First-Principles Characterization and Functionalization of Graphene-Like Materials

Ab initio karakterisatie en functionalisatie van grafeenachtige materialen



Faculteit Wetenschappen Departement Fysica

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¹exception includes text (including equations and tables) of the chapters 4 to 8 2 this particular version, from June 16, 2015, as well as any other corrected versions

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List of abbreviations

- Γ A usual Bouckaert-Smoluchowski-Wigner notation [1] used for labelling zero vector in reciprocal space, it is one of many commonly used letters (M, K, ..) for specific high symmetry points of first Bruilin zone
- 2D Two dimensional
- **3D** Three dimensional
- Å Ångström, unit of length equal to $10^{-10}m$
- **AIM** Atoms in molecules
- ${\bf BZ}\,$ Brillouin zone
- **CMOS** Complementary metal–oxide–semiconductor technology for constructing integrated circuits
- CVD Chemical vapour deposition
- **DFA** Density functional approximation [2]
- **DFT** Density functional theory
- **DFT+U** DFT with Hubbard-corrected energy functionals with explicit on site Coulomb interaction correction terms [3]
- **DOS** Density of states
- **FG** Fluorographene, also known as graphene fluoride, a fully fluorinated graphene with stoichiometry CF and sometimes referred as monolayer in the text
- **GGA** Generalized gradient approximation
- **GW** It refers to GW approximation used to calculate the self-energy of a many-body system of electrons, G stands for Green's function and W for screened Coulomb interaction

Hirshfeld-I Iterative Hirshfeld charge population analysis (see Section 3.4)

HOMO Highest occupied molecular orbital

- LDA Local density approximation
- LUMO Lowest unoccupied molecular orbital
- **MAE** Magnetocrystalline anisotropy energy [4]
- **MD** Molecular dynamics
- \mathbf{MX}_2 Transition metal dichalcogenide general chemical formula, M stands for the metal and X for chalcogen atom
- **NVE** Microcanonical (ensemble), where number of particles in the system (N), the system's volume (V) and the total energy in the system (E) are kept fixed
- PAW Projector augmented waves
- **PBE** Perdew, Burke, and Ernzerhof [5] GGA parametrization
- **SW** Stone-Wales (defect)
- ${\bf TM}\,$ Transition metal
- TMDs Transition metal dichalcogenides
- **VASP** Vienna Ab-initio Simulation Package
- [[[]] Indication symbol for an image (its equivalent or part) that is available at Wikimedia Commons

Preface

Graphene has become the most prominent member and public face of the new wave of research which essentially started after successful isolation of stable monolayer materials in 2004.[6, 7] More than ten years after the first excitement about the "impossible" material graphene, the scientific research bloomed into a large volume of multiple, experimentally observed, ultra-thin materials with even a larger set of unique characteristics. Exploration of the other quasi two-dimensional materials evolved almost parallel with the efforts to bend and shape the electronic and surface properties of graphene via its chemical and mechanical functionalization. These new materials proved to be essential for reaching future goals of superstructures of ultra-thin crystals with tailored applications. Not surprisingly, a large volume of these materials share the hexagonal lattice structure and electronic similarities with graphene and are, in that sense, named graphene-like materials.

The aim of this thesis is to explore the characteristics of a wide group of graphene-like materials. First-principles methods are applied as the main tool for describing as well as engineering of the particular properties via chemical patterning. The extension of the set of studied pristine materials in this thesis evolved as a natural response to the experimental progress in this field, our available scientific methods and the possible industrial applications.

This work mainly focuses on chemical decoration of graphene-like crystals with chemical elements mainly in their single atomic form. This allows mutual comparison and a much more selective approach to tailoring the properties of the derived materials. The following thesis is divided into three main parts. The first one introduces the pristine materials and their precursors in chapter 1, an essential building block of further study. The second part, in Chapters 2 and 3, provides an overview of the applied methods. Finally, the results are grouped in the third part, in Chapters 4 to 8. The results part begins with the investigation of bilayer fluorographene (4), which is a graphene derivative with modified electronic and chemical characteristics. Next, in chapter 5, the patterning of pristine graphene with titanium and its oxide, is discussed. Following two Chapters 6 and 7 contain results about patterned silicene, a later discovered monolayer of silicon, its chemical reactivity and the influence of Stone-Wales defects on its chemical and electronic properties. This part ends with Chapter 8, which discusses a directed decoration of fluorographene and molybdenum disulfide with the aim to engineer the intriguing magnetocrystalline anisotropy properties. Finally a summary with the conclusions is given in Chapter 9.

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Today it seems so clear how the circumstances have evolved into the events. Yet it is unclear how actions and thoughts of people affected one's flow. You read these lines from pure curiosity or from utmost hope to find Your name among the ones which are given an acknowledgement or credit. If the later is the reason of Yours reading, then know, that I express You a true gratefulness, which should never be shown less than by my deeds and more than by an unbreakable commitment.

Despite the idle nature of these words, which should be normally spared for more clear reports, it is appropriate to name the indispensable groups. Those who brought me here, now and in the form of myself. Therefore the siblings, parents, beloved ones, good friends as well as rivals, relatives, masters, peers, colleagues and unknowns are written in these words.

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Part I Introduction

Chapter 1

2D crystals and precursors

The existence and history of 2D crystals is tightly connected with layered bulk materials. Compounds with the intriguing layered structure, including clays, chalcogenides, hydroxides, silicate minerals as well as graphite and hexagonal boron nitride, attract already for a long time the interest of the scientific research community. The research spread across multiple scientific disciplines and industrial applications, from engineering of industrial materials to condensed matter theory.

To properly talk about 2D materials one should inevitably discuss layered materials in the first place, because those are the well recognized precursors to the ultrathin structures. Afterwards the monolayer crystals which are essential for the aims of this thesis will be described to provide a firm and broader base ground for the results.

1.1 Layered bulk materials

Layered materials form a large and important group of the naturally occurring compounds. The aforementioned clays and ceramics found their use in civil engineering, materials engineering as well as in high-temperature superconductivity. The chalcogenides became an essential part of the semiconductor industry and mechanical engineering applications. Materials like graphite and hexagonal boron nitride have reached wide utilization from metallurgy, through artistic media, up to the medicine.

The common and defining feature of these layered materials is their underlying crystal structure of coupled, ultra thin layers. This form determines their mechanical properties as the self-lubrication in the case of graphite or hexagonal boron nitride, [8, 9] but as well their electronic features promoting the effects of quantum confinement. The list of layered materials includes graphite, transition metal dichalcogenides, layered clays and even MoO_3 , GaTe, or Bi_2Se_3 with diverse electrical, mechanical and optical properties.[10]

In the following Sections we discuss only a few of the bulk crystal precursors, consisting of weakly coupled (van der Waals-like interaction) layers with strong in-plane bonding.

1.1.1 Graphite

Graphite, a crystal composed purely out of carbon atoms, is the most abundant carbon allotrope in nature. It belongs to the class of graphitic materials with sp^2 hybridized C atoms (see inset c-e of Fig. 1.1.1), unlike diamond with sp^3 hybridization (see inset a and b in Fig. 1.1.1).



Figure 1.1.1: Few of the many carbon allotropes. a) Diamond, entirely composed of sp^3 hybridized carbon atoms, b) amorphous carbon which is a polycrystal of graphite and diamond, and it is linked together by an amorphous carbon network. Lower row displays graphitic (derived from graphite) carbon allotropes— sp^2 bonded materials: c) zero dimensional fullerene, a C60 bucky-ball, d) one dimensional single walled carbon nanotube and e) graphite, the 3 dimensional material composed of two dimensional graphene sheets. [[12]]

Graphite has a layered crystal structure. Each layer is composed of sp^2 hybridized carbon atoms ordered in a perfectly flat honeycomb lattice with an interatomic distance of 1.42 Å.[11] The weak bonding between the individual sheets, separated at a distance of around 3.35 Å, is carried by the van der Waals forces. It is the underlying crystal form that allows the mechanical

1.1. LAYERED BULK MATERIALS

exfoliation at the macroscopic scale. As can be seen in Fig. 1.1.2 three possible stackings exist. The Bernal AB stacking of the layers is the most energetically favourable as well as abundant form (80 % [12]) compared to simple hexagonal AA (normally not observable in crystalline graphite [13]) or rhombohedral ABC stacking (second most abundant).



Figure 1.1.2: a) Balls and sticks model of AB stacked graphite with highlighted the unit cell composed of 4 atoms. The right panel displays a schematic top view of the structure with various layer stackings: b) ABC stacking, c) most stable AB stacked graphite and d) AA stacking.[14] [[12]]

Graphite is an electric conductor, more specifically it is a material with semimetallic behaviour with low density of states around the Fermi level and a band overlap of about 41 meV (AB stacked form).[15] Its electronic structure is dominated by the in-plane interactions, however the small band overlap is a direct result of the interlayer interactions, with slight variations among the different allotropic structures [11]. Without the interlayer interactions (the 2D situation) the density of states at the Fermi level decreases to zero. The conductance is a result of delocalized π electrons within the carbon layers, and thus it has an anisotropic character.

Due to graphite's electronic and mechanical properties its use is limited to the more conventional industrial applications, for example as electrical conductor in arc electrodes, carbon brushes in commutators or in battery anode constructions or as a dry lubricant for general industrial use.

1.1.2 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) belong to the wider group of compounds, the chalcogenides. The chalcogenides, as the name implies, are materials composed of chalcogen atoms, group VI elements¹, together with an element with lower electronegativity. The specific group of interest is the semiconducting transition metal dichalcogenides, with sixfold coordination bonding of the transition elements with chalcogenides in the prismatic form with general chemical formula MX₂. These TMDs form layered crystal structures.

The individual layers contain strong metal-chalcogenide covalent bonds and the interlayer bonding is provided by the weaker van der Waals' like interaction between chalcogenide atoms. The two alternating layers with hexagonally closed-pack chalcogenide atoms create the so called 2H structure² (see molybdenum disulfide in Fig. 1.1.3) with two alternating layers with trigonal prismatic coordination.[16] Multiple polytypes do exist, the cubic close-packed with rhombohedral symmetry, or the 3R structure, with three distinctive layers with trigonal prismatic coordination of chalcogenide atoms, etc.[17] The possible stackings are similar to the graphite stacking we have mentioned earlier.[18]

Examples of the TMDs with the aforementioned crystal structure include molybdenum disulfide (MoS₂), molybdenum diselenide (MoSe₂), tungsten disulfide (WS₂), tungsten diselenide (WSe₂) and molybdenum ditelluride (MoTe₂). It is worth noting that the alternative CdI₂-like (see 1T structure in Fig. 1.2.6) semimetal structures do exist with similar stackings, however with the octahedral structure of the sixfold coordination bonding of the transition elements with ligands. Examples are titanium disulfide, diselenide or ditelluride (TiS₂, TiSe₂ or TiTe₂).[19, 20]

Due to the layered structure, the TMDs do share similar mechanical properties with graphite and hexagonal boron nitride, and are utilized in e.g. industrial surface protection.[21]. The same mechanical properties enable the mechanical exfoliation of the two dimensional crystals from their bulk counterparts.[22] However, there exist semiconducting MX_2 compounds unlike semimetal graphite.[23] Therefore the investigation of their monolayers is noteworthy and provides a route to an electronically different class of ultrathin materials.

¹Although oxygen belongs to group VI, usually only sulfur, selenium and tellurium atoms are considered because of very different chemical behaviour of oxygen compared to the other elements.

²2H stands for two layers in the unit cell with hexagonal symmetry.



Figure 1.1.3: Ground state structure of the bulk crystal of molybdenum disulfide with hexagonally close-packed sulfur atoms in the alternating layers. In the inset a) the prismatic distribution of the sulfur atoms is clearly visible (sulfur atoms bonded to one Mo atom make up the corners of prism). The b) top and c) side view of the unit cell, consisting of 2 molybdenum and 4 sulfur atoms, displays the alignment. [[\Box]]

1.1.3 Group III-V compounds

Chemical elements of group III and V are known to create binary compounds with crystal structures similar to the previously discussed graphite and other carbon allotropes. For a long time they are already present in the microelectronics and optoelectronics industry, though their importance increased after the large attention that was given to two dimensional materials like graphene.[24–29]

The variety of the crystalline forms of these compounds is comparable to the carbon allotropes and include layered materials with hexagonal symmetry. The range of different compounds include non layered hexagonal wurtzite structures (w-BN, GaN, AlN, α -SiC) with tetrahedrally coordinated atoms like in hexagonal diamond, zincblende structures with atoms in tetrahedral coordination like in the diamond cubic crystal (GaAs, β -BN or c-BN), cubic rock salt structures (binary compounds from group III and VI elements) or finally hexagonal layered crystals (α -BN or h-BN, AlN sheets [30]). One of the leading examples is the diatomic compound, boron nitride (h-BN). It shares many mechanical and chemical properties with graphite. The compounds h-BN, GaN, AlN, GaAs and AlAs are semiconductors with applications in the semiconductor industry, manufacturing of optoelectronic devices, or applications utilizing their mechanical and piezoelectric properties. However, in the context of layered materials and the derived 2D crystals only h-BN [31] and AlN [32] remain promising.

1.2 Two dimensional nanosheets

The separation of layered solids into individual layers was questioned for a long period of time. It was unclear whether it was even possible due to concerns about their stability at finite temperatures [33, 34]. The long lasting stand-off was broken in 2004, when the first successful isolation of two-dimensional atomic crystals was reported by K. S. Novoselov, et al. [33] Among the first isolated crystals were dichalcogenides, graphene, BN, NbSe₂ as well as Bi₂Sr₂CaCu₂O_x. This experimental achievement ultimately made a broad scientific community to focus at this new class of materials with one leading prime member, graphene.

The first separation of 2D materials has been performed by exfoliation of layered bulk materials.³ Thus graphene, boron nitride and molybdenum disulfide have been exfoliated from graphite, hexagonal boron nitride or molybdenite, respectively. The exfoliated sheets are not true two dimensional objects, rather quasi 2D materials with a macroscopic size in two principal dimensions and a thickness of several atoms.

Thanks to the intriguing nature of ultrathin materials the effect of their successful isolation was exceptionally broad. The dimension reduction in the crystals elevate the effects of quantum confinement which could be directly exploited [38] and their planar structure revealed unmatched mechanical [39] and chemical features. Furthermore it seeded theoretical exploration, engineering and even synthesis of a whole class of materials: chemically functionalized materials, e.g. graphene based graphane, fluorographene, their bilayer forms, graphene oxide, "graphene-like" materials such as silicene, germanene, [40–42] stanene, [43] other two dimensional crystal candidates including hydroxides, metal oxides, graphyne, [44] borophene, single-layer black phosphorus (phosphorene), [45, 46] etc. Nowadays, also sandwich-like structures of these different 2D materials are realized, which allows to tune the properties of these layered structures. [47, 48]

 $^{^3}$ For the various materials the exfoliation energy is surprisingly very similar with a value around 20 meVÅ^{-2}.[35–37]

1.2. TWO DIMENSIONAL NANOSHEETS

Further we will discuss a couple of notable examples of ultrathin materials which are relevant for our results discussed further in this thesis, including graphene, chemically modified graphene, silicene and transition metal dichalcogenides. The focus lies on their common properties, synthesis and structure.

1.2.1 Retrieval of the nanosheets

Important aspects of 2D materials can be captured by understanding the conditions and methods used in the process of their synthesis or extraction. Two major method classes exist. The first one includes the top–down procedures, commonly called exfoliation techniques, where the molecular thin crystals are separated or grown from the bulk precursors. The second class of bottom–up practices, represents actual synthesis methods from other chemical compounds.[49]

Exfoliation techniques

The exfoliation methods are the most direct way for obtaining 2D crystals. The group of bulk materials for which the exfoliation technique can be efficiently used includes graphite, hexagonal boron nitride, transition metal dichalcogenides and transition metal oxides. [22]

The mechanical exfoliation is the most direct approach of extraction of single or multiple layers out of layered bulk crystals. The extraction employs mechanical cleaving. The best known example is the mechanical exfoliation of graphene with a technique called the 'scotch-tape method'. The process itself consists of repeatedly peeling of highly oriented pyrolytic graphite (a crystal of almost pure hexagonal graphite [11]) which is performed by repeated sticking of an adhesive tape. In this way the weak interlayer forces can be overcome ending up with a single molecular layer from the layered crystal.[33] ⁴

The direct advantages of the mechanical exfoliation are the simplicity of the method, which can be employed within a couple of hours, and the quality of the obtained samples, which is of high grade, hard to be matched by other techniques.[50] However, the main disadvantage is the lack of scalability, in terms of the sample size as well as the amount of time required for the production. Moreover, the nature of the technique gives little control over the number of exfoliated layers and the actual shape of the crystals.[51]

⁴Exfoliated mono to few layer thick graphite films of the size up to 10 μ m were extracted and they were inspected optically after direct transfer on a Si/SiO₂ substrate.[6]

An alternative approach is the *liquid assisted exfoliation*. The bulk materials are exfoliated in a solvent with or without assistance of intercalation compounds or mechanical acceleration such as sonication. The obtained flakes of a few molecular layers are afterwards transferred to a substrate by spraying, mechanical transfer or by drying the suspension. The variety of method implementations is large, especially because of the number of layered materials and the specific processes (oxidation, intercalation or exchange, treatment by solvents, etc.).[10]

Most of the TMDs are suitable for the liquid-phase exfoliation, [22] the metallic layered compounds TaS_2 and NbS_2 can be exfoliated by intercalation of water, MoS_2 can be exfoliated in an aqueous suspension, [52] graphite flakes can be separated into individual layers by sonication in a dichlorobenzene solution, [53] etc. The discovery of the liquid exfoliation was an important advancement and it is a research field under constant development⁵ as it allows production of large quantities of nanosheets.

Unlike the liquid exfoliation techniques *chemical exfoliation* realizes the final 2D material through intermediate steps with chemically modified compounds which can be exfoliated much more easily in the solvents in the form of a colloidal dispersion. The well known intermediate compound for the production of graphene is graphene oxide. It is produced from graphite that is oxidized with use of strong acids and oxidants, like in the Brodie, Staudenmaier and Hummers method.[54] After oxidation the individual graphene layers are heavily disrupted with a large portion of carbon atoms creating bonds with hydroxyl and epoxy groups. These sheets of layered material are strongly hydrophilic, which makes it easy to intercalate water between the layers and thus to create a colloidal suspension of graphene oxide in a water or other polar solvent with the help of sonication.

The atomic structure of graphene oxide is still not fully understood. On it own it can be used for production of various materials like thin layered paper-like insulating films. However its reduced form is of most interest. The reduction is performed with the assistance of chemical reductants, use of ultraviolet light or with thermal-based methods. The resulting material on the atomic level is disrupted graphene with defects and further treatment to remove residual oxygen and to reconstruct pristine graphene is required to reclaim its electrical conductivity.

Transition metal dichalcogenides like MoS_2 , WS_2 can be easily exfoliated via organolithium reduction chemistry. [55, 56] However these meth-

⁵An example of constant development progress are the new promising solvents like methyl-pyrrolidone suited for hexagonal boron nitride or isopropanol for TMDs. They allow scalable processes with lower sensitivity to environmental conditions (like air or water).[22]

1.2. TWO DIMENSIONAL NANOSHEETS

ods do suffer from low yields and poor quality of produced compounds (defects, structural and chemical changes).[57] Recently high yield methods of chemically driven exfoliation techniques, usable for transition metal dichalcogenides, were reported.[58] The process is similar to the previous attempts albeit much more complicated. The intermediate compounds are made of chalcogenides and lithium, potassium or sodium naphthalenide and in comparison to oxidation/reduction chemistry the process is suited for production of high quality materials.[58]

Synthesis techniques

Synthesis techniques unlike exfoliation ones do not require bulk layered material as precursors. The bottom up approaches are known to be very suitable for the large scale production of two dimensional crystals due to the scalability of the process and the reasonable to superior quality of the produced samples.

Probably the most promising method for scalable and continual production is *chemical vapour deposition* (CVD). In the last decade large attention was given especially to the CVD synthesis of graphene due to its attractive electrical properties as a transparent conductive film, but TMDs, silicene and other monolayers can be produced in a similar fashion.

The synthesis process of graphene consists of exposing a metallic foil (Cu, Ni, Ru, etc.) in a high temperature reactor to the presence of organic compounds as a source of carbon atoms (CH₄, etc.) mixed in the gas atmosphere (H₂, Ar, etc.). After the crystal synthesis the graphene layer can be transferred directly with the use of epoxy resin and polymers [59] or indirectly by a transport film or etching the metal substrate. The known drawbacks of this approach are the low control over the number of graphene layers as well as the polycrystallinity of the material which depends on the polycrystallinity of the substrate metal. Despite shortcomings the method is very attractive for the volume production of large scale transparent conducting films with use in transparent and flexible electronics, materials protecting films, chemical sensors, filters, etc. The possible applications are driving continual improvements.[60]

Under the similar experimental conditions the growth of silicene is possible as well. The first experimental evidence of successful epitaxial growth was reported by Padova et al. [61] followed later by the other experimental groups which have realized and observed silicene sheets grown from evaporated Si on a top of mainly Ag surface in ultra high vacuum. [62, 62–65]

The growth of molybdenum disulfide is much more sensitive to the environmental conditions, including highly crystalline metal substrates or vacuum requirements.[66] However, the successful CVD growth has been reported of the large area MoS_2 and WS_2 samples on amorphous SiO_2 substrates [67] by sulfurization of deposited thin metal films.[68] In the process MoO_3 (or WO_3) and sulfur powder is heated to 650°C which allows the components to diffuse and form one to few layer crystals of chalcogenides on the nearby placed pretreated substrate.

Alternative synthesis methods do exist, specifically for the production of graphene and carbon based materials, with unique features not feasible with exfoliation methods neither CVD methods. First of them is the *epitaxial growth* of graphene, which can be performed with silicon carbide (SiC) by its decomposition at high temperatures and creating few layer graphene on its surface.

The 4H-SiC and 6H-SiC polytypes of semiconducting hexagonal SiC are commonly used, with different stacking of the hexagonal Si-C bilayers.[12] The (0001) surface of SiC is pretreated, to lower the roughness and to remove the coating SiO layer. Afterwards it is annealed in noble gas atmosphere to graphitization temperature (between 1000 and 1500 °C) to allow Si atoms to sublimate and also to diffuse through the growing graphene film. The epitaxial graphene (multi)layer is separated from the underlying surface by the buffer layer and it can be lithographically patterned and contacted with metal contacts. [69] The main advantage of epitaxial growth is the control over the structural uniformity over large areas, because the crystal orientation of graphene is coupled with the crystal structure of the substrate SiC wafers.⁶ Furthermore, this method is a viable candidate for all-carbon post CMOS technology and graphene based electronics, [12] with the advantage of the mass production, high crystal quality and reuse of contemporary silicon based electronics processes. However, the process needs further improvements to resolve sensitivity to the miscut of silicon carbide wafers.[70]

The second method is the *chemical synthesis* of carbon based macromolecules from polycyclic aromatic hydrocarbons, which is a field with long history in chemistry. The route of a chemically driven, bottom-up approach, may not be appealing for the synthesis of large two dimensional sheets of structurally simple materials like graphene, however there is a large set of more complex monolayer crystals without bulk counterparts including graphyne, its boron nitride analogue,[71] graphdiyne,[72] other planar benzenebased macromolecules, nanoribbons (1D structures),[73, 74] etc. which will benefit from the advances in available methods from organic chemistry.

⁶This requirements is especially important in connection to reproducible production and possible graphene ribbon cutting.

1.2.2 Graphene

Graphene is the first known member of the group IV elements 2D crystals with a honeycomb like lattice which can exist in free standing form. The subtle reasons for its stability under the experimental conditions may be provided by the corrugations of its surface with a lateral size of several nanometres and out of plane deformations with heights up to 1 nm.[75]



Figure 1.2.1: a) Ball and sticks model of a single graphene sheet with highlighted in-plane unit cell composed of two carbon atoms. b) Schematic top view on the hexagonal honeycomb lattice with highlighted two sublattices commonly known as A and B. [[12]]

The crystal structure of graphene stems from the graphite structure (see Fig. 1.1.2). Graphene as a single layer of graphite, or macromolecule of aromatic hydrocarbon, is composed of carbon atoms arranged in the honeycomb lattice, with every atom possessing three bonds with its neighbours (see Fig. 1.2.1). The reason for its planar structure is the sp^2 orbital hybridization that induces three in-plane σ bonds, while the remaining electron in the p_z orbital accounts for π bonds and is responsible for the conducting, chemical as well as structural properties.[76] The crystal unit cell has an in-plane lattice parameter of 2.46 Å and includes two equivalent carbon atoms which are usually assigned to the A or B sublattice (see Fig. 1.2.1). The A and B sublattices are two overlapping triangular lattices.

As can be seen from Fig. 1.2.2 graphene can be characterized as a semimetal (or alternatively as a zero band gap semiconductor) with vanishing density of states at the Fermi level. The valence and conduction bands meet together at two independent K and K' points in the first Brillouin zone of the reciprocal space (see Fig. 1.2.3). The energy dispersion at the K points is linear (i.e. the energy is a linear function of the crystal momentum wave vector measured relative to K point) very much like the energy dispersion of massless fermion particles following the Dirac (Dirac-Weyl) equation. The energy dispersion around the Fermi level has the form of $E = \hbar k v_f$, with



Figure 1.2.2: Electronic band structure and corresponding density of states of graphene ($E_F = 0$). Note the vanishing density of states at the Fermi level where conduction and valence band touches at the K point (one can identify two independent K and K' points in the Brillouin zone where the band crossing occurs).

 v_f the Fermi velocity approximately equal to c/300.[12]. Because of the two dimensional nature of graphene crystal, this electronic spectrum can be also, to a great extent, described by the tight-binding model.[49, 77]

Exactly this Dirac spectrum, and related Dirac cones at K symmetric points, are responsible for the large interest in the electronic properties of graphene. The linear character of the energy dispersion theoretically leads to effects such as universal ballistic conductivity, Klein tunnelling [78] and the ambipolar electric field effect.[49] Although these results only apply to the idealized perfect crystal of pristine graphene they provide us very much needed insight into the experimentally observed properties.

However, the Dirac like electronic band structure of graphene is also a major disadvantage for its use in most of the contemporary electronic applications which rely on the presence of a finite band gap. Thus a large portion of the graphene based research is focusing on band gap engineering by applying electric fields, [79, 80] chemical functionalization (changing sp^2 to sp^3 hybridization) of graphene, [81–83] mechanical functionalization (nanoribbons), [84] etc. This handicap of graphene has even more motivated the extensive exploration of other graphene-like and other two dimensional materials.

1.2.3 Silicene

Curiosity and chemical similarity guided scientific research into designing honeycomb structures out of the other group IV elements or of the combination of group III and V elements into binary compounds.[24] A promi-



Figure 1.2.3: a) Real space unit vectors and corresponding b) reciprocal space vectors for graphene lattice (the first Brillouin zone is highlighted). Note the only two dimensional reciprocal space which is effectively used even in the calculations where the periodical unit cell has a finite size in the z direction. Also note that all the compounds with a hexagonal lattice posses the same reciprocal lattice, this includes silicene and TMDs which will be discussed further. [[\Box]]

nent example of such a material is silicene, a monolayer structure of silicon. It has emerged as a few-atom-thick material with a potential to replace graphene by its inherent compatibility with silicon based electronics. This was underlined especially after its successful experimental observation and synthesis.[61–64, 85] The reason for this claim is the fact its proven existence opened a new path for a nanoscale material which might be easily functionalized (like graphene) and incorporated within electronics as we know it today.[86]



Figure 1.2.4: Balls and sticks model of a single layer buckled hexagonal lattice of silicene, the buckling is marked by buckling height δ . The in-plane unit cell composed of two silicon atoms is highlighted. [[$[\Box]$]]

Silicon atoms can create a single layer honeycomb lattice, with considerably larger interatomic distances compared to those of graphene, with a lattice constant of 3.83 Å.[87] Unlike graphene, with sp^2 hybridized carbon atoms and in-plane bonds, silicon atoms form due to their larger size and sp^3 -like hybridization (neither sp^2 nor sp^3) a buckled hexagonal lattice with buckling parameter (δ) of 0.44 Å (see Fig. 1.2.4).[40] The buckling is a feature shared among more hexagonal crystals made of group III, IV and V atoms where the planar form cannot be stabilized with π bonds due to the large interatomic distance. Only the first row element based compounds including SiC, GeC, AlN, GaN, BN, graphene and their mixed compounds form planar sp^2 -only bonds.[24]



Figure 1.2.5: The electronic band structure of free standing silicene with the corresponding density of states ($E_F = 0$). The vanishing density of states at the K symmetry point resembles the band crossing in graphene, however first principles calculations reveal that the significant spin-orbit interaction in silicene leads to a small band gap of 1.47 meV, almost two orders of magnitude more compared to graphene.

As was reported by early theoretical works, silicene is a semimetal with linearly crossing electronic bands with vanishing density of states at the Fermi level in a very similar way as we have observed earlier for graphene. [24, 40, 88] The character of the band dispersion implies similar properties including electrons propagating through the monolayer crystal structure of silicene as massless fermions in the vicinity of the Dirac point. Additionally, some unique features of monolayer silicene such as quantum spin Hall effect, [89] a large spin-orbit interaction, [90] a mechanically tunable bandgap [91] and a valley-polarized metallic phase [92] have been reported by theoretically based studies.

1.2.4 Transition metal dichalcogenides

The last group of two dimensional materials, which we will describe in more detail are the transition metal dichalcogenides.



Figure 1.2.6: The insets a) and b) show two examples of crystal phases of monolayer molybdenum disulfide. The c) and d) inset shows a schematic top view on the 1H and 1T phase of MoS_2 , respectively. The 1H ground state structure has prismatic coordination of sulfur atoms around the transition metal atom and the upper layer lattices of the chalcogenide atoms match with the lower one. The metastable 1T phase shows octahedral coordination of the metal bonds with the upper layer of sulfur atoms rotated by 30° with respect to the lower ones. [[12]]

Unlike the previous one-atom thick hexagonal two dimensional materials, a monolayer of TMDs is formed consisting of three atomic levels: the triangular lattice of transition metal atoms is sandwiched between an upper and lower equilateral triangular lattice formed of chalcogenide atoms. The ground state of the single layer crystal has prismatic coordination, where the upper and lower layer sublattices of the chalcogenide atoms match. This configuration is commonly known as the 1H phase (one layer with hexagonal symmetry). However, a metastable 1T phase (one layer with tetragonal symmetry) does exist.[17] The 1T phase incorporates octahedral coordination of the metal bonds with the ligands and the upper and lower layers of chalcogenide atoms are mutually rotated by 30° as can be seen in the inset d) of Fig. 1.2.6. In addition also other non trivial structures were reported.[55, 93]

Depending on the composition, crystal structure or polytype, the TMDs exhibit semiconducting or metallic properties.[17, 94] As an example, trans-



Figure 1.2.7: Electronic band structure and corresponding density of states of a semiconducting monolayer of MoS₂ in its most stable 1H phase ($E_F = 0$). The direct band gap at the K symmetry point is a feature of the monolayer MoS₂, in the bulk form the indirect band gap appears between valence Γ point and a point between Γ and K in conduction the band.[17]

formation of MoS_2 from a semiconducting material phase to a metal material phase occur with a change from the 1H to 1T structure. Additionally the band gap in TMDs bilayers is tunable, like in graphene, under applied external field.[95]

Several TMDs such as MoS_2 , $MoSe_2$, WS_2 and WSe_2 have large bandgaps that exhibit an indirect to direct band gap transition from their bulk to monolayer form. For example the indirect band gap of 1.3 eV of MoS_2 expands to direct gap of 1.8 eV (see Fig. 1.2.7) in its monolayer form.[96] This indirect to a direct band gap transition enables photoluminescence of monolayer MoS_2 and is of importance for possible photoelectronic applications.[17, 96, 97]

Part II Methodology

Chapter 2

Brief introduction to DFT

The density functional theory (DFT) formalism is probably the most spread *ab initio* quantum mechanical modelling tool in the contemporary solid state matter research. In this Chapter a short introduction and schematic overview of its principles is presented, as it is the method of choice for the results presented later in the manuscript.

DFT is build upon the premise that the properties of many electron systems, such as solid state crystals, molecules and matter in general can be expressed as functionals¹ of the electron density, a single, scalar function. The history of the formalism dates back to 1964 when the two Hohenberg and Kohn theorems were formulated. They express the equivalence between the electronic density and the all-electron wave function of a quantum mechanical many-body system. Shortly after, in 1965 the practical implementation by Kohn and Sham was introduced. However, only the later improvements of exchange-correlation energy, pseudopotentials and projector augmented wave method together with advances in the computational infrastructure allowed for its widespread use.

It can be stated that DFT is loosely based on the Thomas-Fermi model, utilizing only the electron density, which was developed separately from the wave function formalism in 1927. However, even the extension of this model with the Thomas–Fermi–Dirac exchange energy term did not solve the shortcomings. While the Thomas-Fermi model is an example of a simple, fast and to some extent usable method, it largely fails in the fundamental aspects (e.g. description of the atom electron shell structure or molecular bonding). Nevertheless, the Thomas-Fermi model, the first model based on the electron density, is important for fundamental and historical reasons.

Next we discuss the DFT fundamentals and approximations.

¹ In this context functional maps a function space to a space of scalars.

2.1 DFT scheme

2.1.1 Schrödinger equation

The non relativistic solution of a quantum mechanical many electron system can be fully described by the Schrödinger equation. If the Hamiltonian is not an explicit function of time we can restrict ourselves to the stationary states, for which observable properties remain unchanged. The stationary states are defined by:

$$E\Psi = \hat{H}\Psi = \left[\frac{-\hbar^2}{2m_e}\Delta + \hat{V}\right]\Psi$$
(2.1.1)

with E the energy (further referred also as total energy of the system E_{tot}), \hat{H} the Hamiltonian operator, \hat{V} the potential (operator) and Ψ the all electron particle wave function.

The Hamiltonian operator \hat{H} from Equation 2.1.1 can be written for a system of N electrons (all electrons in all atoms) and M atomic nuclei (crystals, molecules, etc.) as:

$$\begin{split} \hat{H} = & \underbrace{-\frac{\hbar^2}{2m_e} \sum_{i}^{N} \Delta_i - \sum_{\alpha}^{M} \frac{\hbar^2}{2M_{\alpha}} \Delta_{\alpha}}_{\hat{T}_n}}_{\hat{T}_e} \\ & \underbrace{-\sum_{i}^{N} \sum_{\alpha}^{M} \frac{1}{4\pi\varepsilon_0} \frac{Z_{\alpha}e^2}{|\vec{r}_i - \vec{R}_{\alpha}|}}_{\hat{V}_{external}} + \frac{1}{2} \sum_{i\neq j}^{N} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}_{ee}} + \frac{1}{2} \sum_{\alpha\neq\beta}^{M} \frac{1}{4\pi\varepsilon_0} \frac{Z_{\alpha}Z_{\beta}e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|}}_{\hat{V}_{nn}} \end{split}$$

with \hat{T}_e the electron kinetic energy operator, \hat{T}_n the nuclei kinetic energy operator, $\hat{V}_{external}$ the external potential created by nuclei acting on electrons, \hat{V}_{ee} the electron-electron interaction operator and \hat{V}_{nn} the nucleus-nucleus interaction operator. One can clearly see the major obstacle of this approach. The size of the phase space (coordinates of all electrons, nuclei, spins and more) rises linearly with the size of the system, beyond practical usability with no analytical solution left for all but a few simple cases (e.g. the hydrogen atom).

A first approximation we will make is the Born-Oppenheimer approximation.

Born-Oppenheimer approximation

The Born-Oppenheimer approximation is also called the adiabatic approximation due to its resemblance to the adiabatic theorem. The slowly acting
external conditions are the positions of the nuclei, which appear fixed due to the large difference of the electron and proton (cores) masses. Therefore we can neglect the kinetic term of the nuclei (inversely proportional to the mass of the particles): $\hat{T}_n = 0$ and we can consider the nucleus-nucleus interaction to be effectively constant: $\hat{V}_{nn} \approx \text{constant}$. Within this approximation the Hamiltonian becomes:

$$\hat{H} = \hat{T}_e + \hat{V}_{external} + \hat{V}_{ee} + \hat{V}_{nn}$$
(2.1.2)

2.1.2 Hohenberg-Kohn theorems

The two fundamental theorems by Hohenberg-Kohn reveal the solution to the unmanageable phase space size.

First Hohenberg-Kohn theorem

The first theorem states that the external potential in the Hamiltonian of the system is a unique functional of the ground state electronic density of the system, apart from a trivial additive constant.[98] In other words, the observable physical properties of a many electron system are fully described (via the functionals) by the scalar electron density function depending only on 3 spatial coordinates.

The actual proof can be performed by means of *reductio ad absurdum* for a non degenerate ground state². The postulate that two distinctive potentials will lead to the same density leads to a contradiction, i.e. the inequality of two identical energies.[49, 98]

Second Hohenberg-Kohn theorem

The second theorem states that the total energy of the system (E), expressed as a functional of the electronic density, reaches its minimum for the ground state electronic density.[98] In other words, the total energy of the system with the external potential as the functional of the electronic density is minimized by the ground state density.

2.1.3 Energy functional

The Hohenberg-Kohn theorems allows one to find the ground state properties of a system by minimizing the total energy expressed as functional of the

 $^{^2 \}mathrm{The}$ restrictions on the non degenerate ground state was removed by the work of Levy.[99]

electronic density. From the aforementioned Hamiltonian operator 2.1.2, we can write the total energy E_{tot} as:

$$E_{tot} = E_{HK} + V_{nn}[\rho]$$

with $V_{nn}[\rho]^3$ a functional of the electronic density and the fixed positions of the nuclei, and E_{HK} (HK stands for Hohenberg-Kohn) equal to:

$$E_{HK} = \underbrace{T[\rho] + V_{ee}[\rho]}_{F_{HK}[\rho]} + V_{external}[\rho] = F_{HK}[\rho] + V_{external}[\rho]$$

with $F_{HK}[\rho]$ the universal functional⁴ and $V_{external}[\rho]$ the potential energy as function of $v_{external}$, the potential of the atomic nuclei (the integration is performed over the entire space Ω):

$$V_{external}[\rho] = \int_{\Omega} \rho(\vec{r}) v_{external}(\vec{r}) d\vec{r}$$

where
$$v_{external}(\vec{r}) = \sum_{\alpha}^{M} \frac{1}{4\pi\varepsilon_0} \frac{Z_{\alpha}e}{|\vec{r} - \vec{R}_{\alpha}|}$$

Hohenberg and Kohn proposed the form of the $F_{HK}[\rho]$ functional as the sum of the dominant classical Coulomb and another G_{HK} universal functional containing the kinetic energy terms and the corrections to the electronelectron interactions not present in following classical Coulomb functional $(V_{ClassicCoulomb})$:

$$F_{HK}[\rho] = \underbrace{\frac{1}{2} \iint_{\Omega} \frac{1}{4\pi\varepsilon_0} \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} d\vec{r'}}_{V_{ClassicCoulomb}} + G_{HK}[\rho]$$

2.1.4 Kohn-Sham approach

The large contribution made by Kohn and Sham in 1965 was the expression of the G_{HK} functional. The Kohn and Sham approach obtains a solution via an auxiliary system of noninteracting particles similar to the Hartree-Fock method, however including exchange as well as correlation corrections.[100]

 $^{{}^{3}}V_{nn}[\rho]\Psi = \hat{V}_{nn}\Psi$

⁴If this functional would be known, the whole problem would be just a minimization problem of the total energy as function of the electronic density. Unfortunately, we do not know it.

2.1. DFT SCHEME

While it is trivial to express the kinetic energy, in the Hamiltonian of the system, as a functional of the many-body wave function (see equation 2.1.1) it is a difficult task to express the kinetic energy as a functional of the electronic density. The idea of the Kohn-Sham approach is the use of an auxiliary system of noninteracting electrons⁵ with the same electronic density $\rho(\vec{r})$ as the original system of interacting particles. However, this second system will experience a non-trivial effective potential composed of a well known analytical part and complicated exchange and correlation corrections. Kohn and Sham themselves suggested the local density approximation (more will be explained later) of the exchange and correlation corrections which allowed them to fully express the energy term. The proposed form of G_{HK} is:

$$G_{KS} = T_S[\rho] + E_{xc}[\rho]$$

with $T_S[\rho]$ the kinetic energy of an auxiliary system of noninteracting electrons and $E_{xc}[\rho]$ the exchange and correlation energy of a system of interacting electrons with density $\rho(\vec{r})$ (a small albeit very important correction). We can trivially express $E_{xc}[\rho]$ as (see previous equations):

$$E_{xc}[\rho] = (T[\rho] - T_S[\rho]) + (V_{ee}[\rho] - V_{ClassicCoulomb}[\rho])$$

Now we can write E_{HK} as:

$$E_{HK} = T_S[\rho] + V_{external}[\rho] + V_{ClassicCoulomb}[\rho] + E_{xc}[\rho]$$

In order to express the effective potential for an auxiliary system, we need to create a link between the system of interacting and noninteracting electrons. The second Hohenberg-Kohn theorem allows us to write the stationary equations for both systems as:

$$\left. \frac{\delta E_{HK}}{\delta \rho} \right|_{\rho_0} = \left. \frac{\delta E_S}{\delta \rho} \right|_{\rho_0} \equiv 0$$

with $E_S[\rho] = T_S[\rho] + V_S[\rho]$ the energy functional for the auxiliary system. Both energies E_{HK} and E_S reach their minimum at the same ground state electronic density $\rho_0(\vec{r})$. $V_S[\rho]$ has the form:

$$V_S[\rho] = V_{external}[\rho] + V_{ClassicCoulomb}[\rho] + V_{xc}[\rho]$$

with V_{xc} part of the effective potential expressed, with use of the stationary property, as a function of the variation of the exchange correlation energy

⁵A system of noninteracting electrons is solved by solving a one-particle Schrödinger equation.

with respect to the electronic density:

$$V_{xc}[\rho] = \int_{\Omega} \rho(\vec{r}) v_{xc}(\rho(\vec{r})) d\vec{r} = \int_{\Omega} \rho(\vec{r}) \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})} d\vec{r}$$

Now, with the effective $V_S[\rho]$ potential, we can write the Kohn-Sham (single particle Schrödinger) equations for an auxiliary system of noninteracting electrons:

$$\begin{bmatrix}
-\frac{\hbar^2}{2m_e}\Delta_i + \hat{V}_S[\rho(\vec{r})]
\end{bmatrix} \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

$$\rho(\vec{r}) = \sum_{spin=1}^2 \sum_i^{N/2} |\psi_i(\vec{r})|^2$$
Kohn-Sham equations
$$\rho(z.1.3)$$

with N the number of the electrons in the system. Note that in the definition of the electronic density $\rho(\vec{r})$ we already assume the Pauli exclusion principle for the electrons (fermions).

Kohn and Sham showed that with the use of the Hohenberg-Kohn theorems the equations for our problem of interacting electrons are identical to the set of equations of noninteracting electrons in an effective potential V_S . Therefore, for a given V_S , determined by the properties of our system, we can search for the solutions of the Kohn-Sham equations and ultimately obtain the ground state electronic density of the system as the sum of the first N'lowest energy solutions $|\psi_i(\vec{r})|^2$ and the ground state energy as:

$$E = \sum_{i}^{N'} \varepsilon_{i} - V_{ClassicCoulomb}[\rho] + (E_{xc}[\rho] - V_{xc}[\rho])$$

One needs to solve the Kohn-Sham equation self-consistently, because V_S depends on the actual electron density ρ . This is performed by constructing an initial guess for the electron density, solving the equations, obtaining a new density and energy (see above) and repeating this process until convergence in both quantities is reached.

This procedure with a known analytical form of the exchange correlation energy E_{xc} provides an exact electronic ground state solution for a given external potential of atomic cores. Additionally, one can find a ground state structure (nuclear positions) with use of the Hellman-Feynman theorem [101].

The Hellman-Feynman theorem relates derivatives of the total energy (like forces) to the expectation value of the derivative of the Hamiltonian:

$$\frac{dE}{d\lambda} = \int_{space} \psi^* \frac{d\hat{H}}{d\lambda} \psi dv \qquad (2.1.4)$$

The optimal configuration (if it exists) of the atomic cores can be found by the following procedure. For an initial guess of the nuclear positions the electronic self consistent loop is performed. Subsequently the forces acting on the ions are calculated with the use of the Hellman-Feynman theorem. Next the atomic cores are moved according to classical mechanics. The procedure is repeated until the forces acting on the ions vanish.

2.2 DFT to DFA

We stated before that DFT is exact. Unfortunately in the real world implementation we are forced to use the density functional approximation (DFA). In the following Sections we discuss the approximations made in the representation of the wave functions and exchange correlation energy. The use of DFA is inevitable for any practical application due to numerical constraints or missing knowledge.

2.2.1 Basis sets and Bloch states

It is convenient to express the wave functions as an expansion in a basis set. There are two distinctive groups of basis sets, localized and nonlocalized. For an isolated system without periodicity, the (atom) localized basis sets (spherical harmonics, Gaussian functions, etc.) can be used. However many systems are, or can be approximated as periodic crystals. The nonlocalized basis set for the wave function representation is suited for periodic systems.

For periodic systems the Bloch theorem provides a natural way to express the wave functions in a plane waves basis set of the single electron states solution, as of the Kohn-Sham equations 2.1.3. The Bloch theorem and the Bloch state describe a single electron moving in the lattice of ions. The wave function of an electron in a periodic potential differs from the one of the free electron by a modulation part (a function with the periodicity of the lattice).[102]

The wave function of an electron in form of Bloch states is (for full explanation of the following form see Appendix A):

$$\psi(\vec{r}) = \sum_{\vec{k} \in 1^{st} BZ} \underbrace{\left| \sum_{\forall \vec{K}} C_{\vec{k} - \vec{K}} e^{-i\vec{K} \cdot \vec{r}} \right|}_{u_{\vec{k}}(\vec{r})} e^{i\vec{k} \cdot \vec{r}}$$
(2.2.1)

where 1^{st} BZ stands for the first Brillouin Zone, with \vec{k} a reciprocal vector in this first Brillouin Zone and \vec{K} the reciprocal lattice point vectors. $u_{\vec{k}}(\vec{r})$ is

lattice periodic function. The used \vec{k} for labelling the Bloch states directly relates to the crystal momentum $\hbar \vec{k}$ of an electron.



Figure 2.2.1: Example of Brillouin zone sampling of hexagonal lattice with a) Γ centred and b) regular $6 \times 6 \times 1$ Monkhorst-Pack grid, the first Brillouin zone is highlighted as well as the irreducible Brillouin zone, which is the first Brillouin zone reduced by all of the point symmetries of the lattice and is used to further reduce numerical costs when applicable. [[1]]

The Bloch states give us more than just an insight into the structure of the solutions, they also provide a possible practical numerical solution. Specifically it provides a recipe for the solution in the form of plane waves (i.e. the summation over \vec{K} in 2.2.1). The use of a plane wave basis set allows the use of fast Fourier transforms, does not depend on ion positions (as in the case of localized basis sets like spherical harmonics, Gaussian functions) and provides a systematic way of refinement.

The practical numerical limitations force us to clip the summation over \vec{K} vectors at a certain length of the vectors. This length is usually expressed in the terms of a maximal energy, and it is named energy cutoff radius E_{cut} :

$$\forall \vec{K}, |\vec{K}| < K_{cut}; \quad E_{cut} = \frac{\hbar^2}{2m_e} K_{cut}^2$$

This constraint results in a limited resolution in real space at the scale:

$$\lambda = \frac{2\pi}{K_{cut}}$$

Similarly, the summation (integration) over \vec{k} in the first Brillouin zone in expression 2.2.1 can be approximated by the sum of well chosen points in the first Brillouin zone. The most widely used set of points is build according to the scheme of Monkhorst and Pack.[103] An example of such a set is shown in Fig. 2.2.1.

2.2.2 Pseudopotentials and PAW

In the previous Section we have outlined the use of a plane wave basis set. However, the wave function typically seen in crystals requires a very large basis set (E_{cut}) due to the large wave function oscillations near the atomic cores. To avoid this obstacle one needs to replace the actual wave function with a smoother one. Because the problematic region lies in the vicinity of the atomic nuclei, the core or inner shell electrons (which are usually dormant) can be subtracted from the total wave function. The price for this approach is the replacement of a simple Coulomb potential ($v_{external}$) created by the nuclei with a much more complicated pseudopotential created by nuclei and chosen number of core electrons.[104] The wave function with omitted core electrons is called a pseudowavefunction, it describes the valence electrons and is identical (due to the construction of the pseudopotential) to the full electron wave function outside a chosen core radius.

The concept of pseudopotentials was further improved by Blöchl who introduced the projector augmented wave (PAW) method.[105] It builds upon the same premise of frozen core electrons which are removed from the calculation. Yet it provides a transparent way to reconstruct all electron wave functions from the valence electron wave function, with the use of projector functions active in the chosen augmentation region close to the atomic nuclei, and it properly describes the potentials from all-electron charge densities. Moreover, the use of the PAW method further increases the calculation efficiency.

2.2.3 Exchange correlation functional

The missing ingredient to the Kohn-Sham equations 2.1.3 is the analytical form of the $E_{xc}[\rho]$ functional. Kohn and Sham originally proposed in their work [100] an exact form of the exchange correlation functional. We know it as the local density approximation (LDA) of the $E_{xc}[\rho]$ functional. For the electronic density which is sufficiently slowly varying, the exchangecorrelation energy can be written in the form:

$$E_{xc}^{LDA}[\rho] = \int_{\Omega} \rho(\vec{r}) e_{xc}(\rho(\vec{r})) d\vec{r}$$

with $e_{xc}(\rho(\vec{r}))$ the exchange and correlation energy per electron in a uniform electron gas with a density equal to $\rho(\vec{r})$, known from the theory of a homogeneous electron gas.

The LDA works surprisingly well for a variety of crystals. The reason for the usability of the LDA lies in the fair amount of error compensation between the exchange and correlation parts of the functional. It is known to slightly underestimate lattice parameters and to reasonably estimate the medium to long range interactions (e.g. van der Waals interaction, hydrogen bonds etc.) due to overestimation of the attractive potential.

Improvement over the LDA approach is the generalized gradient approximation (GGA). If LDA is the first term of the expansion of the exchange and correlation energy in powers of the density gradient, then GGA includes the next term of the series:[100]

$$E_{xc}^{GGA}[\rho] = \int_{\Omega} \rho(\vec{r}) e_{xc}(\rho(\vec{r})) d\vec{r} + \int_{\Omega} |\nabla \rho(\vec{r})|^2 e_{xc}^{(2)}(\rho(\vec{r})) d\vec{r}$$

The improved form of the exchange and correlation energy with the corrections due to gradients in the electronic density is not without drawbacks. GGA functionals are known to generally overcorrect LDA by overestimating the lattice parameters and additional medium to long range interaction corrections are required (e.g. Van der Waals interaction).

The e_{xc} in both LDA and GGA has the form of the two additive parts, representing contributions of exchange energy of electron and correlation between electrons, with various possible representations: [2, 106]

$$e_{xc}(\rho(\vec{r})) = e_x(\rho(\vec{r})) + e_c(\rho(\vec{r}))$$

Chapter 3

Charge transfer methods

The motivation for the charge transfer calculation methods is to evaluate charge transfer (and related physical variables as dipole moments) between the individual atoms (or larger structures) in order to quantify some of the observable properties of the molecules.

In the following we discuss possible methods to determine distribution of charges in crystals. The main goal of all the approaches is to ascribe the obtained multielectron charge density to individual atoms following the concept of atoms in molecules (AIM).¹ The AIM on itself is a construction of the human mind, a tool, and on its own it is not directly observable by experiment nor can be defined unambiguously.[107] The ambiguity originates from the simple quantum mechanical fact that crystals are not just the sum of their charged structural elements, e.g. atoms. This results in a multitude of different techniques. Nevertheless, all these methods provide meaningful and transparent approaches of electronic density division. Furthermore they follow some obvious restrictions, like the computed charge transfer between infinitely separated parts should be zero or that the symmetric compounds exhibit symmetric charge transfers.

One of the early approaches to assign charge to the individual parts in a compound was done by Mulliken.[108] The Mulliken charge population analysis is one example of the many wave function based methods [109] and the actual procedure came at no cost for methods using localized basis sets. However, for DFT formalism methods based on nonlocalized basis sets, the advantage disappears. Moreover, the transferability of the wave function based methods is difficult if not impossible and the major drawback is the large sensitivity to the choice of the basis function set. On the other side there are the electronic density based methods with more intuitive as well

 $^{^1}$ Atoms in molecules is a concept in which atoms and their bonds can be used to express observable properties of molecular systems.

as trustworthy appeal, benefiting from the that the electronic density is well defined and easily obtained in the DFT formalism. In the following, several charge density based methods are discussed.

3.1 Bader charge analysis

The Bader charge analysis was introduced by Richard F. W. Bader in 1990.[110] The method is based on the partitioning of the real space into cells accommodating individual chemical atoms.

The space is divided by the surfaces of zero flux in the gradient of the electronic density. This means the flux in the gradient vector field, of the all electron density, vanishes at this zero flux surface.² Mathematically we can define the surface $S(\vec{r})$ as:

$$\nabla \rho(\vec{r}) \cdot \vec{n}(\vec{r}) = 0; \quad \forall \vec{r} \in S(\vec{r})$$

with $\vec{n}(\vec{r})$ the normal to the surface $S(\vec{r})$.

The dominant feature of the all-electron density in the molecules and crystals is that the density exhibits its maximum at the position of the nuclei. This leads to the intuitive image of the partitioning scheme, where the space is divided by the surfaces determined by the extremes (minima) of the electronic density. In general³ the partitions contain a single nucleus and the charge density enclosed in the separate spatial regions can be ascribed to individual chemical atoms.

The usual form of the electronic charge density, obtained from the DFT based software framework, is a grid sampled function in real space. Thus the practical implementation of the Bader charge analysis is restricted to grid based methods and generally cannot be solved analytically. The reconstruction of the zero flux surface and the subsequent integration, in the so called Bader regions, had caused convergence problems and created additional numerical complexity.

Although the Bader method was first proposed in 1990 the first practical application appeared only in 2006 by Graeme Henkelman et al.[111]. Instead of finding the actual dividing surface, which is particularly difficult, they propose an algorithm which assigns each grid point (with corresponding charge) to the one of the atomic regions by following a steepest ascent path on the charge density grid. This allows robustness (independence on the compound

 $^{^{2}}$ The idea for Bader charge analysis originates from the principle of least action where the zero flux surface appear as one of the required conditions.

 $^{^{3}}$ Sometimes regions without nucleus can occur, then they are assigned to the nearby atom regions.

3.2. VORONOI CHARGE ANALYSIS

structure) and predictable scalability of the algorithm. The resulting Bader charge is then just a sum over the charges at the grid points belonging to the region defined by the common terminal point of the steepest ascent paths.

The aforementioned algorithm was further refined by Edward Sanville et al. in 2007[112] and later by W. Tang et al. in 2009.[113] The improvements included the correction of the grid bias (it causes a systematic deviation from the true Bader surface if ascent trajectories are clipped to grid points) and more accurate division of the charge at the Bader volumes boundary. The improved procedure (with usable implementation available from Henkelman Group at The University of Texas at Austin) also incorporates an iterative approach to improve the speed of the algorithm when dealing with large meshes.

3.2 Voronoi charge analysis

An appealing twist to the Bader partitioning scheme is the Voronoi charge analysis method introduced by F. Matthias Bickelhaupt in 1996 [114] and improved to the Voronoi Deformation Density method by Célia Fonseca Guerra in 2003.[115] The principle is similar to the Bader charge analysis or other minor partitioning schemes,[115] the space is divided to non-overlapping regions defined to be the Voronoi cells⁴ with the seeds the positions of the nuclei.

The actual charge ascribed to the individual atom is the definitive integral of the electronic charge density within the Voronoi cell of the particular atom. The aforementioned improvement of C. F. Guerra was in the use of deformation charge density (this term will be explained with the Hirshfeld method) instead of the all-electon charge density, which results in the better description of the charging effects due to the chemical bonding.

3.3 Hirshfeld method

The origin of the Hirshfeld charge analysis dates back to 1977 when it was first proposed by F. L. Hirshfeld.[116] The main feature of this method is that it assigns to each atom in the molecule its share of charge at each space point of the charge density. There is neither a partitioning scheme

⁴Voronoi cell or polyhedron is the set of points closest to the particular seed point, the Voronoi cells are broadly presented in nature like honeycomb (from triangular seed lattice), basalt stone columns or foam from soap bubbles.

nor dividing surfaces like in the binary approaches where all charge density located at some point is attributed to a specific atom or not.

The total charge density is divided into the atomic contributions:

$$\rho(\vec{r}) = \sum_{\alpha}^{M} \rho_{\alpha}^{b.a.}(\vec{r}) = \sum_{\alpha}^{M} w_{\alpha}(\vec{r})\rho(\vec{r})$$

with $\rho_{\alpha}^{b.a.}(\vec{r})$ the atomic electronic density of bonded atom, M the number of atoms and $w_{\alpha}(\vec{r})$ a sharing (weight) function according to which each point in space is proportionally shared among all the atoms. The sharing function is defined in respect to the isolated atom electronic charge densities:

$$w_{\alpha}(\vec{r}) = \frac{\rho_{\alpha}^{atom}(\vec{r})}{\rho^{proto}(\vec{r})} = \frac{\rho_{\alpha}^{atom}(\vec{r})}{\sum_{\beta}^{M} \rho_{\beta}^{atom}(\vec{r})}$$

with $\rho_{\alpha}^{atom}(\vec{r})$ the electronic density of free standing (isolated) atoms⁵ and $\rho^{proto}(\vec{r})$ molecule (crystal) proto-density (or simply promolecule density) as superposition of the free atom densities of the respective chemical atoms in the compound. The sharing functions are all positive and by definition the sum of all sharing functions is equal to one everywhere.

The core reasoning for such sharing function is the idea that the density of the bonded system is comparable to the artificially created proto-density composed of the free atomic densities. In the extreme case of the free atoms (infinite separation) the aforementioned division of total density is just an identity.

There are two strong points of the Hirshfeld approach compared to the previous partitioning schemes. The first one is that the Hirshfeld method, because of its construction, will show no charge transfer for the artificially created system out of isolated atomic charge densities. The second one is the choice of a stockholder recipe, i.e. charge at every point is divided between all atoms, every atom has its own share, which according to Hirshfeld itself is: "A general and natural choice ... ".

The density of the bonded atom is an overlapping continuously distributed charge density assigned to the specific atom. It is convenient to define the atomic deformation density from the density of bonded atom by $\rho_{\alpha}^{b.a.}(\vec{r})$ sub-tracting the electronic density of a free atom:

$$\delta \rho_{\alpha}(\vec{r}) = \rho_{\alpha}^{b.a.}(\vec{r}) - \rho_{\alpha}^{atom}(\vec{r})$$

⁵to be precise the full description will be: it is suitably positioned, spherically averaged ground-state isolated atomic electronic density

or even molecular deformation density:

$$\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho^{proto}(\vec{r})$$

which are useful for visualization purposes and determination of electrostatic properties of the molecules.

By means of the Hirshfeld charge population analysis one can obtain the total electronic charge of an atom by integrating the density of bonded atom all over the space (Ω) :

$$Q_{\alpha} = \int_{\Omega} \rho_{\alpha}^{b.a.}(\vec{r}) d\vec{r}$$

The net atomic charge can be obtained by addition of nuclear charge or alternatively can be expressed as definitive integral of the atomic deformation density:

$$q_{\alpha} = \int_{\Omega} \delta \rho_{\alpha}^{b.a.}(\vec{r}) d\vec{r}$$

3.4 Iterative Hirshfeld method

On its own the Hirshfeld idea has very solid reasoning. However, it contains one apparent arbitrary decision, it choose the neutral free atoms as a reference systems. This choice leads to deficiencies especially in ionic systems.[117] Patrick Bultinck et al. proposed in 2007 an important extension to the original Hirshfeld scheme [117] and described its characteristics.[118] The extension removed arbitrariness in the choice of promolecule and the known shortcomings of the original approach, such as the small computed charges in the comparison to the other methods or limitation of the method which allowed only description of charge neutral systems.

The proposed algorithm is in essence the iterative refinement scheme for the Hirshfeld charge population analysis. The first step is a regular Hirshfeld method. From that we obtain the calculated valence charges on the bonded atoms Q_{α} . In the consecutive step we use the same approach but instead of the (neutral) isolated atoms (for construction of the sharing function) we make use of the (ionic) isolated atoms with valence charge equal to Q_{α} from the previous step. The iteration scheme is repeated until the convergence in input and output valence charges is reached.

The sharing function becomes:

$$w_{\alpha}(i,\vec{r}) = \frac{\rho_{\alpha}^{atom}(i-1,\vec{r})}{\rho_{proto}(i-1,\vec{r})}; \quad \text{with} \quad \rho_{\alpha}^{atom}(0,\vec{r}) \equiv \rho_{\alpha}^{atom}(\vec{r}) \quad \text{etc.}$$

and $Q_{\alpha}(i)$ the calculated valence charge is used as a new valence charge on isolated atom for the next step:

$$Q_{\alpha}(i) = \int_{\Omega} \rho_{\alpha}^{b.a.}(i,\vec{r})d\vec{r} = \int_{\Omega} \rho_{\alpha}^{atom}(i+1,\vec{r})d\vec{r}$$

with $\rho_{\alpha}^{b.a.}(i, \vec{r}) = w_{\alpha}(i, \vec{r})\rho(\vec{r})$. The process is repeated until the convergence in the charge population difference $\Delta_{\alpha}(i)$ between consecutive steps is sufficiently small.

$$\Delta_{\alpha}(i) = |Q_{\alpha}(i) - Q_{\alpha}(i-1)|$$

The method itself does not require the initial atomic electronic densities $\rho_{\alpha}^{atom}(0, \vec{r})$ representing neutral atoms (the iterative nature will eliminate initial arbitrary choice), albeit it is a common choice as the first step of this iterative Hirshfeld (Hirshfeld-I) analysis returns the original Hirshfeld populations.

The practical representation of the iterative Hirshfeld charge analysis has been recently revived by Danny E. P. Vanpoucke et al., [119] with the focus on the application of the method on periodic materials with the use of the electronic density of fractionally charged isolated atoms constructed as the linear interpolation between isolated atoms with integer charges.[120]

3.5 Modified Hirshfeld method

In 2008 Ortwin Leenaerts introduced yet another modification of the Hirshfeld and iterative Hirshfeld methods named modified Hirshfeld and modified Hirshfeld-I.[121] This method builds directly on the elements of the aforementioned approaches with small yet intriguing change. Instead of the atomic charges he proposes the use of the molecular charges. This is a great simplification especially for large systems where the detailed charge redistribution is of no aim and a full approach is an overcomplication. Probably the simplest example which demonstrates the advantages of this approach is the adsorption of the molecules on the surfaces (e.g. two dimensional crystals). In these systems the only required information is the charge relocation from/to the adsorbent as a whole.

For the system composed of two distinct subsystems A and B the Hirshfeld weight function for the subsystem A will be:

$$w_A(\vec{r}) = \frac{\sum_{\alpha \in A} \rho_\alpha^{atom}(\vec{r})}{\sum_{\beta \in A} \rho_\beta^{atom}(\vec{r}) + \sum_{\gamma \in B} \rho_\gamma^{atom}(\vec{r})}; \quad M_A + M_B = M_B$$

3.5. MODIFIED HIRSHFELD METHOD

The modified Hirshfeld will make use of a different weight function:

$$w_A^{modified}(\vec{r}) = \frac{\rho^A(\vec{r})}{\rho^A(\vec{r}) + \rho^B(\vec{r})}$$

The practical implementation consists of the calculation of the total system electronic density and the subsequent calculation of the electronic density of the subsystems in the same configuration as in the total system. These densities can be afterwards used in the aforementioned modified Hirshfeld method. If the charges are made self-consistent in this way, they will lead to the modified Hirshfeld-I charges. This algorithm allows the total cost of the numerical calculations to be lower compared to the atomic Hirshfeld methods while maintaining most of the advantages of atomic based methods.[121]

Part III Results

Chapter 4

Bilayer fluorographene

In this Chapter¹ fluorinated bilayer graphene, hereafter called bilayer fluorographene (for a better notion of the chemical composition and the structure, see Fig. 4.1.1), is investigated. The reason why the chemical derivative of graphene is studied is the fact that despite unique characteristics of graphene, [79, 123–125] there exists a serious obstacle to use graphene in electronics as we know it today. Graphene is a zero-gap semiconductor, and the absence of a bandgap is protected by inversion and time-reversal symmetry. [126] Among broad set of different approaches, [73, 82–84, 127– 132] the chemical modification, in which p_z electrons are confined into covalent bonds and their hybridization is changed from sp^2 to sp^3 , was chosen. An advantage of the chemical derivatives of graphene is the preservation of the two-dimensional character of the material with vastly different electronic properties. Among the possible derivatives of graphene, there are two that have attracted special attention, namely, graphane and fluorographene (graphene fluoride), which result from the hydrogenation and fluorination of graphene, respectively. They are theoretically predicted [133–140] and experimentally observed [83, 129, 130, 132, 141, 142] to form crystalline materials, in contrast to, for example, graphene oxide. [143, 144]

As is apparent from the title of this Chapter, the process of chemical modification is not restricted to monolayer graphene. It has been proposed before that this process can be expanded to bilayer graphene as well. [145] *Ab initio* calculations showed that the weak van der Waals forces between the graphene layers are replaced by much stronger covalent bonds that stabilize

¹The results of this Chapter can be found in publication: J. Sivek, O. Leenaerts, B. Partoens, and F. M. Peeters, J. Phys. Chem. C **116**, 19240 (2012), "First-principles investigation of bilayer fluorographene".[122] Consult the rights and permissions for the text of this Chapter (including equations and tables) with the publisher of the aforementioned publication.

the structure and that, at full coverage, a bilayer analogue of graphane is formed. The electronic structure of intrinsic monolayer and bilayer graphane are very similar, [146] but their mechanical/elastic properties are expected to be substantially different. And the difference in elastomechanical qualities can be an important issue. It was recently demonstrated [147] that the roughness of monolayer graphane surfaces is considerably larger than that of graphene. This increase of the size of the ripple formation can be explained by the lower stiffness of graphane [148] and its different vibrational properties as compared with graphene. [149] One way to reduce the increased roughness is to consider bilayers instead of single layers. As is well known from experiment, the ripple formation in bilayer graphene is strongly reduced; that is, they are removed by the interlayer interaction. [150] A similar effect can be expected for bilayer graphane where the interlayer interaction is even more important.

Motivated by the previous theoretical and experimental work in this Chapter it is investigated whether it is possible to fluorinate bilayer graphene and to form bilayer fluorographene. Bilayer fluorographene, described further, is a much more stable compound than bilayer graphane, although more fluorination is needed to induce interlayer covalent C–C bonds and its 2D Young's modulus is lowered to approximately 300 N m⁻¹ compared to graphene. The structure of this compound resembles those of monolayer fluorographene and diamond.

Also a comparison is made to graphane, bilayer graphane, and fluorographene. Furthermore the effective masses around the Γ -point for fluorographene and bilayer fluorographene are found to be isotropic, in contrast to earlier reports.

4.1 Calculation details

All our calculations were done within the density functional theory (DFT) formalism as implemented in the VASP package [151] with usage of the local density approximation (LDA) and the Perdew, Burke, and Ernzerhof [5] generalized gradient approximation (GGA) for the exchange-correlation functional. We made use of the projector augmented wave method [105] and a plane-wave basis set with an energy cutoff of 500 eV. The relaxation of atomic positions was performed with forces smaller than 0.01 eV Å⁻¹.

Three types of supercells were used: 3×3 and 2×2 supercells to study the adsorption properties of fluorine on a graphene bilayer for different concentrations and configurations of fluorine and a 1×1 unit cell for the calculation of the properties and electronic band structure of fully fluorinated graphene

4.2. RESULTS

and bilayer graphene.

The sampling of the Brillouin zone was done for the different supercells with the equivalent of a $24 \times 24 \times 1$ Monkhorst-Pack [103] *k*-point grid for the monolayer or bilayer graphene unit cell (containing two carbon atoms per layer). Spin polarization was not included in the calculations because fluorination is not expected to induce magnetism in graphene. [152]

Because periodic boundary conditions were applied in all three dimensions, the height of the supercell was set to 20 Å to include enough vacuum to minimize the interaction between adjacent layers. Additionally, we have performed a convergence test with respect to the planar size of the supercell. We obtain an accuracy in binding energies of less than 0.1 eV and in bond lengths of less than 0.01 Å with the chosen 3×3 supercell.



Figure 4.1.1: Top and side view of bilayer fluorographene. The carbon atoms of the two layers are given by different colours (shades) for clarity and the fluorine atoms are in light green (light circles with the smallest diameter). [[1]]

4.2 Results

4.2.1 Fluorination of bilayer graphene

The main objective of this paper is to investigate chemisorption of fluorine atoms on both sides of bilayer graphene. Hydrogenation and fluorination of the carbon atoms of graphene change their hybridization from sp^2 to sp^3 . In the case of hydrogenation of bilayer graphene, it was demonstrated that stable interlayer C–C bonds are induced at high concentrations of adsorbates.[145] In this Section, we perform a similar study for the case of fluorination and highlight the similarities and differences as compared to hydrogenated bilayer graphene. We make use of the local density approximation, because this approximation gives a better description of the interlayer interaction in bilayer graphene over the generalized gradient approximation.[153]



Figure 4.2.1: Bilayer of AB-stacked graphene with the four different sublattices indicated by different colours. The A and B' sublattices are situated on top of each other, as illustrated by the dotted lines in the lower right inset. The carbon atoms at the corners of the light triangles indicate the six neighbours to be fluorinated. [[1]]

We only consider chemisorption on bilayer graphene with AB stacking because this is the most energetically favourable way of stacking graphene layers. As indicated in Fig. 4.2.1, this gives rise to four sublattices (two in each layer) of which two, namely, the A and B' sublattice, are exactly aligned on top of each other while the sublattices B and A' are not. Since the adsorbates under investigation always chemisorb on top of a single C atom, there are two (inequivalent) adsorption sites, namely, on the A (or B') sublattice and on the B (or A') sublattice. It was found in an earlier study of hydrogen adsorption on bilayer graphene that there is a difference in adsorption energy of approximately 0.03 eV in favour of the B sublattice. [145] The H atoms are, therefore, likely to attach to those carbon atoms that have no direct neighbours in the other layer. For F atoms, we find the same preference for adsorption on the B sublattice. However, the difference in adsorption energy for the two sublattices is only 0.3 meV, which is about 100 times smaller than in the case of hydrogen and practically insignificant. This is caused by the different nature of C-F bonds as compared with C-H bonds: C–H bonds are purely covalent, but C–F bonds have a partially ionic character because of the large difference in electronegativity between C and F.

The formation of a chemical bond between an adsorbate and a C atom

of the bilayer of graphene induces a change in the hybridization of this C atom from sp^2 to sp^3 . If the concentration of attached adsorbates on the preferred sublattice increases, the carbon atoms of the other sublattice also change their hybridization to sp^3 . This allows for the formation of covalent bonds between the two graphene layers. These interlayer bonds are formed between carbon atoms of the A and B' sublattices that are pushed to one another because of the changed hybridization of their neighbours.

For a single interlayer C–C bond, there are six neighbours: three atoms in the B and three in the A' sublattice (Fig. 4.2.1). However, it is not necessary for all of these neighbours to change their hybridization in order for the interlayer bond to be formed, as in the case of hydrogen chemisorption on bilayer graphene, where only four of the neighbouring carbon atoms need to be hydrogenated to induce a covalent interlayer bond.[145]

To study the formation of interlayer bonds upon fluorination in more detail, we gradually increase the number of attached fluorine atoms on neighbouring carbon atoms from one to six. We completely relax the resulting systems and calculate the average and minimum distances between the C atoms of the two layers. The results of these computations are summarized in Table 4.1. From this Table, a gradual decrease of the interlayer distance can be seen upon increasing the concentration of F atoms. At higher concentrations, however, a substantial jump in the minimum distance, d_{\min} , occurs when going from four to five fluorinated neighbours. This jump is about 1 Å in size and clearly indicates the formation of an interlayer bond. It is thus necessary to fluorinate five of the six neighbours to induce an interlayer bond, in contrast to hydrogenation, where four hydrogenated neighbours suffice.

Additional information about the stability of the interlayer bond can be obtained by examining the formation and binding energy of the system at different concentrations of adsorbed F atoms. We define the formation energy $(E_{\rm f})$ as the energy per attached fluorine atom with respect to intrinsic bilayer graphene and the diatomic molecule F₂. The binding energy $(E_{\rm b})$, on the other hand, is defined as the energy per fluorine atom (or CF pair) with respect to intrinsic bilayer graphene and atomic fluorine. Both energies are given in Table 4.1.

The formation energy, $E_{\rm f}$, is negative in all cases, which means that all the configurations are stable against molecular desorption from the graphene surface. This should be contrasted to the same concentrations of hydrogen atoms on the surface of bilayer graphene, where the energy becomes negative only in the case of almost fully hydrogenated bilayer graphene.[145] The value of the formation energies in the case of fluorination is significantly lower (almost 1 eV) than in the case of hydrogen chemisorption. This can be attributed to the weaker bond in the F₂ as compared with the H₂ molecule and is similar to

Table 4.1: Interlayer chemical bond formation in a 3×3 supercell. The binding energy per F atom (E_b) , the formation energy per F atom (E_f) and the average (d_{avg}) and minimum distance (d_{min}) between the C atoms of the two layers are shown for different number of adsorbed fluorine atoms and different configurations. Presence of interlayer bond is marked as chemical bond. Energies are given in eV and distances in Å.

no.	configuration	$E_{\rm b}$	$E_{\rm f}$	d_{avg}	d_{\min}	chemical
F atoms						bond
1	В	-2.525	-0.819	3.326	3.256	no
2	BB	-2.405	-0.700	3.326	3.190	no
2	BA'	-2.555	-0.850	3.213	3.085	no
3	BBB	-2.290	-0.585	3.332	3.126	no
3	BBA'	-2.487	-0.782	3.176	2.979	no
4	BBBA'	-2.384	-0.679	3.150	2.903	no
4	BBA'A'	-2.479	-0.773	3.061	2.821	no
5	BBBA'A'	-2.450	-0.745	2.678	1.757	yes
6	BBBA'A'A'	-2.560	-0.854	2.598	1.737	yes

the previously studied case of monolayer graphane and fluorographene.[137] The calculated binding energies also show that it is energetically favourable for the fluorine atoms to attach themselves on both sides of the bilayer: for the same number of chemisorbed F atoms, the configuration in which these atoms are distributed as equally as possible between the two layers is lower in energy and thus more stable. The fact that adsorbed F atoms on one side of the bilayer make it favourable for other F atoms to adsorb on the other side increases the chance of interlayer bond formation. Because these bonds are stable, we can imagine this process of fluorination and interlayer bond formation to continue until a fully covered bilayer of graphene fluoride is formed.

To test if the aforementioned interlayer bond creation scenario is truly energetically favourable, we considered a 2×2 supercell for a gradual fluorination with different configuration patterns. To be able to choose from the large number of different possible configurations, we need some guidelines for further investigation. As a first guideline, we distribute the F atoms equally on both sides of the bilayer because it is more energetically favourable, as discussed above. Four prevalent configurations are known for the fluorination of graphene: chair, boat, zigzag, and armchair. The chair configuration can be readily extended to the fluorination of bilayer graphene discussed above. The remaining three configurations share as a common feature that they contain dimers, as depicted in the inset of Fig. 4.2.2. Those dimers are used as the

4.2. RESULTS

second guideline to reduce configuration space. The dimer a is composed of F atoms bonded with directly neighbouring C atoms, whereas the dimer b consists of F atoms bonded with distant C atoms on the opposite sides of the hexagonal ring.² For higher fluorine concentrations (above two dimers, one at each side of the bilayer), dimers a and b are combined and create a trimer configuration, as depicted in the inset c of Fig. 4.2.2.

The calculated results are given in Fig. 4.2.2. In this Figure, we present the formation energy per adatom for the different fluorination pathways. These results show that, for low concentrations of F atoms, the dimer b configuration is more stable (carbon atoms from both sublattices are fluorinated, and no interlayer bonds are created). However, higher concentrations of F atoms are not feasible with the dimer configurations as the formation energy increases. However, if only the B and A' sublattices are fluorinated, the formation energy can decrease even more, finally creating bilayer fluorographene, with completely saturated C atoms, as can be seen in Fig. 4.1.1. It is also important to point out that the total formation energy for all adsorbed F atoms (not shown in the Figure) is a monotonically decreasing function of the F atom concentration, and therefore, the local minimum for dimer b will not result in an interruption of the adsorption.

Our calculations also showed that, for both dimer configurations, no interlayer bonding was formed. The dimers a and b transform for higher coverage into the trimer configuration, as indicated by the connection of the plots. For the adsorption on B and A' sublattices, the interlayer bond is created already with only four F atoms. This apparently different result from the previous 3×3 supercell calculations is due to the choice of the size of supercell. Four adatoms in a 2×2 supercell correspond to a higher percentage of F per C atoms than five adatoms in the 3×3 supercell.

We also performed calculations for the case when the A and B' sublattices, lying on top of each other, were fluorinated. As already mentioned, the preference for B (A') over A (B') sublattice for a single adatom is very small and unlikely to conduct the adsorption pattern. With increased F atom coverage, the formation energy per adatom for fluorination of the A and B' sublattice was found to be an increasing function of the total coverage. This results in a very unfavourable alternative over fluorination of B and A' sublattices.

From the calculations on the F adsorption in a 2×2 supercell, we can conclude that the chair configuration is the lowest-energy configuration, the only configuration that leads to interlayer bonding and in which a high fluorine

²The dimers, and respective adatoms positions, can be described in organic chemistry nomenclature as *ortho*- for dimer a and *para*- for dimer b.

concentration can be reached.



Figure 4.2.2: Gradual fluorination of a 2×2 supercell of bilayer graphene. For increasing F concentration the formation energy per fluorine atom is shown. The curves show different distributions of the F atoms: according to dimer configuration *a* (inset a) and *b* (inset b) and only on sublattices B and A'. Dimers *a* and *b* can not be preserved for higher levels of fluorination; instead they transform into the trimer configuration (inset c).

4.2.2 Properties of bilayer fluorographene

In this Section, we examine the properties of bilayer fluorographene in more detail and compare them with those of monolayer fluorographene and diamond. For the study of the geometrical properties, we include also GGA calculations because they give more accurate bond lengths and angles. A summary of the geometrical and electronic properties is given in Tables 4.2 and 4.3. The results for monolayer fluorographene compare well with previous calculations on this system.[135] As can be expected, the cell size and bond lengths and angles of bilayer fluorographene have values between those of monolayer fluorographene and diamond. Overall, the geometrical properties are close to the one of bulk diamond due to the same hybridization of the carbon atoms.[139]

The calculated C–C bond lengths are larger than the ones in diamond. This difference can be explained from a chemical point of view as a result of the depopulation of the bonding orbitals between the carbon atoms after substantial charge transfer to the F atom, which is the result of the difference in electronegativity between C and F atoms.

Additionally, we have observed the shortening of the C–F bond with increasing amount of fluorination on both sides of bilayer fluorographene. In a 3×3 supercell, the C–F bond length varies from 1.50 Å for configuration B to 1.43 Å for configuration BBBA'A'A'. As can be seen from Table 4.2, the C–F bond length decreases even more to 1.38 Å for fully fluorinated bilayer graphene. The source of this behaviour can be attributed to the ionic character of the C–F bond and a gradual transformation from sp² to sp³ hybridization of the C atoms.[152]

Table 4.2: Properties of single layer and bilayer fluorographene: the unit cell length (a), the distances (d) and angles (θ) between neighbouring atoms. Distances are given in Å and angles in deg.

	fluorographene		bilayer		diamond	
			fluorographene			
	LDA	GGA	LDA	GGA	LDA	GGA
a	2.555	2.596	2.525	2.563	2.499	2.527
$d_{\rm C-C}$	1.553	1.576	1.541	1.563	1.531	1.547
$d_{\mathrm{C-C'}}$	n/a	n/a	1.537	1.554	1.531	1.547
$d_{\rm C-F}$	1.365	1.382	1.361	1.377	n/a	n/a
$\theta_{\rm CCC}$	110.7	110.9	110.0	110.2	109.5	109.5
$\theta_{\rm CCC'}$	n/a	n/a	108.9	108.7	109.5	109.5
$\theta_{\rm CCF}$	108.2	108.0	108.9	108.7	n/a	n/a

The electronic properties of monolayer and bilayer fluorographene are given in Table 4.3: we calculated the bandgap of these materials together with the formation energy per atom (in contrast to previously used formation energies per fluorine atom). For comparison, the values of these quantities are also given for diamond. ³

The calculated bandgap for monolayer fluorographene is in good agreement with previously published results when using GGA calculations.[154] Although the computed bandgap value for fluorographene is close to experimentally measured values [83], this should be seen as a coincidence. LDA and GGA calculations are known to largely underestimate the value of the bandgap. The calculated bandgaps are, in fact 2 times lower than more accurate results of many-electron GW calculations.[137] This apparent discrepancy is attributed to the presence of a considerable amount of defects in the experimental samples that induce midgap states (similar to defected graphane.[155])

The bandgap of bilayer fluorographene is found to be larger than the one of monolayer fluorographene by approximately 1 eV. This is different from

 $^{^{3}}$ In the publication the bandgap of diamond is listed as 5.618 eV (LDA) or 5.572 eV (GGA). However, those numerical values were result of a processing error and the correct values are listed in Table 4.3.

the case of hydrogenated graphene, where monolayer graphane is found to have a slightly larger bandgap than bilayer graphane.[145] In fact, within LDA and GGA calculations, graphane has a larger bandgap than monolayer fluorographene,[156, 157] but this observation does not apply to bilayer compounds where bilayer fluorographene surpasses bilayer graphane in the size of the energy gap. Although our calculations are not accurate enough to provide the real bandgap, it is probable that this difference in the size of the bandgap between monolayer and bilayer fluorographene is qualitatively correct. This follows from the fact that LDA and GGA usually produce correct trends in the variation of the bandgap among similar systems. Therefore, the bandgap of bilayer fluorographene has been found to be intermediate between that of fluorographene and that of bulk diamond. In this sense, diamond can be considered as the limit of multilayer fluorographene. This tendency was observed before: for theoretically proposed graphite fluoride materials involving carbon atoms with sp³ hybridization.[158]

The absolute value of the formation energy of bilayer fluorographene is smaller than the one of the monolayer, but still larger than the one of diamond. The main reason for the observed weakening of the formation energy is the drop of the ratio of the amount of fluorine atoms per carbon atom in going from monolayer to bilayer fluorographene. Overall, the qualitative image of the stability of the fluorinated materials corresponds to that of graphane and bilayer graphane in terms of the aforementioned formation energy and the presence of covalent bonds between the graphene layers, which stabilize the structure. Nevertheless, there is a large quantitative difference; the fluorinated materials are much more stable structures than the hydrogenated ones.[134]

Table 4.3: Electronic bandgap E_{gap} and formation energy per atom $(E_f/atom)$
of monolayer and bilayer fluorographene and diamond using LDA and GGA cal-
culations. All the energies are given in eV.

	fluorographene		bilayer		diamond	
			fluorographene			
	LDA	GGA	LDA	GGA	LDA	GGA
$E_{\rm gap}$	2.960	3.089	3.951	4.040	4.132	4.103
$E_{\rm f}/atom$	-1.057	-0.944	-0.722	-0.593	-0.011	0.132

The band structure of bilayer fluorographene is displayed in Fig. 4.2.3 together with a diagram of the density of states. The depicted band structure is seen to be qualitatively similar to the one of monolayer fluorographene [136] with the size of the bandgap as the only obvious difference. We also calculated

4.2. RESULTS

the effective masses of the charge carriers around the Γ -point in order to find other differences or similarities between the two materials.



Figure 4.2.3: Electronic band structure and density of states of bilayer fluorographene. The energies are relative to the Fermi level $(E_F=0)$.

The obtained effective masses of electrons, and heavy and light holes for both studied materials, can be found in Table 4.4. It should be noted that these masses were calculated within the DFT formalism with usage of the LDA for the exchange-correlation functional, which has been shown to give reasonable results.[159]

The effective mass of charge carriers in crystalline materials usually depends on the direction in reciprocal space. Therefore, we have chosen two common directions for the hexagonal lattice at the Γ -point, namely, $\Gamma \to K$ and $\Gamma \to M$. The results for these two directions were found to be indistinguishable, and so we can conclude that the effective masses at the Γ -point are isotropic. The direction independence for the effective masses that we observe contradicts previous results in which the effective masses of monolayer fluorographene were found to be highly anisotropic. [160] Our statement about the isotropic character of the effective masses is supported by a direct plot of the energy value map around the Γ -point. In Fig. 4.2.4 we show a picture of the highest valence band of monolayer fluorographene. The isotropic character of this band is clearly visible close to the Γ -point. Farther away from the Γ -point an anisotropy of the surface map is visible, which can be attributed to fourth- and higher-order effects. However, these higher-order effects do not induce anisotropy in the effective mass, which is a second-order effect. Similar results are found for the light hole and the electrons.

When we compare the effective masses of monolayer and bilayer fluorographene, we observe only a small difference in its values. We, therefore, conclude that both materials have similar electronic properties apart from a difference in the bandgap of about 1 eV.



Figure 4.2.4: Energy levels of the two highest valence bands and lowest conduction band of monolayer fluorographene in reciprocal space. The displayed region is a squared partition of the Brillouin zone with a side length 0.22 of the Γ -M distance. The Γ -point is taken as the origin, and the x axis directed toward the M-point. Contour lines are displayed for a better notion of the symmetry.

Table 4.4: Effective masses of holes and electrons (in units of the electron mass) and the 2D Young's modulus, E, along the Cartesian axes. E is expressed in $N m^{-1}$.

	fluorographene	bilayer		
		fluorographene		
\overline{m}	0.48	0.50		
m_{hh}	1.13	1.10		
m_{lh}	0.41	0.37		
E_x	195	284		
E_{u}	197	293		

In addition to the electronic properties, we calculated the (2D) Young's modulus, E, for monolayer and bilayer fluorographene, which are also included in Table 4.4. We followed the same approach as applied before by Leenaerts *et al.*[136] with 2D Young's modulus computed as:

$$E_x = 2\frac{\Delta E_{tot}}{\Delta x^2} \frac{x_0}{y_0}$$

with E_x the 2D Young's modulus along x axis (in equation x can be mutually interchanged with y), $\Delta E_{tot} = E_{tot} - E_{tot}^0$ the difference of total energy of the system after expansion and total energy of the ground state system, $\Delta x^2 = (x - x_0)^2$ the squared elongation in direction of x-axis (amount of 5% has been used here), x_0 and y_0 the dimensions of the ground state system rectangular supercell along x and y axis.⁴ The 2D Young's modulus of graphene is found to be 307 N m⁻¹ shifted from the experimental value, $E_{exp} = 340 \pm 50$ N m⁻¹,[161] and other theoretical values.[148] The 2D Young's modulus of fluorographene is found to be ¹/₃ smaller in comparison to that of intrinsic graphene, whereas the obtained moduli for bilayer fluorographene reach almost the values of graphene, making these materials very strong. The values unveil the isotropic character of the Young's modulus for both compounds.

The definition of the (2D) Young's modulus is usually accompanied with the definition of the Poisson's ratio. Although it is not used here the following definition is included for completeness:

$$\nu_x = \frac{\Delta y}{\Delta x} \frac{x_0}{y_0}$$

4.3 Conclusions

As an extension to previous work, [136, 145] we studied the potentially interesting case of bilayer fluorographene. We demonstrated that fluorination of bilayer graphene results in more stable structures than hydrogenation. This can be clearly observed by a comparison of the formation energies of the final structures [134] and is accentuated by the fact that the formation energy of partially fluorinated bilayer graphane is always negative, in distinct contrast to partially hydrogenated bilayer graphene. The creation of interlayer chemical bonds occurs at higher amounts of fluorination as compared with hydrogenation.

The calculated bandgap of bilayer fluorographene shows a 30% increase over the one of bilayer graphane, and we also observed quantitatively significant differences between monolayer and bilayer fluorographene. From the value of the Young's modulus, we can conclude that bilayer fluorographene is substantially stronger than monolayer fluorographene and is almost as strong as graphene.

⁴ In the method the ground state structure rectangular cell is stretched in direction of one axis. The elongation is kept fixed and the cell size in the direction of the other axis as well as the ionic positions are fully relaxed.

Chapter 5

Adsorption of Ti and TiO_2 on graphene

The interaction of graphene with metal adsorbates is an important topic as virtually any device assembly incorporating graphene will necessarily include graphene-metal contacts. Titanium has been widely used for metal contacts on graphene and other graphitic surfaces with good adsorption properties.[162, 163] Ti atoms are able to act as adsorption centres for molecular binding.[164] Furthermore, Ti coated nanotubes and graphene have also been proposed as a high-capacity hydrogen storage solution.[165, 166]

However, a recent DFT study,[167] as well as a very recent experimental observation,[168] showed strong structural changes of the adsorbed Ti layer on graphene due to the interaction with oxygen. Experimentally, it was shown that the adsorbed titanium on graphene leads to substantial n-type doping and a reduction of graphene's mobility. The subsequent exposure of the samples to oxygen has restored graphene's gate dependent conductivity to almost intrinsic values, effectively cancelling any previous metal-graphene interaction.[168]

Motivated by these experimental observations, *ab initio* calculations are performed to investigate titanium and titanium dioxide monolayers adsorbed on graphene.¹ The identified ground state structures are presented together with the electronic band structure and a charge population analysis to investigate the character of the charge carrier doping in graphene. A strong n-type doping of graphene induced by adsorbed Ti is found. The highest possible monolayer coverage is identified as the one with stoichiometry Ti_3C_8 . TiO₂ monolayer crystals aligned on top of the graphene surface induce p- or

¹Consult the rights and permissions for the text of this Chapter (including equations and tables) with the author or the future publisher of the publication, if available.[169]

n-type doping of graphene, depending on the nature of the atoms that are exposed closest to graphene with oxygen acting as an acceptor and titanium as a donor.

5.1 Calculations

All calculations in this Chapter were performed within the density functional theory (DFT) formalism as implemented in the VASP package [151] with usage of the local density approximation (LDA) for the exchange-correlation functional with spin polarization. We made use of the projector augmented wave method [105] and a plane-wave basis set with an energy cutoff of 500 eV. The complete relaxation of atomic positions and supercell size was performed up to the level that the forces are smaller than 0.01 eV Å⁻¹.

For all the used supercells, a sampling of the Brillouin zone was done with the equivalent of a $28 \times 28 \times 1$ Monkhorst-Pack [103] *k*-point grid for the graphene unit cell (containing two carbon atoms). Spin polarization was included in the calculations.

Because periodic boundary conditions were applied in all three dimensions, the height of the supercell was set to 20 Å, to include enough vacuum to minimize the interaction between adjacent layers, and dipole corrections were used. All reported quantitative results of the charge transfer were calculated with the iterative Hirshfeld charge population analysis. [117]

5.2 Results and discussion

The binding energies are calculated with respect to intrinsic monolayer graphene and the isolated atom/molecule of which the binding energy is reported. The formation energy for titanium covered graphene is calculated in relation to intrinsic monolayer graphene and the energy of the Ti atoms in a free standing monolayer titanium crystal with hexagonal symmetry.

5.2.1 Properties of Ti monolayer on graphene

Properties of single Ti atom adsorption on a graphene surface were already investigated and the most preferable adsorption site for a Ti atom was found to be the hollow site with a binding energy of -1.58 eV per Ti atom. The top and bridge adsorption site were found to be energetically less favourable by 0.62 eV and result in metastable states.[170]

Also high density coverage of graphene with titanium has been previously investigated and some ground state structures were proposed which have



Figure 5.2.1: Structure g2x2-3Ti: Ti monolayer on a graphene sheet, 3 Ti atoms (light) per 8 C atoms (dark, displayed as a mesh in schematic picture on the left).

stoichiometry TiC₈ and TiC₂ with Ti atoms placed on hollow sites creating monolayer metallic coverage.[171, 172] However, we report here a different ground state structure. As written above, a single Ti atom placed on top of a free standing graphene surface is strongly bonded at the hollow site with a diffusion barrier high enough to prevent its motion on the surface even at room temperature. This fact suggests that the most preferable high coverage structure for titanium on graphene will be the one in which above every single hollow site there is one Ti atom (i.e., one Ti atom per two C atoms). Even the lattice constants compare favourably for this structure with a mismatch of only 5 % (see Table 5.1).

We have calculated binding energies for a variety of structures with stoichiometry TiC₂ and we also investigated the structure g2x2-3Ti (displayed in Fig. 5.2.1) with a lower amount of Ti atoms per C atom (three Ti atoms per eight C atoms) and a larger lattice mismatch of -9 % (Ti atoms are spaced further apart from each other in comparison to the titanium monolayer crystal). The calculated formation energy of -0.93 eV per Ti for g2x2-3Ti system was found to be lowest among all the investigated structures. The lowest formation energy for the TiC₂ system was found to be -0.76 eV per Ti, for the structure consisting of adatoms placed above hollow sites with every fourth Ti atom displaced further from the graphene substrate (see Fig. 5.2.2(d) initial state). Substantial formation energy advantage makes the g2x2-3Ti system virtually the only plausible structure for titanium atoms on graphene at large coverage densities.

We have been surprised by this finding that the structure g2x2-3Ti has the lowest binding energy among studied cases. This has motivated us to perform DFT based molecular dynamics simulations of systems with different Ti coverage densities to identify the ground state configurations that may have been overlooked and/or to support the aforementioned findings.

The simulated systems consist of a 4×4 graphene supercell with 2, 4, 8,



Figure 5.2.2: Top and side view of different graphene structures with different amount of titanium coverage before (left) and after (right) 1 ps of relaxation at T = 500 K. The systems consist of (a) 2, (b) 4, (c) 8 and (d) 16 Ti adatoms (light symbols) placed on the graphene sheet in an unit cell with 32 C atoms (dark symbols).

and 16 Ti adatoms, as displayed in Figs. 5.2.2(a–d). At the temperature of 500 K the different systems were allowed to evolve to more favourable states within a time window exceeding 1 ps.

The system with the highest concentration coverage (TiC_2) , with Ti atoms initially placed above every hollow site, does not remain a monolayer crystal. However, something interesting happens: the Ti atoms rearrange themselves so that they create one monolayer on the graphene surface with the same structure as g2x2-3Ti while the redundant Ti atoms create a second layer.

The systems with lower concentration of Ti atoms per C atoms (TiC₈ and TiC₄, Figs. 5.2.2(b) and 5.2.2(c), respectively) have also undergone structural changes. The separation of adsorbed Ti atoms was too small to prevent atoms from mutual interaction. While adatoms remained adsorbed as a monolayer we have observed the creation of clusters and local rearrangements. Those structural changes occurred despite the presence of the diffusion barrier for adatoms adsorbed on the hollow site (clearly visible for TiC₈, Fig. 5.2.2(b)). Again the comparison with the structure g2x2-3Ti reveals remarkable similarities in local arrangements of Ti adatoms, which is more pronounced in the structure TiC₄ (Fig. 5.2.2(c)) with higher adatom coverage.

The last of the systems investigated using MD calculations is the one
with the lowest Ti concentration: TiC₁₆ (Fig. 5.2.2(a)). We found that this case is the only one that maintained its structural properties during the MD simulations. As can be seen in Fig. 5.2.2(a) the adsorbed atoms are separated by two carbon hexagonal rings. The separation distance of 6.5 Å is found to be sufficient to suppress the mutual adatom interaction observed in the previous cases. The Ti atoms were trapped at the hollow sites and do not pass across the diffusion barrier.

The aforementioned results of the MD calculations can be summarized as follows: (i) Ti atoms placed on a graphene surface can overcome diffusion barriers (for the hollow site) by mutual close range interaction (up to ± 6.5 Å), (ii) the maximal titanium monolayer coverage of graphene has stoichiometry Ti₃C₈ and corresponds to the structure g2x2-3Ti (Fig. 5.2.1).

Experimentally [168] a strong charge transfer from the Ti layer to graphene was observed. Charge population analysis performed on the investigated systems has revealed the same trend of strong to moderate charge transfer from the Ti atoms to the underlying graphene for low and high concentrations, respectively. However, the quantitative values and even qualitative trends for charge transfer were found to be inconsistent among the different methods we used (including the iterative Hirshfeld charge population analysis, modified iterative Hirshfeld method and the Bader and Voronoi cells charge population analysis).[110, 113, 115, 117, 121]

An alternative to obtain directly the charge transfer is by calculating the dipole moment after Ti adsorption. However, the value of the electric dipole moment for the g2x2-3Ti structure is 0.087 eÅ, suggesting a small charge transfer from graphene to Ti. This corresponds neither to the experimental observation of n-type doping, nor with the charge transfer analyses discussed above. As shown by the plane-averaged deformation electron density in Fig. 5.2.3, the strong oscillations in the charge density do not clearly indicate actual charge transfer nor a dipole that will identify such transfer. The opposite total electric dipole moment can be explained by the dominant polarisation inside the carbon layer induced by the positively charged chemisorbed Ti monolayer. The surplus of charge located on the C atoms is shifted towards the Ti atoms thus creating a dipole moment counteracting and exceeding the dipole moment based on the negative charge located on the carbon layer and the positively charged Ti atoms. We expect the polarisation of the carbon layer to be the probable reason for the inconsistent results obtained by the aforementioned charge population analysis methods.

Since the direct charge transfer calculations proved to be insufficient in determining the type of doping we also performed electronic band structure calculations and calculated the work function of the pristine and hybrid materials. As can be seen from the electronic band structure of the g2x2-3Ti



Figure 5.2.3: Plane-averaged deformation electron density of g2x2-3Ti configuration obtained from the difference between the electron density of the g2x2-3Ti structure and the electron densities of the subsystems consisting of only carbon or titanium atoms.

structure	Φ (eV)	a (Å)
graphene	4.49	2.447
hexagonal monolayer Ti	4.72	2.566
rectangular monolayer TiO_2	8.54	3.141
hexagonal monolayer TiO_2	8.51	2.945
graphene + Ti (g $2x2-3Ti$), C side	3.97	4.939
graphene $+$ Ti (g2x2-3Ti), Ti side	4.72	4.939

Table 5.1: Lattice constants and work functions.

configuration (see Fig. 5.2.4), where the preserved Dirac cone is shifted by -2.61 eV below the Fermi level, graphene is strongly n-type doped. The calculation of the work function reveals the same type of doping. As shown in Table 5.1 the work function of free-standing graphene is 4.49 eV, while the work function of an isolated hexagonal titanium monolayer is 4.72 eV. From a simple comparison of these values there is no precondition for charge transfer to occur from Ti to the graphene substrate. However, for closely separated metal-graphene structures (2.1 Å for g2x2-3Ti) the chemical interaction prevails and is responsible for n-type doping even when the work function of the metal is larger than the graphene work function.[173] In the final system the computed work functions on graphene (3.97 eV) and titanium side (4.72 eV) indicate a charge transfer to graphene. The work function difference increases as compared to the difference of work function values of pristine graphene and hexagonal monolayer Ti ($\Phi_{Ti \ side} - \Phi_{C \ side} = 0.81$ eV compared to $\Phi_{hexagonal \ Ti} - \Phi_{graphene} = 0.23$ eV, see Table 5.1).



Figure 5.2.4: Band structure of the g2x2-3Ti configuration. The energies are relative to the Fermi level ($E_F = 0$). The Dirac point, for spin-up states (dark blue), lies -2.61 eV below the Fermi level showing strong n-type doping. The amount of carbon p_z character is indicated by the thickness of the bands.

5.2.2 Properties of TiO₂ monolayer on graphene

Let us now consider the case of TiO₂ adsorption on graphene. As a model approach for studying the interaction of titanium dioxide on graphene surfaces we have chosen monolayer TiO₂ films derived from anatase, (101) with hexagonal and (001) with rectangular symmetry, which were proven to be stable.[174] From the multiple possible configurations the structure g2x2hex-TiO₂ with lattice mismatch of about 4 % (displayed in Fig. 5.2.5(c)) was found to be the most stable. Ti atoms are arranged in a monolayer triangular lattice, similar to the one found in the previously discussed structure g2x2-3Ti, and oxygen atoms are placed between every three neighbouring Ti atoms. The TiO₂ monolayer is buckled due to the alternating displacement of oxygen atoms above or below the plane of Ti atoms. The other displayed model configurations in Figs. 5.2.5(a) and 5.2.5(b), while being metastable, will be discussed below as examples which lead to different doping properties.

The charge population analysis performed on the TiO₂-graphene structures were found to be much more robust than for the titanium covered graphene. The Ti–O bonds exhibit an ionic character with Ti atoms gaining positive charge after loosing two electrons in favour of the O atoms. Besides the charge redistribution in the TiO₂ layer the g2x2-hex-TiO₂ structure shows also p-type doping of the graphene layer. The amount of charge transferred from graphene, calculated with iterative Hirshfeld charge population analysis, is 0.126 e per TiO₂ unit.

The character of the doping is also visible in the electronic band structure shown in Fig. 5.2.6 with a clear hole doping of graphene and a shift of the Dirac cone above the Fermi level by 0.5 eV. The observed doping can be



Figure 5.2.5: Model structures for a TiO_2 monolayer on a graphene sheet. The systems (a) g2x2-aligned hex-TiO₂ and (c) g2x2-hex-TiO₂ contain 3 TiO₂ molecules per 8 C atoms, whereas (b) the g-sq8-TiO₂ configuration has 2 TiO₂ molecules per 8 C atoms. The carbon atoms are given by grey colour (a mesh in schematic picture on the left), Ti atoms are in light grey and O atoms are shown in red (dark, small circles in schematic picture on the left).

explained from geometrical arguments. The bounded oxygen and titanium atoms can induce p- or n-type doping when close to the graphene surface. The TiO₂ monolayer in the g2x2-hex-TiO₂ structure can be seen as consisting of three layers—a titanium layer sandwiched between two oxygen layers, thus exposing oxygen atoms to graphene. Similar charge transfers have been observed at the interface between graphene and rutile TiO₂ (110), where hole doping in graphene and an accompanying shift of the Fermi level relative to the Dirac cone was observed.[175]

The aforementioned reasoning proves to be valid also for the other systems we have investigated. The model structures in Figs. 5.2.5(a) and 5.2.5(b) differ by the amount of oxygen or titanium atoms they expose to the graphene surface. The charge population analysis as well as the electronic band structure provide consistent evidence of p- or n-type doping depending on whether oxygen or titanium atoms are closer to the carbon atoms, respectively. The shift of the Dirac cone with respect to the Fermi level is -1.69 eV for g2x2aligned hex-TiO₂ and 0 eV for g-sq8-TiO₂ structure, and the amount of charge, calculated with iterative Hirshfeld method, transferred from graphene is -0.452 e and 0.026 e, respectively.

Recently it was found experimentally that the graphene gate dependent conductivity can be recovered after oxidation of adsorbed Ti atoms.[168] This



Figure 5.2.6: Band structure of g2x2-hex-TiO₂ configuration. The energies are relative to the Fermi level ($E_F = 0$). The Dirac point lies 0.5 eV above the Fermi level showing p-type doping. The amount of carbon p_z character is indicated by the thickness of the bands.

recovery can be explained with the autocompensation of the titanium dioxide surface [176] exposed to graphene. We showed above that TiO_2 structures can induce both p- or n-type doping in graphene thus opening the possibility of mutual compensation of the doping effects. Although the ground state TiO_2 monolayer induces hole doping to graphene the performed calculations suggest that TiO_2 monolayers can be responsible for the recovery of the graphene gate dependent conductivity. However, the geometrical nature of the autocompensation does not imply that specifically the above considered monolayer TiO_2 crystals are presented on the graphene surface in the experiment. Existence of any TiO_2 nanostructure with both p- or n-type doping face exposed to the graphene surface will lead to similar effects.

5.3 Conclusions

We have demonstrated strong n-type doping of Ti covered graphene. While the various charge population analysis methods failed to provide reasonable quantitative results for the shift of the Dirac point with respect to the Fermi level our investigation of the increased difference of the work functions $(\Phi_M - \Phi_G)$ provided a consistent picture of the character of the induced doping. Titanium is found to be strongly chemisorbed on graphene and the highest monolayer coverage is found to have stoichiometry Ti₃C₈. The studied TiO₂ monolayer crystals aligned on top of graphene induce charge doping that depends on the nature of the atoms that are closest to graphene with oxygen acting as an acceptor and titanium as a donor. The ground state structure of TiO₂ monolayer covered graphene exhibits p-type doping of graphene, nevertheless the calculations suggest various structure states of TiO_2 monolayer can be responsible for the recovery of the graphene gate dependent conductivity after oxidation of adsorbed titanium, as recently found in experiment.[168].

Chapter 6

Atom decoration of silicene

In this Chapter¹ the adsorption and absorption characteristics of silicene [24, 40, 88] are investigated. Silicene is chosen as an alternative two dimensional material, with potential to bypass some of the obstacles existing in the usage of graphene in contemporary electronics.[86] Specifically an incompatibility with present day silicon technology and lack of an energy bandgap.

Within the broad range of chemical decoration [83, 129, 136, 138, 178] and substitutional doping [179–181] of graphene particular attention was given to boron and nitrogen as the first choice elements because of their chemical propinquity to carbon as well as to silicon.[182] The same reasoning apply for the second row elements: Al, Si and P, which doping induce band gap opening in monolayer graphene.[183] Furthermore the substitutional doping with B and N atoms has been realized experimentally via arc discharge using graphite electrodes in the presence of hydrogen and B or N atom incorporating molecules (pyridine, ammonia, B_2H_6),[179] thermal annealing of graphene in the presence of boron oxide [180] or nitrogen plasma treatment of graphene.[181]

The large volume of available evidence on chemically modified graphene and the recent experimental observations and synthesis of silicene [61–64, 85] has motivated similar work on silicene. As an example the adsorption characteristics of alkali, alkaline earth, transition metal atoms and even group-IV elements has been reported on monolayer silicene.[184, 185]

In this Chapter we investigate the adsorption and absorption of B, N, Al and P atoms on the surface of pristine free-standing silicene together with

¹The results of this Chapter can be found in publication: J. Sivek, H. Sahin, B. Partoens, and F. M. Peeters, Phys. Rev. B **87**, 085444 (2013), "Adsorption and absorption of boron, nitrogen, aluminium, and phosphorus on silicene: Stability and electronic and phonon properties".[177] Consult the rights and permissions for the text of this Chapter (including equations and tables) with the publisher of the aforementioned publication.



Figure 6.0.1: (a) Structural parameters for silicene [[$[L^2]$] and (b) possible adsorption sites on the silicene lattice. [[$[L^2]$] (c) Electronic band dispersion and partial density of states for perfect silicene. The energies are relative to the Fermi level (i.e., $E_{\rm F} = 0$). The inset (d) displays the calculated spin-orbit gap of 1.47 meV.

their substitutional doping. Our interest is pointed towards the compound's structure, binding energies of the most stable structures and their electronic, magnetic and phonon properties. We find that the adsorbed B, N and P atoms are strongly bonded to the underlying silicene, attached to its surface but also penetrated into the silicon lattice. Weaker bonding and immersion is observed for the Al atom. These observations differ from the general chemical functionalization of graphene which is highly dependent on the presence of defects and crystal boundaries.[186] The silicene surface (Fig. 6.0.1(a)) is more reactive due to its sp^3 -like lattice structure. The stability of the ground state structures has also been addressed by using *ab initio* molecular dynamics and phonon calculations.

6.1 Computational details

Density functional theory (DFT) is employed as implemented in the VASP package.[151] We have made use of the spin polarized local-density approximation (LDA) [187] for the exchange-correlation functional, the projector augmented wave method [105] and a plane-wave basis set with an energy cutoff of 500 eV. The sampling of the Brillouin zone was done for the supercell with the equivalent of a $24 \times 24 \times 1$ Monkhorst-Pack k-point grid for

a silicene unit cell (containing 2 silicon atoms). The partial occupancies in the electronic ground state calculation were treated using the tetrahedron methodology with Blöchl corrections.[188] The calculation of the density of states was performed with a Gaussian smearing of the energy levels with standard deviation set to 0.1 eV.

To eliminate the interaction emerging from periodic boundary conditions in all three dimensions a 4×4 supercell was used with the height of 15 Å to include enough vacuum, and dipole corrections were used. All reported quantitative results of the charge transfer were obtained by usage of the Bader charge population analysis,[110, 111] and the iterative modified Hirshfeld charge population analysis.[116, 117]

The relaxation of the atomic positions was performed with forces smaller than 0.01 eVÅ⁻¹. To reduce the strain induced by the adsorbates/substituents, the lattice parameters were optimized properly. The phonon frequencies for adatom adsorbed/substituted silicene were calculated using the Small Displacement Method [189] and the calculations were carried out by Doc. dr. Hasan Sahin.

Ab initio molecular dynamics simulations (MD) were performed with use of the non-spin polarized local-density approximation (LDA) [187] for the exchange-correlation functional, the projector augmented wave method [105] and a plane-wave basis set with an energy cutoff of 500 eV. The sampling of the Brillouin zone was done for the supercell with the equivalent of a $12 \times 12 \times 1$ Monkhorst-Pack k-point grid for a silicene unit cell. The integration of Newton's equations of motion was performed using the Verlet algorithm where Harris corrections were used in order to correct the forces. The simulations were performed within the microcanonical (NVE) ensemble with velocities assigned according to the Maxwell-Boltzmann distribution at the temperature of 500 K during the entire calculation. To avoid large temperature fluctuations velocities were normalized every 40 steps. The total duration of the simulation was 2 ps with the time step equal to 1 fs.

6.2 Results

6.2.1 Atomic structure and migration barriers

First, we consider the adsorption of a single atom on a silicene surface. In contrast to the completely flat one-atom-thick surface of graphene, silicene is buckled as can be seen in Fig. 6.0.1(a) and we can expect higher reactivity due to this sp^3 -like lattice structure. Similar to graphene, silicene is a semimetal with linearly crossing bands at the Fermi level with a zero electronic band gap



Figure 6.2.1: Diffusion characteristics of B, N, Al and P adsorbates. The energies are relative to the binding energy of the most preferable adsorption site. Spatial distance is plotted on x axis, the intermediate positions between high symmetry points were obtained by restricting the adatoms movement perpendicular to the silicene surface. The Local minima in diffusion energy plots outside of the four high symmetry adsorption sites do not provide stable binding without aforementioned restrictions.

(Fig. 6.0.1(c)). However, effect of spin-orbit coupling, that yields 1.47 meV spin-orbit gap (Fig. 6.0.1(d)), is much larger than that of graphene's.[190] We define the binding energy for adsorption as: $E_{\rm B} = E_{\rm system} - (E_{\rm silicene} + E_{\rm adatom})$. There are three possible adsorption sites on graphene, while as a consequence of the buckled hexagonal lattice structure of silicene has now four different adsorption sites as shown in Fig. 6.0.1(b): above the centre of the hexagonal silicon rings (Hollow site), on top of the upper silicon atoms (Hill-site), on top of the lower silicon atoms (Valley-site) and on top of the Si-Si bond (Bridge site).

The possible diffusion paths were determined from the energetics of the adatoms on the different lattice points. As shown in Fig. 6.2.1, each N adsorbate has to overcome an energy barrier of ~0.7 eV for diffusion from one bridge site to a neighbouring one via a valley site. B adsorbates, because of their stronger binding energy compared to N atoms, see larger migration barriers. Diffusion of a B atom from one valley site to another one can occur via a hollow site by overcoming the energy barrier of ~2.0 eV. The P adatom has to overcome an energy barrier of ~0.9 eV when diffusing between neighbouring hill sites via the bridge and valley sites. For the Al adatoms the energy barrier is ~0.4 eV between two neighbouring valley sites. After unconstrained relaxation, the four adsorption sites provide stable or metastable binding, albeit with different binding energy. Only the adsorption of an Al atom on a bridge site is found to be unstable.

For the graphene surface the bridge site was found to be the most fa-

vourable adsorption site for both B and N adsorbates.[191] However, we find that the most favourable adsorption sites on the silicene surface are the valley and bridge sites for B and N adsorbates, respectively. While the adsorption of the B (N) atom occurs with a -1.8 (-4.6) eV binding energy on graphene, [191] for silicene the bonding between B (N) and the silicene lattice is stronger with a binding energy of -5.85 (-5.54) eV. The Al and P atom preferential adsorption sites were found to be the valley site with a binding energy of -2.87 eV and the hill site with an adsorption energy of -5.28 eV, respectively. We found the adatoms to considerably distort the underlying silicene layer. A B adsorbate is almost completely immersed into the silicene layer and pushes the underling Si atom down from its original position. The B adatom average distance from the underlying Si layer is only 0.71 A as can be seen in Table 6.1. N atom adsorption on the bridge site results in Si–Si bond breakage. A similar effect as with the B adsorption occurs for P and Al adatoms, albeit with lower intensity and with up to two times larger average distances from the underlying Si layer as can be seen in Table 6.1.

Next we investigate the absorption, i.e., the substitution of a single Si atom with a B, N, Al or P atom. The binding energies for substitutional doping are -6.21, -5.64, -2.28 and -4.84 eV, for a B, N, Al and P atom, respectively. This binding energy for substitution is calculated as follows: $E_{\rm B} = E_{\rm system} - (E_{\rm silicene}(N_{\rm Si} - 1)/N_{\rm Si} + E_{\rm adatom})$. B-Si and N-Si bonds are shorter than the intrinsic Si–Si bond lengths, the P–Si bond is also slightly shorter but the Al–Si bond length is larger by 0.1 Å in comparison to the Si–Si bond length as can be seen in Table 6.1 (comparable to N and B substituted graphene [179]). The B, N and Al substituent atom bonds with neighbouring Si atoms are more flat, reducing local buckling. The P substituent atom exhibits comparable buckling as the Si atoms, the angle θ_{SiPSi} (111.3°) is even smaller compared to θ_{SiSiSi} (116.3°) of pure silicene. With increased distance from the B, N, Al or P atom the buckling of silicene is quickly restored. All the substituents except B atom exhibit a small displacement from the containing Si layer. As already mentioned, the B atom adsorption on the valley site (to some degree P atom adsorption on the hill as well) results in structures resembling substitution structures, with the Si atom pushed out of the silicene plane and adsorbate immersion into the plane. This can be a potential route for chemical doping of silicene via chemical decoration.

The calculated values for the binding energies show that substitutional doping is energetically more favourable for B and N atoms, whereas it is less favourable for Al and P atoms compared to adsorption. This behaviour of the binding energy causes a lower amount of immersion for the Al and P atoms as compared to the B and N atoms.



Figure 6.2.2: Electronic band dispersions, decomposed density of states (DOS) together with side and top view of the final relaxed structures. (a) Adsorption of B on valley site, (b) adsorption of N on bridge site, (c) adsorption of Al on valley site, (d) adsorption of P on hill site, (e) B, (f) N, (g) Al and (h) P substituted silicene layers. The energies are relative to the Fermi level ($E_{\rm F} = 0$). In the legend "A" refers to the adsorbed/substituent atom.

6.2. RESULTS

Table 6.1: Calculated parameters for B, N, Al and P adsorbed/substituted silicene: lattice constant (a); adsorbate–Si bond distance (d_{SiX}); average distance to low-lying Si layer (h); magnetic moment (μ); binding energy per adatom/substituent(E_B); work function (Φ , for the adsorption the value correspond to the value measured from the side of the adsorbate); charge located on adatom/substituent obtained with Bader charge analysis (ρ^B), or iterative Hirshfeld method (ρ^H) and dipole moment (p). The adsorbate and substituent concentration was one to 32 and 31 Si atoms, respectively.

	site	a	$d_{\rm SiX}$	h	μ	$E_{\rm B}$	Φ	$ ho^{ m B}$	$ ho^{ m H}$	p
		Å	Å	Å	μ_{B}	eV	eV	e	e	e∙Å
ads										
В	V	15.16	1.95	0.71	0.0	-5.85	4.73	-1.6	-0.7	-0.02
Ν	В	15.30	1.63	1.42	0.0	-5.54	5.02	-2.0	-0.6	+0.06
Al	V	15.26	2.51	1.71	0.0	-2.87	4.66	+1.0	+0.0	+0.12
Р	Hill	15.19	2.33	1.18	0.5	-5.28	4.89	-0.9	-0.2	-0.16
sub										
В	_	15.21	1.93	0.00	0.0	-6.21	5.15	-1.4	-0.6	-0.08
Ν	—	15.03	1.80	0.14	0.9	-5.64	4.67	-2.1	-0.4	-0.03
Al	_	15.43	2.36	0.44	0.0	-2.28	5.04	+1.6	+0.3	-0.03
Р	_	15.24	2.24	0.47	0.0	-4.84	4.55	-1.2	-0.1	+0.02

We find the adsorbed as well as substituent Al atom to have notable lower absolute value for its binding energy in comparison to the other investigated atoms. The reason for this different behaviour can be explained from a chemical point of view. The Al atom is the only one, due to its lower electronegativity compared to the Si atom, that looses electrons in favour of the neighbouring Si atoms. The induced depopulation of bonding orbitals increases the length of the Si–Al bond (d_{SiAl}) and weakens it.

6.2.2 Electronic structure

In Table 6.1, the electronic properties of B, N, Al or P adsorbed silicene are also presented. Both B and Al atoms adsorbed on the valley site as well as the N atom adsorbed on the bridge site turn the semimetallic silicene into a nonmagnetic metal. Adsorption of P atom on the hill site introduces matallicity with a net magnetic moment of $0.5\mu_{\rm B}$. The work function (measured at the side of the adsorbate) is slightly lowered to 4.73 eV for B and 4.66 eV for Al adsorption from 4.77 eV for intrinsic silicene. On the other hand, adsorption of a N or P atom increases the work function to 5.02 eV and 4.89 eV, respectively.

We also present the partial density of states analysis for B, N, Al and P in Figs. 6.2.2(a-d). For B adsorption, the metallic bands crossing the Fermi level are formed by the hybridization of the B- p_{xy} peaks with the Si- p_{xy} and the Si- p_z states. However, since the adsorption of N occurs on top of a Si-Si bond, mixing of N states with the silicene states is more complex. It appears from Fig. 6.2.2(b) that while the main contribution originates mainly from the hybridization of Si- p_z and N- p_z bands, tails of s and p_{xy} states of both silicene and N play a role in the metallic behaviour. It is also seen that the linearly crossing p bands of silicene at the K symmetry point are disturbed because of the interaction with the $N-p_z$ states albeit not completely removed as for B adsorption. The electronic band dispersion character of Al adsorption is qualitatively identical to the one of the B adsorption, caused by the similar adsorption site and valence electron configuration. The last case of P adsorption shows the metallic bands predominantly formed by the hybridization of the P- p_{xy} states with the Si- p_{xy} and the Si- p_z states and partially produced from silicene s states. The linear crossing of p bands of silicene at the K symmetry point is again completely removed.

On a graphene lattice, upon B adsorption, 0.4 e is transferred to graphene and upon N adsorption 0.7 e is transferred from graphene to N.[191] However, due to its sp^3 -like lattice structure, silicene has a highly reactive surface and therefore some different adsorption characteristics can be expected. The charge transfer occurs from silicene to the adsorbate for the B, N and P adatoms. The opposite charge transfer is observed for the Al adatom. The net charge located on B, N, Al and P adatom has a value of -1.6, -2.0, 1.0 and -0.9 e, respectively. Moreover, in order to examine the reliability of these results, we have also performed a charge population analysis with the iterative modified Hirshfeld method.[116, 117] We found that all the methods provide the same qualitative insight and support for the conclusion that the character of the charge transfer is driven by the differences of electronegativity among the atoms. Silicene donates/accepts electrons to/from adsorbates with higher/smaller electronegativity.

Substitutional doping of silicene induces an opposite change of the work function as compared to adsorption. B or Al substitution increase and N or P substitution slightly decrease the work function. The electronic band structure together with the density of states are shown in Figs. 6.2.2(e-h). The Dirac cone composed of p_z -bands is preserved for B, Al and P substitution. It has been shifted above the Fermi level for B and Al substituents and below the Fermi level for a P atom. It is not altered by the p_{xy} states of the foreign atom which are present as deep bands in the final electronic structure. The character of substitution with a N atom is of a different nature, the linear crossing of *p*-bands is destroyed and the metallic bands in



Figure 6.2.3: The localized p and s states at vicinity of Fermi level at Γ point in N substituted silicene (N atom is located in the centre of sample). The (a) top and (b) detailed angled view is displayed with the isosurface set to $0.25 \cdot 10^{-3}$ e/Å³ (the heat map is skewed to improved clarity, the states are mainly localized at N atom and above its closest neighbour Si atoms visible as small, semi transparent lobes with isosurface set to 10^{-3} e/Å³ encapsulated inside the larger volumes).

the electronic structure are produced from both p and s states located on N and the surrounding Si atoms as can be seen in the Fig. 6.2.3. These states originate from unoccupied states of the free N atom and align with the Fermi level in doped silicene.

The calculated charge transfers for the substitutional doping are of the same magnitude as for adsorption, with 1.4, 2.1, -1.6 and 1.2 e transferred from silicene to a B, N, Al and P atom, respectively. Only N-doped silicene becomes ferromagnetic with a net magnetic moment of 0.9 $\mu_{\rm B}$.

The size of the gap as well as the character of the electronic dispersion bands may be altered by the adsorption or substitution of foreign atoms with the applied spin-orbit interaction as in the case of graphene decorated by 5d transition metal adatoms [192]. We performed calculations with spinorbit coupling included in order to investigate its effect in all the studied systems and found no significant differences in the electronic band dispersion. The variances were found to be in the order of 1 meV and virtually vanishing around the Fermi level. Therefore, we do not report these results in Fig. 6.2.2. The cause of such negligible coupling is the small diameter of the adsorbate/substituent atoms and the small or not existing net magnetic moment of the aforementioned structures.[193]

6.2.3 Stability analysis

Characterization and analysis of the surfaces, crystal structures and molecules can be done by various spectroscopy techniques. Among these particularly Raman spectroscopy allows highly accurate detection and analysis of the vibrational properties of structures even at the nanoscale. Therefore, one can deduce the stability and characteristic vibrational properties of a foreign atom adsorbed/substituted silicene layers via their phonon spectrum. Fig.6.2.4. shows the evolution of the phonon density of states of pristine silicene with adsorption and substitution of B, N, Al and P atoms. Pristine silicene's phonon DOS comprises three main peaks originating from the Γ atomic motions: an acoustic mode at ~100 cm⁻¹, an out-of-plane optical mode at ~175 cm⁻¹ and a degenerate in-plane optical mode at ~571 cm⁻¹. Note that the peaks at 396, 472 and 535 cm⁻¹, are due to the flat slope of the optical branch at the M–K, M and M symmetry points, respectively. We also present adsorbate/substituent-projected phonon DOS and related vibrational motions at the Γ point in Fig. 6.2.4.

Adsorption/substitution of first-row elements B and N do not result in a significant change of the DOS. Due to the coupling of B and N adsorbates/substituents to the acoustical phonon branch of pristine silicene several sharp peaks appear between 200 and 300 cm⁻¹. Obviously, among the



Figure 6.2.4: Phonon dispersion for adsorption and substitution cases of B, N, Al and P on silicene. Total DOS of the structures is shown by the filled area (orange colour). Projected DOS belonging to foreign atoms are represented by lines (red). Γ point vibrational motions are also depicted.

two adsorbates, B and N, the bridge-site-bonded N adatom is more likely to mix with silicene's acoustic branch. In addition to these, high frequency adsorbate/substituent induced modes appear between 700 and 1200 cm⁻¹. Our eigenvector analysis reveals that these high energy modes correspond to in-plane bond-stretching motion of the adatom and the neighbouring silicon atoms.

Consistent with the binding energies calculated in the previous Section, the high frequency in-plane phonon mode of B-substituted silicene takes a higher value than that of the B-adsorbed one. However, such a comparison is not possible for the N atom because of the different geometries of the adsorption and substitution cases. Since the adsorption of a N atom occurs on the bridge site of two silicon atoms, one can expect vibrational characteristics different from those of N-doped graphene. While there is no clear N-induced peak observed in graphene, upon adsorption (substitution) of N to silicene well separated phonon modes (mode) at $\sim 800 \text{ cm}^{-1}$ and ~ 1150 (only at 700) $\rm cm^{-1}$ appear. Furthermore, compared with B-substitution, N substituted silicene's high-frequency mode is softer because of the larger atomic mass of N. These modes correspond to in-plane and out-of-plane motion of the N atom and the nearest two Si atoms. Contributions of second and third nearest neighbour Si atoms are negligible for these high-frequency modes. Because of their bond-stretching nature, adsorbate- and substituent-originated optical branches can be expected to be Raman-active modes.

The experimentally reported atomic weights (covalent atomic radii) of Si, B, N, Al and P are 28.09, 10.81, 14.01, 26.98 and 30.97 amu (111, 84, 71, 121 and 107 pm) and therefore due to the similar properties of second row elements to Si atoms, for the adsorption/substitution of Al and P atoms different effects on the vibrational spectra can be expected. We report a common characteristic for second row elements, that is the absence of highfrequency bond stretching modes. Due to the quite similar atomic weight and radii of Si, Al and P atoms, their effect on the phonon DOS is almost negligible and may not be observed by experimental tools. A widely broadened phonon DOS of Al and P adsorbed silicene, which is different from the narrow peaks in the B and N adsorption case, indicates the larger coupling of Al atoms to the silicene lattice. Similarly, the substitution of Al and P does not result in the presence of high energy modes. It is also seen that while substituent B and N atoms do not couple with optical modes of silicene, Al and P atoms entirely contribute to both acoustic and optical modes.

The discussed structures, that are found to be stable in terms of the total energy optimization and phonon calculations, may not be stable at high temperatures. To address questions regarding thermal stability of a B and N atom adsorbed/substituted silicene monolayers we consider the effect of



Figure 6.2.5: Top and side view of the ground state geometry (left) and the changed geometry at T = 500 K after 2 ps of molecular dynamics (right). The adsorbate/substituent atoms are marked with an open dotted circle for clarity.

temperature by employing *ab initio* MD calculations. MD simulations were performed at a temperature of 500 K for the structures initially optimized at T = 0 K.

In Fig. 6.2.5 geometric structures are presented for the initial and final state of the MD calculations. The simulation of B adsorption, as can be seen in Fig. 6.2.5(a), shows that the B atom stays incorporated within the honeycomb structure but the Si atom, that has been initially pushed down from its position, has started to move towards the neighbouring sites. During the 2 ps of MD simulations it is attached predominantly on the hollow and the top sites. However, the adsorbed B atom remains stable. Similarly, the substituent B atom (Fig. 6.2.5(e)) continues to be bonded to the three Si atoms for the whole simulation period.

Although the adsorption geometry for the N atom is different from Badsorbed silicene, it remains stable after 2 ps at 500 K. Even the characteristic out-of-plane motion of the N atom (from one side to the other one), that can be clearly seen in Fig. 6.2.5(b), is not able to break the strong Si–N–Si bonds. Similar to the B-substitution case, the N-substituted silicene, depicted in Fig. 6.2.5(f), remains in-plane bonded to the three neighbouring silicon atoms after more than 2 ps at 500 K.

Simulation of Al and P adsorption (Figs. 6.2.5(d)) as well as Al and P substitution (Figs. 6.2.5(g) and 6.2.5(h)) shows high stability of the adsorbate/substituent atom with no reconfiguration of the Si lattice in the vicinity of the foreign atoms.

6.3 Conclusions

In summary, we performed an *ab initio* study of atom adsorption and absorption of B, N, Al and P atoms on silicene and we obtained the geometric, electronic and vibrational properties. All the final systems show metallic behaviour. The adatoms are strongly bonded with silicene revealing different preferential adsorption sites for B or N adatoms as compared to graphene. We find the charge transfer to be consistent with the effects ascribed to the element electronegativity. B, N and P atoms behave like acceptors and the Al atom as donor for silicene. Analysis of the vibrational modes shows that adatoms and substituents slightly alter the phonon spectrum of silicene and several adatom/substituent-induced characteristic branches appear, which may be probed by Raman measurements. Finally, we showed the stability of B, N, Al and P adsorbed/substituted silicene layers even at high temperatures. Our work reveals that silicene has a very reactive and functionalizable surface and it can serve as an important and novel playground for silicene

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based novel nanoscale materials.

Chapter 7

Stone-Wales defects in silicene

It is known that physical properties of graphene [6, 9, 161, 194–196] are sensitive to lattice imperfections and adatoms. However, structural and chemical modification opens the possibility for tailoring the electronic and magnetic properties of graphene-based structures.[91, 197–202] It was demonstrated that Stone-Wales (SW) defects [203] can be formed during a rapid quench from high temperature or when graphene is under irradiation.[204] The presence of such defects modifies the chemical reactivity of the graphene lattice.[205, 206] Very recently, Ijäs *et al.* have reported that the presence of SW defects in a honeycomb lattice results in more reactive domains for chlorine atoms as compared to defect-free graphitic structures.[207]

Although the SW type defects are quite likely to be formed in such monolayer systems, the formation of SW-type defects and their effect on the electronic, magnetic and adsorption characteristics of monolayer silicene have remained unexplored. In this Chapter¹ the formation and the electronic properties of SW defects in silicene are investigated. The formation of SW type defects is found to be more likely in silicene compared to graphene and the existence of the underlying Ag(111) surface (common for experimental synthesis) does not significantly affect their formation. Furthermore, once the SW defect is formed in the silicene lattice the doping characteristics are influenced dramatically.

¹The results of this Chapter can be found in publication: H. Sahin, J. Sivek, S. Li, B. Partoens, and F. M. Peeters, Phys. Rev. B **88**, 045434 (2013), "Stone-Wales defects in silicene: Formation, stability, and reactivity of defect sites".[208] Consult the rights and permissions for the text of this Chapter (including equations and tables) with the publisher of the aforementioned publication.

Table 7.1: Calculated structural and electronic properties for silicene and SWdefected silicene: lattice parameter (a), Si–Si distance (d_{Si-Si}) , angle between two of the lattice vectors of a 6×6 supercell (α), total magnetic moment of the system (μ_{Tot}) , formation energy (E_f) , cohesive energy (E_{coh}) and the band gap (E_{gap}) .

	a	d_{Si-Si}	α	μ_{Tot}	E_f	E_{coh}	E_{gap}
	Å	Å	deg	(μ_B)	(eV)	(eV)	(meV)
Silicene	23.21	2.28	60.0	0	0.00	-3.98	1.5
SW-Silicene	23.04	2.19 - 2.28	61.5	0	1.64	-3.96	20

7.1 Computational details

The first-principles calculations are performed based on the plane-wave basis set with a cutoff energy of 500 eV and the projector-augmented wave (PAW) pseudopotentials as implemented in the VASP package.[151, 209] The exchange-correlation functionals are described by the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) approach.[5] The partial occupancies for the total energy ground state calculations were calculated with the tetrahedron methodology with Blöchl corrections.[188]

Periodic boundary conditions were employed for silicene with a vacuum region of 15 Å between neighbouring slabs. For supported silicene on a Ag (111) surface the height of the supercell has been set to 29 Å in order to conveniently include 4 layers of the Ag crystal. In order to determine the equilibrium configuration of silicene with defects, we relaxed all the atomic coordinates and the supercell geometry using the conjugate gradient algorithm with the maximum residual force of less than 0.01 eV/Å. The sampling of the Brillouin zone was done for the supercell with the equivalent of $24 \times 24 \times 1$ Monkhorst-Pack [103] k-point mesh for a silicene unit cell composed of two Si atoms. In order to minimize the interactions between the neighbouring SW defects, for the calculation of geometric and electronic properties, we employed a large supercell derived from a 6×6 supercell of silicene where the distance between neighbouring defects is at least 14.6 Å. The calculations of the formation energetics of a SW defect for supported silicene were performed with a 6×6 supercell of silicene on top of 8×8 supercell of Ag (111) surface.

The phonon dispersions were calculated using the Small Displacement Method [189] and the calculations were carried out by Doc. dr. Hasan Sahin.



Figure 7.1.1: The top and side view of (a) perfect and (b) SW-defected silicene. (c) Energetics of formation of a SW defect in silicene via the bond rotation (highlighted). The curve with open squares is obtained by relaxing the first nearest hexagons to the silicene dimer in free-standing silicene layer. The curves with open circles and triangles are obtained by relaxing up to the second nearest hexagons to the silicon dimer in the free-standing and supported silicene (on a Ag (111) surface), respectively. (d) The actual bond rotation steps $(0^{\circ}, 45^{\circ} \text{ and } 90^{\circ})$ in silicene supported on the Ag (111) surface. The uppermost and lower-lying Ag atoms are shown by grey (light) and black (dark).

7.2 Results

7.2.1 Formation and stability of Stone-Wales defects in silicene

Since the formation of defects is inevitable in crystals, understanding their effect on the mechanical, electronic and structural characteristics plays a key role in nanoscale device applications. The most common defects that have been observed in low-dimensional graphene-like structures are missing atoms, adatom impurities and SW type of disorders. Here we investigate the formation and stability of SW defects in a single layer structure of silicene shown in Fig. 7.1.1(a). Compared to the graphitic materials such as graphite, graphene and carbon nanotubes, the inter-atomic distance is larger in silicene. Furthermore, due to the buckled hexagonal lattice structure, easier formation of various defects in silicene can be expected.

As shown in Fig. 7.1.1(b) a SW defect can be created by the rotation of a silicon dimer by 90° around the centre of the Si–Si bond. From the experimental point of view, such a defect can be formed during the growth process or upon application of irradiation. After the formation of the SW defect, four neighbouring hexagons of silicene are transformed into a pentagon and



Figure 7.2.1: Phonon dispersion of pure (dashed line) and SW-defected silicene (filled curve). Atomic motions for two phonon modes which have imaginary eigenfrequencies are shown on the right. Only the motions of atoms in defect core and neighbouring atoms are shown for clarity. Blue and red arrows represent displacements of Si atoms along -z and +z directions, respectively.

a heptagon pair. As can be seen from Fig. 7.1.1(b), even after the creation of the SW defect, silicene maintains its buckled two-dimensional structure with only a local out-of-plane displacement of the Si atoms. Conversely, large local bumps in the graphene lattice are formed due to the existence of SW defects. Through 90° rotation of a dimer, the Si–Si bond becomes stronger than in defect-free silicene and its length decreases from 2.28 to 2.19 Å. After the shortening of the bond lengths along the direction parallel to the pentagons, the lattice constant decreases from 23.21 to 23.04 Å. Though Si atoms favour buckled configuration in bare silicene the formation of unbuckled Si-dimer in the core of the SW-defect is preferable. Structural properties, energetics and energy band gap of bare and SW-defected silicene are given in Table 7.1.

The transition states and energetics of the formation steps of the SW defect in free standing silicene as well as for silicene supported on the Ag (111) surface are shown in Fig. 7.1.1(c). The intermediate steps are obtained by confining Si atoms at positions interpolated between those of perfect silicene and silicene with a SW defect. The atoms that form two heptagons and two pentagons of the SW defect and the nearest hexagons are allowed to relax. The Si dimer that is gradually rotated is allowed to relax only in the direction perpendicular to the Si layer. It is seen that the formation of such SW defect in a perfect silicene lattice may occur by overcoming the energy barrier of ~2.4 eV for free standing silicene and 2.8 eV for the supported silicene layer. The maximum of the energy barrier corresponds to the ~54° rotation of the bond. In comparison, this barrier in graphitic materials is considerably larger and amounts to 9.2 eV.[205] However, the energy barrier of 0.76 eV

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(1.10 eV for supported silicene) between the intermediate configuration and silicene with a SW defect guaranties the stability of such defects even at high temperatures. This shows that the buckled lattice structure and the softer bonding nature of silicene allows an easier formation of SW-defected structure. The formation energy, E_f , of a SW defect in silicene is given by

$$E_f = E_{Silicene}^{SW} - E_{Silicene} \tag{7.2.1}$$

where $E_{Silicene}^{SW}$ is the total energy of silicene with SW defect and $E_{Silicene}$ is the total energy of perfect silicene. According to this, the formation energy of a SW defect in a $6 \times 6 \times 1$ supercell is calculated to be 1.64 eV. Additionally, the stability of the structure can also be predicted via its cohesive energy which is defined as the energy required for separating the crystal into isolated free atoms.

The cohesive energy of a crystal structure is given by the formula

$$E_{coh} = (E_{Tot}/n) - E_{Si}$$
 (7.2.2)

where E_{Tot} is the total energy of the system, n is the number of atoms in the supercell and E_{Si} is the total energy of an isolated silicon atom. The cohesive energies of silicene and SW-defected silicene are calculated to be -3.98 and -3.96 eV, respectively. The negative cohesive energies of both structures indicate their stability.

Next we extend our discussion on the stability and formation of SWtype defects in single layer silicene by analysing the vibrational spectrum. Although total energy calculations show the stability of the SW defects, our phonon calculations reveals that there are two imaginary eigenfrequencies in the SW-defected silicene spectrum (see Fig. 7.2.1). For a 4×4 supercell of silicene these modes are located at -14 and -20 cm⁻¹. Analysis of the lattice dynamics of structure for these two modes shows that the creation of a SW defect results in large ripples around the defected region. As seen from Fig. 7.2.1, the modes I and II imply the formation of sine like and cosine like lattice distortions with respect to the midpoint of the Si–Si dimer. Therefore the buckled planar structure of SW-defected silicene is a local minimum on the potential energy surface. However, it is worth to note that the stabilization of planar silicene structure by a supporting surface has already been reported by several groups. [62, 86, 210] The existence of sine like and cosine like rippling in silicene is in good agreement with the results for SW-defected graphene.[211] Although our phonon calculations revealed the instability of densely SW-defected silicene, the results also imply the stability provided by the long wavelength ripples. Therefore it is reasonable to assume that the reactivity of defect cores for planar and long-wavelengthrippled silicene do not differ significantly. Additionally, we perform molecular dynamics calculations in order to further examine the thermal stability of SW-defected silicene. At the temperature of 500 K, we choose time steps of 1 and also 2 fs. The SW defect and the surrounding bonds in silicene remain stable and there is no indication of defect-healing throughout the molecular dynamics simulations with duration of 2 ps at 500 K.

In Figs. 7.2.2(a) and (b) the electronic band dispersion of perfect and SW-defected silicene are presented. It is worth to note that for a 6×6 supercell, the K and K' symmetry points of the unit cell of silicene are folded onto the Γ point. Therefore, both valence band maximums are transferred to the Γ point of the supercell. Clearly, as seen in Fig. 7.1.1(b), after the formation of a SW defect the lattice symmetry of silicene is broken. Since the formation of the SW defect breaks the six-fold symmetry of the silicene lattice, that results in linearly crossing bands and the existence of highly mobile fermions in the vicinity of the Dirac point, a band gap opening occurs at the crossing point. [212] The band gap opening for SW-defected silicene in a 6×6 supercell is calculated to be 0.02 eV. It correspond to the system with a defect concentration of $1.9 \cdot 10^{13}$ cm⁻². The actual value of the band gap depends on the concentration of the SW defects. In the case of a 5×5 supercell with a single SW defect $(2.7 \cdot 10^{13} \text{ cm}^{-2})$ the energy band gap increases to 0.1 eV. Here it is also worth to note that the choice of a hexagonal supercell results in band edges that appear at the K symmetry point (Γ for $3n \times 3n$ supercells) and a temporarily ordered defect configuration may result in a different band dispersion. Since there are no dangling bonds introduced into the silicene lattice with the creation of a SW defect, all the atomic orbitals of the Si atoms at the vicinity of the defect are paired and hence there is no defect-originated magnetism.

7.2.2 N-doped silicene: effect of Stone-Wales defects

Doping materials with foreign atoms is an efficient way to manipulate their electronic, magnetic and chemical properties. For carbon-based materials such as graphite, graphene and nanotubes the doping especially with Group III or V atoms is desirable since they induce n or p type doping and the density of the charge carriers can be tuned by the concentration of the substituents. It has been demonstrated that synthesis of N doped graphene samples can be achieved by annealing in the presence of pyridine or NH₃ molecules and by chemical vapour deposition (CVD) and the observed features of N-doped graphene are quite desirable for device applications. [179, 213–216] The formation energy of N substitution in graphene is 0.32 eV



Figure 7.2.2: The electronic band structure for a 6×6 supercell of (a) perfect and (b) SW-defected silicene. (c) Band decomposed charge densities of the conduction band around the Fermi level at Γ , K and M symmetry points (the isosurface is set to $0.57 \cdot 10^{-3} \text{ e/Å}^3$)



Figure 7.2.3: (a) The electronic band structure of N-doped silicene, (b) top and side view of the structure. (c) 3D and contour plot of difference charge density $(\rho_{\uparrow} - \rho_{\downarrow})$. The slicing plane is marked by dot-dashed line in (b).

per N atom.[217] Since N atom in graphene forms three σ bonds and p_z orbital is filled by two electrons, N-doped graphene shows non-magnetic behaviour.[213] The N doping induces *n*-type doping of graphene and shifts the Fermi level up by ~ 0.6 eV for the case of 2 % N concentration.[179]

The substitutional doping of silicene with a N atom is of a different nature as compared to the doping of graphene. The N–Si bond length in substituted silicene (1.83 Å) is significantly shorter than the Si–Si bond length in pristine silicene (2.28 Å) and the shorter bonds induce a local in plane shrink deformation in the structure as presented in Fig. 7.2.3(b). The nitrogen bonds with the neighbouring Si atoms are in the plane, which reduces the amount of local buckling. However, perfect silicene's lattice structure is restored just several bonds away from the substituent atom. The formation energy of N-doping in silicene is defined as

$$E_f = E_{Tot} - (E_{Silicene} - \mu_{Si}) - \mu_N \tag{7.2.3}$$

where E_{tot} is the total energy of the N-doped silicene and $E_{Silicene}$ is the total energy of perfect silicene, μ_{Si} is the chemical potential of a single silicon atom (calculated from the total energy of monolayer silicene), and μ_N is the chemical potential of a nitrogen atom, defined as one-half of the total energy of the N_2 molecule in the gas phase. This choice of chemical potentials is made to account for the stability of N-doped silicene against N_2 molecular desorption. The binding energy of N-doped silicene is here defined as:

$$E_{bind} = E_{Tot} - (E_{Silicene}(n_{Si} - 1)/n_{Si}) - E_N$$
(7.2.4)

where n_{Si} is the number of Si atoms in a supercell of pristine silicene and E_N is the total energy of an isolated N atom. The binding energy of a N atom in N-doped silicene is -4.60 eV. On the other hand, the calculated formation energy is 0.59 eV as a consequence of the large bond-dissociation energy of the N_2 molecule.

From the electronic band structure of N-doped silicene, displayed in Fig. 7.2.3(a), it is seen that the substitutional N atom turns semimetallic silicene into a ferromagnetic metal with total magnetic moment of 1.0 μ_B . The magnetic character of N substituted silicene can be seen from the 3D and the contour plot of the difference charge density $(\rho_{\uparrow} - \rho_{\downarrow})$ in Fig. 7.2.3(c). It appears that the N-originated state is delocalized over the nearest Si atoms and therefore N substitution results in long-range spin polarization of the surrounding sp³-like orbitals even in a large 6×6 supercell. The magnetic behaviour of N-doped silicene and delocalization of the N-originated states are consistent with previously-reported results obtained with the use of LDA functionals.[177, 184]



Figure 7.2.4: The substitutional sites of the SW defect in silicene with associated letter, and the side view of the same structure. [[]]



Figure 7.2.5: (a) Large local lattice deformation around small N substituent atom at A site destabilize the structure. (b) Much larger P atom, on the other hand, can form stable bonding.

Next we investigate the effect of the presence of a SW-defect on substitutional nitrogen doping in silicene. As a result of local deformations induced by the creation of a SW-defect (Fig. 7.1.1(b)) every single Si atom in the surroundings of a SW-defect provides a unique place for substitution. Since the surrounding atoms still maintain their buckled hexagonal nature we will focus only on the Si atoms that are part of the heptagons or pentagons in the SW-defect. As a consequence of the lattice symmetry with respect to the Si– Si dimer at the defect core a similar behaviour of adsorbates on site I and II can be expected. However, in order to not exclude the possible effects of lattice distortion on N substitution, calculations were performed for all 16 sites of the SW defect. Possible positions for substitutional doping with one substituent atom are displayed in Fig. 7.2.4. Additionally, we present structural properties, total magnetic moment, formation energies and binding energy values in Table 7.2.²

The substitution positions can be divided into the four groups. The first group contains the lattice sites that belong to edges of heptagons A, B, H and I. We found that Si–N bonds at the edges of heptagons are not stable and hence the substitution of a N atom on A, B, H and I positions cannot be realized. The formation of the stable structure is made impossible due to the large local lattice deformation at the substitution site (see N substituent atom in Fig. 7.2.5(a) and compare to less stressed system with P substituent atom in Fig. 7.2.5(b)).

The second group is composed of C, and G substitution sites that locate at the outermost intersection of heptagons and the pentagons of the defect core. Though C and G sites are geometrically and energetically similar, because of the lattice distortion induced by N-doping and buckled nature of the silicene lattice, these adsorption sites are not identical. Similar to doping in perfect silicene the substitution of a N atom on C and G site result in spin polarization of 1 μ_B . The binding energies on these lattice sites are smaller compared to intrinsic silicene.

The third group of possible substitution points are I and II sides of E which are located in the middle of the defect core. Clearly, both sides of E are equal for N-doping. When a N atom is substituted over E site, the resulting structure has a total magnetic moment of 1 μ_B and doping on these sites is by 0.4 eV more favourable than doping on C and G sites.

² An attentive reader will be surprised by the binding energy of nitrogen atom in silicene, because the results in Table 7.2 and Table 6.1 differ by more than 1eV. This apparent discrepancy is mainly caused by the overbinding in the LDA calculations.[218, 219] The difference of total energies for the structures will be large between LDA and GGA calculation then the difference of the total energies of isolated atoms between LDA and GGA calculation (see Equation 7.2.4).

7.3. CONCLUSIONS

Table 7.2: Calculated values for N-doped on SW-defected 6×6 silicene; bond length of N–Si (d_{N-Si}) , angle between two of the lattice vectors of supercell of N-doped structure (α) , total magnetic moment of the system (μ_{Tot}) , formation energy (E_f) and binding energy (E_{bind}) .

defect site	d_{N-Si}	α	μ_{Tot}	E_f	E_{bind}
	(Å)	(deg)	(μ_B)	(eV)	(eV)
N in pure silicene	1.83 1.83 1.83	60.0	1.0	0.59	-4.6
N at site A,B,H,I		-	-	-	-
N at site C	$1.86 \ 1.82 \ 1.80$	61.7	1.0	1.8	-3.4
N at site D	$1.78 \ 1.82 \ 1.80$	61.5	0.7	1.1	-4.0
N at site E	$1.83 \ 1.83 \ 1.76$	61.3	1.0	1.5	-3.7
N at site F	$1.80 \ 1.78 \ 1.82$	61.5	0.7	1.1	-4.0
N at site G	$1.79\ 1.82\ 1.83$	61.7	1.0	1.8	-3.3

The last group includes D and F substitution sites, which belong to the pentagons of the SW-defect. The Si–N bond lengths in these lattice sites are smaller or equal to the bond lengths in N-doped silicene. For those structures we also observe large rippling of the order of 2 Å. We found that substitutional doping on D and F positions does not give rise to a shrinkage of the lattice parameters. D and F points are energetically most favourable sites on a SW defect with a binding energy of -4.0 eV. It is seen that nitrogen substitution results in a net magnetic moment of 0.7 μ_B . Similar to N-doping in perfect silicene, SW-defected silicene shows metallic behaviour for all possible substitution sites that belong to the core of SW defect.

7.3 Conclusions

In this study we performed *ab initio* calculations in order to investigate the formation of SW defects in silicene and to show the effect of these defects on the reactivity of the silicene with respect to nitrogen doping. We found the formation of a SW-defect to be much easier in the buckled lattice structure of silicene as compared to graphene. The softer bonding nature of silicene allows easier formation of a SW defect with a smaller energy barrier for both free standing as well as supported silicene. The presence of a SW defect in silicene breaks the symmetry and results in a band gap opening in electronic band structure with size depending on the defect concentration. Additionally, our vibrational analysis reveals that the formation of SW defects in freestanding silicene inevitably leads to the formation of large ripples. Moreover, the presence of an underlying Ag(111) supporting surface increases the barrier

for the formation of SW defects from 2.4 to 2.8 eV. We also found that the buckled nature of silicene provides a large energy barrier for healing of SW defect and therefore defective silicene is quite stable even at high temperatures.

Furthermore, the presence of SW defects significantly modifies the doping characteristics of silicene. While doping defect-free silicene by N atoms is favourable with a little lattice shrinking, the presence of a SW defect limits the number of possible doping sites. We found that all the nitrogen substitution sites on the defect core are less preferable than defect-free silicene. Among the possible sites of defect the edges of heptagons are least favourable sites while doping of the N atoms at the edges of pentagons is most preferable. Our findings on the reactivity of SW-defected silicene domains agree well with the very recent study that reports the chlorine adsorption on SW-defected graphene and carbon nanotube.[207] We believe that our results provide a basis for the understanding of the characteristic properties of defected silicene which are essential for its utilization in future electronics.

Chapter 8

Inducing giant magnetic anisotropy

Controllable doping provides a directed and effective approach to elevate or induce specific characteristics of two dimensional crystals.[220] One of the more intriguing material properties is magnetic anisotropy. Materials with a high magnetocrystalline anisotropy [221] are of interest for magnetoelectronics technology to manufacture data storage components,[222] as well as for spintronics applications where increased anisotropy is used to realise a high degree of spin polarization.[223] The search for nanostructures with high magnetic anisotropy is also fuelled by the need to reduce the size of ferromagnetic components, e.g. for long-term magnetic data storage.

In the past it was demonstrated that magnetic anisotropy can be induced by chemical functionalization of pristine materials, e.g. in graphene decorated with transition metal atoms the strong hybridization between adatoms and the graphene C atoms induce magnetic anisotropy,[224-227] in MoS₂ crystals the magnetic anisotropy can be controlled by hydrogenation and proton irradiation,[228] and this is valid especially for ultrathin materials.[229]Especially adsorbates with 4d and 5d transition metals (TM) have shown promising results for the realisation of large uniaxial magnetic anisotropies with magnetocrystalline anisotropy energy (MAE) value of the order of several 10 meV's,[192, 227] or even up to the 100meV for transition metal dimers on graphitic surfaces.[227] Such large MAE values are of high interest because they allow for applications with a long retention time for the magnetization at high temperatures.

In this Chapter¹, we investigate monolayer structures of fluorographene

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(FG) and molybdenum disulfide (MoS₂) as a chemically and structurally stable basis for the chemical functionalization by TM atoms in order to induce a large magnetic anisotropy. We present the structural stability, magnetic properties and MAE's of single layer S-vacant MoS₂ and F-vacant FG decorated with W, Os, Ir, Pt, Ru, Rh or Co atoms located at the vacancies. F vacancy has been chosen for its potential feasibility in fluorographene synthesis and the S vacancy in MoS₂ has been chosen due to its frequent presence in experiments.[230]

8.1 Computational details

All geometry optimizations and electronic structure calculations were carried out by means of the VASP package [151] and with the use of spin polarized Perdew, Burke, and Ernzerhof [5] (PBE) generalized gradient (GGA) parametrization for the exchange-correlation functional. We made use of the projector augmented wave method [105] and a plane-wave basis set with an energy cutoff of 500 eV. The sampling of the Brillouin zone was done for the supercell with the equivalent of a $24 \times 24 \times 1$ Monkhorst-Pack k-point grid for both the FG and MoS₂ primitive unit cell. The partial occupancies in the electronic ground state calculation were treated using the tetrahedron methodology with Blöchl corrections.[188] The reported quantitative results of the charge transfers were obtained using the Bader charge population analysis.[110, 111]

MAE values were calculated by employing a direct, two step process. First, a Kohn-Sham based calculation with collinear electron density and without spin-orbit coupling corrections (this allows fixing the orientation of all magnetic moments which is important for determining of MAE) was performed in order to obtain a self-consistent ground state electronic charge density. In the second step, the obtained charge density was used as an input for the non self-consistent spin-orbit coupling and non-collinear calculations with varying orientation of the magnetic moments. In other words the magnetization charge density from the first, self-consistent, calculation is interpreted as magnetization in a specific direction during the second, non self-consistent, calculation. This procedure is allowed by changing the quantisation axis for spin to an arbitrary direction. Naturally, this is only possible with use of charge charge density with collinear orientation of spins.

The fundamentals of the employed *ab initio* methodology allows one to obtain a self-consistent relativistic potential directly from the pseudowavefunctions following the construction methods in studies of Hamann et al,[104] Kleinman [231] and Błoński et al.[232]


Figure 8.2.1: Top and side view of the relaxed structures of (a) fluorographene and (b) molybdenum disulfide. C, F, Mo, S and adatoms are depicted with grey, green (light), green (dark), yellow (light) and red (murky) colours, respectively. The carbon-transition metal distance d_{CX} and the molybdenum-transition metal distance d_{MoX} is displayed as well.

The spin-orbit interaction is evaluated in the Hamiltonian with the following contribution from each atom in the supercell (with only spherical dependence on the potential within the restricted region)[233]:

$$H^{so} = \frac{1}{2(m_e c)^2} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S}$$
(8.1.1)

with m_e the electron mass, r the radial distance from individual atom nuclei, V the pseudopotential, L and S the orbital momentum and spin operator.

The spin-orbit induced nondiagonal terms in Eq. (8.1.1) lead to the nonzero MAE for the adatom-monolayer crystal structures, considered in this study, when varying direction of magnetic moments. As long as the spin-orbit coupling is ignored rotation of all the magnetic moments in the system by the same angle results in the same total energy.

8.2 Results

8.2.1 Structural and stability properties

The systems under study are composed of a 3×3 supercell of FG and MoS₂ with a single F or S atom vacancy, respectively, in which a transition metal atom is adsorbed. This is equivalent to ~ 5.5 % coverage of TM atoms per C and/or Mo atom. The structure and placement of the adsorbed atom is indicated in Fig. 8.2.1. The structural properties including the lattice parameter as well as the TM atom to C (or Mo) atom distance are reported in Table 8.1. The adsorption of the metal atom on the vacant site of the

MoS₂ does not result in a significant lattice distortion. Compared to the pristine MoS₂ lattice parameter 9.56 Å (for a 3×3 supercell) the adsorption induces a moderate decrease by as much as ~ 0.5 %, with one exception for the Os atom, where the lattice parameter is enlarged by ~ 0.1 %. A similar decrease of lattice constant, by as much as ~ 0.6 %, is found for doped FG with a pristine lattice parameter of 7.84 Å (for a 3×3 supercell).

In order to address the stability of the predicted structures we evaluate the binding energy. It is defined as $E_{\rm b} = (E_{\rm vacant} + E_{\rm TM}) - E_{\rm system}$, with $E_{\rm system}$ the total energy of the system with adsorbed TM atom, $E_{\rm vacant}$ the total energy of the system with the vacancy, and $E_{\rm TM}$ the energy of a single TM atom, all in the corresponding supercell. All the TM decorated systems are stable as can be seen from the considerable positive values of the binding energies, in Table 8.1, ranging from 3.78 to 5.24 eV per adatom for doped MoS₂ and 2.45 to 3.14 eV per adatom for doped FG. The binding of TM atoms to MoS₂ is up to 2.5 eV larger compared to FG, this is especially prominent for Pt, Ir and Os adatoms. Consistent with the electronegativity of the elements, with the C atom carrying the highest value, all the TM atoms are positively charged and donate electrons mainly to the bonded C atom when adsorbed on F-vacant FG. On the other hand Pt, Ir and partially Os adatoms behave like acceptors on S-vacant MoS₂.

 MoS_2 as well as FG are materials composed of three atomic layers. Due to the difference in the electronegativity the outer layers composed of F atoms or S atoms are charged negatively while leaving the middle layer composed of positively charged C atoms or Mo atoms. Addition of the TM adatom, which has a smaller electronegativity compared to both F or S atoms, into the single vacancy creates locally a decrease of the electron density, reducing the amount of surplus of the negative charge in the upper layer compared to the bottom layer. This change induces a dipole moment pointing from the pristine to the adsorbed side of 0.39 to 0.58 e·Å for FG and 0.16 to 0.32 e·Å for MoS₂.

8.2.2 Magnetic properties

The magnetocrystalline anisotropy energy is the energy difference between in plane magnetization (E_{\parallel}) and perpendicular magnetization (E_{\perp}) which is given by the formula:

$$MAE = E_{\parallel} - E_{\perp} \tag{8.2.1}$$

The positive (negative) value of the MAE implies that the easy magnetization axis is perpendicular (parallel) to the surface of the two dimensional crystal. The easy magnetization axis, or just easy axis, is an energetically

8.2. RESULTS

favourable direction (without orientation) of the crystal ground state magnetization (orientation of magnetic moment). The xy-axis was selected as plane magnetization axis. The effect of in-plane rotation of the magnetization axis is discussed later. Presence of such an anisotropic behaviour in a crystal structure stems from the interaction of the spins with the field generated by the electron orbital motion and it is fundamentally a relativistic effect.

Inducing MAE in fluorographene

The calculated MAE values of the chemically decorated F vacant FG are given in Table 8.1. The Os, Ir and W atoms induce a strong magnetocrys-talline anisotropy with MAE values of -100.46 meV, 52.79 meV and -47.02 meV, respectively. With exception of Os, W and Ru adatoms, the perpendicular direction corresponds to the easy axis.

An essential requirement to realize a non zero MAE is the presence of a net magnetic moment. The magnetization of the ground state is consequently reflected in the MAE values. As shown in Table 8.1, higher MAE values are reached for strongly magnetized TM atoms. Adsorption of a TM atom results in a spin-polarized ground state with the magnetic moment gradually decreasing with increase TM atomic number in the corresponding row of the periodic table of elements. Vacant FG itself possesses a magnetic moment of 1 $\mu_{\rm B}$ per one F vacancy originating from the dangling bond of the sp^3 hybridized C atom. The TM adatom s and d states partially hybridize and create a bond with this underlying C atom. The resulting magnetic moment of the compound originates from an antiferromagnetic coupling between the TM atom valence electrons and the C atom p_z orbital. Thus, the absolute value of the magnetic moment per TM atom is equal to the number of unpaired electrons in the free standing TM atom valence electron shell minus one. This gradual decrease of the magnetic moment is identifiable on the magnetization charge density displayed in Fig. 8.2.3 where magnetic states are strongly localized on adsorbed TM atom.

Furthermore, the magnetic anisotropy depends on the spin-orbit coupling of the adatoms. This characteristic is dominant for a Pt atom which induces a higher MAE of 5.46 meV, compared to 1.24 meV for a Co atom, despite its lower magnetic moment.

While magnetization of adatom decorated FG could be manipulated by an external magnetic field in different directions, the stability of a specific magnetization direction is determined by the TM atom bonding coordination, the geometry, as well as by the occupation of the electronic states close to the Fermi level and the interplay between the HOMO and LUMO states. From the calculated orbital projected density of states, see Fig. 8.2.2, we



Figure 8.2.2: Orbital projected density of states for TM atom decorated FG and MoS_2 . The total density of states includes only adatoms and bonded atoms from substrate (three neighbouring Mo atoms in MoS_2 and four C atoms in FG, first and second nearest neighbour). The majority of the pictured midgap states do have origin in TM adatoms and their orbital character is denoted in the legend with labels starting with "TM" prefix. The Fermi energy is set to 0 eV.



Figure 8.2.3: The magnetization charge densities of TM adsorbed fluorographene (the isosurface is set to 10^{-2} e/Å³ for majority, orange (bright), and minority, blue (dark), spin charge densities). In lower the plots of the variations of MAE values are projected on sphere surface for Os and Ir adsorbed FG. The displayed values are computed as: $MAE = E_{axis} - E_{\perp}$, with E_{axis} the magnetization energy with the magnetization axis corresponding to the point on the sphere.

Table 8.1: Electronic, magnetic and structural properties of transition metal adatom bonded to single layer MoS_2 and fluorographene. These atoms are attached at the position of missing sulfur or fluorine atom, respectively. The table provides the following parameters: the lattice constant (*a*), substitute–carbon (or molybdenum) distance (*d*), binding energy per TM atom (E_b), magnetic moment per TM atom (μ), charge located on the adatom (ρ), dipole moment per TM atom (*p*) and magnetocrystalline anisotropy energy (MAE) per TM atom.

	a	d	\mathbf{E}_{b}	μ	ρ	p	MAE
	Å	Å	eV	μ_B	е	e∙Å	meV
Pt-FG	7.81	2.03	2.71	1	0.36	0.43	5.46
Rh-FG	7.79	2.11	3.14	2	0.56	0.55	7.77
Ru-FG	7.79	2.13	2.84	3	0.66	0.56	-11.24
Co-FG	7.79	1.98	3.01	2	0.67	0.58	1.24
Ir-FG	7.81	2.05	2.72	2	0.44	0.42	52.79
Os-FG	7.80	2.08	2.45	3	0.54	0.40	-100.46
W-FG	7.80	2.25	2.58	5	0.73	0.39	-47.02
$Pt-MoS_2$	9.54	2.63	5.24	0	-0.38	0.16	0.00
$\operatorname{Rh-MoS}_2$	9.53	2.62	4.66	1	-0.12	0.19	-3.21
$\operatorname{Ru-MoS}_2$	9.53	2.62	4.58	2	0.06	0.23	9.92
$\operatorname{Co-MoS}_2$	9.51	2.49	3.78	1	0.12	0.19	2.24
$\operatorname{Ir-MoS}_2$	9.54	2.52	5.15	1	-0.31	0.16	31.14
$Os-MoS_2$	9.58	2.57	4.88	2	-0.11	0.22	36.30
$W-MoS_2$	9.54	2.60	4.62	2	0.44	0.32	-40.65

can make a link between the geometrical character of the valence states and the easy axis orientation. The Os adatom induces a giant negative MAE with a value of -100.46 meV and shows perpendicularly oriented d_{xz} and d_{yz} HOMO states (lower left panel in Fig. 8.2.2). On the other hand Pt, Ir and Co adatoms induce a perpendicular easy axis, and create valence states dominated by planar d_{xy} and $d_{x^2-y^2}$ states. All this in the consent with the model where the orientation of the easy axis corresponds with the direction of the dominant orbital magnetic moment near the Fermi level, very similar to the consequences of the the Bruno model for magnetocrystalline anisotropy.[229] The same trend is observable for Ru and partially for Rh adatoms, the observations are of opposite nature for W decorated FG. Moreover, the splitting in energy bands of Pt, Ir and Os decorated FG correlates with the absolute value of the MAE.



Figure 8.2.4: The magnetization charge densities of TM adsorbed MoS₂ (the isosurface is set to 10^{-2} e/Å³ for majority, orange (bright), and minority, blue (dark), spin charge densities). In lower the plots of the variations of MAE values are projected on sphere surface for W, Os and Ir adsorbed MoS₂. The displayed values are computed as: $MAE = E_{axis} - E_{\perp}$, with E_{axis} the magnetization energy with the magnetization axis corresponding to the point on the sphere.

Inducing MAE in MoS₂

The calculated MAE values of the chemically decorated vacant MoS_2 are given in Table 8.1. Although the induced MAE values are lower compared to FG, we observe a strong induced magnetocrystalline anisotropy for adsorbed W, Os and Ir atoms with MAE values of -40.65 meV, 36.3 meV and 31.14 meV, respectively. All, but W and Rh, adatoms induce a perpendicular easy axis.

The origin of the magnetic moment in doped MoS_2 is of a different nature and can have mixture of causes. The magnetic states in decorated S vacant MoS_2 are more spread compared to FG as they extend up to the nearest Mo neighbour atoms for Co and Ir adsorption and even the next nearest Mo neighbour atoms for Os adsorption (compare the magnetization charge density for the example of Os adatom on MoS_2 in Fig. 8.2.3 with the Os on FG case in Fig. 8.2.3). Co, Rh, Ir and Pt atoms are after adsorption in the low spin configuration. Unlike free atoms, with all the d orbitals at the same energy level, the Mo neighbours induce large d level splitting in the bonded TM atoms. The splitting of the d orbitals is reflected in the lower ground state magnetic moment of the confined atom. However, the Os, Ru and W atoms remains in the high spin configuration after adsorption in a single S vacancy. Furthermore, the magnetic moment of the Ir, Rh and Co adsorbed structure stems from the small fractional charge transfer to and from (in case of Co) TM atoms and the different coupling of the valence shell electrons of TM atoms with its bonded Mo atom which results in unified observable total magnetic moment of $1\mu_B$ per adatom.

Unlike in decorated FG the TM adatoms on MoS_2 exhibit three coordination bonding to the neighbouring Mo atoms. As can be seen in Fig. 8.2.3 for the example of the Os adatom, the magnetization charge density induced by the TM atom adsorbed on MoS_2 is not axially symmetric and its symmetry does not correspond to the three fold symmetry implied by the bonding. This discrepancy in the symmetries induces slightly asymmetric bonds.

It is also important to discuss the effect of this magnetization charge density symmetry on the calculated MAE values. Fig. 8.2.3 and 8.2.3 show the MAE values for various TM atoms on FG and MoS₂, respectively, for arbitrary magnetization axes. In combined Fig. 8.2.4 it can be easily shown that the strong anisotropy of the magnetization charge density induced by TM atoms adsorbed on MoS_2 markedly induces a dependence of the MAE value on the orientation of the parallel magnetization axis. The effect is negligible for decorated FG.

The aforementioned observations of the relation between the magnetic moment, the character of the HOMO and LUMO levels and the magnetic anisotropy in FG can now be applied to doped MoS_2 . Stronger hybridization between Mo and adatom states and a large splitting of the d orbitals of the TM adatoms result in relatively smaller net magnetic moments of the compounds, compared to FG. The lower magnetic moments consequently affect the lower amplitudes of the MAE (see Table 8.1), up to the point of Pt decoration of MoS_2 with a rather strong binding energy (5.24 eV) and a non-magnetic ground state leading to zero MAE (compared to 5.46 meV for Pt-FG). The MAE value for the Os adatom case, 36.30 meV, is larger than for the Ir adatom, 31.14 meV, thanks to a larger magnetic moment. Next, we can deduce the orientation of the easy axis. The Co, Ru, Ir as well as Os adatoms induce HOMO states predominantly composed out of planar d_{xy} and $d_{x^2-y^2}$ states. The geometrical character is translated into an easy axis perpendicular to the surface. The same trend can not be applied for adsorbed Rh and W atoms, however W adatom shows compatible behaviour for MoS_2 and FG substrate. In accordance with doped FG, the increased band gap in doped MoS_2 properly indicates the differences in the absolute size of MAE.

We observe mutually compatible majority trends for the magnetic anisotropy of doped MoS_2 and FG. The clues in the form of the net magnetic moment of the structure, the atomic radius and the orbital character of the HOMO and LUMO states are found to be sufficient to provide general insight into the calculated magnetocrystalline anisotropy. Nevertheless, it is important to note that the aforementioned recipe for large MAE values does not give a comprehensive explanation of the origin of the magnetic anisotropy. This fact is underlined by the connection between orbital character of the HOMO states and easy magnetization axis, we described as general trend earlier, which is of a different nature than the one described in earlier works of J. Honolka et al. [234]. The fundamental adatom properties like larger covalent radius, structure of the atomic shell that has a direct influence on the larger spin-orbit interaction, or the magnetic moment per adatom which enhances the calculated MAE values (for calculated magnetic moments up to the 3 μ_B per adatom the corresponding MAE values increase respectively with magnetic moment), are indispensable indicators of the magnetic anisotropy, yet they are just parts of the complex origin of this physical property. It is worth to note that here presented results have been computed with DFT based formalism without incorporating Hubbard corrections to DFT energy functional (also known as DFT+U). To our knowledge, the additional corrections do not alter orientation of the observed easy axis, while they can lower the magnetocrystalline anisotropy energy. The amplitude of the correction effects is comparable to the aforementioned variations of the MAE values for different orientation of in-plane reference magnetization axis. Furthermore we believe the explicit use of these corrections could lead to more misleading results, where the Coulomb and exchange interaction parameters are not known experimentally, hence they require non-trivial scheme to be determined.

8.3 Conclusions

In summary, we performed an *ab initio* study of transition metal atom (W, Os, Ir, Pt, Ru, Rh and Co) adsorption in single F-vacant (S-vacant) FG (MoS_2). It was shown that transition metal atoms form stable structures when adsorbed in vacant sites on monolayer FG and MoS_2 . We found giant magnetocrystalline anisotropy energy values for these low-dimensional crystal structures. The reduced symmetry, due to the asymmetric charge distribution at adatom adsorption sites, spin-polarized ground state of the compound and orbital character of the electronic band states around the Fermi level result in the observed magnetocrystalline anisotropy. The obtained results should provide a useful base for further study of magnetocrystalline anisotropy and motivation for potential design of monolayer optoelectronic devices with novel functionalities.

Part IV Summary

Chapter 9

Summary

In this thesis we characterized, using first-principles calculations, chemically derived materials from graphene including fluorographene, bilayer fluorographene and chemically decorated graphene with Ti atoms and their oxides. Furthermore we expanded the study to include adsorption, absorption and defect formation characteristics of the rather novel material silicene. Finally, the set of studied graphene-like materials was expanded further with molybdenum disulfide in order to comprehensively investigate magnetic property engineering of these two-dimensional materials. All the reported results were based on the density functional theory formalism as the method of choice for the first-principles study.

The results part began with the investigation of bilayer fluorographene in Chapter 4. The first studied structure was chosen as an extension to the previous works on bilayer graphane.[136, 145] It was demonstrated that fluorination of bilayer graphene results in more stable structures than hydrogenation with a strength comparable with the elastic strength of graphene. Furthermore the calculated band gap of bilayer fluorographene shows a 30% increase over the one of bilayer graphane, and we also observed quantitatively significant differences between monolayer and bilayer fluorographene.

The following Chapter 5 continued in the direction of chemical functionalization of graphene with titanium and its oxide. Strong n-type doping of Ti covered graphene was demonstrated with supporting evidence from calculation of the work functions. Titanium was found to be strongly chemisorbed on graphene with the monolayer coverage limit with stoichiometry Ti_3C_8 . The studied TiO_2 monolayer crystals aligned on top of graphene were found to induce charge doping that depends on the nature of the atoms that are closest to graphene with oxygen acting as an acceptor and titanium as a donor.

In Chapters 6 and 7 the results about patterned silicene were discussed.

First a study was performed with atom adsorption and absorption with B, N, Al and P atoms on silicene. The obtained final systems were found to be metallic. The foreign atom created strong bonding with silicene and led to a geometry very different compared to the similar graphene based systems. Analysis of the vibrational modes showed phonon spectrum alterations and several adatom/substituent-induced characteristic branches, which can be used as guide for experimental Raman measurements. The stability of the studied structures was tested at high temperatures with use of DFT based molecular dynamics simulations. Second, the formation of SW defects in silicene was described and the induced effects on its electronic and chemical properties were studied. It was found that the formation of a stable SW defect is much easier in the buckled lattice structure of silicene compared to graphene, even on a Ag(111) supporting surface. The presence of a SW defect results in a tunable band gap opening in the electronic band structure and it decreases the number of favourable doping sites. The findings were found to be in agreement with a recent study that reported chlorine adsorption on SW-defected graphene and carbon nanotubes. [207] The aforementioned chapters revealed the very reactive and functionalizable silicene surface as an important playground for silicene based nanoscale materials.

The results presented in this thesis are finalized with Chapter 8, presenting the study of transition metal atom (Os, Ir, Pt and Co) adsorption in single F-vacant (S-vacant) FG (MoS₂). It was shown that transition metal atoms form stable structures when adsorbed in vacant sites on monolayer FG and MoS₂ and induce a giant magnetic anisotropy with observable connections with orbital character of the electronic band states around the Fermi level. The chemical decoration proved to be a robust method for directed functionalization of these low dimensional materials.

9.1 Outlook

In the following paragraphs an extended set of perspective problems is outlined, which covers first-principles characterization of graphene-like materials.

An interesting problem regarding the results discussed in Chapter 5, is the study of the oxidation process of Ti atoms bonded to the graphene surface. The analysis of the intermediate structures and electronic properties is an intriguing problem of which the results could be compared with experimental observations. This study probably requires the examination of large scale systems with an increased structural complexity, so that other computational tools, like classical molecular dynamics, might be useful.

9.1. OUTLOOK

There also remain some exciting questions on the adsorption and absorption properties of silicene. The results presented in Chapter 6 and 7 provide enough motivation to study large-scale patterning of silicene sheets with substituted or adsorbed foreign atoms. An important aspect of this study will be the examination of the mutual interactions among the adsorbates with respect to the structural changes of the silicene surface. In this way, it will be possible to explore the experimental viability of functionalized silicene. It was also shown that the presence of the SW defects in the silicene lattice considerably affects its absorption properties. Therefore, the study of other defects, such as Si vacancies, could be a valuable extension of the presented research. Knowing the influence of the lattice defects on the surface properties of silicene could be helpful to improve its experimental analysis.

Another possible topic is related to Chapter 8 on giant magnetic anisotropies. It will be intriguing to include more graphene-like materials (such as those presented in this thesis, as well as other experimentally accessible ones) into the study of inducing a giant magnetic anisotropy. This topic is especially important in the light of any future practical use of ultrathin materials with large magnetic anisotropy. The study of different substitution sites, large scale patterning with induced group behaviour of the substituents, and the inclusion of different chemical elements, are some of the main possible topics to be included in such a work.

In addition to the simple scaling of the system size, two more fundamental points will be of high value for fundamental research. First, the application of the DFT+U method to improve the DFT models for systems with localized, strongly correlated d and f electrons. However, such corrections require non-trivial insight or even experimental input. The second point is the involvement of lighter chemical elements, including Fe and Co, which are frequently used in experimental set-ups and industrial applications. By using chemical elements, which on their own have only weak to moderate spin-orbit coupling, the effects of the substrate, crystal structure and group effects in complex functionalized materials will play a more important role. And there is a potential to produce novel compounds with large magnetic anisotropy from experimentally more accessible materials.

Chapter 10 Samenvatting

In deze thesis karakteriseerden we van grafeen afgeleide materialen zoals fluorografeen, bilaag fluorografeen en grafeen chemisch gedecoreerd met Ti atomen en hun oxides, gebruik makende van ab initio berekeningen. Daarnaast breidden we de studie uit om adsorptie, absorptie en de vorming van defecten te bestuderen van het nieuwe materiaal siliceen. Tenslotte werd de set van grafeenachtige materialen uitgebreid met molybdeen disulfide om een volledige studie te maken van de controle van de magnetische eigenschappen van deze twee-dimensionale materialen. Al de bekomen resultaten zijn gebaseerd op het dichtheidsfunctionaal formalisme.

Het deel met resultaten begon met de studie van bilaag fluorografeen in hoofdstuk 4. Deze structuur werd gekozen als een uitbreiding van gelijkaardig, eerder werk voor een bilaag grafaan.[136, 145] We toonden aan dat fluorinatie van bilaag grafeen resulteert in een stabielere structuur dan hydrogenatie met een sterkte vergelijkbaar met de elastische sterkte van grafeen. Daarnaast toont de berekende bandkloof van bilaag fluorografeen een stijging van 30% in vergelijking met die van bilaag grafaan en we merkten ook significante, kwantitatieve verschillen op tussen monolaag en bilaag fluorografeen.

Het volgende hoofdstuk 5 handelde over het chemisch functionaliseren van grafeen met titanium en zijn oxide. We vonden een sterke n-type dotering van met Ti bedekt grafeen. Dit resultaat werd ondersteund door de berekening van de werkfuncties. We toonden ook aan dat titanium sterk chemisch adsorbeert op grafeen met als stoichiometrie voor de monoloog bedekkingslimiet Ti_3C_8 . De bestudeerde TiO_2 monolaag kristallen, gealigneerd bovenop grafeen bleken een ladingsdotering te induceren die afhangt van het type van atomen dat zich het dichtst bij grafeen bevindt, met zuurstof dat zich als een acceptor gedraagt en titanium als een donor.

In hoofdstukken 6 en 7 werden de resultaten over chemisch gedecoreerd siliceen besproken. Eerst werd een studie gemaakt van de adsorptie en absorptie van B, N, Al en P atomen op siliceen. De bekomen systemen bleken metallisch te zijn. De aanwezigheid van een extrinsiek atoom creëerde een sterke binding met siliceen en leidde tot een geometrie die sterk verschilt met die van gelijkaardige, op grafeen gebaseerde systemen. Verdere analyse van de vibrationele modes toonde wijzigingen in het fononspectrum en verschillende adatoom/substituent-geïnduceerde karakteristieke takken, die via Raman metingen zouden kunnen gedetecteerd worden. De stabiliteit van de bestudeerde structuren werd getest bij hoge temperaturen d.m.v. op DFT gebaseerde moleculaire dynamica simulaties. Ten tweede werd de vorming van SW defecten in siliceen beschreven en de geïnduceerde effecten op de elektronische en chemische eigenschappen werden bestudeerd. We vonden dat de vorming van een stabiel SW defect veel makkelijker is in de geknikte roosterstructuur van siliceen dan in grafeen, zelfs op een Ag(111) ondersteunend oppervlak. De aanwezigheid van een SW defect resulteert in de opening van een bandkloof in de elektronische bandenstructuur alsook in de afname van voordelige adsorptiesites. Deze bevindingen zijn in overeenstemming met de recente studie over adsorptie van chloor op grafeen en koolstof nanobuisjes met SW defecten. [207] Deze hoofdstukken toonden dat siliceen een erg reactief en functionaliseerbaar oppervlak heeft en dat het een belangerijk test model is voor op siliceen gebaseerde nanoschaal materialen.

De resultaten voorgesteld in deze thesis worden afgerond in hoofdstuk 8, met de studie van adsobtie van transitiemetaalatomen in F-vacant (S-vacant) fluorografeen (MoS_2). We toonden aan dat transitiemetaal atomen, geadsorbeerd in vacatures op monolaag FG en MoS_2 een stabiele structuur vormen en een grote magnetische anisotropie induceren met merkbare connecties met het orbitaal karakter van de elektronische bandtoestanden rond het Fermi niveau. De chemische decoratie bleek een robuuste methode voor gerichte functionalisatie van deze laag-dimensionele materialen.

Appendix A

Bloch states

Following the Bloch states, and their use as the basis sets, are discussed in more detail.

The lattice points of the crystal (the set \vec{R}) can be written as:

$$\vec{R} = \sum_{i=1}^{3} n_i \vec{a}_i; \quad \forall n_i, n_i \in \mathbb{Z}$$

with \vec{a}_i the lattice vectors (see Fig. 1.2.3). The potential in the time independent Schrödinger equation:

$$E\Psi = \left[\frac{-\hbar^2}{2m_e}\Delta + V(\vec{r})\right]\Psi \tag{A.0.1}$$

is then a lattice periodic function: $V(\vec{r} + \vec{R}) = V(\vec{r})$. This fact allows one to write the potential as a Fourier series (ordinary Fourier series just written in the different form):

$$V(\vec{r}) = \sum_{\forall \vec{K}} \underbrace{\left[\frac{1}{V_{PrimitiveCell}} \int_{PrimitiveCell} V(\vec{r}')e^{-i\vec{K}\vec{r}'}d\vec{r}'\right]}_{V_{\vec{K}}} e^{i\vec{K}\vec{r}} \qquad (A.0.2)$$

with \vec{K} the set of reciprocal lattice points:

$$\vec{K} = \sum_{i=1}^{3} m_i \vec{b}_i; \quad \forall m_i, m_i \in \mathbb{Z}$$

and reciprocal lattice vectors:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

The reciprocal lattice is designed to simplify Fourier expansion by the following identity:

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$$

Furthermore the wave function can be expressed as Fourier series:

$$\psi(\vec{r}) = \sum_{\forall \vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$
(A.0.3)

with

$$\vec{k} = \sum_{i=1}^{3} \frac{n_i}{N_i} \vec{b}_i; \quad \forall n_i, n_i \in \mathbb{Z}$$

where N_i is the number of crystal unit cells of the bulk crystal in the direction of \vec{a}_i lattice vector (in reality N_i is very large number and we can look on the set of \vec{k} as continuum).

This form of the \vec{k} vector fulfils periodic boundary conditions for the wave function solution of the bulk crystal (wave function are stitched together, thus they can differ only by factor equal to 1 at the boundary):

$$\forall i \in \{1, 2, 3\}; \quad \psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r})$$

If one inserts series A.0.2 into the one particle Equation A.0.1 together with A.0.3, and compare the expressions standing next to the *same* basis functions, the set of linear algebraic equations binding the Fourier coefficients will be obtained:

$$\left(E - \frac{\hbar^2}{2m_e}k^2\right)C_{\vec{k}} = \sum_{\forall \vec{K}} V_{\vec{K}}C_{\vec{k}-\vec{K}}$$

Due to this coefficient binding the solution wave function contains whole classes of \vec{k} components which differ by the vector \vec{K} . The original A.0.3 can be written as (the following form is called a Bloch state):

$$\psi(\vec{r}) = \sum_{\vec{k} \in 1^{st} BZ} \sum_{\forall \vec{K}} C_{\vec{k}-\vec{K}} e^{i(\vec{k}-\vec{K})\cdot\vec{r}} = \sum_{\vec{k} \in 1^{st} BZ} \underbrace{\left| \sum_{\forall \vec{K}} C_{\vec{k}-\vec{K}} e^{-i\vec{K}\cdot\vec{r}} \right|}_{u_{\vec{k}}(\vec{r})} e^{i\vec{k}\cdot\vec{r}}$$

where BZ stands for Brillouin Zone. The $u_{\vec{k}}(\vec{r})$ is the lattice periodic function (due to \vec{K} in basis set).

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List of publications

- Sivek, Leenaerts, Partoens, and Peeters. First-principles investigation of bilayer fluorographene. J. Phys. Chem. C, 116(36):19240–19245, 2012.[122]
- Sivek, Leenaerts, Partoens, and Peeters. Adsorption of titanium and titanium dioxide on graphene: n and p-type doping. URL http://arxiv.org/abs/1301.3654.[169]
- Sivek, Sahin, Partoens, and Peeters. Adsorption and absorption of boron, nitrogen, aluminum, and phosphorus on silicene: Stability and electronic and phonon properties. *Phys. Rev. B*, 87(8):085444, 2013.[177]
- Sahin, Sivek, Li, Partoens, and Peeters. Stone-Wales defects in silicene: Formation, stability, and reactivity of defect sites. *Phys. Rev. B*, 88 (4):045434, 2013.[208]
- Sivek, Sahin, Partoens, and Peeters. Giant Magnetic Anisotropy in Doped Single Layer Molybdenum Disulfide and Fluorographene. In review process.

Software

Computational results, graphics and the thesis itself made use of the following computer software which was not necessary mentioned before:

blacksci Post-processing, computational and aiding tools (https://code. launchpad.net/blacksci) (disclaimer: author of this thesis is also author of the blacksci software)

GIMP Raster graphics editor (http://www.gimp.org/)

Gnuplot Graphing utility (http://www.gnuplot.info/)

Inkscape Vector graphics editor (https://inkscape.org/)

Jmol Visualization tool (http://jmol.sourceforge.net/)

Latex Document preparation system (http://latex-project.org/)

VASP DFT formalism based software (http://www.vasp.at/)

And other including Debian (https://www.debian.org/), GNU tools and utilities (https://gnu.org/) and more libre software.

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