Proximity Mechanisms in Graphene: Insights from Density Functional Theory

Dissertation by
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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

King Abdullah University of Science and Technology
Thuwal, Kingdom of Saudi Arabia

November, 2018
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ABSTRACT

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One of the challenges in graphene fabrication is the production of large scale, high quality sheets. To study a possible approach to achieve quasi-freestanding graphene on a substrate by the intercalation of alkali metal atoms, Cs intercalation between graphene and Ni(111) is investigated. It is known that direct contact between graphene and Ni(111) perturbs the Dirac states. Cs intercalation restores the linear dispersion characteristic of Dirac fermions, which agrees with experiments, but the Dirac cone is shifted to lower energy, i.e., the graphene sheet is n-doped. Cs decouples the graphene sheet, while the spin polarization of Ni(111) does not extend through the intercalated atoms to the graphene sheet, for which we find virtually spin-degeneracy. In order to employ graphene in electronic applications, one requires a finite band gap. We engineer a band gap in metallic bilayer graphene by substitutional B and/or N doping. Specifically, the introduction of B-N pairs into bilayer graphene can be used to create a band gap that is stable against thermal fluctuations at room temperature. Introduction of B-N pairs into B and/or N doped bilayer graphene likewise hardly modifies the band dispersions, however, the size of the band gap is effectively tuned. We also study the influence of terrace edges on the electronic properties of graphene, considering bare edges and H, F, Cl, NH$_2$ terminations. Periodic structural reconstruction is observed for the Cl and NH$_2$ edge terminations due to interaction between the terminating atoms/groups. We observe that Cl edge termination p-dopes the terraces, while NH$_2$ edge termination results in n-doping.
ACKNOWLEDGEMENTS

This dissertation would not have been possible without the kind support and help of many individuals. I would like to express my gratitude to my advisor, Prof. Udo Schwingenschlogl, for providing invaluable insight, guidance, and encouragement. My gratitude is extended to the committee members, Prof. Boon Ooi, Prof. Enzo Di Fabrizio, and Dr. Wajood Diery. I would also like to thank my group members and my colleague Sumit Ghosh for fruitful discussions. Special thanks to my friend Najebah Alsaleh for being a great emotional supporter. My best friend Salma Alrasheed, you have not only made this journey bearable, but also so delightful. Thank you for being on my side, always. Werfi, my gratitude to you is beyond words, you have always been my rock. I am ever thankful to have you in my life. To my family members, you are a blessing from heaven. Thank you very much for all the love and support. Last but not least, my beloved daughter Mayar, thank you for your patience and kindness. I dedicate this thesis to you. I am so lucky to be your mother.
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Chapter 1

Introduction

1.1 Carbon Nanostructures and Hybridization

Carbon, the fourth most abundant element in the universe, is unique in its ability to form various geometries in all dimensions, such as (0D) fullerenes, (1D) graphene nanotubes and nanoribbons, (2D) graphene sheets, and (3D) graphite and diamonds [1]. Different structures can have significantly different physical properties [2, 3, 4, 5, 6]. For example, it is well known that diamond and graphene are among the stroggest materials known, while graphite is soft enough to produce pencils. Carbon nanostructures also differ in their electronic properties. A C$_{60}$ fullerene is an insulator and can be tuned to both a semiconductor and superconductor [7]. The chirality of a graphene nanotube determines whether it behaves as metal or semiconductor [8]. Graphite is a metal and graphene is a zero gap metal, while diamond is an insulator. Figure 1.1 shows examples of different-dimensional structures in C materials.

1.2 Graphene

A C atom possesses two core electrons, while are not participating in bond formation, and four valence electrons that can participate. In graphene, a one atom thick sheet of carbon, arranged in a planer honeycomb structure, three electrons form sp$^2$ bonds while the fourth electron is available for $\pi$ bonds [9], see Figure 1.2. Due to its sp$^2$ hybridization, is the building block of many C materials such as: (i) graphite, which consists of a number of graphene layers connected by van der Waals forces and can
have a Bernal (ABA) or a rhombohedral (ABC) stacking configuration [10, 11, 12] as shown in Figure 1.3; (ii) carbon nanotube, made by rolling up a graphene sheet into a cylinder [13]; and (iii) graphene nanoribbon, formed by cutting a graphene sheet [14]. Graphene was theoretically predicted in 1947 [2], but only 2004 it was successfully isolated [15] and since then, gained great attention for many unique properties. At room temperature, graphene has a high electron mobility of 200,000 cm²/Vs [6] and a thermal conductivity of 5000 W/mK [16], which is about 10 times larger than that of copper. It is also almost transparent, absorbing only about 2% of the incident white light [17]. With a breaking strength of 42 N/m, it is about 100 times stronger than steel [18]. It has a large surface area per gram (2630 m²/g) [19]. As shown in Figure 1.4(a), the two dimensional honeycomb lattice structure consists of two non-equivalent triangular sublattices of C atoms (A and B), with a C-C bond length of 1.24 Å and a lattice parameter of 2.46 Å. The sp² orbital gives rise to in-plane σ bonds. The remaining pₓ orbital, which is perpendicular to the σ bonds, interacts
with neighboring $p_z$ orbitals to form $\pi$ bonds \cite{3}, see Figure 1.4(a) and (b). The $\pi$ electrons are responsible for graphene’s electronic properties \cite{9}, giving rise to a cone-shaped dispersion in the vicinity of the Fermi energy, called “Dirac cone”, with the “Dirac point” exactly at the Fermi energy. Those Dirac points are located at the corners of the Brillouin zone at the K and K’ points, which is discussed in detail in section 2.2. Figure 1.4(c) shows the three dimensional band dispersion of graphene along its high symmetry lines in the Brillouin zone, with the zoomed Dirac cone on the right showing the $\pi$ and $\pi^*$ states (valance and conduction bands). This particular electronic dispersion makes graphene a zero gap metal. The electrons at the Dirac point act as massless fermions \cite{9}. Fermions are particles that have half integer spin and therefore obey the Pauli exclusion principle. Bilayer graphene can have massless or massive fermions in the vicinity of the Fermi energy depending on the stacking...
configuration. In AA stacking the material consists of two graphene layers located directly on top of each other, whereas in AB stacking half of the C atoms from one layer sits on top of C atoms of the other layer and the other half sits on top of hollow sites, see Figure 1.5. AA stacked bilayer graphene has two Dirac cones which meet at two points at the Fermi energy. The AB stacked bilayer graphene, on the other hand, has two parabolic bands that intersect at two points at the Fermi energy, i.e., the fermions are massive [21].

1.3 Graphene Nanoribbons

Graphene nanoribbons can have armchair or zigzag edges, or a mixture of both [5]. Tight binding calculations and calculations based on Dirac’s equation for massless particles suggest that zigzag graphene nanoribbons are metallic and armchair graphene
nanoribbons are either metallic or semiconducting \[5, 22\]. Density functional theory, on the other hand, shows that both zigzag and armchair graphene nanoribbons can have finite band gaps, inversely proportional to the width of the nanoribbon, when considering spin polarization \[23, 24\]. The width of graphene nanoribbons is counted by the number \(N\) of zigzag chains. An armchair graphene nanoribbon is metallic if \(N = 3p+2\) (where \(p\) is a positive integer), otherwise it is a semiconductor. The band gap of a zigzag graphene nanoribbon is determined by the magnetic configuration of the edges \[26\], with the ground state being given by ferromagnetic ordering within each edge and antiferromagnetic coupling between the edges \[23, 26, 27, 28\]. Antiferromagnetic coupling between the edges results in a semiconductor and ferromagnetic coupling in a metal \[29\]. The band gap of graphene nanoribbons facilitates their use in nanoelectronic devices, for example, for low noise applications. It was found experimentally and theoretically for a graphene zigzag nanoribbons that for a width of 70 Å the band gap drops from about 200 meV to zero and the nanoribbon shows a transformation from antiferromagnetic to ferromagnetic coupling between the edges \[25\]. In Figure 1.6 tunneling spectroscopy is used to measure the band gap as a function of the nanoribbon width. The edge magnetization of a graphene zigzag nanoribbon can be suppressed if supported by a metal substrate \[30\]. Supporting an antiferromagnetic graphene zigzag nanoribbon by a graphene sheet, however, is reported in

\[a\] \hspace{1cm} \[b\]  

Figure 1.5: Top view of bilayer graphene in an (a) AA and (b) AB stacking configuration, where the red color represents the top layer and the blue color is for the bottom layer.
Ref. \[31\] to have no effect on the edge magnetic moment. Graphene zigzag nanoribbons with widths above 30 Å supported by a graphene sheet exhibit electron-electron interaction effects \[32\].

### 1.4 Cs Intercalation between Graphene and Ni(111) Substrate

While the electronic properties are interesting for many applications \[33\], graphene still faces the challenge of growth in high quality and large scale. During growth, graphene may experience defects \[34\] or form wrinkles, the result of relaxing the strain in the lattice \[35\], which will reduce its mobility \[36\]. Therefore, it is important to preserve the Dirac cone, which is considered to be the main electronic feature of graphene. A popular method to prepare graphene is chemical vapor deposition \[37\], which has been successfully used for metallic substrates, such as Cu \[38\], Au \[39\], Co
Ni(111) and Co(0001), in particular, are considered to be good substrates due to their small lattice mismatches of only 1.3\% \textsuperscript{44} and 1.9\% \textsuperscript{45}, respectively.

Figure 1.7: Experimental and simulated scanning tunneling microscopy images for graphene on Ni(111) substrate. The right hand side shows a scanning tunneling microscopy image together with simulated structural configurations. Image from Ref. \textsuperscript{46}.

Figure 1.7(a) shows a scanning tunneling microscopy image demonstrating the coexistence of three configurations of graphene on Ni(111) substrate in one sample. We see a transition between the top-fcc, top-bridge, and top-hcp configurations. The transition is smooth between the top-fcc and top-bridge configurations, with a small distortion of the carbon hexagon. On the other hand, the transition between the top-bridge and top-hcp configurations is sharp, with a domain boundary forming. Figure 1.7(b) shows a grid highlighting the Ni atoms from the top layer of the substrate.
Zooming into the domain boundary region in Figure 1.7(c) we can see how the two configurations are merging (green and blue dots represent the positions of the C atoms in the top-bridge and top-hcp configurations, respectively). Figure 1.7(d) shows a stick-and-ball-model and Figure 1.7(e) a simulated scanning tunneling microscopy image of the relaxed domain boundary (red: C atoms, blue: Ni atoms), illustrating Stone-Wales defects (pentagonal and octagonal rings) between the top-bridge and top-hcp configurations [46].

Some metallic substrates, such as Ni(111) [47], interact strongly with graphene and distort the Dirac cone [48], whereas for Pt(111) [35], for example, the interaction is weaker. The small distance (2.1 Å) realized between graphene and Ni(111) results in significant hybridization of the Ni 3d and C 2p orbitals, which explains the strong modification of the band structure [49, 50]. It has been shown experimentally [51] and theoretically [52] that C magnetic moments are induced. A well known method for decoupling layered structures is intercalation, i.e., foreign atoms or molecules are inserted to increase the interlayer distance and reduce the undesirable interaction [53], see Figure 1.8.

Intercalation of noble metal atoms can restore the original band structure to give rise to quasi-freestanding graphene [54]. Ag intercalation into the graphene/Ni(111)
system has been studied by density functional theory and it has been found that the Ag atoms decouple graphene from the substrate electronically [55]. The band gap decreases when the Ag concentration grows, as the interaction with the substrate is reduced. Ni then has no other role than to support the noble metal atoms. For Au intercalation the concentration also has a noticeable impact on the shape of the graphene $\pi$ bands [56]. Already low Au concentration largely recovers the Dirac cone but leaves a band gap and a sizable shift of the Dirac point below the Fermi level. Increasing the Au coverage, on the other hand, almost removes the band gap and shifts the Dirac cone back to the Fermi level [41]. Figure 1.9 shows an angle-resolved photoemission electronic structure of graphene on Ni(111) (a) before and (b) after intercalation of 1 monolayer of Au, resulting in a 2 eV shift toward higher energy.

Figure 1.9: Angle-resolved photoemission electronic structure of graphene on Ni(111). Image from Ref. [41].
and closing the gap at the K point. The zoomed image in Figure 1.9(c) x shows the dispersion of the π states near the Fermi energy. Metal intercalation is not restricted to noble metals. In particular, alkali metals have been studied experimentally [47] and theoretically [57]. They also weaken the interaction between graphene and Ni(111) by enlarging the interlayer distance [58, 59].

1.5 Doping in Bilayer Graphene

Absence of a band gap limits applications of graphene in electronics, calling for band gap engineering [9, 60]. Many methods were used to create a band gap including strain [61], vacancies [62], interaction with substrates [41], and formation of nanoribbons [63]. Substitutional doping with foreign atoms, however, is considered the main approach to intrinsically alter the electronic properties [64–66]. In particular, graphene is often doped with B [67] and N [68], as these atoms have radii (B: 87 pm; N: 56 pm) similar to that of C (67 pm) and the planar geometry therefore is preserved [69, 70]. Gradual transition from n-type to p-type character in contact with air can be neutralized by intentional overdoping [71, 72, 73, 74, 75, 76]. Bilayer graphene early has been proposed as viable alternative to the monolayer [77]. Both AA and AB stacking have been observed experimentally [78, 79], AB stacking being 5 meV per C atom lower in energy than AA stacking [80], and nowadays can be grown in high quality and with large area [81]. It has been demonstrated that both B and N doping requires less energy than in the monolayer [82].

Introduction of one B or one N atom into AB stacked bilayer graphene has been studied in Ref. [83] both for the top and hollow sites (which refers here and in the following to the position of the dopant atom relative to the other layer) and similar electronic band structures have been found for the two sites in each case. B and N favor hollow sites over top sites by 11 meV and 16 meV, respectively [82]. In AB stacked bilayer graphene with one N atom in each layer the total energy declines significantly
for increasing distance between the two dopant atoms, while for corresponding doping
with B atoms hardly any dependence of the total energy on the distance is found [84].
Codoping of B and N in graphene (monolayer) is energetically favorable in the form
of B-N pairs in ortho position, for example, by 20 meV as compared to next nearest
neighbours [85]. Ref. [86] has studied bilayer graphene with one B atom in one layer
and one N atom in the other, claiming that the electronic properties depend on the
occupied sublattice rather than on the mutual distance.

1.6 Terrace Effects on the Electronic Properties of Graphene

Multilayer graphene samples can show large variations due to the presence of terrace
edges with different terminations [87]. This is particularly problematic as large scale
growth of multilayer graphene results almost inevitably in terraces and terrace edges
on the surface [88] [89]. Depending on the method of growth, the topology can range
from 10-100 nm wide terraces (distance between terrace edges) in the case of chemical
vapor deposition [90] to highly uniform terraces with widths of 300-700 nm or 3-5 μm
(carrier mobility above 3000 cm²/V·s and carrier density of 10¹² cm⁻²) in the case of
thermal decomposition of silicon carbide [91] [92]. In Ref. [93], 500 nm wide graphene
islands were observed on a terrace of 4 μm width [94]. The presence of terraces
decreases the carrier mobility due to scattering steps [95]. Figure 1.10(a) shows an
atomic force microscopy image of graphene on 6H-SiC(0001) and Figure 1.10(b) a
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starts at step edges.
Figure 1.10: (a) Atomic force microscopy and (b) low-energy electron microscopy images for graphene on 6H-SiC(0001). Light, medium, and dark grey color corresponds to a thickness of 0, 1 and 2 monolayers, respectively. (c) Zoomed view of (b). (d) Zoomed view of (a) and height profile. Image from Ref. [91].

It can be expected that terrace edges are highly reactive, similar to the edges of graphene nanoribbons, due to the presence of dangling bonds [96], leading to edge termination, which can be determined by comparing experimental and calculated Raman spectra [97]. For zigzag graphene nanoribbons, H results in lower formation energy per terminating atom (0.14 eV) than noble metals (1.20 eV for Ag, for ex-
ample) and transition metals (1.74 eV for Ni and 1.86 eV for Fe, for example) [98]. Zigzag graphene nanoribbons terminated with H (one and two atoms per edge C atom), hydroxyl, ketone, and ether were addressed in Ref. [99] to study the effect of the edge termination on the band gap. It turned out that forming a ketone is easier than hydrogenation and leads to a metallic behavior due to the high electronegativity of O relative to C. Hydroxylated edges are stabilized by the formation of hydrogen bonds between adjacent hydroxyl groups [100]. Modifications of the electronic structure of thin zigzag graphene nanoribbons due to NH$_2$ termination are described in Ref. [65].
Chapter 2

Method of Calculations

2.1 Density Functional Theory

Density functional theory is considered one of the most successful and powerful approaches to describe the ground state properties of a material, in terms of the electron density. It can predict the structural, electronic, and magnetic properties as well as vibrational frequencies, for example. It is based on fundamental theorems by Hohenberg, Kohn, and Sham. Hohenberg and Kohn [101] suggested a way of solving a many-body problem using the electron density rather than the wave function. They stated that there is a relation between the electron density and the ground state total energy. Kohn and Sham [102] later put forward a theorem for finding this electron density. Key to this approach is the exchange correlation functional, which must be approximated depending on the system under consideration. A widely used approximation to the exchange-correlation functional is the generalized gradient approximation. It employs the electron density and local gradient of the electron density. One commonly used parameterization is due to Perdew-Burke-Ernzerhof [103]. The generalized gradient approximation is employed throughout our investigations. Figure 2.1 shows an iteration scheme for density functional theory calculations.
2.2 Honeycomb Lattice and Brillouin Zone

The graphene unit cell consists of two C atoms (A and B) and has basis vectors $a_1$ and $a_2$, as shown in Figure 2.2(a), where $b_1$, $b_2$, and $b_3$ are the connecting vectors from sublattice A to sublattice B. Figure 2.2(b) shows the reciprocal lattice with vectors $k_1$ and $k_2$, and the first Brillouin zone shaded in yellow with the high symmetry points $\Gamma$ (center) and $K$ (corners of the hexagon); $K' = -K$. Different graphene supercells have different Brillouin zones due to band back folding. The first Brillouin zone, see the small black hexagons in Figure 2.3, has the high symmetry points $\Gamma$, $K$, $K'$, and
2.2 Lattice and Brillouin Zone of Graphene

Figure 2.2: The (a) lattice and (b) Brillouin zone of graphene. Image from Ref. [104].

M. The red hexagon is the second Brillouin zone and we can see that the K point is folded back to the K′ point. Similarly, for the third Brillouin zone (green hexagon) the K point is folded back to the Γ point. Any high symmetry point will be folded back to a high symmetry point in the first Brillouin zone [105].

2.3 Computational Methods

We perform first-principles calculations using the Vienna Ab-initio Simulation Package, employing ultrasoft pseudopotentials [106]. The code is biased on density functional theory. Projected densities of states are used to evaluate the roles of particular
orbitals of specified atoms. In the total density of states all partial densities of states are summed. Weighted band structures provide the contributions of particular orbitals of specified atoms to an electronic state at a given energy and momentum. Electronic charges on individual atoms are calculated using Bader’s theory of atoms in molecules or crystals \[107\]. This approach provides a good approximation for the total electronic charge of an atom by estimating the charge confined within its Bader volume (partitioning scheme based on zero-flux surfaces).
Chapter 3

Quasi-freestanding graphene on Ni(111) by Cs intercalation

In this chapter we will discuss the effect of Cs alkali metal atoms when intercalated between graphene and Ni(111). We start by describing the computational methods. We then investigate different structural configurations and concentrations to search for induced spin polarization.

3.1 Computational Methods

Density functional theory is employed using the Vienna Ab-initio Simulation Package [106] and the generalized gradient approximation (Perdew-Burke-Ernzerhof parametrization [103]) along with ultrasoft pseudopotentials. London forces are considered in all calculations [108] and the plane wave cutoff energy is set to 500 eV. Supercells are created using the xy-plane the lattice parameter of Ni (2.49 Å) and adding a vacuum slab of about 15 Å thickness in the z-direction. For a 1 × 1 unit cell of graphene on Ni(111) a 32 × 32 × 1 k-mesh (Monkhorst-Pack scheme [109]) is used for the Brillouin zone integration (16 × 16 × 1 for the structure relaxation). We built a 2 × 2 supercell containing 24 atoms (8 C and 16 Ni) and introduce one Cs atom, giving a total number of 25 atoms. Also 3 × 3 and 4 × 4 supercells are constructed to examine the effect of the Cs concentration. These supercells are relaxed using 4 × 4 × 1 and 2 × 2 × 1 k-meshes, respectively, and 8 × 8 × 1 and 4 × 4 × 1 k-meshes are employed for the self-consistency calculation.
3.2 Possible Configurations

The 1×1 unit cell of the graphene on Ni(111) consists of 4 Ni layers and 1 C layer on top. To determine the favorable lateral shift between the two materials, we study four structural configurations: (i) Hollow, where each atom of the topmost Ni layer is in the center of a C honeycomb. (ii) Face centered cubic (fcc), where three of the C honeycomb atoms are located on top of atoms of the topmost Ni layer and the center of the C honeycomb is located on top of an atom of the second Ni layer. (iii) Hexagonal close packed (hcp), which is similar to the fcc case but with the center of the C honeycomb located on top of an atom of the third Ni layer. (iv) Bridge, where the center of the C honeycomb is located between two atoms of the topmost Ni layer. Figure 3.1 illustrates the four cases and Table 1 summarizes key findings. In agreement with previous studies [110], the fcc configuration turns out to have the lowest formation energy

\[ E_{\text{formation}} = E_{\text{system}} - E_{\text{Ni}} - E_{\text{C}}, \]  

where \( E_{\text{Ni}} \) is the total energy per atom in bulk Ni and \( E_{\text{C}} \) is the total energy per C atom in graphene. The fact that the bridge configuration is only 10 meV higher in energy than the fcc configuration implies that it is accessible as well. Even the hcp configuration might be accessible with low probability. Indeed, these configurations experimentally can coexist [111, 46]. The hollow configuration, on the other hand, is rather unlikely to be formed.
Figure 3.1: Top view of the structural configurations considered for graphene on Ni(111), where the C atoms (yellow) occupy (a) hollow, (b) fcc, (c) hcp, and (d) bridge sites on the Ni(111) surface.

<table>
<thead>
<tr>
<th></th>
<th>hollow</th>
<th>fcc</th>
<th>hcp</th>
<th>bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{C/\text{Ni}}$ (Å)</td>
<td>3.3</td>
<td>2.1</td>
<td>3.0</td>
<td>2.2</td>
</tr>
<tr>
<td>$E_{\text{formation}}$ (eV)</td>
<td>−4.01</td>
<td>−4.19</td>
<td>−4.11</td>
<td>−4.18</td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of different configurations of graphene on Ni(111).

### 3.3 Graphene on Ni(111)

The C-C bond length in the fcc configuration is 1.44 Å, whereas it is 1.42 Å in pristine graphene. This small tensile strain corresponds to the mentioned small lattice mismatch. The obtained perpendicular distance between graphene and the Ni(111) surface, $d_{C/\text{Ni}}$, see Table 1, is in very close agreement with previous experimental [112] and theoretical [113] findings. For the fcc configuration, Figure 3.2 shows the band structure for the spin up and down channels. The Dirac cone is strongly perturbed with a 0.3 eV splitting at the K point, reflecting a strong hybridization between the C 2p and Ni 3d states as a consequence of the small $d_{C/\text{Ni}}$. We obtain finite though small magnetic moments of $-0.02$ and $0.03 \mu_B$ on the two C atoms due to
Figure 3.2: Graphene on Ni(111): Band structure of the (a) spin up and (b) spin down channels.

Ni-C hybridization, in agreement with the results reported in Ref. [114], and charge transfers of 0.03 and $-0.01$ electrons from the Ni 3d to the C 2p states.

### 3.4 Increase of Interlayer Distance

We next consider a $2 \times 2$ supercell with graphene artificially placed in a distance of 6 Å from the Ni(111) substrate, see Figure 3.3(c). As expected, this distance yields a weak interaction between the Ni 3d and C 2p states, compare the almost vanishing Ni-C hybridization, leading to a restoration of the Dirac cone with a minor splitting. In fact, hybridization effects start vanishing in distances larger than 3 Å. Figure 3.3(a,b) shows the band structures of the spin up and down channels. We obtain a shift of the Dirac point by 0.2 eV above the Fermi level, reflecting p-doped graphene. The Dirac cone appears in the two spin channels at the same energy, implying that there is no C magnetic moment. The Ni bands, on the other hand, show a rigid shift due to spin polarization. Projected densities of states in Figure 3.3(c) confirm that the magnetic moments on the C atoms are zero and that the total magnetic moment of 10.8 $\mu_B$
comes from the Ni atoms, where atoms in the first layer show magnetic moments of \(0.67 \mu_B\) and atoms in the other layers show \(0.68 \mu_B\).

Figure 3.3: Band structure of the (a) spin up and (b) spin down channels for \(d_{C/Ni} = 6 \text{ Å}\). (c) Atomic structure with real and artificially exaggerated distance between the graphene sheet and Ni substrate. (d) Projected densities of states.
3.5 Intercalating Cs between Graphene and Ni(111)

We find that intercalation of Cs enlarges the distance between the graphene sheet and the Ni(111) substrate to 6.0 Å post relaxation (3.1 Å from graphene to Cs and 2.9 Å from Cs to Ni). The in-plane Cs-Cs distance is 5.0 Å. We note that the graphene sheet shows no significant structural modification, see Figure 3.4(c), in particular hardly any buckling. According to Figure 3.4(a,b), the electronic structure, on the other hand, is altered substantially by the Cs intercalation. In particular, a multitude of bands appears from $-1.5$ to $0.5$ eV. To understand the origin of these bands we use a weighted band analysis. Figure 3.5(b) shows that the cone-like bands originate from the C 2p states, while the other bands are due to the Ni 3d states. The Dirac cone is restored with a negligible splitting. It appears about 1.1 eV below the Fermi level, representing prominently n-doped graphene. The C atoms carry no magnetic moment, see also Figure 3.4(d), implying that Cs does not transfer spin polarization from Ni to graphene. In the Ni(111) substrate the magnetic moments decrease towards Cs from a value of 0.68 $\mu_B$, which is close to the bulk Ni value of 0.67 $\mu_B$, to values of 0.49 $\mu_B$ for the atom directly below Cs and 0.59 $\mu_B$ for the other atoms in the same layer.
Figure 3.4: Band structure of the (a) spin up and (b) spin down channels for the graphene/Cs/Ni(111) system (2 × 2 supercell). (c) Atomic structure with intercalated Cs (gray). (d) Projected densities of states.
3.6 Different Concentrations of Cs Intercalation

We next consider larger supercells, see Figure 3.5 on top, to study the effect of the Cs concentration. The weighted band structures obtained for $2 \times 2$ (without and with the intercalation), $3 \times 3$, and $4 \times 4$ supercells in Figure 3.5 demonstrate a shift of the Dirac point upwards to the Fermi level when the Cs concentration is reduced. The higher the Cs concentration the stronger is the n-doping of graphene. The Dirac point is located 1.12 eV, 0.61 eV, and 0.59 eV below the Fermi level, respectively, for the $2 \times 2$, $3 \times 3$, and $4 \times 4$ supercell, which corresponds to a charge transfer of 0.045, 0.012, and 0.011 electrons in the case of pristine graphene.

Figure 3.5: Atomic structures and weighted bands for the (a,b) $2 \times 2$ supercell without/with intercalation, (c) $3 \times 3$ supercell, and (d) $4 \times 4$ supercells. The size of the dots represent the sum of all C $p_z$ contributions.
3.7 Intercalating Cs between Graphene and Co(0001)

Figure 3.6: Band structure of the (a) spin up and (b) spin down channels for the graphene/Cs/Co(0001) system (2 × 2 supercell). (c) Projected densities of states.

As another ferromagnetic substrate we have also considered Co(0001) to check whether our results for Ni(111) are of general validity. The band structure of the 2 × 2 supercell, see Figure 3.6(a,b), is found to show close similarity to the case of the Ni(111) substrate, only the Dirac point is shifted slightly more (1.17 eV) below the Fermi level. The projected densities of states in Figure 6(c), on the other hand, indicate that Co is subject to a stronger exchange splitting as compared to Ni.
3.8 Summary

We have investigated the effect of Cs intercalation on the structural, electronic, and magnetic properties of graphene on Ni(111) and Co(0001). An fcc configuration is found to be energetically favorable in agreement with previous experimental and theoretical results, and therefore is chosen for studying the intercalation. Different supercell sizes have been considered to examine the effect of the Cs concentration. In agreement with experimental results, the Cs intercalation restores the Dirac cone, since it decouples graphene from the substrate, resulting in n-doped quasi-freestanding graphene. Both for the Ni(111) and Co(0001) substrates the graphene sheet exhibits no trace of spin polarization.
Chapter 4

Band Gap Control in Bilayer Graphene by Co-Doping with B-N Pairs

In this chapter we discuss the electronic band structure of bilayer graphene and systematically study it in the presence of substitutional B and/or N doping. Various configurations are considered to understand the role of additional B-N pairs.

4.1 Computational Methods

Spin-polarized first-principles calculations are performed using the Vienna ab-initio simulation package [106] and the generalized gradient approximation for the exchange-correlation potential (Perdew-Burke-Ernzerhof parameterization), taking into account a van der Waals correction with Becke-Johnson damping [120]. The plane wave energy cutoff is set to 500 eV. We employ a Γ-centered $2 \times 2 \times 1$ k-mesh for the structure optimization and a Γ-centered $8 \times 8 \times 1$ k-mesh for evaluating the electronic properties. Both for AA and AB stacking, a $5 \times 5$ supercell of bilayer graphene is constructed with a total of 100 C atoms (to consider doping effects) to which a 16 Å thick vacuum layer is attached along the c-axis in order to avoid artificial interaction between periodic images. The interlayer distance after structure optimization turns out to be 3.6 Å for AA stacking and 3.4 Å for AB stacking, in agreement with the experimental observations in Refs. [115] and [116]. These values are not modified by the presence of dopant atoms for the concentrations considered in this study. We obtain for both stackings an in-plane lattice parameter of 2.46 Å and a C-C bond length of 1.42 Å.
As in no case atoms develop significant magnetic moments ($\leq 0.01 \mu_B$), we present in the following spin-degenerate band structures.

4.2 Undoped and Doped Bilayer Graphene

For reference, we show the electronic band structure of AB stacked bilayer graphene (see the atomic structure in Figure 4.1) in Figure 4.2(a) in the undoped case, in Figure 4.2(b) doped with one N atom in one layer, and in Figure 4.2(c) doped with one B atom in one layer. All these results agree with the existing literature [83, 117]. We next introduce one B atom into one layer and one N atom into the other, representing a dopant concentration of 2%, and examine different distances between them as well as doping at both the top and hollow sites. In each case we obtain minimal energy for minimal distance between the dopant atoms.

Figure 4.1: Atomic structure of AB stacked bilayer graphene: (a) undoped, (b) doped with one N atom in one layer, (c) doped with one B atom in one layer, (d) doped with one N atom in one layer and one B atom in the other, and (e) doped with one B-N pair in one layer.
The energetically favorable configuration with AB stacking has 467 meV (∼5 meV per C atom) lower energy than that with AA stacking. In the case of AB stacking, when B sits at a top site and N at a hollow site the energy is 14 meV lower than when both sit at hollow sites, 75 meV lower than when N sits at a top site and B at a hollow site, and 65 meV lower than when both sit at top sites. The electronic band structure of the minimum energy configuration, see Figure 4.1(d), agrees with the result of Ref. [86]. There are two buried Dirac cones at the K point, which can be attributed to the layers doped with B (unoccupied cone) and N (occupied cone), and we obtain a band gap of 298 meV.

Turning to the situation that both the B and N atoms are located in the same layer while the other layer is undoped, we confirm that for both AA and AB stacking the formation of a B-N pair is energetically favorable, as a strong covalent bond is formed [118]. Concerning the position of the B-N pair relative to the other layer we find that N occupying the hollow site gives an energy advantage of 22 meV, which agrees with the finding of Ref. [82] that N favors in bilayer graphene the hollow site more strongly than B (by 22 meV). It turns out that the total energy is 590 meV (∼6 meV per C atom) lower for AB stacking than for AA stacking. The electronic band structure of the minimum energy configuration is shown in Figure 4.2(e). We observe parabolic bands in the vicinity of the Fermi energy, as expected for AB stacked bilayer graphene (see Figure 4.2(a) and Ref. [119]), with a band gap of 70 meV due to the presence of the B-N pair. As a remark, we note that the electronic properties depend on the sites (top or hollow) occupied by the dopant atoms rather than on the occupied sublattice as claimed in Ref. [86].
Figure 4.2: Electronic band structure of AB stacked bilayer graphene: (a) undoped, (b) doped with one N atom in one layer, (c) doped with one B atom in one layer, (d) doped with one N atom in one layer and one B atom in the other, and (e) doped with one B-N pair in one layer.
4.3 Doping One Layer with a B-N Pair and the Other Layer with One N Atom

We next study, for different relative positions, one B-N pair in one layer and one N atom in the other. It turns out that the N atom still favors the hollow site. The numbers in Figure 4.3(a) are total energy differences in meV for location of the N atom at the respective site relative to the minimum energy location. We observe significant variations in the total energy. Comparing the electronic band structures obtained for the highest and lowest energy configurations (at distances of 2.13 Å and 6.41 Å, respectively), however, shows close similarity, see Figure 4.3(b). We observe a sizeable shift of all bands to lower energy, with respect to Figure 4.2(e), reflecting an n-type character due to the extra charge of the N atom. On the other hand, the band dispersions in the vicinity of the Fermi energy closely resemble those of Figure 4.2(b). It turns out that incorporation of the B-N pair in the undoped layer increases the binding energy to the layer with the N atom by 37 meV, showing that B-N pairs can be used to enhance the interlayer interaction.
Figure 4.3: (a) Top view of AB stacked bilayer graphene with one B-N pair in the bottom layer (B blue, N yellow, top layer gray, bottom layer red). The numbers represent the total energy in meV for location of an additional N atom at the respective site of the other (top) layer (relative to the minimum energy location). (b) Electronic band structures for location of the N atom at the sites indicated in (a) by red numbers: next to the B-N pair (blue solid line) and far from the B-N pair (green dashed line).
4.4 Doping One Layer with a B-N Pair and an Additional B Atom, Keeping the Other Layer Undoped

Keeping one layer undoped, we now add one B atom to the layer containing the B-N pair. The numbers in Figure 4.4(a) are the total energy differences in eV for location of the B atom at the respective site relative to the minimum energy location. We observe a strong tendency of the additional B atom to bond to the N atom of the B-N pair, forming a B-N-B triple, by occupying a top site (where the determining factor is not whether it is a top or hollow site but the proximity to N). Despite large differences in the total energy, Figure 4.4(b) demonstrates that the electronic band structures are similar for different positions of the additional B atom. We also observe that the band dispersions in the vicinity of the Fermi energy are closely related to those of Figure 4.2(c).
Figure 4.4: (a) Top view of AB stacked bilayer graphene with one B-N pair in the top layer (B blue, N yellow, top layer gray, bottom layer red). The numbers represent the total energy in eV for location of an additional B atom at the respective site of the same (top) layer (relative to the minimum energy location). (b) Electronic band structures for location of the B atom at the sites indicated in (a) by red numbers: next to the B-N pair (blue solid line) and far from the B-N pair (green dashed line).
4.5 Doping One Layer with a B-N-B triple and the Other Layer with One N Atom

We finally study, for different relative positions, one N atom in one layer and one B-N-B triple in the other. The numbers in Figure 4.5(a) are the total energy differences in meV for location of the N atom at the respective site relative to the minimum energy location. Similar to the situation of Figure 4.3, the N atom favors hollow over top sites. We compare in Figure 4.5(b) the electronic band structures obtained for the highest (N far from the B-N-B triple) and lowest (N next to the two B atoms of the B-N-B triple) energy configurations, finding close similarity, however, with a difference of 43 meV in the size of the band gap. The band dispersions in the vicinity of the Fermi energy resemble those of Figure 4.2(d), while the band gap is much smaller (148 meV instead of 298 meV for the lowest energy configuration, for example). The fact that the presence of B-N pairs in bilayer graphene hardly affects the shape of the electronic bands but strongly alters the size of the band gap makes it possible to tune these quantities independently of each other.
Figure 4.5: (a) Top view of AB stacked bilayer graphene with one B-N-B triple in the bottom layer (B blue, N yellow, top layer gray, bottom layer red). The numbers represent the total energy in meV for location of an additional N atom at the respective site of the other (top) layer (relative to the minimum energy location). (b) Electronic band structures for location of the N atom at the sites indicated in (a) by red numbers: next to the B-N-B triple (blue solid line) and far from the B-N-B triple (green dashed line).
4.6 Doping One Layer with a B-N Pair and the Other Layer with One B Atom

Similarly to the case in section 4.3, we dope one B-N pair in one layer while the other layer is doped with one B atom. Unlike the case in section 4.3, the B atom is found to have minimum energy when located as close as possible to the B-N pair and at a hollow site, see Figure 4.6(a), though there is no strong preference over top sites. The electronic band structures obtained for the highest and lowest energy configurations at the hollow site are almost identical, see Figure 4.6(b).
Figure 4.6: (a) Top view of AB stacked bilayer graphene with one B-N pair in the bottom layer (B blue, N yellow, top layer gray, bottom layer red). The numbers represent the total energy in meV for location of an additional B atom at the respective site of the other (top) layer (relative to the minimum energy location). (b) Electronic band structures for location of the N atom at the sites indicated in (a) by red numbers: next to the B-N pair (blue solid line) and far from the B-N pair (green dashed line).
4.7 Doping One Layer with a B-N Pair and an Additional N Atom, Keeping the Other Layer Undoped

Having one layer undoped, we now add one N atom to the layer containing the B-N pair. The numbers in Figure 4.7(a) are the total energy differences in eV for location of the N atom at the respective site relative to the minimum energy location. We observe a similar behavior to the case in section 4.4, where the additional N atom has a strong tendency to bond to the B atom of the B-N pair, forming a N-B-N triple, by occupying a hollow site (where the determining factor is not whether it is a top or hollow site but the proximity to B). Despite large differences in the total energy, Figure 4.7(b) demonstrates that the electronic band structures are similar for different positions of the additional B atom. We also observe that the band dispersion in the vicinity of the Fermi energy are closely related to those of Figure 4.2(c).
Figure 4.7: (a) Top view of AB stacked bilayer graphene with one B-N pair in the top layer (B blue, N yellow, top layer gray, bottom layer red). The numbers represent the total energy in eV for location of an additional N atom at the respective site of the same (top) layer (relative to the minimum energy location). (b) Electronic band structures for location of the B atom at the sites indicated in (a) by red numbers: next to the B-N pair (blue solid line) and far from the B-N pair (green dashed line).

4.8 Weighted Band Structures for Different Configurations

We calculate weighted band structures for AB stacked bilayer graphene when doped with: (a) N in one layer and B in the other, (b) a B-N-B triple in one layer and N in
the other, (c) N in one layer, (d) N in each layer, and (e) a B-N pair in one layer and N in the other. We also study (f) undoped AB stacked bilayer graphene decorated with an O\textsubscript{2} molecule. The purple color in the band structure represents the C \textit{p\textsubscript{z}} states of the top layer and the blue color the C \textit{p\textsubscript{z}} states of the bottom layer. In Figure 4.8(a) we see two Dirac cones at the K point, where the purple cone is not occupied (B doped layer) and the blue cone is fully occupied (N doped layer). The cases of Figure 4.8(b), (c) and (e) were already described in the above sections. For the case that each layer is doped with one N atom, we obtain minimum energy when the N atoms are separated from one another as far as possible. Only one color is observed in Figure 4.8(d) as the purple and blue bands are degenerate. Figure 4.8(f) shows undoped AB stacked bilayer graphene decorated by an O molecule. One can see spin degeneracy at most points of the Brillouin zone. We find a charge transfer to bilayer graphene of 0.01 electron per C atom. Linear bands in dark blue and green represent the \textit{p\textsubscript{x}+p\textsubscript{y}} and \textit{p\textsubscript{z}} states, respectively.
Figure 4.8: Weighted band structure of AB stacked bilayer graphene: (a) doped with N in one layer and B in the other, (b) doped with a B-N-B triple in one layer and N in the other, (c) doped with N in one layer, (d) doped with N in each layer, (e) doped with a B-N pair in one layer and N in the other, and (f) decorated with an O$_2$ molecule. The purple and blue colors represent the C p$_z$ states of the top and bottom layers, respectively. In (e) the dark blue and green colors represent the O p$_x$+p$_y$ and p$_z$ states, respectively.
4.9 Summary

In conclusion, the effects of B and/or N doping on bilayer graphene have been studied by first-principles calculations based on density functional theory. Special attention has been given to the modifications of the electronic band structure due to the presence of B-N pairs. We have demonstrated that such B-N pairs hardly modify the band dispersions in bilayer graphene, while opening a substantial band gap (of 70 meV in the case of 2% dopant concentration, for example). Similarly, introduction of B-N pairs into N and/or B doped bilayer graphene largely maintains the electronic band structure (for any relative position between the dopant species). Interestingly, for semiconducting systems (same amount of B and N dopants) our results show that the presence of B-N pairs shifts the band edges (almost rigidly) towards each other, i.e., the band gap shrinks. For this reason, introduction of B-N pairs into bilayer graphene can be used to tune the size of the band gap without critically affecting the band dispersions.
Chapter 5

Terrace Effects on the Electronic Properties of Graphene

5.1 Introduction

In this chapter we discuss how the electronic properties of graphene can be effected by terraces edges. We have study bare edges along with H, F, Cl, NH$_2$ edge terminations. Most of which remain liner with the ribbon geometry, except for Cl, NH$_2$, which is tilted with respect to the ribbon due to strong interaction between neighboring terminating atoms. The electronic properties of the liner and deformed structures where investigated. Our results shows that Cl and NH$_2$ edge terminations will p-dope and n-dope the terraces, respectively. Little is known about the properties of terrace edges in multilayer graphene and, in particular, about the consequences of termination. We therefore investigate the electronic states in the vicinity of such terrace edges using density functional theory.

5.2 Computational Methods

Spin-polarized first-principles calculations are performed using the Vienna Ab-initio Simulation Package [106] and the generalized gradient approximation of the exchange-correlation potential (Perdew-Burke-Ernzerhof parametrization) with van der Waals corrections [120]. Ultrasoft pseudopotentials are used and the plane wave cutoff energy is set to 500 eV. To understand the electronic states at terrace edges, we first study 8-chain zigzag graphene nanoribbons of 15.6 Å width (y-direction) and 2.5 Å length (x-direction) with bare edges and H, F, Cl, NH$_2$ terminations in a unit cells
of dimension 2.5 Å × 34.2 Å × 23.0 Å. All calculations are performed spin-polarized, because the ground state is characterized by ferromagnetic ordering within the edges and antiferromagnetic ordering between them \[23, 26, 27, 28\]. The simulation cells contain 16 C atoms in total. Terraces with zigzag edges are simulated by placing the nanoribbons on top of graphene sheets (in the energetically favorable AB stacking), using the same unit cell size. The simulation cells contain 48 C atoms in total. As the simulation cells of the nanoribbons and terraces have the same size, we use in both cases a Γ-centered 14 × 1 × 1 k-mesh in the structure optimization and a Γ-centered 28 × 2 × 3 k-mesh to examine the electronic properties. We also create 2 × 1 × 1 supercells for the Cl and NH\(_2\) terminations (containing 32 C atoms in the case of the nanoribbons and 104 C atoms in the case of the terraces), for which we use a Γ-centered 7 × 1 × 1 k-mesh in the structure optimization and a Γ-centered 14 × 2 × 3 k-mesh to examine the electronic properties.

### 5.3 Zigzag Graphene Nanoribbon with Bare and Terminated Edges

Figure 5.1 shows the atomic configurations and electronic band structures of a bare nanoribbon and of H and F terminated nanoribbons. The structure is flat in all cases. All band structures show semiconducting states and only spin-degenerate bands. According to Figure 5.1(a), the bare nanoribbon is characterized by two bands that are almost symmetric around the Fermi energy (with a band gap of 665 meV). The part close to the X point originates from the p\(_z\) orbitals of the edge C atoms, in agreement with the findings in Refs. \[121\] and \[122\]. The other part originates from the p\(_z\) orbitals of the non-edge C atoms. We also notice a rather flat band, originating from the p\(_y\) orbitals of the edge C atoms, in agreement with Ref. \[99\]. The two C edge atoms contribute each one spin channel to this band, while the other spin channels (not visible in the figure) appear below −1 eV. Bader charge analysis shows that each
Figure 5.1: Graphene zigzag nanoribbons and corresponding electronic band structures: (a) bare and with (b) H and (c) F edge terminations (H: white, F: orange, C: blue). All bands are spin-degenerate.
edge C atom loses 0.05 electrons to the body of the nanoribbon. They carry magnetic moments of 0.13 $\mu_B$, which agrees with the findings of Ref. [31].

In Figure 5.1(b) the H atoms realize a distance of 1.09 Å to the edge C atoms. Similar to the bare nanoribbon, we observe two bands (due to the $p_z$ orbitals of the edge C atoms) that are almost symmetric around the Fermi energy. However, the band gap is reduced to 440 meV. Bader charge analysis shows that each edge C atom gains 0.07 electrons, with respect to the bare nanoribbon, from the neighbouring H atom. We have also considered a $2 \times 1 \times 1$ supercell to check whether the terminating atoms realize any kind of structural ordering, however, this is not the case. In Figure 5.1(c) the F atoms realize a distance of 1.35 Å to the edge C atoms. The band structure is analogous to the previous cases but with a band gap of 399 meV. Unlike the H-terminated nanoribbon, where the H s states play no relevant role, the F $p_z$ orbitals slightly contribute to the almost flat bands around the X point due to $\pi$-bonding with the C $p_z$ orbitals. They mainly contribute below $-6$ eV. The F $p_x$ orbitals (can interact with each other) contribute below $-3$ eV and the F $p_y$ orbitals below $-8$ eV and above 5 eV. According to Bader charge analysis, each F atom gains $\sim 0.6$ electrons, mainly from the neighbouring C atom. A $2 \times 1 \times 1$ supercell calculation does not show any structural ordering of the terminating F atoms.

Figure 5.2: Top and side views of graphene terraces: (a) bare and with (b) H and (c) F edge terminations (H: white, F: orange, C: blue/gray).
5.4 Graphene Terraces

In the terrace models the two edges have different relative positions with respect to the graphene sheet (top or hollow sites), as shown in Figure 5.2. In each model we observe significant bending of the graphene sheet. In Figure 5.2(a) the interlayer distance (shortest distance between atoms) is 3.55 Å at the center and 3.50 Å at the edges. In Figure 5.2(b,c) it is 3.42 Å at the center, i.e., the same as in AB-stacked bilayer graphene \[116\], and 3.32 Å at the edges. The distances between the edge C atoms and the terminating atoms are the same as in the corresponding nanoribbons (see above). The electronic band structures obtained for the models of Figure 5.2 are shown in Figure 5.3. Almost flat bands are visible in each case around the X point, similar to Figure 5.1. The spin degeneracy is (slightly) lifted for all bands. For the bare terrace edges [Figure 5.3(a)] we find the same bands as in Figure 5.1(a) and, as an additional feature, cone-shaped C p\(_z\) bands with the Dirac point at the Fermi energy. The position of the Dirac cone in the Brillouin zone is marked by a red dashed line, which we also draw in all following figures as guide to the eye. The Dirac cone reveals a minor splitting of 15 meV. Analysis of the eigenvectors demonstrates that the states of the Dirac cone belong entirely to the graphene sheet. Furthermore, Bader charge analysis shows that, in contrast to the bare nanoribbon, one edge C atom (hollow site) gains 0.07 electrons while the other edge C atom (top site) loses 0.04 electrons. For the H-terminated [Figure 5.3(b)] and F-terminated [Figure 5.3(c)] terrace edges the band structure closely resembles Figure 5.1(b) and 5.1(c), respectively, except for the Dirac cone, which here reveals a splitting of 16 meV and 7 meV. By Bader charge analysis, we observe in the case of H termination that, in contrast to the nanoribbon, both edge C atoms lose charge (0.19 and 0.04 electrons, respectively) with respect to the bare model. The H atoms still lose 0.08 electrons. In the case of F termination, each F atom again gains \(\sim 0.6\) electrons from the neighbouring C atom.
Figure 5.3: Electronic band structures of the graphene terraces of Figure 5.2: (a) bare and with (b) H and (c) F edge terminations. Black and blue bands represent the spin channels. Red dashed lines show the position of the Dirac cone.
Figure 5.4: Example of band backfolding: $2 \times 1 \times 1$ supercell of the bare graphene nanoribbon.

5.5 Cl and NH$_2$-Terminations

Cl and NH$_2$-terminated nanoribbons in the following are studied in $2 \times 1 \times 1$ supercells, because there is strong interaction between the terminating atoms/groups. We demonstrate the consequences of the band backfolding in this supercell for the H-terminated nanoribbon in Figure 5.4. The electronic band structure in the range X-$\Gamma$-X is shown on the left hand side and the corresponding backfolded band structure on the right hand side. Sections (1) and (4) are backfolded onto sections (3) and (2), respectively. The blue dash-dotted line marks the $X_s = X/2$ point, where the subscript indicates the supercell. The X point falls on the $\Gamma_s = \Gamma$ point. We notice that starting the relaxation of the Cl and NH$_2$-terminated nanoribbons from
a flat structure results in a metastable flat structure with much higher energy (1.2 eV per Cl atom; 1.3 eV per NH$_2$ group) than the ground state. It turns out that the energetically favorable structure has the edge atoms/groups alternatingly tilted upwards and downwards, see Figure 5.5(a,b). In the case of Cl termination, the Cl atoms realize a distance of 1.74 Å to the edge C atoms. The electronic band structure in Figure 5.5(a) shows the expected behavior with an indirect band gap of 164 meV. Bader charge analysis demonstrates that each Cl atom gains 0.17 electrons from the neighbouring C atom. In the case of NH$_2$ termination, the N atoms realize a distance of 1.41 Å to the edge C atoms. The N-H bond length is 1.02 Å and the H-N-H bond angle is 113°. The electronic band structure again shows the expected behavior with an indirect band gap of 317 meV. Bader charge analysis demonstrates that the NH$_2$ groups gain 0.35 electrons while the edge C atoms lose more charge (0.45 and 0.30 electrons), i.e., there is a significant charge redistribution within the nanoribbon.

Figure 5.5(c) shows for the case of the Cl-terminated terrace edges that the Cl atoms are bent upwards. The lower Cl atoms realize distances of 2.63 Å (top site) and 2.95 Å (hollow site) to the graphene sheet. Away from the edges we observe the same interlayer distance as in AB-stacked bilayer graphene (3.4 Å). Interestingly, the system develops a metallic character with the Dirac point 86 meV above the Fermi energy (p-doping). Each Cl atom gains 0.18 electrons, both edge C atoms lose charge (0.18 and 0.04 electrons, respectively), and the graphene sheet loses a total of 0.08 electrons. According to Figure 5.5(d), the atomic structure at the NH$_2$-terminated terrace edges resembles that of the NH$_2$-terminated nanoribbon, including the atomic distances. The distance between the H atoms and graphene sheet is 2.89 Å. The system is metallic with the Dirac point 338 meV below the Fermi energy (n-doping). Note that the flat band at the Fermi energy is not completely filled. Bader charge analysis shows that the NH$_2$ groups gain 0.33 electrons, both edge C atoms lose charge (0.45 and 0.37 electrons), and the graphene sheet gains a total of 0.24 electrons.
Figure 5.5: Graphene zigzag nanoribbons and terraces with (a,c) Cl and (b,d) NH$_2$ edge terminations (H: white, N: gray, Cl: yellow, C: blue/gray) and corresponding electronic band structures. Black and blue bands represent the spin channels.
5.6 Summary

In conclusion, we have studied the electronic properties of graphene terrace edges terminated with different atoms/groups. It turns out that H and F terminations result in flat structures, while for Cl and NH$_2$ terminations alternating tilts of the edge atoms/groups are observed. H and F terminations hardly modify the Dirac cone at the Fermi energy, while Cl and NH$_2$ terminations lead to significant energetical shifts (86 meV to higher energy and 338 meV to lower energy, respectively). Therefore, Cl-terminated terrace edges induce p-doping and NH$_2$-terminated terrace edges n-doping. The observed energetical shifts are, in good approximation, proportional to the amount of charge transferred from and to the graphene sheet (loss of 0.08 electrons and gain of 0.24 electrons, respectively).
Chapter 6

Concluding Remarks

6.1 Summary

In this thesis, graphene has been investigated in the framework of first principles calculations, incorporating van der Waals corrections, aiming at solutions to selected problems of technological relevance.

A possible approach to achieve quasi-freestanding graphene on a Ni(111) substrate is the intercalation of Cs atoms. Our results show that Cs intercalation indeed restores the linear dispersion characteristic of Dirac fermions, which agrees with experiments. The Dirac cone is shifted to lower energy, i.e., the graphene sheet is n-doped. Cs intercalation therefore decouples the graphene sheet from the substrate and results in a charge transfer. On the other hand, the spin polarization of Ni(111) does not extend through the intercalated atoms to the graphene sheet, for which we find virtually spin-degeneracy.

Motivated by experiments, the electronic band structure of bilayer graphene has been studied systematically in the presence of substitutional B and/or N doping. We show that introduction of B-N pairs into bilayer graphene can be used to create a substantial band gap, stable against thermal fluctuations at room temperature, but otherwise leaves the electronic band structure in the vicinity of the Fermi energy largely unaffected. Introduction of B-N pairs into B and/or N doped bilayer graphene likewise hardly modifies the band dispersions. In semiconducting systems (same amount of B and N dopants), however, the size of the band gap is effectively
tuned in the presence of B-N pairs.

A systematic study of the effects of terrace edges on the electronic properties of graphene demonstrate that H and F edge terminations result in flat structures. Periodic structural reconstruction, on the other hand, is observed for Cl and NH$_2$ edge terminations due to interaction between the terminating atoms/groups. It turns out that Cl edge termination p-dopes the terraces while NH$_2$ edge termination results in n-doping. The amount of charge transferred from and to the graphene sheet is 0.08 electrons and 0.24 electrons, respectively.
REFERENCES


7 Papers Submitted and Under Preparation

