produced by the interaction of the two graphitic layers and with that hybridization of the different band species. Gd being in between can therefore be excluded. If Gd was in between, the interlayer distance would drastically increase. Starting from an initial spacing of graphite with 3.35 Å, one could then assume a layer spacing on the order of 5 Å as a reasonable scenario. In some comparable graphite intercalation compounds like BaC$_6$, EuC$_6$ and SmC$_6$ the interlayer spacing is 5.25 Å, 4.86 Å and 5.03 Å, respectively [203]. Simulations by Guo et al. [204] showed that under these conditions the interlayer interaction in terms of orbital overlap can be neglected, whereas the renormalizations at $E_{D2}$ or the gap at $E_{D1}$ would be basically non-existing.
Photon energy dependent ARPES measurements

A commonly made observation, characteristic for few layer graphene, is the fact that the relative intensity of the different band branches oscillates, when altering the photon energy and with that the kinetic energy of the photoelectrons due to interference effects [33, 199, 205]. As the higher and lower doped bands in the Gd intercalated samples are related to bilayer graphene (see previous paragraph), one can expect similar oscillations here. In this manner, photon energy dependent ARPES measurements in the energy range of 20 eV to 165 eV were made on the Gd intercalated samples. A representative series of ARPES cuts through \( \overline{K} \) taken parallel to \( \Gamma \bar{K} \) is plotted in Fig. 5.9 (a). It is clearly visible, that the intensities of the higher and lower doped bands are altered with respect to each other, when varying the photon energy. However, it is expected that the intensity modulations themselves are not periodic in kinetic energy of the electrons and therefore photon energy, but in the quantity \( k_\perp \). \( k_\perp \) represents the photoelectrons’ momentum.

Fig. 5.9: Photon energy dependent ARPES measurements on Gd intercalated MLG: (a) ARPES spectral cut through \( \overline{K} \) taken parallel to the \( \Gamma \bar{K} \) direction with different photon energies. (b) Intensity ratios of the lower (blue) and higher doped (red) bands at 0.1 eV binding energy.
perpendicular to the graphene plane. The general expression is given in Eq. 2.9, yet the kinetic energy $E_{\text{kin}}$ has to be expressed in terms of the photon energy $E_{\text{ph}}$ by $E_{\text{kin}} = E_{\text{ph}} - \phi - E_B$ (Eq. 2.1). $\phi$ is the work function of the analyzer, which is in this case $\approx 4.5$ eV, and $E_B$ the binding energy of the respective electrons. Using Eq. 2.7, one can easily rewrite Eq. 2.9 to:

$$k_{\perp} = \sqrt{\frac{2m}{\hbar^2} (E_{\text{ph}} + V_0 - \phi - E_B) - k_{\parallel}^2},$$ (5.3)

The inner potential $V_0$ is the energy difference between the bottom of the conduction band and the vacuum level [53]. For graphite, it was reported to be 16.5 eV [205]. As the bands here are shifted by about 1 eV with respect to the Fermi level (i.e. $E_{\text{D}2}$, see paragraph 5.2.1), this corresponds to 17.5 eV in our case. In order to circumvent effects related to renormalizations close the Fermi level, the intensities are evaluated at 0.1 eV binding energy. $k_{\parallel}$ denotes the momentum of the photoelectrons parallel to the graphene plane. For $k_{\parallel}$ a mean value between the higher and lower doped bands at 0.1 eV binding energy was used (1.9 Å$^{-1}$). In order to follow the oscillations, the relative intensity of the two band species is plotted in Fig. 5.9 (b). The graph presents a clear oscillatory behavior with the periodicity being 1.86 Å$^{-1}$. The maxima are marked by the orange lines. This periodicity corresponds to a real space lattice vector of $2\pi/1.86$ Å$^{-1} = 3.38$ Å, which is in agreement with the interlayer distance of graphite (3.4 Å) and previous findings [33].

The presented behavior is very characteristic for bilayer graphene on SiC(0001). The agreement of the extracted real space vector with other comparable systems strongly suggests a comparable interlayer spacing, which is yet again incompatible with Gd being in between the graphene sheets. As already pointed out in paragraph 5.2.2, if Gd was in between, one could assume an increase in layer spacing by a factor of about 1.5 compared to bilayer graphene.

Summing up this section, the combination of all results, worked out here, must yield the conclusion that bilayer graphene was fabricated by the intercalation of Gd in MLG on SiC(0001). Furthermore, the interlayer distance coincides with that of other multilayer graphene systems and graphite. The Gd induces strong doping but also a strong asymmetry potential in this bilayer system. The intensity oscillations in the photon energy dependent ARPES measurements (paragraph 5.2.3) and the doping dependent spectral changes in ARPES (paragraph 5.2.2) are only
compatible with this scenario. The detailed analysis and quantification of the characteristic energies and energy gaps shows the incompatibility of the gap value $E_{G2}$ with the used tight binding model (paragraph 5.2.1). One must thus assume, that these findings have to be produced by an effect, not taken into account by tight binding here. This will be elaborated in the following.

### 5.3 Interpretation of the spectral properties

Concomitantly to the energy shifts introduced by additional Rb deposition in paragraph 5.2.2, one would expect distinct changes in the values of the energy gaps $E_{G1}$ and $E_{G2}$ (defined in Fig. 5.10 (a)). These values together with the asymmetry potential $U$ were also obtained from the fitting procedure in paragraph 5.2.2 (further described in paragraph 5.2.1). The respective data points from the different Rb-deposition and measurement cycles are plotted in Fig. 5.10 (b). An increase is evident for $E_{G1}$ with decreasing $U$, which is in agreement with the expected course from tight binding with $\gamma_1 = 0.4$ eV (following Eq. 1.3). The slight differences to the pristine sample ($\gamma_1 = 0.42$ eV, see paragraph 5.2.1) can be attributed to increased band broadening due to the introduction of additional scattering centers by the Rb. As already pointed out in paragraph 5.2.1, the Gd data is not compatible with this model regarding $E_{G2}$. Yet, a slight decrease of the gap value with decreasing $U$ is evident in the data and present in the model. The graph in Fig. 5.10 (b) also contains the data points obtained from Au intercalated MLG on SiC(0001) (see paragraph 5.2.1) to demonstrate consistency.

Although the discrepancy in $E_{G2}$ is obvious, the origin is yet to be understood. In order to do so, we turn to simulations made by Wang et al. [206] based on density functional theory for AB bilayer graphene. The resulting values for $E_{G1}$ and $E_{G2}$ are plotted in Fig. 5.10 (d) dependent on the electric field perpendicular to the graphene plane. In the view of a plate capacitor, however, the electric field is about proportional to the asymmetry potential (see sketch in Fig. 5.10 (c)). The plot also contains the results from the tight binding calculations used in Fig. 5.10 (b). For $E_{G1}$ the magnitude and course are very similar in both theories and in agreement with the experiment. For $E_{G2}$, two separate regimes are distinguishable. Below about 3 V/nm, the value is about proportional to the electric field and basically corresponds to the asymmetry potential $U$, thus the curves overlap in both theories. Going beyond, both curves deviate. The values
5.3 Interpretation of the spectral properties

Fig. 5.10: Doping dependent evolution of the energy gaps: (a) Sketch of tight binding bands defining the energies. (b) Evolution of the extracted $E_{G1}$ and $E_{G2}$ with asymmetry potential. Superimposed is the course predicted from tight binding ($\gamma_1 = 0.4$ eV). The differently colored points represent data sets obtained from different deposition cycles, whereas the color code corresponds to Fig. 5.8 (e). The data points of Au intercalated MLG (see paragraph 5.2.1) are also plotted. (c) Illustration of the connection between the electric field perpendicular to the graphene plane and the asymmetry potential $U$ in bilayer graphene. (d) Theoretical evolution of $E_{G1}$ and $E_{G2}$ with an electric field perpendicular to the graphene plane, which corresponds here to the evolution with asymmetry potential $U$. The two colors correspond to the tight binding data used in (b) and simulations adapted from Wang et al. [206], respectively. The regions of Au intercalated MLG and doped Gd intercalated MLG are marked.

From Wang et al. [206] are significantly lower than in tight binding. Here, the Au case is in a transition region (marked green in Fig. 5.10 (d)). The electric fields corresponding to a part of the asymmetry potential of the doped Gd case in Fig. 5.10 (b) is marked orange. Indeed, the experimental values for $E_{G2}$ are reproduced well by the results from Wang et al. [206]. Following their argumentation, under a sufficiently strong electric field perpendicular to the graphene plane, the charge carriers within the respective layers rearrange. The charge density is shifted such that an additional dipole moment emerges between the sites with a direct neighbor in the other layer. This is not covered by the tight binding model used here. This charge redistribution re-
roduces the effective interlayer hopping, thus interaction. Yet, due to the cause of this reduction, $E_{G1}$ and $E_{G2}$ are affected differently. While $E_{G2}$ is directly affected through the hopping parameter, in other words hybridization of the layers’ $\pi$ bands [207], $E_{G1}$ is also related to the sublattice asymmetry within one layer. As the reduction of interlayer hopping is accompanied with an increased sublattice asymmetry, these effects compensate for $E_{G1}$.

The correspondence between theory and experiment points towards a general characteristic of bilayer graphene under a large asymmetry potential. Our detailed study of the system Gd intercalated MLG thus provides proof for this effect with a strong credibility. It has to be pointed out here, that spectral pictures similar to Gd intercalated MLG were found in other intercalation systems, which will be discussed in paragraph 5.5. However, the interpretation there was different, which is strongly opposed by our results.

5.4 CLS on Gd intercalated MLG

In the scope of comparing the Gd intercalated MLG and ZLG systems, the chemistry was investigated by CLS for the MLG case. Starting first with the Si 2p spectrum of both systems in Fig. 5.11 (a), the observed components are completely analogous for both systems (see also paragraph 4.1.3). One more intense component can be found at about 100 eV binding energy, assigned to bulk SiC, and one less intense component at about 99 eV, assigned to silicon bound to Gd. Like in the ZLG case, these two components are distinguishable by altering the photon energy, i.e. surface sensitivity and therefore height distribution (see Fig. 5.11 (a)). The Gd-Si component is more pronounced in the more surface sensitive probe (photon energy 330 eV). Analogously to the argumentation in paragraph 4.1.3, the small relative intensity of the Gd-Si component points towards a partial bonding of the Gd to the topmost Si atoms of the SiC. Initially, no significant differences can be expected for the Si 2p, produced by the additional graphitic layer on top. As in the case of standard mono- to fewlayer graphene on SiC(0001) the chemistry at the interface as well as the band bending on the SiC(0001) surface should not be affected significantly [208].

The C 1s spectrum on the other hand does show differences in the two cases. Comparing the spectra obtained with 450 eV photon energy in Fig. 5.11 (b) for both systems, similar broad graphitic features can be found in the region 284-
Fig. 5.11: CLS measurements on Gd intercalated MLG and ZLG: The respective experimental parameters and systems are specified in the legend. (a) Comparison of the Si 2p spectra for the two systems at different photon energies. The red spectrum is set off for clarity. The region of the two different components (bulk SiC, Gd-Si) are illustrated by the different background color. (b) Top: Comparison of the C 1s spectra for both systems at different photon energies. The C 1s spectra are normalized to the region greater than 286 eV binding energy. Bottom: Difference spectrum of the spectra from Gd intercalated MLG in the top panel together with a fit. (c) Sketch illustrating the mechanism producing the changes in shape of the C 1s core level with photon energy (see text). The different background colors (light blue and light red) represent the layers producing the C 1s signal in the marked binding energy regions in (b).

289 eV besides the SiC bulk component around 282.5 eV. This broad distribution was assigned to energy losses mainly due to plasmon creation during the photoemission process in the ZLG case [105] (see paragraph 4.1.3). It is thus reasonable to assume a similar behavior in the MLG case. The energy loss mechanisms can be connected to the size of the Fermi surface [105], which is similar for the higher doped bands in the Gd intercalated MLG (see paragraph 5.1) and ZLG case (see paragraph 4.1.1). Yet, an additional component at about 284.5 eV appears to be present in the intercalated MLG case. The same component can also be recognized, when comparing spectra in the MLG case for two different photon energies and therefore surface sensitivity (also in Fig. 5.11 (b)). To extract this component, the difference spectrum of the spectra in the MLG case is plotted in the same graph. This spectrum can be fitted well with a Doniach-Šunjic line shape with reasonable width (Gaussian: 0.01 eV, Lorentzian: 0.16 eV) and asymmetry (0.1), which is in agreement with standard MLG on SiC(0001) [48]. Also, the binding energy (284.66 eV) is near the value of pristine MLG on SiC(0001) (284.7 eV) [48, 209].

Connecting the results, two different graphitic C subsystems can be distinguished.
by their plasmonic energy loss mechanisms. The atoms producing the respective components in CLS are distinguishable by their arrangement in depth. The signal resembling that of Gd intercalated ZLG, and therefore highly doped graphene, has to be produced by C located below the surface. On the other hand, the signal resembling MLG on SiC(0001), and therefore low doped graphene, has to be produced by C located on the surface. This is sketched in the ball and stick model in Fig. 5.11 (c), where different background colors are reflected by the different background colors of the components Fig. 5.11 (b). It is reasonable to assume, that the respective energy loss characteristics are directly connected to the respective sections of the FS, produced by the higher and lower doped band branches (see paragraph 5.1) [55, 105]. Consequently, it comes naturally to mind that the real space wave functions associated with the higher and lower doped band branches are not smeared over both layers equally. They rather have to be located at the respective layer (see sketch in Fig. 5.11 (c)). This, however, can be connected to information gathered earlier on (see paragraph 5.2). Namely, the charge carriers introduced by the Gd are rather located at the graphitic layer nearby the Gd (layer beneath the surface), which introduces the strong asymmetry in the bilayer graphene.

Concluding this paragraph, the interface chemistry (Si 2p) in the Gd intercalated MLG is completely analogous to the ZLG case. In the C 1s spectra, differences are found for both system. The comparison of the C 1s signal of Gd intercalated MLG with the ZLG case and standard MLG on SiC(0001) brings the insight, that the different band branches observed in ARPES can be assigned to the different layers. This can be viewed as an inherent consequence of charge separation, thus layer asymmetry. In this respect, the two sublayers can be viewed as two coupled layers to some extent instead of one bilayer system, which is the case in the absence of asymmetry.

5.5 Comparison to literature

A great body of work is available on different dopant atoms intercalated in the MLG on SiC(0001) system and BLG on SiC(0001) in literature. In Fig. 5.12 a selection of ARPES measurements on these systems is shown. All of these measurements were taken at \( \overrightarrow{K} \) perpendicular to the \( \overrightarrow{\Gamma K} \) direction and are lined up by doping level/asymmetry with the C case (standard BLG on SiC(0001)) hav-
5.5 Comparison to literature

Fig. 5.12: ARPES comparison of the Gd intercalated MLG to related systems in the literature; ARPES cuts through $\overline{K}$ taken perpendicular to $\overline{\Gamma K}$. The different panels indicated different intercalated materials (see bottom sketch) in the MLG on SiC(0001)-system, besides the C case, which is standard BLG on SiC(0001). Yb was adapted from ref. [191] (see also refs. [98, 107]), Na from ref. [192], Li from ref. [193] and C from ref. [51]. The Au data was obtained within this thesis (see paragraph 5.2.1). Tight binding bands of bilayer graphene were superimposed in the Li and Na case as a guide to the eye. Although the conclusions drawn by the respective authors in the Li, Na and Yb cases did not assign the spectral features to bilayer graphene, an assignment is reasonable (see text).

ing the least doping level/asymmetry. Starting with the C case [51], the bands can be fitted well by the tight binding model specified in paragraph 1.1.1 with $\gamma_1 = 0.4$ eV [7]. In the Au case this is also valid (see paragraph 5.2.1). Although the data sets for Li [193] and Na [192] are more diffuse, the similarities to bilayer graphene are evident in the tight binding bands with $\gamma_1 = 0.4$ eV superimposed. At last, in the case of Yb, the picture converges to the Gd case. All these measurements share the fact, that bands are found which connect the valence and conduction band. As elaborated in paragraph 5.2.1, this might be produced by electron-electron interaction [195–198, 210] or rotational disorder [199]. However, as it is evident for the Li, Na and Yb case, the tight binding model fails to describe the gap $E_{G2}$ around $E_{D2}$ (marked by the orange arrow in Fig. 5.12) at higher asymmetry. As worked out in paragraph 5.2.1 & 5.3, this effect has to be separated from the mentioned bands connecting the valence and conduction bands.
However, in the case of Yb [98, 107, 191], Na [192] and Li [193] the systems were interpreted in a different way compared to the Gd case here. It was stated, that the intercalant was also in between the graphitic sheets and/or spatial inhomogeneity was involved. This must be objected by considering the similarities to the Gd case and the complete work done for Gd intercalated MLG within this thesis. The misinterpretation in literature was firstly steered by the mentioned deviations from tight binding. Yet, it must be mentioned that CLS measurements, especially with altering photon energies, on these systems resembled the rather unusual behavior of the Gd case (see paragraph 5.4), which further led to the mentioned misinterpretation. This was explained with different photoelectron energy loss mechanisms within the two layers in paragraph 5.4.

Concluding, one can state that all of the results for Gd intercalated MLG elaborated thus far are indisputably reflected by several systems in literature. Yet, in literature, the systems were interpreted differently. Considering the complete work done for Gd intercalated MLG here, the conclusion suggests itself, that these systems must be interpreted like our Gd case. Furthermore, this consistency strongly supports the thesis, that the deviations in $E_{G2}$ compared to tight binding (paragraph 5.3) as well as the layer distinguishably at high layer asymmetry (paragraph 5.4) are a universal property of bilayer graphene.

### 5.6 Quasiparticle dynamics

As worked out in paragraph 5.1, the similarities in shape of the lower doped branch in Gd intercalated MLG and pristine MLG on SiC(0001) are obvious. However, the introduction of a band gap at the Dirac point $E_{D1}$ (defined in Fig. 5.4) severely alters it’s properties. In this manner, the differences in the quasiparticle dynamics are examined here. To quantify the deviations in the two systems, single MDCs were fitted with single Lorentzian functions to obtain a center of spectral weight and a spectral width. The respective ARPES cut of the lower doped branch parallel to $\Gamma K$, alongside with fitted positions is shown in Fig. 5.13 (a). Taking the derivative of the fitted band position as the band velocity (see Fig. 5.13 (b)), two diverging points are visible. The energy difference is about 150 meV, which is in agreement with the gap values extracted in paragraph 5.2.1 and proves consistency. The evolution of the linewidth in Fig. 5.13 (c) further gives a clear distinction between pristine (adapted from ref. [57]) and Gd intercalated MLG in this
branch. The spectral width of the intercalated sample increases much slower with binding energy as a consequence of less pronounced many-body renormalizations, which leads to a larger lifetime of the respective states. When one compares the evolution of the spectral width in greater detail severe implications on the quasiparticle dynamics can be drawn. Following Bostwick et al. [57], the many-body effects producing this picture in pristine MLG are Auger processes and electron-plasmon coupling, aside from electron-phonon coupling (see also paragraph 1.2.3). The dimensionless electron-phonon coupling constant $\lambda$ for the intercalated case can be estimated with $\lambda = \frac{v_{ph}}{v_{FE}} - 1$ [194], where $v_{FE}$ is the band velocity at the Fermi level and $v_{ph}$ the velocity below the phonon kink (see also paragraph 1.2.3). This yields a value of about 0.07, which is very low and in agreement with previous observations on MLG on SiC(0001) [152, 211]. This means, that the observed deviations in the linewidth in Fig. 5.13 (c) have to be assigned to the mentioned Auger processes and electron-plasmon coupling.
The observations can then be connected to the bandgap introduced at the lower doped bands’ Dirac point in the intercalated case. Let’s assume, the system is in an excited state, where a state at a certain binding energy below the Fermi level is empty. Following the sketches in Fig. 5.13 (d, left), it is clear, that many different Auger processes can take place in linear bands, as both energy and momentum are always conserved [212]. In quadratic bands on the other hand, this is much more restricted. Within one band, Auger processes are forbidden in this simple picture Fig. 5.13 (d, middle). Auger processes satisfying energy and momentum conservation can however occur in a two band system in a symmetric fashion, like sketched in Fig. 5.13 (d, right). The minimum binding energy of the initial empty state has to be twice the energy difference of the midgap energy to the Fermi level in a symmetric valence and conduction band system. In the Gd intercalated system this corresponds to about 0.92 eV. Considering electron-plasmon coupling, also the linear band structure of graphene exhibits a special case, as electron-plasmon renormalizations at such small energies are forbidden for parabolic bands [57, 194].

Concluding, the found differences in band width evolution for monolayer and bilayer graphene are a direct consequence of differing many-body properties of these systems produced by the introduction of a band gap. In this manner, implications must be suspected for all of the materials’ properties and also for possible applications. As an example, this could contribute in the application of graphene in photonics and plasmonic devices [213], where the increased lifetime of an excited state is beneficial.

5.7 Conclusion for Gd intercalated MLG

The successful intercalation of Gd in the MLG on SiC(0001) system was reported here. It was shown in a systematic and conclusive way, that highly doped bilayer graphene with a large asymmetry potential between the layers was formed (see paragraph 5.2). As a consequence of the large asymmetry, the interlayer coupling in the bilayer graphene gets lowered significantly (see paragraph 5.3). These observations are in agreement with recent theoretical studies of biased bilayer graphene [206] and point towards a general characteristic of bilayer graphene. Our studies thereby lead to the reinterpretation of observations made for many complementary intercalation systems based on MLG on SiC(0001) like Li [193, 214],
Na [192] or Yb [107, 191]. Besides the importance on a basic research level, this observation draws implications for potential technical applications. The introduction of a bandgap in bilayer graphene, driven by an asymmetry potential, is a promising root for the implementation in logical devices [7]. In this manner, mechanisms influencing the interlayer hopping and with that the bandgap formation are of uttermost importance. Furthermore, the studies made, point towards the fact, that the bilayer system indeed shows characteristics of two coupled layers instead. By comparing the CLS measurements of Gd intercalated MLG with those of pristine MLG and Gd intercalated ZLG, different band branches could be assigned to different C 1s components, which could then be assigned to the different layers (see paragraph 5.4). This is in contrast to unbiased bilayer graphene, where the layers are indistinguishable. Despite the similar doping levels reached and the similar spectral picture in ARPES (see paragraph 5.1), the eVHs regime was not reached in this system, in contrast to Gd intercalated ZLG (see paragraph 4.1.1). This points towards a general discrepancy between monolayer and bilayer graphene. The analysis of the ARPES data in terms of spectral width shed light on the differences of monolayer and bilayer graphene in the view of quasiparticle dynamics (see paragraph 5.6). This means, the basic difference between a gapped/parabolic and a non-gapped/linear electronic spectrum was elaborated in the scope of electron-electron interaction.
CHAPTER 6

The role of the interface in Au intercalated graphene - an alternative view to intercalation

Only considering the number of charge carriers introduced in graphene by the different intercalated atom species misses key aspects of the total intercalation system. Since graphene is a quasi two-dimensional construct, the environment on both sides can have influence indirectly. It was shown for instance, that different intercalants can build up different dielectric environments, altering the effective dielectric constant of the system [50]. This can have strong influence on properties governed by Coulomb interactions, like for instance electron-electron interaction in graphene [215–217]. On the other hand, especially the question for intercalant related bands is of importance. One can take the example of certain graphite intercalation compounds like CaC$_6$, where a so-called interlayer state gets occupied, which is a hybrid band of graphene and intercalant related states [218, 219]. It was claimed that the emerging superconductivity in these systems is related to the occupation of this interlayer state [158, 160, 162].

One of the first publications on intercalation in graphene on SiC(0001) showed, that by evaporating Au onto ZLG on SiC(0001) and upon subsequent annealing to about 800 °C, the deposited material intercalates [100]. However, since then, techniques for graphene growth have drastically improved. While earlier, the SiC wafers were graphitized in UHV conditions, state of the art techniques are based on annealing in Ar atmosphere, providing superior homogeneity [27]. Addi-
tionally, intercalation procedures were developed, where much more homogeneous results could be obtained (see for instance appendix A & B). Taking advantage of this progress, it is crucial to reexamine the Au intercalated system, as data of superior quality can be obtained and evaluated more rigorously. The Au case itself denotes an especially interesting case, as two different stable phases can be obtained, where one or two Au layers are intercalated [100]. The two phases are foremost characterized by strongly differing charge carrier densities in the graphene. The single Au layer phase introduces an n-type charge carrier density of about $5 \times 10^{13} \text{ cm}^{-2}$, whereas the double Au layer phase introduces a p-type charge carrier density of about $7 \times 10^{11} \text{ cm}^{-2}$.

6.1 Properties of the n-phase

Starting here with the n-phase of Au intercalated ZLG, the focus is firstly put on a thorough characterization of the Au in the interface, named Au-interface in the following. This includes the structural, chemical and electronic properties. Afterwards, the influence on graphene’s properties is examined. Details about the intercalation procedure can be found in appendix A.

6.1.1 Interface chemistry & structure

In order to examine the chemical bonding situation in the Au-interface, CLS measurements were conducted. Representative spectra of the Au 4f and Si 2p core levels are shown in Fig. 6.1 (a) & (b), respectively. The Au 4f spectrum can be fitted well with a single doublet Voigt function (see Fig. 6.1 (a)). On the other hand, the Si 2p spectrum can be fitted well with a double doublet Voigt function (see Fig. 6.1 (b)). For the Au 4f, spin splitting was set to 3.68 eV and the branching ratio was 0.57. Standard constraints were set for the Si 2p fit, such as spin splitting of 0.63 eV and branching ratio of 0.5 for the single doublets. Within the respective doublets, both components were set to the same Lorentzian and Gaussian widths. The resulting fitting parameters can be found in Tab. 6.1. The small Lorentzian and Gaussian widths for the Au 4f levels are indicative for the presence of only one chemical species of Au. The f_{7/2} component’s binding energy of 84.35 eV is shifted by about 350 meV towards higher binding energy
Fig. 6.1: CLS and LEED on n-phase Au intercalated ZLG: (a) & (b) Au 4f and Si 2p related core level spectra together with their respective fits. (c) μLEED pattern and the closeup around the (0,0) spot. The prominent diffraction spots are marked and specified. (d) Ball and stick model, illustrating the n-phase atomic configuration.

compared to metallic Au. This means firstly, that one can exclude the presence of Au clusters on the sample surface, as it was observed earlier [100]. Also, all Au atoms within the interface have the same chemical environment. Judging from the two very distinct chemical components in the Si 2p spectrum, it is reasonable to assume that these Au atoms are chemically bound to the topmost Si of the SiC(0001) surface. All components of the Si 2p spectrum show a Lorentzian broadening of 0.12 eV, which can be viewed standard for this core level. The Gaussian width is 0.32 eV in the 100.78 eV binding energy doublet.

<table>
<thead>
<tr>
<th></th>
<th>E_B (eV)</th>
<th>ω_L (eV)</th>
<th>ω_G (eV)</th>
<th>ratio (%)</th>
</tr>
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<tbody>
<tr>
<td>Au 4f_{7/2}</td>
<td>84.35</td>
<td>0.15</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Si 2p_{3/2}, bulk SiC</td>
<td>100.78</td>
<td>0.12</td>
<td>0.32</td>
<td>68</td>
</tr>
<tr>
<td>Si 2p_{3/2}, Au-Si</td>
<td>100.31</td>
<td>0.12</td>
<td>0.13</td>
<td>32</td>
</tr>
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Table 6.1: Fit parameters of the Si 2p_{3/2} and the Au 4f_{7/2} components of the n-phase Au intercalated ZLG. The binding energies of the respective doublet partners are given by the spin splitting mentioned in the text, which was set as a constrain for the fit.
and 0.13 eV in the 100.31 eV doublet (both binding energies denote to the $2p_{3/2}$ components). A Gaussian broadening of 0.32 eV is generally observed for bulk SiC even if the experimental resolution is much better (see also Gd intercalation in paragraph 4.1.3). However, the Gaussian width of Si 2p spectra can be much smaller in other materials, as it is the case for instance in the $(7 \times 7)$-reconstruction of the Si(111) surface [220]. This peculiar broadness within the SiC system is not understood up until now; yet it can be seen as characteristic for bulk SiC. It is therefore reasonable to assign the narrower component to Si, which is covalently bound to Au on the surface of the SiC.

Stoltz et al. [221] have investigated Au adsorbed on the (0001) surface of 4H-SiC. They report a shift of the Au 4f component towards higher binding energy of 540 meV compared to the metallic Au reference. Also, they report a Si 2p component distribution, which is similar to our case, but with slightly different binding energies. There, they also assign the higher binding energy component to Si in the bulk of the SiC and the lower binding energy component to Si, which is bound to Au on the surface. The differences in binding energy can be caused by the different SiC polytype used here (6H-SiC) and also by the additional graphene layer on top in our case. Both have influence on the band alignment and accompanied surface band bending in the SiC [52, 55], which alters the observed binding energies.

It must be mentioned here that one can compare the intensity ratio of the signal produced by the two chemical Si species to other intercalation systems based on graphene on SiC(0001). The intensity ratio from Si in the bulk SiC and Si bound to Au is 68:32. In the case of H intercalation, the intensity ratio of Si in the bulk SiC to Si bound to H is 63:37 and 67:33 for photon energies 140 eV and 330 eV, respectively [41]. In this case, every Si atom on the surface of the SiC is bound to one H. Keeping in mind that the photon energy in the measurements presented here is 210 eV, it is reasonable to assume that also in the Au case here all Si atoms on the surface are bound to Au.

This information can now be connected to structural information, obtained from LEED. A characteristic diffraction pattern obtained with $\mu$LEED is shown in Fig. 6.1 (c). As could be expected, no spots are discernible, which are characteristic for the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$-SiC(0001) reconstruction. The insertion of the Au breaks the chemical bonds between the graphitic layer and the substrate, which lifts the reconstruction (see paragraph 1.1.3 and refs. [22, 100]). However, three
prominent features can be observed in this diffraction pattern. These consist of intense spots characteristic for (1\times1)-graphene and (1\times1)-SiC(0001) structures. Also, additional spots can be seen around the (0,0) spot, which are on a (13\times13)-graphene grid (see also closeup Fig. 6.1 (c)). These are characteristic for epitaxial graphene on SiC(0001), as they mark the total periodicity of this system. This points towards a well ordered Au subsystem at the interface, as disorder in the interface would suppress these spots. No additional spots are discernible, which can directly be connected to the interfacial Au. One must thereby assume, that this layer is ordered either as a (1\times1)-graphene or a (1\times1)-SiC(0001). Since we have shown by CLS, that the Au is covalently bound to Si, a (1\times1)-SiC(0001) suggests itself. We take now the argument, that the topmost Si of the SiC(0001) surface is covalently bound to three C atoms beneath. Therefore, these Si atoms have only one free bond for Si in the sp$^3$ configuration, respectively. Also including the arguments, that only one chemical species of Au is present and the different Si 2p components have the mentioned characteristic intensity ratio, one must conclude, that every Au atom is bound to only one Si atom. A sketch of this configuration can be found in Fig. 6.1 (d).

In other words, since Si forms a simple triangular lattice on the bare SiC(0001) surface, the Au atoms must also build a simple triangular lattice with the same lattice constant. Compared to the Au(111) surface, the lattice is stretched by about 7%. This structure must firstly be mediated by at least partial covalent bonding of the Au atoms to the topmost Si atoms of the SiC. Yet, as such a structure does not form for Au, which is simply adsorbed on SiC(0001) [221], this structure must be stabilized by the graphene cover. Similar effects were observed for complementary systems, like the oxygen intercalation underneath graphene on Ir(111) [222].

6.1.2 Interface related electronic spectrum

As shown in the previous paragraph, the interfacial Au arranges as a triangular lattice with the lattice constant coinciding with the SiC(0001) surface. The lattice constant of the interfacial triangular Au lattice is 3.08 Å, which is stretched by about 7% compared to Au(111). This is much more densely packed compared to for instance intercalated Gd in the simplified ($\sqrt{3}$$\times$$\sqrt{3}$)R30°-graphene structure,
which is also a simple triangular lattice with a lattice constant of 4.26 Å (see paragraph 4.1.4). Consequently, the configuration in the Au case is generally much more favorable to have significant overlap of the respective atomic orbitals. In the simple picture of tight binding in the sense of linear combination of atomic orbitals (LCAO) [34], the Au system is therefore more favorable for the formation of bands than the Gd case. In the Gd intercalated system no distinct interface related band structure was found (see paragraph 4.1.1). Yet, one can ask, if this is also the case for the Au intercalation.

ARPES measurements were conducted with the aim of identifying such interface related bands. We start with the complete Fermi surface of the system as measured by ARPES in Fig. 6.2 (a). Apart from graphene related pockets around graphene’s \( \bar{K} \) points (\( \bar{K}_{gr} \)), one can identify additional strong spectral weight around the \( \bar{K} \) points of the SiC(0001)’s surface BZ. This BZ is coinciding with the Au-interface BZ and therefore the respective \( \bar{K} \) point is marked as \( \bar{K}_{Au} \). The additional features are absent in any other graphene/SiC(0001) based system. They display a triangular geometry, whereas a distinct contour, defining a pocket structure like in graphene’s \( \pi \) bands, cannot be identified. In order to examine the course of these bands, two spectral cuts are shown in Fig. 6.2 (b), which give the dispersion along the high symmetry directions \( \bar{\Gamma}\bar{K}_{Au}\bar{M}_{Au} \) and \( \bar{\Gamma}\bar{M}_{Au}\bar{\Gamma}' \). The band course from \( \bar{\Gamma} \) towards \( \bar{K}_{Au} \) is very steep. From \( \bar{K}_{Au} \) towards \( \bar{M}_{Au} \), the course is rather flat. At \( \bar{K}_{Au} \) a maximum and at \( \bar{M}_{Au} \) a saddle point is present. No distinct

![Graphene Brillouin zone](image)

**Fig. 6.2:** ARPES on the interface related bands: (a) Complete symmetrized FS. Graphene’s BZ is marked blue. The Au-interface and the coinciding SiC(0001) surface BZ is marked in red. (b) Left: Spectral cut ranging from \( \bar{\Gamma} \) over \( \bar{K}_{Au} \) to \( \bar{M}_{Au} \) showing the Au-interface related bands. Right: spectral cut around \( \bar{M}_{Au} \) perpendicular to the left plot. Nearest neighbor tight binding bands of a simple triangular lattice (see text) are superimposed. The measurements were taken with 95 eV photon energy.
crossing of the Fermi level can be found, which is in line with the missing Fermi surface contour in Fig. 6.2 (a).

It is obvious to associate this structure with the interfacial Au layer. As this layer is arranged as a simple triangular lattice, we compare the observed bands first to a tight binding model on this lattice. The model follows [223]:

\[
E(\vec{k}) = E_0 - 2t \left( \cos(k_x a) + 2 \cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \right),
\]

where \(a\) is the lattice constant and \(t\) the hopping parameter. The corresponding bands with \(a = 3.08\) Å (lattice parameter of the interfacial Au layer) and \(t = 1\) eV is superimposed in Fig. 6.2 (b). It is obvious that the band topology is identical in theory and experiment. Also, the extrema are placed at the same crystal momentum, which proves the right choice of \(a\). Although this model also roughly reproduces the band course, some deviations are present, especially at \(\overline{M}_{Au}\). However, it cannot be expected that the used simplified model is sufficient to describe the experiment. For this, the nature of the involved orbitals have to be taken into account more realistically.

A more realistic model in this sense was utilized by Hsu et al. [224] for this system within density functional theory (adapted in Fig. 6.3 (a)). These simulations show the formation of Au-interface related bands, similar to the ones observed in the experiment. The calculations are built upon an atomic model with the unit cell of a \((\sqrt{3} \times \sqrt{3})R30^\circ\)-SiC(0001) matching a \((2 \times 2)\)-graphene. Therefore, the Au related bands are folded towards \(\Gamma\) and the high symmetry points cannot be directly connected to the experiment. Yet, the band branch going from \(\overline{K}\) towards \(\Gamma\) in the calculations can be compared to the branch going from \(\Gamma\) towards \(\overline{K}_{Au}\) in the experiment. In Fig. 6.3 (b, right) the respective ARPES cut is shown, which was taken with higher resolution than the one in Fig. 6.2 (b). The bands in the simulations appear to just touch the the Fermi level at \(\overline{\Gamma}\), which is in agreement with the experimental bands at \(\overline{K}_{Au}\). As a distinct Fermi contour is missing in this system, one can expect a comparatively low charge carrier density or even a complete filling. This follows directly from Luttinger’s theorem [85], where the free charge carrier density in a crystal is defined by the area enclosed by the Fermi surface compared to the size of the BZ. In the calculations, the Au-interface related bands appear to be strongly spin split, such that they exhibit a Rashba-like spin texture [224]. We do find a strong correspondence to this in the experimental band
structure in Fig. 6.3 (b, right). Away from $K_{Au}$, these bands are unambiguously doubled. The bands in the simulations also appear to hybridize strongly with the graphene related bands between 1 eV and 1.5 eV (marked orange in Fig. 6.3 (a)). We found no indication for strong hybridization at this energy in the experimental graphene related bands, which are plotted in Fig. 6.3 (c). Yet, it has to be pointed out, that the features caused by hybridization in the DFT-simulations could be an artifact produced by the choice of the unit cell (i.e. $(\sqrt{3} \times \sqrt{3})R30^\circ$-SiC(0001) matched to $(2 \times 2)$-graphene).

Finally, we also observe additional bands around $\Gamma$ (see Fig. 6.3 (b, left)). These bands, however, are about a factor of 10 less intense than the previous elaborated bands around $K_{Au}$ and $M_{Au}$. The structure is such that two individual main bands symmetric to $\Gamma$ cross at $\Gamma$. The individual branches, on the other hand, show the same band course than the bands around $K_{Au}$, which is illustrated by the green arrow in Fig. 6.3 (b). This gives an indication, that these bands
around \( \Gamma \) cannot be identified with real bands, but rather with a superposition of replica bands, produced by photoelectron scattering at the graphene lattice. When taking a closer look, one sees that the individual branches are doubled, just like the bands around \( K_{\text{Au}} \) (purple arrows in Fig. 6.3 (b)). This again points towards spin splitting, which is again a strong argument for replica bands in the following considerations. Band crossing without hybridization is generally only allowed, if the different band branches have differing spin (e.g. surface state of topological insulators) or if the branches can be assigned a pseudospin, denoting for example differing orbitals or a special crystal structure (e.g. graphene). Due to the simplicity of the Au-interface’s crystal structure, the presence of a pseudospin is rather unlikely. Also, due to the fact, that these bands are symmetric around \( \Gamma \), one would expect the same orbital character. Therefore, as the single branches themselves are apparently spin split, a crossing at \( \Gamma \) is not allowed with real bands. These bands would have to hybridize, resulting in the well known anti-crossing gap [34], which is not observed in the experiment.

To sum things up, in the n-phase the Au-interface forms bands. The interface bands’ shape and symmetry is reproduced by a simple tight binding model on a simple triangular lattice. DFT simulations in ref. [224] reproduce the band course, the apparent spin splitting and exact binding energies. The BZ of the Au-interface does not coincide with graphene’s BZ and the bands of these two systems do not hybridize strongly. One can state therefore that the Au-interface forms a two-dimensional electron system, which is in first approximation independent of the graphene.

6.1.3

Plasmarons in graphene’s electronic spectrum

As it was shown up to this point, that the interface in this system forms its own two-dimensional electronic structure, the influence on graphene’s electronic properties is investigated here. An ARPES cut through graphene’s \( \overline{K} \) point taken parallel to \( \overline{\Gamma K} \) is shown in Fig. 6.4 (a). The quality of the data allows to determine a certain spectral feature, often observed in monolayer graphene on SiC(0001), namely, a prominent band splitting in a wider range around the Dirac point \( E_D \). This spectral feature was assigned to the formation of a certain type of polaron by Bostwick et al. [58]. This means that due to strong electron-plasmon coupling,
so-called plasmarons as new quasiparticles are formed with a defined lifetime, consisting of coupled electrons and plasmons [50, 58]. Plasmarons are thereby the plasmon pendant to the phonon case, described in paragraphs 1.2 & 4.2.2.

Following the procedure developed by Walter et al. [50], one can directly extract the electron-plasmon coupling constant $\alpha_G$ from the experiment by evaluating the energy splitting. With that it is possible to compare different monolayer graphene-based systems. One can fit the EDC at the $\overline{K}$ point with a sum of two Voigt functions, as it is done in Fig. 6.4 (b) for our data. The energy separation $\Delta E$ of these two Voights is 0.253 eV, whereas the lower binding energy branch is located at $E_0 = 0.686$ eV. It was shown by Walter et al. [50], that $\Delta E$ and $E_0$ scale for a constant coupling constant, thus we can proceed with the ratio of these values as the scaled splitting $\delta E = 0.369$. Comparing to the systems in ref. [50], the value lies between potassium doped fluorine intercalated ZLG and standard MLG on SiC(0001). In ref. [50], the fluorine intercalated samples and the standard MLG samples were doped to an n-type charge carrier density of about
6 × 10^{13} \text{cm}^{-2} \text{ by potassium deposition to introduce a convenient n-doping. This doping level is in fact comparable to the n-phase of Au intercalation here [100]. By further comparison to simulations in ref. [50] (adapted in Fig. 6.4 (c)), one can estimate an } \alpha \text{ of about 0.31 for our system. Interestingly, this value is about a factor of 6 higher than in the p-phase Au intercalated ZLG in ref. [50]. There, the p-phase was again n-doped to about } 6 \times 10^{13} \text{cm}^{-2} \text{ by potassium deposition for the mentioned reason. A strongly differing spectral picture is already apparent, when comparing the bare ARPES cuts of our n-phase (see Fig. 6.4 (a)) and the potassium doped p-phase from ref. [50] (adapted in Fig. 6.4 (d)). While the splitting is very pronounced in the n-phase, it is barely discernible in the p-phase. An orange line is superimposed to the plots in Fig. 6.4 (a) & (d) as a guide to the eye. To sum up the results for the n-phase, CLS experiments in combination with LEED show, that the interfacial Au forms a simple triangular lattice with lattice constant corresponding the SiC(0001) surface. ARPES measurements reveal a well defined two-dimensional band structure related to this Au-interface. The topology of these bands is identical to tight binding bands of a simple triangular lattice, whereas the BZ of this system is defined by the lattice constant of the SiC(0001) surface. This establishes the point, that the interface’s electronic subsystem can be seen as a two-dimensional electron system, which is independent of graphene’s electronic system in first approximation. The interface bands exhibit a strong spin splitting, which is reflected by DFT simulations from Hsu et al. [224]. Due to the missing distinct Fermi surface of the interface’s bands, one can expect a low free charge carrier density, or even a semiconducting behavior. In contrast to the simulations by Hsu et al. [224], graphene’s } \pi \text{ bands and the Au-interface bands do not hybridize strongly. The total system can therefore be interpreted as a van der Waals heterostack [225–229], which is supported by SiC. Further, ARPES measurements on graphene’s } \pi \text{ bands in this system reveal strong coupling to plasmons, such that plasmarons as new coupled electron-plasmon quasiparticles emerge. The comparison to results from literature [50] shows, that the coupling strength is strongly increased compared to the p-phase. The cause of the different coupling strengths will be discussed in section 6.2.1.}
6.2 Dielectric properties of Au-intercalated ZLG

As worked out in the previous paragraph, graphene in the n-phase of Au intercalation shows strongly enhanced electron-plasmon coupling compared to the p-phase case. According to Walter et al. [50] and Lischner et al. [230], the difference in coupling constants are directly related to the dielectric environment experienced by the graphene. This means, an environment, which is more polarizable, screens the interaction and with that decreases the coupling constant. The coupling constants consequently translate into an effective dielectric constant $\epsilon$, as an inherent quantity governing Coulomb interactions in the graphene. $\epsilon$ can be approximated by the relation $\epsilon = e^2 / \alpha G \hbar v_F \sim 2.2 / \alpha G$ and one can estimate the substrate’s contribution $\epsilon_S$ to this by $\epsilon_S \approx 2 \epsilon - 1$ [50]. For the p-phase this yields $\epsilon_S = 87$ [50], whereas for the n-phase, elaborated in the previous paragraph, one obtains about 13. The cause of these differences in this respect must be found in the Au-interface. One can argue here, that the presence of a larger amount of a heavy atom species like Au nearby the graphene in the p-phase [100] increases screening of the charge carriers in the graphene. Yet, in a conservative estimation, an increase in $\epsilon_S$ to less than a factor of two would be plausible. In any case, an increase to about a factor of 6.7 cannot be explained by this. One must assume a general difference in polarizability of the Au-interface in both cases and with that of the respective electronic properties.

6.2.1 Interface band structure in the p-phase

In the scope of finding the origin of the different dielectric properties, it is straightforward to characterize the p-phase and in particular the Au-interface more deeply. Similar to the n-phase, also p-phase Au intercalated samples were prepared following the procedure described in appendix A. In Fig. 6.5 (a) a representative ARPES cut of graphene’s $\pi$ bands at $\bar{K}$ ($\bar{K}_g$) is shown, taken perpendicular to $\overline{\Gamma K}_g$. The characteristic p-type doping [100] is reproduced. Yet, one can see that these bands are modified compared to regular graphene. Around 1.2 eV binding energy, strong renormalizations appear. Following DFT band simulations by Chuang et al. [231], this energy corresponds to the crossing point of graphene and Au-interface related bands. The simulations are adapted in Fig. 6.5 (b), where
Fig. 6.5: ARPES of p-phase Au intercalated ZLG on SiC(0001): (a) Spectral cut through graphene’s $K$ point ($K_{gr}$) perpendicular to the $\Gamma K_{gr}$ direction. The hybridization gaps with Au related states are marked by the green arrows. (b) DFT simulations adapted from ref. [231] of the p-phase Au intercalated ZLG on SiC(0001). Due to the atomic model in these simulations (see text), the high symmetry points in this graph do not coincide with the ones in the other panels. Graphene related bands are marked in purple and Au-interface related bands are plain black. The crossings of graphene and Au-interface related bands are marked green. (c) Spectral cut going from $\Gamma$ towards $M_{gr}$ showing the Au related bands. Superimposed in orange/yellow are sketched bands as guide to the eye. (d) Symmetrized FS of the Au-interface related bands. Graphene’s BZ is marked blue, which is in scale with the Fermi surface. The Fermi surface of the Au-interface related bands marked orange in (c) are also marked orange in this plot. The connection of the orange marked features in (c) and (d) to the orange marked band in (b) is given in the text. (a) was taken with 40 eV and (c) & (d) were taken with 75 eV photon energy.

the crossing of the two band species is marked green. These simulations show that similarly to the n-phase (see paragraph 6.1.2), defined Au-interface related bands are meant to form in the p-phase. One has to note here, that the simulations are built upon an atomic model with the unit cell of a $(\sqrt{3} \times \sqrt{3})R30^\circ$-SiC(0001) matching a $(2 \times 2)$-graphene. The Au related bands are thereby folded towards $\Gamma$, which produces a rather complex band structure and the high symmetry points cannot be directly connected to the experiment. However, indeed distinct bands are present in the experiment, which can conclusively be connected to the simulations. In Fig. 6.5 (c) an ARPES cut ranging from $\Gamma$ towards graphene’s $\overline{M}$ point ($\overline{M}_{gr}$) is shown. Multiple bands emerge, which have a rather complex course.
Three band branches are most prominent in this graph. The band marked orange in the plot exhibits a minimum and the band marked yellow a maximum around $\Gamma$. Going towards $\mathbb{M}_{gr}$, a structure similar to an anti-crossing gap is formed, where the two marked bands would meet. Finally, the Fermi level is crossed by one of these bands. The band, crossing the Fermi level in the experiment, can be associated with the band going from $\mathbb{K}$ towards $\Gamma$ in the simulations (marked orange in Fig. 6.5 (b)). The third band forms a small parabola around $\Gamma$, which is also reflected by the simulations at $\Gamma$. Besides these bands, multiple bands with lower intensity can be distinguished, which cross the Fermi level. The small parabola around $\Gamma$ forms a small electron pocket in the Fermi surface in Fig. 6.5 (d). The less intense bands show as concentric hexagonal pockets around $\Gamma$. Although the data is not complete for the band marked orange in Fig. 6.5 (c), one can assume that a rather large electron pocket centered around $\Gamma$ is formed. This pocket is marked orange as guide to the eye in the FS plot in Fig. 6.5 (d).

Considering the simplest presumptions [34], one must assume a metallic behavior in the interface’s electronic system with multiple conducting channels originating from multiple bands. Well defined closed structures in the Fermi surface imply partial filling of bands. Considering for simplicity only the largest pocket, one can assume a rather large free charge carrier density. This thought originates from a criterion given by Luttinger [85], which states that the area enclosed by the Fermi surface normalized by the size of the BZ is proportional to the filling of a band and thereby to the free charge carrier density associated with this band. Although at the moment the exact structure and chemistry of the interface in the p-phase is not clear, one can put the size of graphene’s BZ as ultimate limit in this system. The ratio of the area enclosed by the Fermi surface and graphene’s BZ is about 1:2. Considering the small or non-existing FS of the interface in the n-phase (see paragraph 6.1.2), a drastically different behavior for the interfaces in the two phases can be expected. The free charge carrier density in the interface for the two phases must be orders of magnitude apart.

Concluding this paragraph, we have shown, that in the p-phase a defined two-dimensional electron system is formed by the Au-interface similarly to the n-phase (see paragraph 6.1.2). This is in agreement with theory [231]. These bands strongly hybridize with graphene’s $\pi$ bands, which is in contrast to the n-phase. Also in contrast to the n-phase, this subsystem is very likely to exhibit a metallic behavior with a considerably large free charge carrier density.
6.2.2 Interpretation of the dielectric properties

As we have shown until now, besides the different doping levels induced in the respective graphene, both phases of Au intercalation strongly differ in two main aspects. Firstly, the two systems are influenced by strongly differing dielectric environments (see paragraph 6.1.3). As all other experimental parameters are comparable, this must be associated with differences in the Au-interface. Secondly, although the Au-interface in both cases forms a defined two-dimensional band structure, the interface in the n-phase is rather semiconducting to insulating (see paragraph 6.1.2) whereas it is metallic in the p-phase (see paragraph 6.2.1). The different electronic structures of these phases are sketched in Fig. 6.6. It is now straightforward to connect these observations. As the Au-interface layer is nearby the graphene in both cases, Coulomb interactions within the graphene could be screened by free charge carriers in the neighboring layer [232]. This stems from the differing polarizability of an insulator and a metal. Consequently, electron-electron interaction by Coulomb forces in the respective graphene subsystem is more efficiently screened by the respective Au-interface subsystem in the p-phase than in the n-phase. Differing electron-electron interaction, on the other hand, is key for differing electron-plasmon coupling constants and with that the effective dielectric constants [50, 230], extracted in paragraph 6.1.3.

Fig. 6.6: Band structure of the two phases of Au intercalated ZLG on SiC(0001), sketched with tight binding bands. The respective band structures are cut at the Fermi level.
6.3 Conclusion for Au intercalated ZLG

Concluding this chapter, we have thoroughly investigated the two phases of Au intercalation in ZLG on SiC(0001). In both phases, the Au-interface forms a defined two-dimensional band structure. From ARPES experiments one expects a rather semiconducting to insulating behavior in the n-phase and metallic behavior in the p-phase (see paragraphs 6.1.2 & 6.2.1). The electronic system of the Au-interface subsystem can be viewed as an independent electronic system in first approximation. The interface subsystems themselves are in the tradition of the extensively studied metal adsorbate on semiconductor systems [233–242]. Yet, combining this with graphene on top brings a new dimension to both, graphene and the metal adsorbate system. In this view, the Au intercalated systems forge ahead into the field of Van der Waals heterostacks [225–229]. We could thereby show for the first time, that such a system can be produced by the technique intercalation on SiC(0001). Further, we could show that the graphene in the two phases is characterized by strongly differing electron-plasmon coupling strengths as a consequence of their differing dielectric environments (see paragraph 6.1.3). This could be connected to the differing nature of the Au-interface, i.e. semiconducting/insulating and metallic. Our studies thereby also worked out a general aspect to these Van der Waals heterostacks.
Experimental outlook

The experimental results obtained in this thesis give deeper insight in substantial properties of graphene. Yet, at the same time, these results open up further possibilities. In this chapter, a collection of ideas and substantial questions will be listed in this respect.

**eVHs in graphene with different dielectric environment**  It is interesting to compare graphene with very high doping levels on different substrates. Fedorov et al. [68] for instance have shown, that doping levels, which are comparable to Gd intercalated ZLG on SiC(0001), can be achieved in graphene on Ni(111) thin films on W(110) crystals by Ca intercalation. Interestingly, in this case, the eVHs regime was not reached. As the eVHs is steered by electron-electron interaction (see paragraph 4.2.1), one can speculate, that interactions within the electronic system are damped by the metal compared to the semiconducting SiC as substrates. These differences might therefore be triggered by screening of the interaction within the graphene by free electrons in the metal near by. The argumentation is thus similar to the one made for electron-plasmon coupling in Au intercalated graphene on SiC(0001) (see paragraph 6.2.2). In fact, as it was shown theoretically by Rösner et al. [232], the realistic Coulomb interactions in graphene can be drastically decreased by the dielectric environment. In order to tackle this question experimentally, the eVHs state in Gd intercalated ZLG could be manipulated for instance by depositing material onto these samples. A controlled ARPES
Experiment could be conducted with these Gd intercalated samples, where metallic layers are deposited on top. In order to not alter the doping level significantly, a material would have to be chosen with low doping efficiency with respect to the graphene. For technical reasons, these ARPES experiments have to be conducted with photon energies in the hundreds of electron volts. At these photon energies, the kinetic energy of the photoelectrons is high enough to have a suitable mean free path. For the LaAlO$_3$/SrTiO$_3$ interface with its 18 Å deep buried electron system, this was shown by Cancellieri et al. [174].

Electron-phonon coupling in monolayer graphene The intercalation of Gd in the ZLG system proved that electron-phonon coupling can be drastically enhanced by coupling to lower energy phonons without occupying additional interlayer states (see paragraph 4.2.2). Up until now, it was believed, that this is a crucial criterion to achieve this enhancement in graphite intercalation compounds [162, 243] and also Li decorated monolayer graphene [158]. The enhanced coupling is also most probably responsible for emergent superconductivity in these systems [157, 160, 244]. Our results thus at least partially question this to be the ultimate explanation for the observed phenomena. Building up on this view, it would be crucial to unambiguously identify the evolved phonon modes in order to find the exact microscopic mechanism steering this. A possibility to do so is by conducting high resolution electron energy loss spectroscopy (HREELS), which gives the possibility to extract the phononic spectral function [245]. The involved phonon modes should then be easily identified by exhibiting Kohn anomalies [67, 168, 246], as dips in the phonon dispersion produced by electron-phonon coupling. In this scope it might also be interesting to alter the doping level of the samples and therewith the size and shape of the Fermi surface. This could be done by the Gd-Au hybrid-intercalation described later in this chapter. The crystal-momentum of the involved phonon modes should then be altered, as scattering between different Fermi surface sections is modified [151].

Altering the Gd structure by exposing the samples to air Gd intercalated ZLG or MLG on SiC(0001) samples suffer degeneration, when exposed directly to air. The induced changes are very distinct and can be tracked by CLS, LEED and ARPES. Changes can be followed by the ARPES series in Fig. 7.1. After exposure, graphene bands emerge, that only show very slight n-doping for
Fig. 7.1: ARPES study of Gd intercalated samples exposed to air: (a) and (b) ARPES cuts through the K point taken perpendicular to ΓK for Gd intercalated ZLG and MLG, respectively. The series shows measurements for in situ prepared samples, after exposing them to air and flashing them again within UHV. The last panel in (a) shows an ARPES cut in KM direction. The middle panel in (b) is accompanied by tight binding bands.

both the ZLG and MLG case. In both cases, $E_D$ is shifted by about 0.5 eV with respect to the Fermi level. In the MLG case, the picture is very similar to standard BLG on SiC(0001) with an interlayer coupling on the order of 0.4 eV (see band sketch in Fig. 7.1 (b)). The mentioned degeneration processes appear to take place on a time scale of seconds and minutes for the ZLG and MLG case, respectively. This, however, is intuitive, as in the MLG case an additional protection layer is present. The whole process can, however, be reversed to some extent. When heating the samples to about 1200 °C for the ZLG and 1300 °C in the MLG case for about 5 s (flashing), strongly doped bands start to appear again. In the ZLG case, the eVHs regime (see also chapter 4) is reached again (see Fig. 7.1 (a) last panel), which points towards a similar doping level than before air exposure. Similarly, in the MLG case the bands again resemble bilayer graphene with reduced interlayer coupling (see paragraph 5.2).

Judging from CLS measurements, the degeneration is accompanied with the ap-
pearance of a strong O 1s signal (see Fig. 7.2 (a)). This signal persists for outgasing

to 900 °C, which is a sign that the oxygen is not adsorbed on the graphene. It is reasonable to assume, that oxygen or water migrates beneath the graphene layer during air exposure in this system, oxidizing the Gd and thereby reducing the doping efficiency with respect to the graphene, similarly to the observations made for Yb intercalated MLG [98]. After flashing, a shift in binding energy of the O 1s of 0.5 eV is observed (see Fig. 7.2 (a)). Yet, the intensity of the O 1s and therefore the amount of oxygen, is only slightly altered. Besides these observations, also a new (2×2)-SiC(0001) structure in LEED can be determined (see Fig. 7.2 (b)), which is distinct from all other observed structures in the Gd intercalated systems (see paragraph 4.1.4). It is therefore reasonable to assume, that the topmost Si of the SiC, the Gd and the oxygen build up a structure, which still induces extremely high doping levels in the graphene.

These findings give the opportunity to examine the properties of the Gd intercalated samples by altering the structure/chemistry of the intercalant. Thus, it might be possible to further separate doping/asymmetry potential induced effects from effects induced by the structure/chemistry of the intercalant. This may then lead to even greater insight in the phenomena observed in chapters 4 & 5.

**Further examining layer decoupling by asymmetry in bilayer graphene**

In the scope of asymmetry potential driven decrease of interlayer coupling in bilayer graphene, further investigations are desirable. An interesting starting point would be tuning the asymmetry to a further extent than shown in paragraph 5.2.2, especially towards lower asymmetry. Although the simulations by
Wang et al. [206] point towards a smooth decrease of interlayer coupling with asymmetry, their model might not be accurate enough. These simulations, pointing towards intralayer charge redistribution, are based on single particle models. Yet, correlation effects could strongly affect the physics involved, as especially onsite Coulomb repulsion of the electrons involved might compete with intralayer charge redistribution [195, 197, 198] at realistic Coulomb repulsion strengths [247]. For this reason, a full series of asymmetry dependent ARPES measurements, like described in paragraph 5.2.2, has to be made. This should be done preferably at cryogenic temperatures, as the mentioned mechanisms could drive phase transitions to interesting ground states, like charge ordering.

Utilizing quasiparticle dynamics in bilayer graphene  Besides the similarities to standard MLG on SiC(0001), the lower doped branch in Gd intercalated MLG exhibits severe differences in quasiparticle dynamics, as shown in paragraph 5.6. The apparent blocking of Auger and/or plasmonic processes in the Gd intercalated samples could lead to drastic advantages. The quasiparticle dynamics determined by ARPES translates directly to the thermalization dynamics of the system excited for instance by light pulses [248]. In other words, the lifetime of electrons in the respective states is increased and therefore relaxation is slowed down, when the mentioned processes are blocked. It was shown in time-resolved ARPES experiments, that for H intercalated ZLG on SiC(0001), a short lived population inversion can be achieved [249]. A major limiting factor for the timescale of the population inversion are Auger processes. Therefore, the timescale for population inversion could be further enhanced in the Gd intercalated MLG system, as further thermalization channels are blocked. Population inversion is a basic physical necessity for stimulated emission in the construction of a laser. The energy of the stimulated photons would then correspond to the bandgap in the Gd intercalated samples, which is about 150 meV. This is in the highly desired THz regime [250–252], therefore examining the Gd intercalated samples in this scope would be desirable.

Technical application of the differing dielectric properties in the Au intercalation  The strongly differing dielectric environments of the p-phase compared to the n-phase in Au intercalation (discussed in chapter 6) brings many opportunities. One ansatz could be the controlled combination of both phases
in a nano-structured device. The technical possibility for this was shown for the case of Ge [24], where similarly to the Au case two differently doped intercalation phases were found [23]. Arrays of patterned junctions with different dielectric properties could be produced with Au intercalation. The spatially altering coupling of $\pi$-electrons in graphene to plasmons [50, 253] could bring the opportunity for applications in plasmonics and optoelectronics [213, 254–258].

Examining the Au intercalated ZLG in the scope of a VdW heterobilayer As mentioned previously, VdW heterostructures are at the forefront of recent research in the scope of possible applications and also on a basic research level [225]. The interesting aspect in the n-phase Au intercalated graphene system is the combination of a conducting and a presumably semiconducting layer (see section 6.1.2). Such a combination of two-dimensional materials put into prospect applications like light-emitting diodes [259] and also efficient light detection for ultra thin films [260]. Further, many ground breaking discoveries were made in similar systems. The combination of graphene and hexagonal boron nitride led to a massive increase of graphene’s performance, i.e. mobility and carrier homogeneity [261]. Also, the introduction of a superlattice on the graphene in this system led to the first observation of the long sought Hofstadter butterfly pattern in magnetotransport measurements [262–264]. A peculiarity in the n-phase Au intercalated graphene is also the strong spin splitting of the interface bands, which is suggested by the measurements and theory [224]. A considerable spin splitting might therewith be induced in graphene’s $\pi$ bands due to a proximity effect, as it was shown for the graphene tungsten disulfide heterostack [265].

In the p-phase, the combination of two metallic layers stands out (see section 6.2.1). In contrast to the mutual screening (see chapter 6), the charge carriers in the two layers can also directly interact by Coulomb forces and move synchronously through the layers (see sketch in Fig. 7.3). This phenomenon, also called Coulomb drag [266–268], can thus lead to ordered ground states like superconducting or excitonic insulating condensates [269–271].

It would be desirable to conduct additional experiments in this scope on such samples, such as electronic transport. For this, the substrate SiC provides an excellent playground due to its semiconducting nature. Furthermore, the production of such samples is well controllable on a larger scale compared to other methods, where for instance different layers are manually stacked upon each other.
Gd-Au hybrid intercalation  In the course of finding the Gd intercalation parameters for the ZLG it appeared, that the interface between the graphitic layer and the SiC can be filled up continuously. The intercalated material itself presumably is disordered or forms nano-islands at incomplete intercalation stages (see appendix B). With this finding, the question arose, if such an incomplete intercalation state can be filled up by a different material. For this reason, such an incompletely intercalated sample was prepared with a gradient in Gd amount on a length scale of about 8 mm. There, all stages described in appendix B were found spread over the sample. Subsequently, the sample was treated like described in appendix A in order to intercalate Au. Afterwards, ARPES measurements showed a mixture of two differently doped graphene phases (see Fig. 7.4 (a)). Further annealing to 1000 °C, however, changed the picture drastically to only single phases at the respective positions on the sample. The doping level on the other hand varied, following the initial Gd gradient. A series of ARPES cuts at these different positions on the sample can be found in Fig. 7.4 (b). Apparently, at these preparation conditions, the Gd and the Au mix at the interface and one can produce graphene with varying doping level. Furthermore, also these mixed intercalation phases build up bands corresponding to the Au-interface related bands in the sole Au intercalated n-phase (see paragraph 6.1.2), whereas these bands are also shifted towards higher binding energy (compare Fig. 7.4 (c) & (d)).

These findings bring the opportunity to explore graphene’s properties all the way from very low doping levels to the eVHs regime with measurement techniques that are not compatible with UHV conditions. In the special case of Au intercalation, the same argument holds for the Au-interface related bands. Furthermore, replacing the Au with other intercalants is thinkable to even achieve a greater versatility.
Fig. 7.4: ARPES on Au-Gd hybrid-intercalated ZLG on SiC(0001): (a) ARPES cut through graphene’s K point taken perpendicular to the ΓK direction of a ZLG sample intercalated with both Gd and Au before further heating to 1000 °C (see test). (b) ARPES series of Gd and Au intercalated ZLG after heating to 1000 °C with different Au/Gd ratios. (c) & (d) ARPES on the Au-related bands of Au-only and Gd-Au hybrid intercalation samples, respectively.
In the mid 2000s, first targeted experiments on the quasi two-dimensional crystal graphene led to a whole new branch within solid state research. In the following decade, much effort was put on characterizing and modifying the extraordinary properties of this material. Especially the fact that graphene’s electronic low-energy excitations at low doping levels resemble the behavior of massless Dirac Fermions [31] was meant to be a key for achieving possible technical applications. Despite this, new paths are still opened up for this material. In the view of basic research, unusual conditions like for example extremely high doping levels are interesting. Many ideas aim directly on many-body effects like strong electron-electron interaction or electron-phonon coupling, which could lead to interesting ordered ground states. Especially the Van Hove singularity (VHs) in the density of states, which is associated with the saddle point at \( \overline{M} \) in graphene’s dispersion, should be reached at the Fermi level. At these conditions, graphene is predicted to exhibit exotic properties, like unconventional chiral superconductivity [90, 91]. 

The main part of the presented thesis deals with the controlled modification of graphene to introduce ultra high n-doping and explore graphene’s properties therein. The technique intercalation in epitaxial graphene on SiC(0001), produced by thermal decomposition of the SiC [27], was used for producing such samples within this work. Here, intercalation can be seen as the controlled insertion of foreign atom species between the graphene and its substrate. Among others, the intercalant serves there as a dopant for the graphene. Besides the production of such samples, the characterization by means of classical surface science techniques like core-level spectroscopy (CLS), low-energy electron diffraction (LEED)
and microscopy (LEEM), photoemission electron microscopy (PEEM) and X-ray magnetic circular dicroism (XMCD) was essential. Yet, the most important point was the characterization of the low-energy electronic band structure by means of angle-resolved photoelectron spectroscopy (ARPES). Furthermore, a characterization of the transport behavior by means of magnetotransport was conducted. Within this thesis, three main aspects/achievements stand out: By the intercalation of gadolinium in the system zerolayer graphene on SiC(0001) (ZLG), highly doped monolayer graphene could be produced (see chapter 4). In this system, the growth stage of one epitaxial graphitic layer on SiC(0001) is generally named ZLG. The introduced charge carrier density of $4.5 \times 10^{14} \text{ cm}^{-2}$ was sufficient for reaching the mentioned VHs at the Fermi level. As determined by ARPES, reaching the VHs regime was accompanied with strong renormalizations of the electronic spectrum, such that parts of the dispersion were squeezed to a flat band at the Fermi level. Theoretical models gave evidence, that this is driven by strong correlations in the electronic system, being a universal property of graphene. Apart from the extremely strong doping efficiency, Gd exhibited a special case among other intercalants. Combining results obtained with LEED and CLS led to the insight, that the Gd arranged with both, the SiC substrate and the graphene, resulting in an exceptionally large $(13\sqrt{3} \times 13\sqrt{3})R30^\circ$-graphene superstructure. A detailed analysis of the ARPES data in the scope of electron-phonon coupling brought the insight, that coupling constants were strongly enhanced in this system. On the one hand, the spectral function determined by ARPES showed signs of the formation of polarons as new quasiparticles, consisting of coupled electrons and high-energy phonons. This appeared to be connected to the eVHs state, which can be viewed as an effect intrinsic to graphene. On the other hand, resonant coupling to additional low-energy phonon modes was observed. This appeared to be connected to the ordered Gd adlayer as an extrinsic effect. Interestingly, coupling to such low-energy phonon modes in related graphitic materials like graphite intercalation compounds was accompanied by the occupation of a so-called interlayer band. Theoretical models connected these two phenomena [160, 162], as additional resonant phonon-driven interband scattering paths of the electrons would be opened up. However, no such interlayer state is occupied in the Gd case according to ARPES. Therefore, this mechanism could be excluded for this system, which challenges the universality of the mentioned theoretical picture. In order to provide information on a possible ordered magnetic ground
state, XMCD experiments were carried out. However, ferromagnetism could be excluded down to 1.6 K. LEEM provided proof for a superb homogeneity on a mesoscopic scale. Having brought graphene into the eVHs regime by intercalation produces samples, which are comparatively stable. The homogeneity and stability brought the possibility to characterize graphene in this regime with techniques not compatible with UHV conditions like magnetotransport at mK temperatures.

By the intercalation of gadolinium in the system monolayer graphene on SiC(0001) (MLG), highly doped AB-stacked bilayer graphene could be produced (see chapter 5). In this system, the growth stage of two epitaxial graphitic layers on SiC(0001), i.e. one additional graphitic layer compared to the ZLG stage, is generally named MLG. It was shown in a systematic study, that no Gd was in between the graphene sheets. Despite the similarities to Gd intercalated ZLG, observed by ARPES, the eVHs state was not built up in Gd intercalated MLG. This points towards a general discrepancy between monolayer and bilayer graphene in terms of electron-electron interaction. As a consequence of the intercalation geometry a strongly asymmetric charge carrier density for the two graphitic layers was introduced. Inherent for AB-stacked bilayer graphene, a band gap is developed between the valence and conduction bands under this condition. Yet, well targeted ARPES experiments and their detailed analysis proved that this band gap was strongly reduced, compared to expectations derived from a tight binding model. DFT simulations [206], however, supported the conclusion, that the two layers get decoupled at this strong charge carrier asymmetry. The strongly asymmetric charge carrier distribution between the layers results in a charge density rearrangement within the layers. The accompanying additional dipole moment reduces effectively the interlayer interaction, which in turn is a quantity responsible for the band gap formation in this case. As a further consequence of this layer-asymmetric charge distribution, the bilayer may better be viewed as two separate but strongly interacting systems. Both layers could be distinguished by a differing C 1s signal in CLS experiments. The different C 1s signal on the other hand could be assigned to different electronic bands and therewith to different electronic subsystems. Therefore, both layers could be assigned different yet interacting electronic subsystems. Contrary to this, in bilayer graphene without charge carrier asymmetry, both layers share the same valence electronic system as they are indistinguishable. Such an effect was not reported thus far in literature to our knowledge. Furthermore, these experiments revealed general characteris-
tics of bilayer graphene and led to the reinterpretation of experimental results obtained for related intercalation systems in literature [98, 107, 191–193]. As the mentioned band gap is of great importance for a possible application in a transistor setup, the results reported in this thesis have to be considered in the construction of such electronic components.

Finally, the two phases of gold intercalation in ZLG on SiC(0001) were reexamined (see chapter 6). As described by Gierz et al. [100], a phase where the graphene is n-doped and a phase where the graphene is p-doped is built up, depending on the amount of intercalated Au. Here, it was found that in both phases, the interfacial Au-layer forms a defined two-dimensional band structure. The electronic system of the Au-interface subsystems can be viewed as independent electronic systems with respect to the graphene in first approximation. ARPES measurements suggest a rather semiconducting/insulating behavior of the Au-interface in the n-phase and metallic behavior in the p-phase. The interface subsystems themselves are in the tradition of the extensively studied metal adsorbate on semiconductor systems [233–242]. Yet, combining this with graphene on top brings a new dimension to both, graphene and the metal adsorbate system. In this view, the Au intercalated systems could be viewed as Van der Waals heterostacks [225–229]. We could thereby show that such a system can be produced by the technique intercalation on SiC(0001), which brought this technique onto a different level. Further, we could show by comparison to literature [50] that the graphene in the two phases is characterized by strongly differing electron-plasmon coupling strengths as a consequence of their dielectric environment. This can be connected to the differing nature of the Au-interface, i.e. semiconducting/insulating versus metallic. In this manner, our studies worked out a general aspect to the interaction of different layers in such Van der Waals heterostacks.

Vornehmlich sollte die Van-Hove-Singularität (VHS) in der Zustandsdichte, welche mit dem Sattelpunkt am M-Punkt der Dispersionsrelation von Graphen einhergeht, am Fermineiveau erreicht werden. Es wurde theoretisch gezeigt, dass Graphen dabei einen unkonventionellen supraleitenden Zustand ausbilden könnte [90, 91]. Ein Großteil der vorgestellten Arbeit beschäftigt sich mit der kontrollierten Modifizierung von Graphen, sodass eine ultra-hohe n-Dotierung erreicht wird um daraufhin die Eigenschaften von Graphen unter diesen Bedingungen genauer erforschen zu können. Im Fokus lag dabei die Technik der Interkalation im System epitaktischen Graphens auf SiC(0001), welches durch thermische Dekomposition des SiC-Substrats hergestellt wurde [27]. Interkalation kann in diesem
Zusammenfassung

Fall als die gezielte Einbringung von Fremdatomen zwischen dem Graphen und seinem Substrat erachtet werden. Diese Fremdatome fungieren dabei unter anderem als Dotieratome. Neben der Herstellung solcher Proben war die Charakterisierung mit klassischen Oberflächenphysiktechniken wie Atomrumpfniveauspektroskopie (CLS), Beugung langsamer Elektronen (LEED) und deren Mikroskopie (LEEM), Photoemissionselektronenmikroskopie (PEEM) und zirkularem magnetischen Röntgendiff röismus (XMCD) ein wichtiger Bestandteil. Das Hauptaugenmerk wurde jedoch auf die Charakterisierung der niedrigerenergetischen elektro nischen Struktur mit Hilfe von winkelaufgelöster Photoelektronenspektroskopie (ARPES) gelegt. Außerdem wurden die elektronischen Transporteigenschaften untersucht.

Die vorliegende Arbeit kann in drei Hauptaspekte unterteilt werden:

Durch die Interkalation von Gadolinium unter das sogenannte Nulllagengraphen (von engl. *zero-layer graphene*) auf SiC(0001) (ZLG) konnten Monolagengraphen mit einem extrem hohen Dotierungsniveau hergestellt werden (siehe Kapitel 4). In diesem System wird die Wachstumsstufe der ersten graphenartigen Lage auf SiC(0001) als ZLG bezeichnet. Die durch das Gd eingebrachte Ladungsträgerdichte von $4.5 \times 10^{14}$ cm$^{-2}$ war dabei ausreichend, um die erwähnte VHS am Fermineiveau zu erreichen. ARPES-Messungen zeigten, dass das Erreichen des VHS-Regimes mit starken Renormalisierungseffekten der elektronischen Bandstruktur verbunden war, sodass Teile der Dispersion zu einem flachen Band nahe des Fermineiveaus zusammengestaucht wurde. Theoretische Modelle brachten dabei die Erkenntnis, dass dieser Effekt durch starke Elektron-Elektron-Wechselwirkungen erzeugt wird und eine allgemeine Eigenschaft von Graphen darstellt. Abgesehen von der im Graphen eingebrachten herausragend starken Dotierung stellte Gd als Interkalan t einen sehr speziellen Fall dar. Die Kombination von Erkenntnissen aus CLS- und LEED-Messungen legten nahe, dass das interkalierte Gd teilweise kovalent an das SiC-Substrat bindet, sich jedoch auch nach der Graphenstruktur ausrichtet, sodass eine außerordentlich große $13\sqrt{3} \times 13\sqrt{3}$R$30^\circ$-Graphen Überstruktur ausgebildet wird. Die detaillierte Auswertung der ARPES-Messungen an diesem System zeigte, dass Elektron-Phonon-Kopplungskonstanten stark erhöht waren. Einerseits zeigte die elektronische Spektralfunktion eine verstärkte Kopplung zu höherenergetische Phononen, sodass Anzeichen für die Ausbildung von Polaronen, als kohärent gekoppelte Elektron-Phonon-Quasiteilchen, gefunden wurden. Dies schien mit der eVHS verbunden zu sein, was als ein dem

Durch die Interkalation von Gadolinium unter epitaktisches Monolagengraphen auf SiC(0001) (MLG) konnte Bilagengraphen mit einem extrem hohen Dotierungsniveau hergestellt werden (siehe Kapitel 5). In diesem System wird die Wachstumsstufe zweier graphenartiger Lagen auf SiC(0001), d. h. eine zusätzliche epitaktische Graphenschicht im Vergleich zur ZLG, als MLG bezeichnet. Mit Hilfe einer systematischen ARPES-Studie wurde gezeigt, dass sich kein Gd zwischen den Graphenlagen befand. Trotz der spektralen Ähnlichkeiten in ARPES zu Gd interkaliertem ZLG, wurde hier die eVHS nicht ausgebildet, was auf eine generelle Diskrepanz zwischen Monolagen- und Bilagengraphen in Bezug auf Elektron-Elektron-Wechselwirkung hindeutet. Als Folge der atomaren Geometrie bei der

Im dritten Hauptteil wurde die Interkalation von Gold in das ZLG-System tiefer untersucht (siehe Kapitel 6). Wie schon früher gezeigt, werden zwei unterschiedliche Interkalationsphasen ausgebildet, welche sich durch unterschiedliche Mengen an interkaliertem Au und durch n- und p-Dotierung im Graphensystem auszeichnen [100]. Es wurde in der vorliegenden Arbeit gezeigt, dass die interkalierte
Appendices
Intercalation procedure of Au in the ZLG and MLG system

In contrast to the procedure described by Gierz et al. [100], a different approach to intercalation was pursued here, which drastically increased the quality of the intercalated samples. The exact procedure was developed by Dr. Stiven Forti. Instead of depositing the material to be intercalated in UHV with the sample kept at room temperature (RT), as it was done previously [100], we deposited it on the hot sample. The differences in these two intercalation procedures can be followed by the chart in Fig. A.1. After depositing the material to be intercalated (here Au with a standard Knudsen cell) at RT, a thin film is formed on top of the sample. To carry out the intercalation, the samples have to be heated up to about 700 °C. During heating, a part of the Au intercalates and a part clusterizes on top of the samples, which produces stable droplets [100]. These droplets represent scattering centers, which drastically reduce the quality of the data, obtained by the measurements conducted. For instance, it can broaden spectral features observed in ARPES and produce a strong background or even additional bands, which makes interpretations difficult. This is especially important, considering the conclusions made in chapter 6. In many cases, as it is also the case for Au, the intercalated configuration is less stable, than the clusters. This leads to the fact, that at further heating deintercalation takes place before the clusters evaporate. This clusterization, however, can be avoided, by deposition onto a heated sample
Fig. A.1: Illustration of the two intercalation procedures: (Top) Room temperature intercalation procedure. (Bottom) High temperature intercalation procedure.

(about 700 °C). There, the evaporated material intercalates before clusterization could take place. This procedure is successful for the ZLG as well as the MLG system on SiC(0001). The preparation of the different Au intercalation phases is then well controllable by the sample temperature as well as the deposited amount, in agreement with the previous procedure described in ref. [100].
Intercalation procedure of Gd in the ZLG and MLG system

In order to find the right conditions for intercalating Gd in ZLG and MLG on SiC(0001) systems a systematic approach was pursued. In this special case, it turned out, that intercalation does not take place at all, when depositing Gd at RT with subsequent annealing, in contrast to the Au case [100]. Gd clusterizes, as determined by AFM measurements (not shown), and a significant part also oxidizes during deposition at a pressure of about $5 \times 10^{-9}$ mbar, as determined by CLS (not shown). When depositing at about 800 °C sample temperature, the material intercalates immediately (see also appendix A). No clusterization or oxidation takes place. Also, in contrast to the Au case the parameters temperature and deposited amount have to be met very precisely. In this case, an e-beam evaporator was used, as the deposited amount can be controlled more precisely compared to Knudsen cells, commonly used. Yet, controlling the amount by calibrating the source and depositing an amount commonly needed for intercalation in other materials ($\frac{1}{3}$ or 1 ML for Au [100], 5 ML in the Ge case [23]) lacks in precision. Thus, the necessary amount was determined by an empirical approach. The amount of Gd deposited was regulated by the deposition time and systematically increased until the optimum result was reached (determined by LEED, CLS and ARPES). In Fig. B.1 (Top) a sequence, dependent on the deposition time, is shown.
Fig. B.1: Different stages of Gd intercalation in the ZLG system: (Top) LEED and ARPES measurement series with varying intercalated amount of Gd. The amount is proportional to the time of deposition. (Bottom) Two different stages after the flashing procedure. The ARPES measurements were done with He II radiation and the LEED measurements at 67.5 eV electron energy. The sketches represent the sample surface before and after the flashing procedure for an incomplete and complete intercalation stage.

It is clearly visible in this series, that bands in ARPES and accompanied $(1 \times 1)$-graphene spots in LEED appear at 15 min deposition time, corresponding to about $\frac{1}{3}$ needed for complete intercalation. The bands and the diffraction spots get more intense and sharper, when increasing the deposition time. This trend is followed until a deposition time of about 40 min is reached, which corresponds to about 0.75-0.8 ML of Gd deposited (determined with a quartz crystal balance). Going beyond this point, the bands strongly increase in width and the diffraction
spots decrease in intensity. It is obvious in the ARPES series, that not only the band width and intensity changes with deposited amount, but also the shape itself. When looking at the second ARPES cut, a clear elongation at the Dirac point is visible, that decreases with deposition time. The elongation at the Dirac point resembles that of graphene’s $\pi$ bands with a band gap on the order of 1 eV, yet intensity is evident within the gap. Such effects are, however, common for strongly distorted graphene [272–278]. We thus conclude, that the intercalated Gd does not form a stable ordered configuration at these preparation conditions. It has to be noted, that none of these stages show the distinct $(13\sqrt{3} \times 13\sqrt{3})R30^\circ$-graphene diffraction pattern, discussed in paragraph 4.1.4. To achieve this, another step has to be executed. The samples were shortly heated (flashed, about 5 s) up to 1250 °C, subsequent to the prior mentioned procedure. This temperature has to be met very precisely, as ±50 °C gives a noticeably inferior result and the superstructure does not develop. After this step, the bands in ARPES as well as the $(1 \times 1)$-graphene spots get much more intense and narrower (see Fig. B.1 (Bottom)). The Flashing procedure also yields sharper and more intense bands and $(1 \times 1)$-graphene spots, when executed at a stage with less Gd intercalated (also in Fig. B.1 (Bottom)). Yet, an elongation at the Dirac point and distinct $(13 \times 13)$-graphene spots in LEED remain and also the $(13\sqrt{3} \times 13\sqrt{3})R30^\circ$-graphene spots do not appear. Our interpretation of this behavior is as follows (see also sketches in the inset of Fig. B.1): The Gd can be incorporated between the graphitic layer and the SiC at about 800 °C, yet it remains disordered and thus the interface can be filled up continuously. A similar behavior was found for the intercalation of Li in graphene on Ir(111) [112, 279, 280]. Flashing forces the intercalated material to cumulate and form nano-islands at the interface in a non-fully intercalated stage. This introduces the remaining elongation. When flashing the completely intercalated stage, the Gd is forced into a long range order with the complete area being intercalated.

The intercalation procedure for MLG on SiC(0001) builds upon the knowledge gained in the ZLG case, yet it had to be slightly refined. Intercalation was carried out at about 900 °C, whereas the amount needed for intercalation was comparable with the ZLG case. The most important difference, however, had to be made in the flashing procedure. The optimum result was achieved by flashing to temperatures of about 1300 °C. Reaching this temperature, the system is very stable. No differences can be determined in ARPES and LEED after heating the samples
up to 1400 °C. A consequence of this increased flashing temperature shows in the fact that the \( (13\sqrt{3} \times 13\sqrt{3})R30^\circ \)-graphene spots in LEED, characteristic for the ZLG case, could not be determined in the MLG case.
Self energy extraction

The procedure of extracting the bare band $\epsilon_b(k)$ and the self energy $\Sigma(E)$ from the spectral function determined by ARPES was adapted from the procedure developed by Pletikosić et al. [66]. It is based on a self consistent recursive approach and is strictly only valid for bands crossing the Fermi level with low to medium many-body renormalizations. From the experimental spectral distribution, one firstly has to determine the spectral width $w_m$ and the band position $k_m$ in terms of momentum by fitting Lorentzian functions to the respective MDCs indexed with $m$ in the examined energy window. The course of the subsequent procedure can be followed by the chart in Fig. C.1 [66]. In order to execute the procedure, one has to start by making an initial guess $E_b(k)$ for the bare band. Utilizing $w_m$
and \( k_m \), a first attempt to \( \Im \Sigma(E_m) \) is extracted for all MDCs \( m \). The used Eq. (a) in the chart is thereby valid for the mentioned low to medium strong many-body renormalizations \[281\]. As it was already pointed out in paragraph 1.2, the real and imaginary part of the self energy are connected by Kramer-Kronig transformation. This is used here to extract \( \Re \Sigma(E_m) \) in a self consistent way from \( \Im \Sigma(E_m) \). As the real part of the self energy denotes to the energy renormalization, a new bare band \( E_b(k_m)' \) can be calculated by using Eq. (b) in the chart \[281\]. This new \( E_b(k_m)' \) can subsequently serve as a new guess for the algorithm. As experimental data suffers from statistical noise, it is beneficial for numerical reasons to not directly use this \( E_b(k_m)' \) further, but use a function \( E_b(k)' \) obtained for instance by a polynomial fit. After few iteration steps (<10) for this procedure, the polynomial fit parameters converge and a decent approximation for the self energy and the bare band is received.
Bibliography
Bibliography


[46] U. Starke and C. Riedl: Epitaxial graphene on SiC(0001) and SiC(000\bar{1}) : from surface reconstructions to carbon electronics, Journal of Physics: Condensed Matter 21, 134016 (2009)


D. M. Guzman, H. M. Alyahyaei, and R. A. Jishi: Superconductivity in graphene-lithium, 2D Materials 1, 021005 (2014)


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