2D Materials and Van der Waals Heterostructures

Zhen Jiao

Composition of graduation committee:

<i>Chairman and secretary:</i>	Prof. dr. J.L. Herek
<i>Supervisor:</i>	Prof. dr. ir. H.J.W. Zandvliet
<i>Co-supervisor:</i>	Dr. A. van Houselt
<i>Members:</i>	Prof. dr. ir. F.A. Zwanenburg Prof. dr. ir. J.E. ten Elshof Prof. dr. A. Colak Prof. dr. ir. N. Oncel

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2D MATERIALS AND VAN DER WAALS HETEROSTRUCTURES

DISSERTATION

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on account of decision of the Doctorate Board
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by

Zhen Jiao
born on 16th of September, 1991
in Henan, China

This dissertation has been approved by the supervisor:
Prof. dr. ir. H.J.W. Zandvliet

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Introduction

1.1 Introduction

Two-dimensional (2D) materials are materials that have a thickness of only a single layer. The blooming research field of 2D materials started in 2004 by the successful isolation of graphene by Geim and Novoselov.^{1,2} Graphene is a single layer of carbon atoms that arranged in a honeycomb structure.³ Geim and Novoselov used a sticky tape to exfoliate graphene multilayers from a highly oriented pyrolytic graphite substrate. They repeated this exfoliation process until they obtained a single graphene layer. This was quite a surprise as theory predicts that a single 2D layer should be thermodynamically unstable. Later on it turned out that the key to the stability of graphene lies in the fact that the long-range fluctuations are suppressed due to an anharmonic coupling between the stretching and bending modes in the graphene. Simple tight binding calculations have revealed that graphene is a semimetal, i.e. the maximum of the valence band and minimum of the conduction band touch at the Fermi level.⁴ In addition, the energy bands in the vicinity of the Fermi level have a linear energy-momentum dispersion relation, which implies that the electrons in graphene behave as massless relativistic particles that obey the Dirac equation, i.e. the relativistic variant of the Schrödinger equation.⁵ Graphene is a particularly interesting material that exhibits a myriad of interesting physical properties, which has led to a true revolution in contemporary condensed matter physics. Graphene exhibits a high electrical conductivity, good thermal conductivity, high mechanical strength and has an excellent flexibility.^{6,7} However, the material also has a severe drawback: graphene is gapless, which implies that graphene cannot be used for field-effect based applications.

1.1.1 The group IV graphene-like materials

THE electronic structure of the elements silicon, germanium and tin are very similar to carbon. These group IV elements of the periodic table all have two electrons in their outermost s and p shells and therefore it is very likely that they can also form a graphene-like honeycomb structure.⁸ Unfortunately, the silicon, germanium and tin analogues of graphene, which are referred to as silicene, germanene and stanene, do not occur in Nature and therefore these materials have to be synthesized. In 2012 silicene has been successfully synthesized,⁹ followed by germanene in 2014 and stanene in 2015.^{10,11} Silicene, germanene and stanene are sometimes also referred to

Figure 1.1: Ball-and-stick model of graphene (a)-(b) and silicene/germanene (c)-(d). (a) and (c) are top views. (b) and (d) are side views. The honeycomb lattice of graphene is fully planar, whereas the honeycomb lattices of silicene and germanene are buckled. The red and blue balls in panels (c) and (d) represent the two interpenetrating triangular sub-lattices of the honeycomb lattice.

as the group IV 2D Xenes. Despite the fact the group IV 2D Xenes share many properties with their carbon counterpart graphene, there are also a few differences. The honeycomb lattice of graphene is fully planar, whereas the honeycomb lattice of the 2D Xenes is buckled. The two interpenetrating triangular sub-lattices are displaced with respect to each other in a direction normal to the 2D material. This displacement, which is often referred to as buckling, is about 0.045 nm for silicene, 0.065 nm for germanene and 0.085 nm for stanene (see Figure 1.1).⁸ The broken symmetry of the buckled honeycomb lattice allows to open a bandgap by the application of a transversal electric field. The application of a transversal electric field leads a charge shift from one triangular sub-lattice to the other triangular sub-lattice. There is another salient difference between graphene and the other group IV 2D Xenes: graphene has a very tiny spin-orbit of only a few μeV , but silicene,

germanene and stanene have sizeable spin-orbit gaps of 1.5 meV, 24 meV and 100 meV, respectively.^{8,12} Owing to this spin-orbit gap, the 2D Xenes are strictly speaking not semimetals, but two-dimensional topological insulators. Silicene, germanene and stanene are therefore the ideal candidates to exhibit the quantum spin Hall effect.

1.1.2 Germanene

IN this thesis we will focus our attention on germanene as the group has already obtained some experience with the growth and characterization of this material. Unfortunately, natural germanene does not exist and therefore the material has to be synthesized or grown on a substrate. In the past decade various metallic and nonmetallic substrates have been selected as template for the growth of germanene. The choice of a substrate is motivated by structural as well as electronic band structure related considerations. Preferably the substrate has the same crystal structure and only a small lattice mismatch with germanene. In order to electronically decouple the key electronic states of germanene from the underlying substrate, an insulating or semiconducting substrate is very desirable. Substrates with a bandgap are appealing because near the Fermi level there are simply no states to hybridize with. However, also some metals, such as Pt(111), Cu(111) and Au(111), have also been used as templates for the growth of germanene.^{13–24}

The first report on the successful synthesis of germanene was by Li et al.¹⁸ They deposited germanium on a Pt(111) substrate. Using low energy electron diffraction (LEED) and scanning tunneling microscopy they observed a $(\sqrt{19} \times \sqrt{19})$ periodicity with respect to the Pt(111) substrate. They ascribed this continuous and well-ordered $(\sqrt{19} \times \sqrt{19})$ superstructure to a single germanene layer on the Pt(111) substrate. Unfortunately, they did not manage to achieve atomic resolution. The $(\sqrt{19} \times \sqrt{19})$ superstructure has a corrugation of about 0.6 Å and only the upward buckled atoms were visible in their scanning tunneling microscopy images. The density functional theory calculations showed that $(\sqrt{19} \times \sqrt{19})$ superstructure coincides with a (3×3) germanene layer. The claims by Li et al. have been refuted by Švec et al.²⁵ Švec et al. pointed out that the $(\sqrt{19} \times \sqrt{19})$ reconstruction on Pt(111) is not due to a germanene layer, but rather a surface alloy composed of Ge₃Pt tetramers that resembles a twisted kagome lattice. This conclusion was based on a detailed study of the closely related Si/Pt(111) system.

Shortly after the appearance of the paper of Li et al. a second paper was

published by Davila et al.¹⁰ The substrate used for germanium deposition was changed to an Au(111) substrate. Using low energy electron diffraction they found (5×5) , (7×7) ($\sqrt{19} \times \sqrt{19}$) superstructures. They ascribed the (7×7) structure to the formation of a germanene layer. Two years later, however, the same authors arrived in a more detailed study at the conclusion that the germanium layer actually does not exhibit a (7×7) , but rather a (8×8) structure with respect to the unreconstructed Au(111) substrate.²⁶ They pointed out that the (8×8) unit cell coincides with a $(3\sqrt{3} \times 3\sqrt{3})$ germanene cell. Angle resolved photoemission measurements revealed the presence of Dirac cones located about 0.8 eV below the Fermi level at the K points of the $(3\sqrt{3} \times 3\sqrt{3})$ unit cell. A few years later Wang and Uhrberg studied the structural properties of the germanium on Au(111) system using low energy electron diffraction, scanning tunneling microscopy and photoemission electron microscopy.²⁷ They found that a $\begin{pmatrix} 5 & 0 \\ 8 & -14 \end{pmatrix}$ unit cell provides a much better fit with the experimental results than the (8×8) superstructure reported by Davila and Le Lay.²⁶ The core levels spectra indicated that Ge atoms do not stay at the interface, but rather diffuse into the Au substrate.

Just a few days after the appearance of the paper by Davila et al.¹⁰ our group also reported the successful synthesis of germanene. The method we (Bampoulis et al.²⁸) used was totally different from the others. Rather than depositing germanium on platinum, we deposited platinum on a germanium substrate. Subsequently, we annealed the germanium substrate to a temperature well above the eutectic temperature of the Ge/Pt alloy. At these high temperatures micrometer sized eutectic droplets form on the germanium substrate. The Ge/Pt system has an eutectic temperature of 1043K at a composition of 22% platinum and 78% germanium. As soon as the temperature drops below the eutectic temperature, the eutectic droplets undergo spinodal decomposition into a Ge_2Pt phase and a pure Ge phase. Owing to the lower surface free energy of Ge as compared to Ge_2Pt the germanium atoms segregate to the droplet/vacuum interface. The Ge atoms form a buckled honeycomb lattice with a lattice constant of about 4.2 Å. Bampoulis et al.²⁸ was the first to show an atomically resolved image of germanene and demonstrated that the honeycomb lattice is buckled as predicted by density functional theory calculations. In a follow-up paper Zhang et al.²⁹ measured the density of states of the germanene. They found a V-shaped density of states, which is one of the hallmarks of two-dimensional Dirac system. Al-

though the system Pt/Ge is very promising, it also suffers from a severe drawback: the eutectic droplets have a sizes in the micrometer range, i.e. way too small for any technological application.

In 2016 Zhang et al.²⁹ managed to grow germanene on molybdenum disulfide (MoS₂). MoS₂ is transition metal dichalcogenide with a bulk bandgap of about 1.3 eV. The transition metal dichalcogenides belong to the class of 2D van der Waals materials that are characterized by a strong covalent interaction between neighboring atoms within a layer and a weak van der Waals interaction between the layers. They found that the formation of hexagonal islands within a lattice constant of about 3.8 Å, which is substantially larger than the lattice constant of MoS₂ (3.15 Å).²⁹ The monatomic germanene islands are about 3.2 Å high, which is indicative of a weak interaction between the germanene layer and the MoS₂ substrate. Scanning tunneling spectroscopy measurements revealed a well-defined V-shaped density of states for the germanene islands, whereas the density of states for the MoS₂ substrate has a typical U-shape, which is characteristic for a semiconductor.

Figure 1.2: Ball-and-stick model of molybdenum disulfide (MoS₂)

1.2 Transition metal (di)chalcogenides (TM(D)Cs)

IN this thesis we will study two transition metal chalcogenides: MoS₂ a transition metal dichalcogenide and GeSe a transition metal monochalcogenide.^{30–33} Both materials belong to the class of 2D Van der Waals materials.

MoS₂ consists of trilayers, i.e. one layer of Mo atoms sandwiched between two S layers. In nature MoS₂ occurs in two phases the so-called 2H and 3R phases. The 2H phase, which we consider here, has a hexagonal symmetry with a lattice constant of 3.16 Å, whereas the 3R phase exhibits a rhombohedral symmetry.³⁴ There is a third, metastable, phase which is referred to as the 1T-MoS₂ phase. This phase is metallic and has a tetragonal symmetry. The 2H phase has an indirect bulk bandgap of about 1.3 eV. A single MoS₂ layer has a direct bandgap of about 1.8 eV.^{34,35}

Figure 1.3: Ball-and-stick model of germanium selenide (GeSe)

GeSe has a structure that is very similar to black phosphorus.³¹ The rectangular centered unit cell contains a Ge atom and a Se atom and has dimensions of 3.8 Å by 4.4 Å. Like black phosphorus, which is sometimes also referred to as phosphorene, also GeSe is a semiconductor. In contrast to phosphorene GeSe is less susceptible to the adsorption of oxygen and water than phosphorene.³⁶

In this thesis project we aim to use both substrates for the growth or deposition of germanene and graphene. To the best of our knowledge the GeSe surface has never been imaged with atomic resolution and therefore we decided to study the structural and electronic properties using scanning tunneling microscopy and spectroscopy.

1.3 Heterostructures of 2D materials

2D Van der Waals materials cover an amazing range of electrical, chemical, optical and mechanical properties, perhaps the most astounding discovery is that new materials can be created by simply stacking single layers of different 2D materials on top of each other.³⁷ In this way an infinitely number of new materials can be created. The reason that this stacking of these materials is so easy has to do with the fact that the materials possess a very strong covalent intralayer interaction and a very weak interlayer interaction.³⁸ The weak interlayer allows to easy exfoliate a single layer flake from a bulk substrate and subsequently place this single layer flake on another Van der Waals material. The stacking of Van der Waals materials is often done with an all-dry viscoelastic stamping set-up that is equipped with an optical microscope, XYZ translation manipulator and sample holder mounted on a rotation stage. (see Figure 1.4).

Figure 1.4: Stamping device at the PIN group. (a) Photograph of the 2D transfer system. (b) Schematic diagram of the 2D transfer system. Copyright, PIN group.

In Figure 1.5 (a) an optical image of twisted bilayer graphene (twist angle of about 1.1°) on a hexagonal boron nitride sample is shown. Owing to the twist angle between the two graphene layers a moiré structure develops (see Figure 1.5 (b) for a high-resolution scanning tunneling microscopy image).

A moiré structure is a beating pattern produced by overlaying similar, but slightly shifted or rotated periodic structures. A particularly promising way to create moiré materials is by stacking two crystalline two-dimensional (2D) materials that are slightly twisted with respect to each other.^{39–41} In this way, one can create new materials with unit cell sizes that can be tuned from

Figure 1.5: (a) Photograph of a twisted bilayer graphene on an h -BN substrate. (b) Scanning Tunneling Microscopy image ($15 \text{ nm} \times 15 \text{ nm}^2$) of twisted bilayer graphene ($\theta=2.3^\circ$) taken at 77 K. Copyright, PIN group.

a few Ångström to tens of nanometres by changing the twist angle.^{42,43} The twist angle between the two layers is a new degree of freedom that does not only modify structural properties, but also and more importantly many other physical properties.^{41,44–49} As moiré patterns can only be realized with 2D materials, the discovery of graphene, the first truly 2D material, paved the way to a new and, by now booming, research field.

In this thesis we will study twisted stacks of 2D van der Waals materials consisting of elemental 2D-Xenes (graphene and germanene) on transition metal (di)chalcogenides. This broad range of 2D materials provides additional degrees of freedom to be exploited, such as the spin-orbit coupling, buckling of the lattice, and electronic band structure. The availability of these twisted 2D materials does not only provide ideal model systems to systematically study and tune the formation of electronic instabilities, but it also offers a wealth of input to advance modern theories of complex quantum phases of matter.

1.4 Outline of this thesis

IN this thesis, we aim to study heterostructures of 2D materials. The experimental techniques that we will use in our investigations are introduced and discussed in Chapter 2. In this Chapter we also provide information on

the experimental set-up as well as the different methods to synthesize, grow or transfer 2D materials to a substrate. In Chapter 3 we will focus our attention on the synthesis and characterization of germanene on a molybdenum disulfide substrate (MoS_2). This is an interesting system because MoS_2 has a substantial bandgap of about 1.3 eV, which allows to keep the key electronics states of the germanene layer, which are located in the vicinity of the Fermi level, intact. The germanene layer will be grown using molecular beam epitaxy. In Chapter 4 we study the electronic properties of the germanene layer. Special attention will be paid to formation of charge puddles. In Chapter 5 we elaborate on the possibility to alter the quantum state of matter of a 2D Dirac material with a buckled honeycomb lattice using an external transversal electric field. We will show that beyond a critical transversal electric field the 2D Dirac material undergoes a topological phase transition from a 2D topological insulator to a normal band insulator. In Chapter 6 we present a detailed study of the structural and electronic properties of germanium selenide (GeSe). GeSe is a transition metal chalcogenide with a bandgap that is very comparable to the bandgap of MoS_2 . The structure of both 2D materials is, however, different: GeSe has a rectangular unit cell, whereas MoS_2 has a hexagonal unit cell. Chapter 7 deals with the structural and electronic properties of graphene on a MoS_2 substrate. A graphene flake is placed on the substrate via the solvent transfer technique. In this chapter we also present a new technique to measure the Fermi velocity of graphene. This new technique relies on an analysis of the voltage dependent inverse decay length of the electrons that tunnel from tip to substrate, or vice versa. Finally, Chapter 8 provides a brief summary of the work performed in thesis project as well as a brief outlook.

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Experimental

2.1 Fundamentals of scanning tunneling microscopy

SCANNING tunneling microscope (STM) is a very powerful microscopic technique that has attracted quite some attention since its discovery. STM relies on the principle of quantum mechanical tunneling, which is different from traditional optical and electron microscopy. Since the invention of STM by Gerd Binnig and Heinrich Rohrer in 1981,¹⁻³ we cannot only obtain structural and electronic information of materials down to the atomic scale, but also move and displace individual atoms.⁴

We first briefly elaborate on the working principle of the scanning tunneling microscope. We will restrict ourselves to a simple one-dimensional system consisting of a tip, a vacuum barrier and a substrate⁵. Subsequently, we will discuss various scanning tunneling spectroscopy modes as well as atomic force microscopy. In the last two sections we will introduce our experimental set-up and some methods we have used to prepare the samples that we have used in this project.

2.1.1 The basic concept of quantum mechanical tunneling

WE consider an electron that moves in one-dimension and feels a potential $U(z)$. The wave function of the electron, $\Psi(z)$, obeys the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial z^2} + U\Psi = E\Psi \quad (2.1)$$

where $\hbar$ refers to the reduced Plancks constant, also referred to as the constant of Dirac, m to the effective mass of electron, z to the position and E to the energy. When $E > |U|$, the solutions of Schrödinger equation are given by $\Psi(z) = \Psi(0)e^{\pm ikz}$, where the wave vector k , is given by $\frac{\sqrt{2m(E-U)}}{\hbar}$. In the case that ($E < |U|$), the wave function of electron can be represented by $\Psi(z) = \Psi(0)e^{-\beta z}$, where $\beta = \frac{\sqrt{2m(U-E)}}{\hbar}$ is the inverse decay length of the electron. If we consider an incoming electron wave from the left, the total wave function in the different regions (left of the barrier, in the barrier and right of the barrier, respectively) can be written as,

$$\Psi_S(z) = Ae^{ikz} + Re^{-ikz} \quad (2.2)$$

$$\Psi_B(z) = Be^{\beta z} + Ce^{-\beta z} \quad (2.3)$$

$$\Psi_T(z) = De^{ikz} \quad (2.4)$$

The probability of find the electron in a certain interval $[z, z + dz]$ is given by $P(z)dz = \Psi^*(z)\Psi(z)dz$. For a plane wave $\Psi = Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}$ one finds $P(z)dz = |A|^2 dz$. The current density, J , is given by $J = |A|^2 \frac{\hbar k}{m}$. The barrier transmission coefficient T is given by,

$$T = \frac{J_T}{J_I} = \left| \frac{D}{A} \right|^2 \quad (2.5)$$

Using appropriate boundary conditions and equation (2.2), (2.3) and (2.4), the transmission coefficient T can be rewritten as,

$$T = \left| \frac{D}{A} \right|^2 = \frac{16k^2\beta^2}{(k^2 + \beta^2)^2} e^{-2\beta z} \quad (2.6)$$

For small sample biases the tunnel current is given by,

$$I \propto V \rho_s \rho_t e^{-\beta z} \quad (2.7)$$

where ρ_s and ρ_t are density of states of sample and tip, respectively. As can be seen in the equation (2.7), the tunneling current depends exponentially on the sample-tip distance. Accordingly, a small change in sample-tip distance leads to a huge change in the tunneling current. Owing to this sensitivity the scanning tunneling microscope (STM) can measure subtle changes in the surface topography. In case of a sufficiently sharp tip, images can be recorded with atomic resolution.⁶

As described in Figure 2.1, STM can be operate in constant current mode and in constant height mode.⁷ In the constant current mode, the tunnel current (I) and bias voltage (V) are kept constant. The feedback loop regulates the tunnel current and therefore an image at constant tip-substrate separation is obtained. In the constant height mode the tip is scanned across the surface at a fixed height, resulting in varying tunnel current. This tunneling current is a measure of the surface topography.

Figure 2.1: The simple diagram of the two major STM operation modes: a) the constant current mode and b) the constant height mode.

2.1.2 Scanning tunneling spectroscopy

IN addition to measure the surface topography of the sample, STM can also be used to provide information on the local electronic state features of the sample surface. The technique to determine this information is referred to as scanning tunneling spectroscopy (STS). The most common spectroscopy modes are current-voltage ($I(V)$), current-distance ($I(Z)$) and current-time ($I(t)$) spectroscopy.⁸ Often $I(V)$ spectra are used to determine the differential conductivity, i.e. dI/dV , which is proportional to the density of states.

Well before the discovery of STM Bardeen already used first-order time-dependent perturbation theory to study tunneling processes.⁹ In the case of STM the electronic structure of the substrate as well as the tip should be taken into account. Since the electronic structure of the STM tip is not known, Tersoff and Hamann proposed a model, based on Bardeen's tunneling theory,¹⁰ which assumes a spherically symmetric wave function for the STM tip. In case that the density of states of the STM tip and the tunneling matrix element are approximately constant, the tunneling current is given by,

$$I = \int_0^{eV} \rho_s(E) \rho_t(E - eV) T(z, V, E) dE \quad (2.8)$$

If the feedback loop is disabled and the bias voltage is ramped, the tunnel current will be measured as a function of the sample bias, $I(V)$ is measured at a constant tip-sample distance. By differentiating equation (2.8) one can extract the differential conductivity, dI/dV , which is proportional to the density of states,

$$\frac{dI}{dV} = \frac{d}{dV} \int_0^{eV} \rho_s(E) \rho_t(E - eV) T(z, V, E) dE \quad (2.9)$$

$$\frac{dI}{dV} \propto e \rho_s(E) \rho_t(0) e^{-2z \sqrt{\frac{2m(U-E)}{\hbar}}} \quad (2.10)$$

Figure 2.2: A typical STS current-voltage curve. The sample bias is modulate with a small high frequency sinusoidal voltage, which also leads to a modulation of the tunnel current.

There is also another way to directly measure the differential conductivity. A small and high frequency sinusoidal modulation voltage is added to the sample bias. This high frequency modulation of the sample bias results in a tunnel current that is modulated with the same frequency. By feeding this signal into a lock-in amplifier and demodulate it, one directly obtain the differential conductivity¹¹. In Figure 2.2 the effect of the modulation of the sample bias on the tunnel current is shown. Owing to a change of the sample bias the tunnel current will change as well,

$$I(V + \Delta V) \propto \int_0^{e(V+\Delta V)} \rho_s(E) dE \quad (2.11)$$

Equation (2.11) can be written as a Taylor expansion,

$$\begin{aligned} I(V + \Delta V) &= I(V) + \frac{dI}{dV}|_V V_m \sin(\omega t) + \frac{1}{2} \frac{d^2 I}{dV^2}|_V V_m^2 \sin^2(\omega t) + \dots \\ &\propto \int_0^{eV} \rho_s(E) dE + eV_m \rho_s(eV) \sin(\omega t) + \frac{e^2 V_m^2}{2} \rho_s(eV) \sin^2(\omega t) + \dots \end{aligned} \quad (2.12)$$

The second right hand term is obtained with a lock-in amplifier.

Besides $I - V$ spectroscopy there is also the $I - Z$ spectroscopy technique. The $I - Z$ spectroscopy (current-distance spectroscopy) can be used to determine the tunnel barrier height. In this spectroscopic mode the sample bias is fixed and the z -piezo voltage is modulated with a small high frequency sinusoidal voltage. This results in a tunnel current that is modulated with the same frequency. Using equation (2.7) we can extract the following expression,

$$\frac{d \ln I}{dz} \propto \sqrt{\phi} \quad (2.13)$$

where $\phi = (\phi_{\text{sample}} + \phi_{\text{tip}})/2$ is averaged work function of tip and sample. By plotting $d \ln(I)/dz$ versus z the averaged work function can be determined.

The third spectroscopic mode we want briefly elaborate on is $I(t)$ (current-time spectroscopy). In this mode the tip is fixed at a pre-defined location, the feedback loop is disabled and the tunnel current is measured as a function of time. As the bandwidth of STM IV converters is typically in range of a few hundreds of kHz, the temporal resolution of this technique is in the μs range. This technique is extremely powerful for the study of dynamics of individual atoms or molecules on surfaces.

2.2 Atomic force microscopy

ALTHOUGH STM has the potential to produce high-resolution atomically resolved images, the technique is limited to conducting samples, i.e. metals and semiconductors. The Atomic Force Microscope (AFM), a descendant of the Scanning Tunneling Microscope (STM), can, however, also image materials that are not conducting. The key element of this instrument is a tiny sharp tip, which is located at the end of a cantilever. When the tip is moved towards the sample, using a piezo actuator, it will at some point start to experience a force that results in bending of the cantilever. This force can have many different origins and is in most cases attractive for large separations, but repulsive for small separations. By setting the bending of the cantilever at a fixed value, using a feedback system, the force between tip and sample surface can be kept constant. In order to measure the bending of the cantilever accurately, atomic force microscopes make use of a laser beam that is reflected at the end of the cantilever and subsequently detected by a four-quadrant photodetector. A topographic image of the surface of a sample is obtained by scanning the tip across the surface and recording either the z -piezo displacement (constant force mode) or the deflection of the cantilever (constant distance mode). Since the tip is in contact with the surface, the stiffness of the cantilever needs to be smaller than the effective spring constant that holds the atoms together, which is typically of the order of about $1 - 10$ N/m. The constant distance mode can only be applied in cases that the surface is very flat.

Like STM, AFM is able to provide images with a resolution down to the atomic scale.¹² In contact mode the friction can be measured by the torsion of the cantilever. Besides the conventional contact mode, most AFMs can also be operated in the non-contact mode, also referred to as tapping mode. In this mode the tip is not in contact with the surface resulting in less wear and thus to longer tip lifetimes. In the non-contact mode, the tip is oscillated at its resonance frequency, which is typically of the order of $50 - 300$ kHz, at a small, but fixed, amplitude. When the tip is brought in the vicinity of the sample surface, the tip oscillation is damped and the resonance frequency is shifted, owing to the interactions with the substrate. Both the amplitude (amplitude modulation) as well as the frequency (frequency modulation) can be used as feedback parameters. The most popular mode is the amplitude modulation as it has higher stability and reacts more rapidly to distortions.

Besides the topography also the phase of feedback signal can be recorded. This phase signal is very valuable as the phase contrast is a strong indication for chemical inhomogeneities.

2.3 Experimental set-up

Figure 2.3: The photograph of the Omicron STM-1 system.

2.3.1 Ultra-high vacuum system

THE STM results are mainly obtained by a commercially available Omicron STM-1, which is kept at room temperature and under high vacuum ($10^{-10} - 10^{-11}$ mbar) conditions during operation. As shown in Figure 2.3, the setup of STM-1 consists of three sub-chambers, a load-lock, a prepara-

tion chamber and an STM chamber. The function of load-lock is to quickly transfer samples to the STM without breaking the vacuum. In the preparation chamber the samples can be cleaned using Argon ion bombardment and annealing. In addition, in the preparation chamber we can also deposit various materials, like Pt, Ge and Sb.

Figure 2.4: The schematic diagram of tip repair by dipping the STM tip in a metal substrate.

2.3.2 Tip repair

THE STM tips we use are made from tungsten (W) or platinum iridium (Pt/Ir). The W tips we use are prepared by electrochemical etching, whereas the Pt/Ir tips are prepared by simply cutting a Pt/Ir wire under an angle. Tungsten oxidize at ambient conditions, but this oxide can be removed by a high temperature anneal or prolonged scanning and dipping the STM tip in a noble metal substrate. During the STM scanning process, the STM tip is sometimes of insufficient quality for atomic resolution. There are, however, ways to improve the quality of the tip. These tip repair methods can be ex-situ as well as in-situ.¹³ In ultra-high vacuum the tip can be improved by argon ion bombardment in combination with high temperature annealing or

by electric field induced field evaporation. The latter is realized by increasing the separation between tip and substrate to a distance of at least a few hundreds of nanometers. Subsequently a high voltage is applied across the junction and the field emission current is recorded. During scanning on a metal substrate, for instance Au or Pt, the STM tip can also be improved by simply dipping the tip gently into a noble metal substrate.

Figure 2.5: A large size (30 x 30 nm) STM image of pristine Au(111). The sample bias is 0.3 V and tunnel current is 1 nA.

The quality of the tip can be checked by recording a conventional topographic image. In Figure 2.5, STM image of Au(111) is shown after a successful tip repair process. The image shows the characteristic Au(111) herringbone reconstruction.

However, due to the weak interaction between Pt/Ir tip and gold atoms, the adsorption repair Pt/Ir tip shown in Figure 2.4(c) is difficult to achieve. It usually takes several days to get a very good tip. Compared with a gold sample, it is more effective to improve the tip quality with platinum or iridium samples. As shown in the Figure 2.6, when the Pt/Ir tip is moved to a position close to the platinum or iridium sample, the stronger interaction with tip atoms allows the tip to be repaired in just tens of minutes.

Figure 2.6: The schematic image of tip improvement by Noble metal sample.

2.4 Sample transfer method

NORMALLY, We have transferred graphene flakes to another substrate via two methods, the so-called thermal treatment technique and the solvents transfer technique. In Figure 2.7 we show a schematic diagram of the different steps of both transfer techniques. In the case of the thermal treatment transfer method, the first step is to release the monolayer graphene with sacrificial layer from the polymer substrate. This is done by putting the polymer with graphene and sacrificial layer in water and subsequently use take of the graphene with sacrificial layer flakes from the water by approaching the flake from the below by our substrate. Subsequently the substrate/flake sample is annealed at $150\text{ }^{\circ}\text{C}$ on a hot plate to remove any residual water. Finally, the sacrificial layer is removed by annealing the sample to $450\text{ }^{\circ}\text{C}$ for 2 hours in an inert atmosphere. In the second method the last step is replaced by a solvent step to remove the sacrificial layer. We have to notice here that the anneal step put limits to the choice of substrates, as not every substrate can withstand prolonged heating at elevated temperatures.

Figure 2.7: (a) and (b) show the schematic diagrams of thermal treatment technique and solvents transfer technique, respectively.

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Germanium/MoS₂: competition between the growth of germanene and intercalation

In this chapter, We have scrutinized the growth of germanium (Ge) on molybdenum disulfide (MoS₂) using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations to resolve the question whether Ge atoms prefer to intercalate between the MoS₂ layers or rather form germanene islands on-top of the MoS₂ substrate. At a fixed growth temperature, germanene islands are formed on top of the MoS₂ at high deposition rates, whereas at low deposition rates the Ge intercalates between the MoS₂ layers. Scanning tunneling spectra (STS) recorded on the germanene islands reveal a *V*-shaped density of states, which is one of the hallmarks of a 2D Dirac material. The intercalated Ge clusters have a bandgap of 0.5-0.6 eV. Density functional theory calculations have been conducted in order to study the stability and electronic band structure of several intercalated Ge cluster configurations. Based on these calculations, two promising stable configurations with bandgap can be compared well with the experimental observations. STS measurement recorded on the intercalated Ge clusters reveal well-defined signatures of Coulomb blockade.

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3.1 Introduction

THE successful isolation of a single layer of graphene, i.e., a truly two-dimensional material, by Geim and Novoselov has led to numerous exciting discoveries.^{1–3} Graphene consists of sp^2 hybridized carbon atoms that are arranged in a two-dimensional honeycomb structure. Shortly after the discovery of graphene many scientists have attempted to synthesize other two-dimensional materials. The most appealing candidates are the group IV elements, i.e. silicon and germanium, because they have, just like carbon, also four electrons in their outermost s and p shells. In contrast to carbon the most stable configuration of silicon and germanium is, however, not the sp^2 hybridized graphite-like structure, but rather the sp^3 hybridized diamond structure. Silicene and germanene, i.e. the silicon and germanium analogous of graphene, do not occur in nature and therefore these materials have to be synthesized. Despite the fact that silicene and germanene are in many aspects very similar to graphene, there are also a few differences. The most eye-catching difference is the buckling of the honeycomb lattice.^{4–7} In the case of graphene the two interpenetrating triangular sub-lattices, that form the honeycomb lattice, lie in exactly the same plane, i.e. graphene is perfectly planar. In the case of silicene or germanene, however, the two triangular sub-lattices are displaced with respect to each other in a direction normal to the two-dimensional sheet. Despite this buckling the electrons in silicene and germanene are still predicted to behave as massless relativistic particles that have a linear dispersion relation with Fermi velocities that are only slightly lower than graphene.⁴

Silicene has been synthesized in 2012 by Vogt et al.⁸ as well as Fleurence et al.⁹ The synthesis of its germanium counterpart followed a few years later.^{10–13} Initially silicene and germanene were mainly grown or synthesized on metallic substrates, which is not optimal because the important electronic states of the two-dimensional material that are located near the Fermi level can hybridize with the electronic states of the underlying metallic substrate. In order to electronically decouple the electronic states of the two-dimensional Dirac material, a substrate with a band gap is required. The first results of the growth of silicene on a bandgap material were reported by Chiappe et al.¹⁴ These authors used MoS₂, a transition metal dichalcogenide with a bulk band gap of 1.3 eV, as a substrate.^{14,15} Van Bremen et al.¹⁶ basically followed the same growth procedure, but they found that the

deposited silicon intercalates between the MoS₂ layers. Similar results were obtained for the growth of silicon on WSe₂ by Yao et al.¹⁷ Zhang et al.¹⁸ found that for the related system Ge on MoS₂, germanene islands are formed on-top of the MoS₂ substrate. In addition, Zhang et al.¹⁸ also showed that the differential conductivity, which is proportional to the local density states, of the germanene islands exhibits a well-defined V-shape, which is one of the hallmarks of a two-dimensional Dirac material. The exact position of the Dirac point, however, varies across the germanene surface owing to the formation of charge puddles, which are induced by charged defects or impurities in the underlying MoS₂ substrate.¹⁹

As has been mentioned above the results of the growth of silicon and germanium on MoS₂ vary substantially, which is difficult to understand as these materials are in many aspects so similar. It is the aim of this chapter to revisit the growth of germanium on MoS₂. The deposition of germanium can be tuned from intercalation between the MoS₂ layers to the growth on-top of the MoS₂ substrate. The key parameters that govern the growth are: the growth temperature, the deposition rate and the defect concentration of the MoS₂ substrate. Since growth experiments are very time consuming we have fixed the growth temperature and the defect concentration of the MoS₂ substrate and only varied the deposition rate. The electronic band structure of the intercalated germanium islands will be studied with scanning tunneling spectroscopy and density functional theory calculations.

3.2 Experimental and theory details

EXPERIMENTS were performed in an ultra-high vacuum system with a base pressure below 3×10^{-11} mbar that is equipped with a room temperature scanning tunneling microscope (Omicron STM-1). The MoS₂ samples were purchased from HQ graphene. The MoS₂ samples were clamped on a Ge crystal that can be resistively heated. The latter allowed us to vary the temperature of the MoS₂ samples. The temperature of the MoS₂ sample is measured with a Cr/Al thermocouple. Before the MoS₂ samples were transferred to the load-lock of the ultra-high vacuum system, a few layers of the MoS₂ crystal were peeled off by mechanical exfoliation. Germanium was deposited using a home-built evaporator consisting of a resistively heated Ge crystal. After the deposition of Ge, the MoS₂ substrate was transferred to the scanning tunneling microscopy chamber. Electrochemically etched tungsten

tips were used for imaging.

The density functional theory calculations were carried out using the projected augmented wave formalism²⁰ as implemented in the Vienna ab initio simulation package (VASP).^{21,22} The exchange-correlation effects were taken into account by using the dispersion-corrected nonlocal optB88-vdW functional.²³ A 600 eV energy cutoff for the plane-waves and a convergence threshold of 10^{-7} eV have been used. The Brillouin zone was sampled by a (64×64) k-point mesh. The supercell was built by one germanium layer sandwiched between two MoS₂ layers. In order to avoid interactions between the supercell structures in the nonperiodic direction, a 20 Å thick vacuum slab was added in the direction normal to the MoS₂ sheet. We consider 2- and 3-atom-thick commensurate structures of encapsulated germanium clusters in different stackings, making up five different structures as shown in the next paragraph. The atomic positions in the supercell were relaxed until the residual forces were less than 10^{-3} eV/Å. The lateral lattice constant was fixed to the MoS₂ equilibrium value of 3.16 Å.¹⁸ The formation energy of the encapsulated germanium layer was calculated as $E_f = E_{\text{MoS}_2+n\text{Ge}} - 2E_{\text{MoS}_2} - n\mu_{\text{Ge}}$, where $E_{\text{MoS}_2+n\text{Ge}}$ is the total energy of n-atom-thick germanium encapsulated between two MoS₂ layers, E_{MoS_2} is the energy of an isolated MoS₂ layer, and μ_{Ge} is the chemical potential of the Ge atom derived from the energy of free-standing germanene.

3.3 Results and discussion

3.3.1 Characterization of MoS₂

IN Figure 3.1(a) a scanning tunneling microscopy (STM) image of a pristine MoS₂ substrate is shown. The lattice constant of the hexagonal MoS₂ surface is 3.16 Å.^{24,25} The STM image of the MoS₂ is taken at sample bias of 0.3 V, which is located in the bulk bandgap of MoS₂. As shown in Refs. [24,25] MoS₂ can be imaged with scanning tunneling microscopy at sample biases located in the bulk bandgap of MoS₂. A scanning tunneling spectrum of the pristine MoS₂ is shown in Figure 3.1(b). The pristine MoS₂ is slightly *n*-type, has a bandgap of about 1.3 eV and is nearly defect-free.

Figure 3.1: (a) Scanning tunneling microscopy image ($6 \text{ nm} \times 6 \text{ nm}$) STM image of pristine MoS_2 . The sample bias is 0.3 V and tunnel current is 800 pA and (b) Scanning tunneling spectroscopy of pristine MoS_2 . Set points: sample bias -1.6 V and tunnel current 1.05 nA.

3.3.2 The growth of germanene/ intercalated Ge clusters

SUBSEQUENTLY, we have deposited Ge on the pristine MoS_2 substrate at two different deposition rates of 0.10 and 0.03 monolayers per minute, respectively (here 1 monolayer corresponds to a (5×5) germanene honeycomb cell on a (6×6) honeycomb cell of the MoS_2 substrate. In Figure 3.2(b) an STM image after 1 minute deposition of Ge at the high deposition rate of 0.10 monolayers per minute resulting in a total amount of 0.1 monolayers is shown. During the deposition the temperature of the MoS_2 increased by a few degrees owing to the radiative heating of the Ge evaporator. The deposited Ge atoms form islands with a hexagonal structure (see 3.2(a)). The lattice constant and height of the islands are $3.8 \pm 0.2 \text{ \AA}$ and $3.2 \pm 0.1 \text{ \AA}$, respectively. The lattice constant of $3.8 \pm 0.2 \text{ \AA}$ is somewhat smaller than the lattice constant of free-standing germanene, which is $\sim 4.0 \text{ \AA}$.^{4,5} A possible explanation of this deviation could be attributed to the substrate-induced stress which, along with relatively high flexibility of germanene,²⁶ leads to its lateral contraction. It is noteworthy to mention that there is a one monolayer deep hexagonal-shaped vacancy island in the interior of all germanene islands. These vacancy islands are terminated by zigzag edges. The origin of these vacancy islands is still unknown. The periodicity of the islands does not correspond to a $(\sqrt{3} \times$

$\sqrt{3}R30^\circ$ periodicity. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity, which is observed when depositing Si or Ge on highly oriented pyrolytic graphite,²⁷ is a direct result of intervalley scattering.²⁸ Furthermore, in contrast to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains that occur for the systems Si and Ge on highly oriented pyrolytic graphite, the islands we observe on MoS₂ are terminated by edges with a height of about 3.2 Å and the electronic structure of the islands on MoS₂ deviates substantially from MoS₂. A step height larger than ~ 3 Å is what one would typically expect for stacked two-dimensional van der Waals materials. Density functional theory calculations have revealed that the germanene is under a small compressive stress resulting in a decrease of the lattice constant and an increase of the buckling.¹⁸ The calculated buckling of germanene on MoS₂ (~ 0.86 Å) is larger than the buckling in free-standing germanene (~ 0.65 Å). Unfortunately, we were not able to resolve simultaneously both triangular sub-lattices of the germanene islands. It is very likely that this is due to the relatively large buckling, which makes it difficult to image the lower lying sub-lattice.

In a second series of experiments we decreased the deposition rate to 0.03 monolayers per minute. The deposition time was 5 minutes, resulting in a total deposited amount of 0.15 monolayers. The deposition resulted in a hill and valley structure with height variations in the range of a few Å to occasionally 1-2 nm, see Figure 3.2(d). The lattice constant of the honeycomb pattern is the same as the lattice constant of pristine MoS₂, i.e. 3.16 Å. Since the surface lattice constant of germanium and germanene are substantially larger than 3.16 Å we have very compelling evidence that the deposited Ge atoms have been intercalated and form islands or clusters underneath the MoS₂ top layer (see Figure 3.2(c)). These findings are very similar to the findings of van Bremen et al. and Yao et al. for the Si/MoS₂ and Si/WSe₂ systems, respectively.^{16,17} The STM images by van Bremen et al.¹⁶ are also very comparable to the STM images obtained by Chiappe et al.¹⁴ for the Si/MoS₂ system, however Chiappe et al.¹⁴ concluded that the deposited Si forms a highly strained silicene layer on top of the MoS₂ substrate with a lattice constant that is exactly the same as the lattice constant of MoS₂. The latter is quite remarkable given the fact that silicene and MoS₂ are both van der Waals materials and thus the interaction between both two-dimensional materials is expected to be very weak.

We note that the sequence of STM images shown in Figure 3.3 reveals that the intercalated islands or clusters are not static. The encircled regions

clearly show that the intercalated islands or clusters are dynamic.

Figure 3.2: (a) Cartoon of a germanene island on MoS₂, (b) STM image (7 nm by 7 nm) of a MoS₂ substrate after the deposition of 0.10 monolayers of Ge, $V=0.5$ V and $I=300$ pA. This figure is a cropped version of Figure 2(a) from ref. [18]. Inset: line scan recorded along the black line in (b), (c) cartoon of an intercalated germanium island on MoS₂ (d) STM image (15 nm by 15 nm) of a MoS₂ substrate after the deposition of 0.15 monolayers of Ge, $V=0.8$ V and $I=900$ pA. Inset: line scan recorded along the black line in (d). All measurements are recorded at room temperature.

MoS₂ is a two-dimensional Van der Waals material and therefore the diffusion barrier for the Ge atoms is expected to be very low. This low diffusion barrier combined with the fact that the deposition rate is rather low allows the deposited Ge atoms to visit many crystal sites without meeting another Ge atom. In the case that the Ge atom encounters an intercalation portal, e.g. a step edge or a large vacancy cluster, before it meets another Ge atom

it is very likely that the Ge atom intercalates between the MoS₂ layers. In the first series of deposition experiments the deposition rate was more than 3 times larger and therefore the deposited Ge atoms have a much larger probability to encounter another Ge atom or a defect. As shown by Zhang et al.¹⁸ the defects in the MoS₂ surface act as nucleation centers for the deposited Ge atoms. Although the exact size of the critical nucleus is not known, we found that the edges of the germanene islands (see Figure 3.2(b)) have a fuzzy appearance, which is due to the continuous attachment and detachment of Ge atoms during imaging.

Figure 3.3: In sequence of STM images of the area shown in Figure 3.2d revealing that the intercalated structures are dynamic (see encircled areas). Image size 15 nm by 15 nm, sample bias 0.8 V and tunnel current 900 pA.

3.3.3 The electronic properties

THE electronic properties of the germanene island and intercalated germanium clusters have been studied by recording grid $I(V)$ curves with the feedback loop disabled. The differential conductivity (dI/dV), which is proportional to the density of states, is obtained by numerically differentiating the $I(V)$ curves. As shown in Figure 3.4(a), the differential conductivity displays a V -shape, which is one of the signatures of a two-dimensional Dirac material (see for more details ref. [18]).

Figure 3.4: (a) differential conductivity (dI/dV) recorded on the germanene island shown in Figure 3.2(b). Set points: $V = -0.8 \text{ V}$ and $I = 400 \text{ pA}$ and (b) differential conductivity (dI/dV) recorded on two embedded Ge clusters with areal sizes of 15 nm^2 (top panel) and 20 nm^2 (bottom panel), respectively. Set points: $V = -0.8 \text{ V}$ and $I = 600 \text{ pA}$.

In principle we would expect to observe particle-in-a-box-like states in the dI/dV spectrum of the germanene islands. The absence of these quantum confined states is probably caused by the fact that the germanene islands are terminated by zigzag edges. In 2D Dirac materials with a honeycomb lattice intra-valley scattering is strongly suppressed because the pseudospin is locked to the momentum. Inter-valley scattering (scattering from valley to valley) is in principle, however, possible. Park et al.³⁰ have demonstrated that the armchair edges show almost perfect inter-valley scattering with pseudospin invariance, but the inter-valley scattering of the zigzag edges is strongly suppressed. The latter implies that quantum confinement will be strongly suppressed if zigzag edge boundaries are involved. As can be seen in Figure

3.2(b) the outer edges of germanene island are aligned along the inner edges (the edges of the vacancy islands). The edges of the vacancy islands are zigzag edges and therefore the outer edges are zigzag edges too.

In order to obtain more information on the Ge that has been intercalated between the MoS₂ layers we have performed spatially resolved scanning tunneling spectroscopy measurements on the intercalated Ge clusters, see Figure 3.4(b). The differential conductivity spectrum shows a bandgap of about 0.6 eV, reminiscent of bulk germanium, which has a bandgap of 0.67 eV. In addition, this bandgap is also substantially smaller than the 1.3 eV bandgap of the pristine MoS₂ regions.

3.3.4 The potential models for intercalated Ge clusters

IN order to identify possible atomic configurations of intercalated germanium clusters, we have performed density functional calculations of several commensurate germanium clusters encapsulated between MoS₂ layers. Schematic atomic structures, cohesive energies, and densities of states (DOS) are shown in Figure 3.5. In the experiments we are dealing with finite size clusters, but in the density functional theory calculations we are limited to regular and periodic clusters. Furthermore, we note that the bandgaps shown in Figure 3.5 may be underestimated due to the well-known deficiency of exchange functionals based on local and semi-local approximations.

In contrast to germanene on MoS₂, the commensurate 2-atom-thick structures 1A and 1B are highly buckled with a vertical displacement between the two sublattices of 2.2 Å. The corresponding DOS projected on MoS₂ exhibits a bandgap of ~ 0.9 eV, which is smaller than the bandgap in pristine MoS₂. The DOS of germanium is non-zero with a well-defined peak in the vicinity of the Fermi energy, which is almost insensitive to the DOS of MoS₂. Among the 3-atom-thick structures, structure 2C appears to be a less favorable candidate because its DOS exhibits multiple midgap states, clearly visible even in the DOS projected on MoS₂. It is worth noting that 4-atom-thick and more thicker structures (not shown here) have similar DOS with multiple midgap states and no clear bandgap. On the other hand, structures 2A and 2B allow us to identify a bandgap in the MoS₂ states to be 1.2-1.3 eV, which is comparable to the bandgap in pristine MoS₂. In these cases, the states of germanium give rise to a plateau in the total DOS. As a result, the region with zero DOS is narrowing down to ~ 0.6 eV. This value is comparable with the experimental observations given that the fact that scanning probe tech-

Figure 3.5: Schematic atomic structure, cohesive energies, and DOS calculated within the density functional theory for five different structures of germanium encapsulated between two MoS₂ layers. Zero energy corresponds to the Fermi energy. The formation energies are given per Ge atom, and are calculated with respect to the chemical potential μ_{Ge} of Ge atoms in free-standing germanene. If the chemical potential of bulk diamond-structure germanium is considered, the lowest formation energy (Structure 2A) turns 0.26 eV.

niques are mostly sensitive to the surface states. From an energetic point of view, all structures have comparable cohesive energies, yet structures 2A and 2B turn out to be the most energetically favorable. Therefore, these structures appear to be the most promising atomic models for the encapsulated germanium clusters observed in the experiment. However, we do not exclude the formation of incommensurate structures with more complex geometries.

3.3.5 Coulomb blockade

As a final point we want to elaborate on another interesting feature in the differential conductivity spectrum of the intercalated Ge clusters. In the conduction and valence bands of the clusters oscillations are observed with a constant energy separation. The exact width varies from cluster to cluster. In the two examples shown in Figure 3.4(b) the energy separations are 0.10-0.11 eV and 0.09 eV, respectively. We interpret these oscillations as Coulomb blockade oscillations due to charging of the germanium cluster in the MoS₂/germanium cluster/MoS₂/vacuum/tip tunnel junction. Coulomb

blockade can be observed in IV and dI/dV spectra if the following requirements are met: (1) the charging energy, e^2/C , should be large than the thermal energy, and (2) the tunnel resistances of both junctions should be large than the quantum of resistance ($h/2e^2$). The energy separation of the oscillations is given by e/C , where C is the total capacitance of the Ge cluster. The mutual capacitance of the embedded germanium cluster and the two contacts (substrate and tip) can be estimated by the self-capacitance of the embedded cluster. The self-capacitance of a sphere of radius R embedded in a medium is $4\epsilon_r\epsilon_0\pi R$,³⁸ where ϵ_r is the relative dielectric constant of the medium (here MoS₂, which has a relative dielectric constant of 2.5). The areal sizes of the germanium clusters in Figure 3.4(b) are $A_1=15\text{ nm}^2$ and $A_2=20\text{ nm}^2$, respectively. By making use of the aforementioned approximation of the total capacitance of the embedded germanium clusters we find energy separations of 0.13 eV and 0.11 eV, respectively. These values are somewhat larger than our experimental observations, but given the crudeness of our model they are quite acceptable. The conclusion that these oscillations are indeed due to Coulomb blockade is reinforced by the fact that the oscillations are absent for larger clusters due to thermal broadening, i.e. $e/C \ll kT$.

3.4 Conclusions

WE have studied the growth of Ge on MoS₂ and found that for, a low deposition rate Ge atoms have a high probability to find an intercalation portal in the MoS₂ substrate and intercalate before meeting another Ge atom or a defect. For higher deposition rates there is fair change that the deposited Ge atoms find a defect or another Ge atom and nucleate on the MoS₂ substrate before they find an intercalation portal in the MoS₂ substrate. The intercalated germanium clusters exhibit, in contrast to the germanene islands that grow on top of the MoS₂, a substantial bandgap of 0.5-0.6 eV. In addition, we observed well-defined Coulomb blockade oscillations in the valence and conduction bands of intercalated germanium clusters. Based on density functional theory calculations and our experimental observations we have identified a few promising structural models for the intercalated germanium islands.

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Charge puddles in germanene

In this chapter, We report an investigation of the electronic inhomogeneities in a single germanene layer grown on a molybdenum disulfide (MoS_2) substrate. Using scanning tunneling microscopy and spectroscopy we have recorded spatial maps of the Dirac point of germanene. The Dirac point maps reveal the presence of charge puddles in the germanene sheet. The Dirac point varies from -30 meV to +15 meV, corresponding to a charge density in the puddles in the range of 2.6×10^{-3} electrons to 6.6×10^{-4} holes per nm^2 . The radius of these puddles is about 10-20 nm, resulting in a total charge of the order of one charge carrier per puddle. The defect concentration in the top layer of the MoS_2 substrate is very comparable to the density of charge puddles, suggesting that the charge puddles are caused by the charged defects in the top layer of the MoS_2 substrate.

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4.1 Introduction

GRAPHENE is a semimetal with linearly dispersing energy bands at the K and K' points of the Brillouin zone. Owing to these linearly dispersing energy bands the electrons in graphene behave as massless relativistic particles.^{1–4} An ideal graphene sheet, i.e. a sheet that is undoped, perfectly flat and completely free from defects and charged impurities, has its charge neutrality point, also referred to as Dirac point, located at the Fermi level. The density of states of this ideal graphene sheet vanishes at the Dirac point. Recent experiments have revealed that graphene placed on a substrate often exhibits a spatially varying Dirac point, resulting in electron-holes puddles. The exact origin of these charge puddles is still under debate. Possible candidates for the occurrence of these charge puddles are: (1) charged impurities in the substrate on which the graphene is placed,^{5,6} (2) charged species which are intercalated between the graphene sheet and the substrate⁷ and (3) local curvature of the graphene sheet.^{8–10}

The first experimental evidence for the occurrence of charge puddles in two-dimensional materials dates back to 2008. Martin et al.⁵ used a scanning single-electron transistor to spatially map out the charge inhomogeneities in graphene on SiO_2 . One year later, Zhang et al.⁶ used a scanning tunneling microscope to map out the charge density inhomogeneities in graphene on SiO_2 by a new technique, referred to as Dirac-point mapping, with a charge density spatial resolution that is substantially higher than what can be achieved by the scanning single-electron transistor. These authors arrived at the conclusion that the electron-hole puddles originate from charge donating defects and/or impurities in the SiO_2 substrate. As demonstrated by Martin et al.⁷ also atoms or molecules intercalated between graphene and its support can result in the formation of charge puddles. Gibertini et al.^{9,10} used density functional theory calculations to show that structural corrugations are in principle sufficient to explain the formation of charge puddles in graphene. They also pointed out that the locations of these electron-hole puddles, which have a typical dimension of a few nanometers, do not exhibit a clear correlation with the topography of the graphene sheet. It is worth mentioning that electron-hole puddles are also found in bilayer graphene.¹¹ To the best of our knowledge charge puddles have only been found in graphene and not in any other elemental two-dimensional material.

The electronic structures of silicon and germanium are very similar to car-

bon, and therefore, it is worthwhile to check if these materials can form two-dimensional honeycomb lattices. Theoretical calculations have revealed that the graphene-like allotropes of silicon and germanium referred to as silicene and germanene, respectively, are indeed stable.^{12–14} Unfortunately, silicene and germanene do not occur in nature and therefore these materials have to be synthesized. In 2012 silicene was successfully synthesized,^{15,16} followed a few years later by germanene^{17–20}. Initially metallic substrates, particularly transition metal (111) surfaces, were used as template. In order to electronically decouple the relevant electronic states of the two-dimensional material, which are located near the Fermi level, a band gap substrate is required. A suitable substrate would be MoS₂, a material with a bulk band gap of about 1.3 eV. Earlier work revealed that the unique electronic properties of graphene are preserved if MoS₂ is used as a substrate.²¹ Inspired by this success, Zhang et al. have successfully grown germanene on MoS₂.²² Scanning tunneling spectroscopy measurements revealed that the density of states of germanene synthesized on MoS₂ exhibits a V-shaped density of states, which is one of the hallmarks of a two-dimensional Dirac material.

In this chapter, we have investigated the electronic disorder of germanene sheets grown on bulk MoS₂ by using scanning tunneling microscopy. Inspired by the observation of charge puddles in graphene sheets we have scrutinized if such charge inhomogeneities are also present in germanene. In order to map out the charge density of the germanene sheet, we have used the aforementioned Dirac point mapping technique.

4.2 Experimental details

THE scanning tunneling microscopy (STM) and spectroscopy (STS) experiments have been performed at room temperature with an ultra-high vacuum STM (Omicron STM-1). The base pressure of the ultra-high vacuum system is 3×10^{-11} mbar. MoS₂ samples were freshly cleaved from synthesized 2H-MoS₂ (purchased from 2D Semiconductors) before inserting into the vacuum system. The MoS₂ samples are mounted on a Mo sample holder. Germanium was deposited onto the MoS₂ substrate, which was held at room temperature, by resistively heating a small piece of a Ge(001) wafer at a temperature of ~ 1150 K. Prior to the deposition process the Ge(001) wafer was cleaned by outgassing at a temperature of 700 K for about 24 h followed by several cycles of argon ion bombardment at 800 eV and annealing

at 1100 K.²³ The Ge source was located at a distance of ~ 10 mm from the MoS₂ substrate. After the deposition of germanium, the MoS₂ sample was inserted into the STM.

4.3 Results and discussion

4.3.1 Characterization of MoS₂

THE MoS₂ is a transition metal dichalcogenide that consists of a covalently bonded Mo layer encapsulated between two S layers. The MoS₂ trilayers are held together by weak Van der Waals bonds. The material is a semiconductor with a bulk band gap of 1.3 eV. The MoS₂ surface has a hexagonal unit cell with a lattice constant of 0.316 nm. Despite the fact that the lattice constant of MoS₂ is substantially smaller than the lattice constant of germanene, MoS₂ is a good substrate for growth of germanene owing to the relatively weak Van der Waals interaction between the two materials.

Figure 4.1: (a) Scanning tunneling microscopy image of the pristine MoS₂ surface. Inset: small scale scanning tunneling microscopy image. The sample bias is -0.3 V, and the tunnel current is 500 pA. (b) dI/dV spectrum of the pristine MoS₂ surface. The set point values are -1.1 V and 500 pA.

In Figures 4.1(a)-(b) a large-scale scanning tunneling microscopy image and a scanning tunneling spectroscopy spectrum of the pristine MoS₂ surface are shown. By examining several large-scale scanning tunneling microscopy images, similar to one shown in Figure 4.1(a), we have found that the defect

density is about $3 \times 10^{-3} \text{ nm}^{-2}$. This defect density, which includes the dark as well as the dimmer defects shown in Figure 4.1(a), compares well with a previous study of the defects of MoS₂ using conductive atom force microscopy by Bampoulis et al.²⁴ The dark features in Figure 4.1(a) are defects in the first MoS₂ trilayer, whereas the dimmer features are defects located in the second MoS₂ trilayer.²⁴ As shown by Bampoulis et al.²⁴ the dark and dim defects are both electronic nature since they only show up in conductive atomic force microscopy images and not in topographic atomic force microscopy images.

The differential conductivity spectrum displayed in Figure 4.1(b) demonstrates that the MoS₂ substrate has a sizeable band gap. The defects in MoS₂ have been extensively studied (see e.g. Ref. [25] and references therein). MoS₂ exhibits n-type as well as p-type defects, which are explained by sulfur-deficient and sulfur-rich regions, respectively.²⁵

Figure 4.2: (a) Large scale scanning tunneling microscopy image (100 nm by 100 nm) of a complete germanene layer grown on MoS₂. Inset: small scale scanning tunneling microscopy image of germanene layer. The Sample bias is -1 V, and the tunnel current is 300 pA. (b) Differential conductivity of germanene. The set point values are -1.4 V and 600 pA.

4.3.2 The electronic properties of germanene

IN Figure 4.2(a) a scanning tunneling microscopy image of a germanene layer grown on MoS₂ is shown. As we have already shown in a study,²²

Ge atoms deposited on the MoS₂ substrate nucleate at pre-existing defects of the MoS₂ surface. The germanene islands have a height of 3.2 Å and exhibit a hexagonal symmetry with a lattice constant of 3.8-3.9 Å, which is about 20% larger than the lattice constant of pristine MoS₂. This relatively large interlayer spacing of 3.2 Å between the germanene sheet and the MoS₂ substrate hints to a relatively weak interaction between the layers as one expects for materials that are held together by Van der Waals interactions. The deposition of more Ge eventually leads to a complete germanene layer.²² Owing to the large buckling of germanene on MoS₂, only one of the two triangular sub-lattices is visible in the scanning tunneling microscopy images.

The electronic properties of the germanene layer have been studied by recording grid $I(V)$ curves with the feedback loop disabled. The typical grid size is 60×60 for a 100 nm by 100 nm scan. The differential conductivity (dI/dV), which is proportional to the density of states, is obtained by numerically differentiating the $I(V)$ curves. The averaged dI/dV curve is shown in Figure 4.2(b). The differential conductivity displays a V -shape, which is one of the signatures of a two-dimensional Dirac material. The density of states does not completely vanish at the Dirac point. The dI/dV curve is asymmetric, a feature that we have observed before.²² The asymmetry of the dI/dV curve could be caused by the electronic structure of the STM tip. In addition, it should be noted that the rounded shape near the Dirac point cannot be fully explained by thermal broadening. A much improved fit is, however, obtained by introducing a band gap of about 25 meV. This band gap could be caused by the spin-orbit coupling in germanene, which is substantially larger than in graphene.²⁶

Density functional theory calculations shown in Ref. [22] reveal that besides the linear bands at the K and K' points of the Brillouin zone there are also two parabolic bands in the vicinity of the Fermi level at the Γ point. It is very well possible that these two parabolic bands near the Γ point are responsible for the non-zero density of states at the Dirac point, however, the non-zero density of states could also be caused by the electronic structure of the scanning tunneling microscopy tip.

4.3.3 The charge puddles

SINCE the dI/dV curve shown in Figure 4.2(b) is averaged over 3600 different positions on the surface, it is worthwhile to have a detailed look at the spatial variation of the dI/dV curves. In order to do this, we have de-

terminated the exact position of the minimum of all individual dI/dV curves. The minimum of the V -shaped dI/dV curve is located at the charge neutrality point, i.e. the Dirac point. As we will show below, the Dirac point provides information on the local charge density. The dispersion relation of a two-dimensional Dirac material is $E = \hbar\nu_F |k|$, where $\hbar$ is the reduced Planck constant, ν_F the Fermi velocity, E the energy of the electron and k the momentum of the electron. The density of states of a two-dimensional Dirac material is given by,

$$D(E) = \frac{2|E - E_D|}{\pi\hbar^2\nu_F^2} \quad (4.1)$$

where E_D the Dirac point. The map of the Dirac point can be converted into a map of the charge density by using,

$$\rho(x, y) = \int_0^{E_D} \frac{2|E - E_D|}{\pi\hbar^2\nu_F^2} dE = -\frac{E_D^2}{\pi\hbar^2\nu_F^2} \text{sign}(E_D) \quad (4.2)$$

In Figure 4.3, spatial maps of the Dirac and charge character of a 100 nm by 100 nm germanene/MoS₂ are shown, respectively. The images consist of 60×60 pixels, and each pixel corresponds to a single $I(V)$ curve. It should be emphasized here that we are dealing with raw data and we have not applied any smoothening of the $I(V)$ curves in order to determine the minimum of each $I(V)$ curve. The spatial maps of the variation of the Dirac point and charge character reveal that the germanene sheet consists of electron and hole puddles with a typical radius of 10-20 nm embedded in an intrinsic, i.e. undoped, background. The electrostatic screening in two-dimensional Dirac materials is significantly different from electrostatic screening in conventional two-dimensional electron systems. The Dirac point varies from -30 meV to 15 meV corresponding to a charge fluctuation of 2.6×10^{-3} electrons/nm² to 6.6×10^{-4} holes/nm², assuming a Fermi velocity of 5×10^5 m/s.²⁷ Since the germanene sheet is atomically flat on a length scale exceeding the typical size of the charge puddles we have to rule out to the possibility that charge puddles are caused by structural corrugations or bending of germanene sheet. The germanene sheet are grown and subsequently studied at ultra-high vacuum conditions and therefore we can also rule out intercalation of atoms or molecules as being the cause of the charge puddles. The only remaining source are charge donating impurities in the MoS₂ substrate. By analyzing several large-scale scanning tunneling microscopy images of our pristine and

freshly cleaved MoS₂ substrate we find a defect density of $3 \times 10^{-3} \text{ nm}^{-2}$. This value compares favorably well with the charge puddle density we have determined for the germanene sheet. Based on these findings we suggest that the charge puddles are caused by charge donating defects of the MoS₂ substrate.

Figure 4.3: (a) Spatial map (60×60 pixels) of the Dirac point of germanene/MoS₂. Image size is 100 nm by 100 nm. The color code refers to the position of the Dirac point. (b) Spatial map (60×60 pixels) of the charge character of germanene/MoS₂ (red: intrinsic, black: n-type and white: p-type). Image size is 100 nm by 100 nm.

The typical radius of the charge puddles in germanene is about 10-20 nm. A crude estimate for the size of the charge puddle is the Thomas-Fermi screened length. In conventional two-dimensional electron systems, the density of states in energy space is constant, and therefore, the Thomas-Fermi screening length, which is inversely proportional to the density of states at the Fermi level, is constant.²⁸⁻³¹ In two-dimensional Dirac systems, however, the density of states is proportional to the energy. This results in a Thomas-Fermi screening length of $2\pi k\hbar v_F / 4e^2 \sqrt{\pi n}$, where n is the charge density.³¹ Assuming a Fermi velocity of $5 \times 10^5 \text{ m/s}$ and a charge density of $3 \times 10^{-3} \text{ nm}^{-2}$ (one charge carrier per defect), we find for germanene on molybdenum disulfide a Thomas-Fermi length of $\sim 10 \text{ nm}$, which is somewhat smaller than our experimental observations. In addition, the size of the charge puddles in germanene is very comparable to the size of the charge puddles found in graphene at a comparable charge density.^{6,7} Please note that the charge density in Ref. [7] is substantially larger than in our case as well as Ref. [6],

resulting in, as expected, smaller charge puddles.

In a previous study,²² our group found a qualitative good agreement between the dI/dV spectrum and the density functional theory calculations. There is, however, an overall energy shift of about 0.3 eV between the experimental and theoretical spectra. In Ref. [22] our group tentatively ascribed this energy shift to the presence of defects and/or impurities with an acceptor character. In this work, we have not found any evidence for the presence of these acceptor type of defects and/or impurities in the germanene layer and therefore we have to discard this interpretation.

4.4 Conclusions

IN conclusion, we have studied the charge inhomogeneities of germanene grown on MoS₂. The charge fluctuations in germanene have been mapped out by using a Dirac point map. Spatial maps of the Dirac point and the charge character reveal that the germanene sheet consists of electron and hole puddles with a typical radius of 10 – 20 nm embedded in an intrinsic, i.e undoped, background. The typical charge per puddle is of the order of one electron or hole. The defect density of the MoS₂ is determined by analysis of several large-scale scanning tunneling microscopy images and compares very well with the charge density of the germanene sheet. We found strong indications that the charge puddles in germanene are caused by charge-donating defects and impurities in the MoS₂ substrate. Our results demonstrate that even in Van der Waals heteroepitaxy the quality of the substrate plays a key role. Charge donating defects or impurities result in electronic inhomogeneities in the two-dimensional material.

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Tailoring and probing the quantum states of matter of 2D Dirac materials with a buckled honeycomb structure

In this chapter, the quantum state of matter of a two-dimensional Dirac material with a buckled honeycomb structure can be tuned by an electric field. In the absence of an external electric field the material is a topological insulator owing to the spin-orbit coupling, which opens a band gap at the K and K' points of the Brillouin zone. The size of this band gap decreases with increasing electric field until eventually the band gap completely closes at a critical electric field E_c and the material becomes a semi-metal. For electric fields exceeding E_c the band gaps reopens again and the material undergoes a topological phase transition from a semi-metal to a normal band insulator. The electric field in a tunnel junction depends on the applied voltage bias across the junction as well as the difference in work function of the two electrodes. Here we show how scanning tunneling microscopy (STM) can be employed to simultaneously apply an electric field and study the electronic structure of a 2D Dirac material with a buckled honeycomb structure. The electric field applied by the STM offers the possibility to locally alter the quantum state of matter of 2D topological insulator to a semi-metal or normal band insulator. This results in the development of topologically protected spin polarized edge states within the material. We present a spectroscopic method to probe these topologically protected edge states.

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5.1 Introduction

THE successful isolation of graphene,^{1,2} i.e. a single layer of sp^2 hybridized carbon atoms arranged in a honeycomb structure, has resulted into the opening of a new research field. Graphene exhibits many interesting and unique properties. Most of these properties are intimately related to the linear dispersion relation of the electrons in the vicinity of the Fermi level.³⁻⁶ Near the K and K' points of the Brillouin zone the linearly dispersing energy bands lead to Dirac cones. If spin-orbit coupling is not taken into account, graphene has no band gap and a vanishing density of states at the Fermi level. If, however, spin-orbit coupling is taken into account a band gap at the K and K' points of the Brillouin zone opens. The spin-orbit gap in graphene is only about 20 μeV and therefore it will not be detectable at any experimentally accessible temperature.^{7,8}

Silicon, germanium and tin atoms have a similar electronic configuration as carbon atoms and therefore these atoms might also form a two-dimensional honeycomb lattice.⁹⁻¹⁶ Theoretical studies have revealed that the graphene-like allotropes of silicon, germanium and tin referred to as silicene, germanene and stanene respectively, can indeed exist. These two-dimensional materials share many properties with their carbon counterpart.¹⁷⁻²¹ For instance, the energy bands near the K and K' points of the Brillouin zone are linear and the charge carrier mobilities and Fermi velocities are very comparable to graphene. Unfortunately, silicene, germanene and stanene do not occur in nature and therefore these materials have to be synthesized. Silicene has been successfully synthesized in 2012, followed by germanene in 2014 and stanene,^{9,10,12-16} sometimes also referred to as tinene in 2015.²²

Silicene, germanene and stanene also exhibit some properties that are different from graphene. The most eye-catching difference with graphene is the corrugation: the honeycomb lattices of silicene, germanene and stanene are buckled,²¹ i.e. the two triangular sub-lattices of the honeycomb lattice are displaced with respect to each other in a direction normal to the two-dimensional layer. This buckling is caused by the relatively large, at least as compared to carbon, ionic radii of silicon, germanium and tin, which prohibits the formation of a perfectly planar honeycomb lattice. The buckling breaks the symmetry of the honeycomb lattice and offers the appealing possibility to transfer charge from one triangular sub-lattice to the other via, for instance, the application of an external electric field.^{23,24} This charge transfer

results into the opening of a band gap, which paves the way to the tailoring of the quantum state of matter of these two-dimensional material as well as field-effect based device applications. Like graphene, silicene, germanene and stanene belong to the class of Z_2 topological insulators.^{25,26} The spin-orbit coupling in silicene (3.9 meV), germanene (43 meV) and stanene (100 meV) results in the opening of a spin-orbit band gap at the K and K' points of the Brillouin zone.^{27–29} As shown by Drummond, Ztolyomi and Falko²³ as well as Ezawa²⁴ the application of a transverse electric field first closes and then reopens the band gap. With increasing electric field silicene, germanene and stanene undergo a topological phase transition from a topological insulator to a semi-metal and subsequently to a normal band insulator.^{23,24,30,31} It has been pointed out that the application of an inhomogeneous electric field, for instance by using a scanning tunneling microscope, can result in the development of topologically protected and spin polarized edge states anywhere within the two-dimensional material.

Inspired by Ezawas work we are dedicated to search for an experimental method to prove the existence of these topologically protected edge states within a material. The requirement of a high spatial resolution puts severe constraints and basically limits our search to scanning probe microscope-based techniques. Scanning tunneling microscopy and spectroscopy are often employed to study the structural and electronic properties of two-dimensional materials. There is, however, also a point of concern when using scanning tunneling microscopy. The voltage drop across the tunnel junction, which can be as a few Volts per nm can affect the electronic structure of the material under scrutiny. Here, however, this electric field is advantageous since it allows us to modify the electronic band structure of the buckled two-dimensional materials.

In this chapter, we will not only study the effect of an electric field on the density of states of a buckled two-dimensional material with a honeycomb lattice, but we also put forward a method that allows to study the formation of topologically protected edge states within the material. Our method relies on the presence of topologically protected edge states at the boundary between a the two-dimensional topological insulator and a semi-metal or normal band insulator.²⁴ The topologically protected edge states act as barriers for incoming electron waves resulting in standing wave patterns, which will show up as peaks in the scanning tunneling spectroscopy spectra.

5.2 Quantum states of matter of buckled 2D Dirac materials

TWO-dimensional elemental materials such as silicene and germanene exhibit a buckled honeycomb lattice, which is composed of two triangular sub-lattices. These two triangular sub-lattices are slightly displaced with respect to each other in a direction normal to the two-dimensional sheet. The displacement or buckling is denoted by Δ . The buckling of free-standing silicene and germanene is 0.44 Å and 0.66 Å, respectively. For the sake of simplicity we consider here a perfect, i.e. defect free and impurity free, single sheet of a buckled two-dimensional elemental material. As shown in ref. [24] the energy dispersion in the vicinity of the K and K' points of the Brillouin zone is given by,

$$E_{\pm} = \pm \sqrt{\hbar^2 \nu_F^2 k^2 + \left(\frac{\Delta}{2} e E_z - \zeta s \lambda_{SO} \right)^2} \quad (5.1)$$

where $\zeta = \pm 1$ refers to the K (K') point, $s = \pm 1$ to the spin, E_z to the electric field, e to the unit of elementary charge, λ_{SO} to the spin-orbit gap, ν_F to the Fermi velocity, k to the momentum and $\hbar$ to the reduced Plancks constant. For a vanishing spin-orbit coupling and electric field the well-known Dirac cones are recovered, i.e. $E_{\pm} = \pm \hbar \nu_F k$. We would like to emphasize here that this method is not applicable to graphene owing to its planar structure, which prohibits the transfer of charge from one sub-lattice to the other sub-lattice.

The electric field E_z can have different contributions. For instance, in a scanning tunneling microscope junction the electric field has in general two components. The first component is caused by the applied sample bias, V , resulting in an electric field $\frac{V}{d}$, where d is the tip-sample distance. The second component is due to a difference in work function between tip and substrate. This difference in work function, $\delta W = W_t - W_s$, results in an electric field $(\frac{\delta W}{e})/d$. The total electric field, E_z , in the tunnel junction is then given by $(V + \frac{\delta W}{e})/d$.

For completeness we also include a Rashba coupling, λ_R , but as we will see later the Rashba coupling has no effect on the actual size of the band gap at the Dirac points.^{24,30} The full expression of the dispersion relations in the vicinity of the K point that includes a spin-orbit coupling, an electric field and a Rashba coupling is given by,

$$E_{\pm} = \pm \sqrt{\hbar^2 \nu_F^2 k^2 + \left(\frac{\Delta}{2} \left(\frac{eV + \delta W}{d} \right) - \zeta s \sqrt{\lambda_{SO}^2 + \alpha^2 \lambda_R^2 k^2} \right)^2} \quad (5.2)$$

where α is a constant. Please note that equation (5.2) reduces to equation (5.1) at the Dirac points, i.e. at $k = 0$. In Figure 5.1 we show an overview of the different topological quantum states of matter of a two-dimensional Dirac material with a buckled honeycomb lattice. For a vanishing electric field the material is a two-dimensional topological insulator (left panel). In the middle panel the applied electric field is just large enough to close the spin-orbit gap for the spin up and spin down bands at the K and K' points, respectively. At this condition the material behaves as a perfect semi-metal. For electric fields that exceeds the spin-orbit gap, the band gap reopens again and the material becomes a normal band insulator.

Figure 5.1: Schematic cartoon of the electronic band structure of a two-dimensional Dirac material with a buckled honeycomb lattice. Left panel: electric field smaller than spin-orbit gap. The material is a topological insulator. Middle panel: electric field is equal to spin-orbit gap. The material is a semi-metal. Right panel: electric field is larger than spin-orbit gap. The material is a normal band insulator. Blue: spin down bands. Orange: spin up bands.

At $k = 0$ we find in principle two branches with a band gap,

$$E_{gap} = 2 \left| \frac{\Delta}{2} eE_z - \zeta s \lambda_{SO} \right| \quad (5.3)$$

where $\zeta s = \pm 1$. The band gap closes at the critical electric field $E_C = \pm \frac{2}{\Delta e} \lambda_{SO}$. The critical fields for silicene and germanene are ± 0.18 V/nm and

± 1.3 V/nm, respectively. In Figure 5.2(a) schematic figure of the energy bands at the K point versus the electric field is depicted.

Figure 5.2: The energy bands at the K point of the Brillouin zone versus electric field. Blue: spin down bands. Orange: spin up bands.

An ideal technique to explore the effect of an electric field on the quantum state of matter is scanning tunneling microscopy. The density of states can be obtained by recording a current (I)- curve (V) trace at constant tip-sample distance. The differential conductivity (dI/dV) is proportional to the density of states. Since the electric field in the tunneling junction also depends on the tip-sample bias we have to disentangle this effect from the measured density of states. For the sake of simplicity we consider here the case that the work function difference between tip and substrate, which results in an offset of the electric field, is zero. In the absence of an electric field, i.e. $E_z = 0$, the density of states, $D(E)$, of both spin branches at the K point are given by,

$$D(E) = \frac{D(k)2\pi k dk}{(\frac{dE}{dk})} = \frac{|E - \lambda_{SO}|}{2\pi\hbar^2\nu_F^2} \quad (5.4)$$

The total density of states at energy E is then (K and K' points and two spin bands),

$$D(E) = \frac{|E - \lambda_{SO}|}{\pi \hbar^2 \nu_F^2} \quad (5.5)$$

For an applied electric field, E_z , the spin up and spin down gaps at the K point are given by,

$$E_{g,s=+1} = 2 \left| \frac{\Delta}{2} e E_z - \lambda_{SO} \right| \quad (5.6)$$

and

$$E_{g,s=-1} = 2 \left| \frac{\Delta}{2} e E_z + \lambda_{SO} \right| \quad (5.7)$$

Similar expressions can be derived for the K' point. The only difference is the sign in front of the λ_{SO} term. Here we restrict ourselves to (1) the E_+ branch at the K point and (2) positive electric fields, i.e. $E_z > 0$. The application of a voltage, V , across the scanning tunneling microscopy junction results in an electric field $\frac{V}{d}$, which will lead to charge transfer from one triangular sub-lattice to the other triangular sub-lattice. This charge transfer will lead to an increase (decrease) of the band gap of the spin up (down) band. From a scanning tunneling spectroscopy measurement one can extract the exact location of these two band gaps. The first gap is found that a threshold voltage V_1 ,

$$eV_1 = \lambda_{SO} - \frac{e\Delta}{2d} V_1 \quad (5.8)$$

In the density of states a kink will be found when the second spin band comes into play. The second gap has a threshold voltage V_2 ,

$$eV_2 = \lambda_{SO} + \frac{e\Delta}{2d} V_2 \quad (5.9)$$

The density of states can be found by simply adding up the two spin bands and multiply with a factor of two due to the two different K points. The total density of states is then given by,

$$D(E) = 0 \quad \text{for} \quad 0 \leq eV \leq \frac{\lambda_{SO}}{(1 + \frac{\Delta}{2d})} \quad (5.10a)$$

$$D(E) = \frac{eV(1 + \frac{\Delta}{2d}) - \lambda_{SO}}{\pi \hbar^2 \nu_F^2} \quad \text{for} \quad \frac{\lambda_{SO}}{(1 + \frac{\Delta}{2d})} \leq eV \leq \frac{\lambda_{SO}}{(1 - \frac{\Delta}{2d})} \quad (5.10b)$$

$$D(E) = \frac{2(eV - \lambda_{SO})}{\pi \hbar^2 \nu_F^2} \quad \text{for} \quad \frac{\lambda_{SO}}{(1 - \frac{\Delta}{2d})} \leq eV \leq \frac{2d\lambda_{SO}}{\Delta} \quad (5.10c)$$

$$D(E) = \frac{2eV(1 - \frac{\Delta}{2d})}{\pi \hbar^2 \nu_F^2} \quad \text{for} \quad eV \geq \frac{2d\lambda_{SO}}{\Delta} \quad (5.10d)$$

Similar expressions can be found for negative sample biases. Usually the tunneling current is dominated by electronic states at the Γ point of the surface Brillouin zone, since this results in the smallest inverse decay length.³² However, if there are no states available at the Γ point tunneling will occur to, or from, electronic states with a non-zero parallel momentum.³² In the vicinity of the Fermi level of two-dimensional elemental materials, such as graphene, silicene and germanene, there are only electronic states at the K and K' points of the Brillouin zone and therefore the density of states only comes from these k -points.

We now return to equations (5.10) to discuss the impact of the electric field of the scanning tunneling microscopy junction on the density of states. The slope of the density of states changes with increasing energy from 0 to $(1 + \frac{\Delta}{2d})$ to 2 and finally to $2(1 - \frac{\Delta}{2d})$. Since $d \gg \Delta$ ($\frac{\Delta}{2d}$ is about 0.022 for silicene and 0.033 for germanene) the most pronounced change in the density of states occurs at $eV \approx \lambda_{SO}$.

Let's assume that we set the electric field to a value larger than its critical value, i.e. $E_C = \frac{2\lambda_{SO}}{e\Delta}$, which implies that the circular region underneath the tip has become a normal band insulator (see Figure 5.3). For the sake of simplicity we consider the STM tip as a simple rod with radius R . The interface between the small circular semi-metal with radius R and the surrounding topological insulator host will act as a barrier for incoming electron waves leading to an electron interference patterns. For simplicity we reduce this problem to that of a quantum mechanical particle trapped in an infinitely deep circular well with a radius R . A few remarks are in place here: (1) in reality the transition from a normal band insulator to a the two-dimensional topological insulator leads a barrier of finite height, where the

Figure 5.3: Schematic picture of the development of topologically protected helical zero modes due to the electric field of a scanning tunneling microscope. Underneath the scanning tunneling microscope tip the quantum state of matter can be changed from a two-dimensional topological insulator to a semimetal or normal band gap insulator. The electron standing wave pattern results in resonances in the $z(V)$ signal.

incoming electrons are scattered and (2) we assume that the electrons at the bottom of conduction have a parabolic dispersion relation with an effective mass m_{eff} . The energy eigenfunctions and energy eigenvalues are given by,

$$\Psi(\gamma, \theta) = C J_m \left(\frac{z_{m,n}}{R} \gamma \right) e^{ima} \quad (5.11)$$

and

$$E_{m,n} = \frac{\hbar^2}{2m_{eff}} \left(\frac{z_{m,n}}{R} \right)^2 \quad (5.12)$$

where γ and θ are the polar coordinates, C a constant, J_m the Bessel function of the first kind and order m , $m \in \mathbb{Z}$, $n \in \mathbb{N}$ and $z_{m,n}$ the n th

zero of the Bessel function of the first kind and order m . For instance for $m = 0$ the first 4 zeros are given by 2.4048, 5.5207, 8.6537 and 11.7915 respectively.³³ For $m = 0$ these electron standing waves patterns will exhibit a strong maximum in the middle of the circle, i.e. precisely at the location of the scanning tunneling microscope tip, see Figure 5.3. If we record the z -piezo displacement versus sample bias, i.e. $z(V)$, at constant tunnel current we will find a resonance in the $z(V)$ signal if a standing wave pattern occurs. The $z(V)$ signal provides direct information on the position of the energy eigenvalues of this system.^{34–36} However, more important is the fact that the presence of these electron standing waves implies that we must have formed topologically protected edges state within the material.

For electric fields exceeding the critical field the region just underneath the scanning tunneling microscope tip will become a normal band insulator. Since the energy of tunneling electrons is higher (lower) than the minimum (maximum) of the conduction (valence band) and therefore we expect also in this case the development of electron standing waves patterns. In order to avoid field emission resonances, which can occur at voltages exceeding the work function of the substrate, it is advisable to keep the maximum voltage in the $z(V)$ measurement below the work function of the substrate.

5.3 Conclusions

THE quantum state of matter of a two-dimensional Dirac material with a buckled honeycomb lattice can be tuned from a topological insulator to a semimetal or a normal band insulator by applying an external electric field. The application of an spatially inhomogeneous electric field, by for instance an STM, allows to locally change the quantum state of matter. The STM can simultaneously be used to probe the changes in electronic structure upon the application of an electric field. Here we show how the electric field of the scanning tunneling microscope affects the electronic structure of a buckled two-dimensional Dirac material. In addition, we have proposed a method, that relies on $z(V)$ spectroscopy, to obtain more information on the presence of topologically protected edge states within the material.

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Structural and electronic properties of the α -GeSe surface

In this chapter, the structural and electronic properties of the α -GeSe surface are investigated by atomic force microscopy, scanning tunneling microscopy and density functional theory calculations. GeSe belongs to the group-VI transition metal monochalcogenides and occurs in two polymorphs, α -GeSe and β -GeSe. The most redundant polymorph, i.e. α -GeSe, has a structure that is very similar to black phosphorene. The α -GeSe surface has a centered rectangular unit cell with dimensions $a=3.8$ Å and $b=4.4$ Å, respectively. In scanning tunneling microscopy images only the Se atoms are resolved owing to the substantial transfer of electrons from the Ge to the Se surface atoms. This experimental finding is fully in line with density functional theory calculations. Scanning tunneling spectroscopy reveals that the α -GeSe surface is a p -type semiconductor with a band gap of 1.0 eV. Despite the fact that GeSe is exfoliated at ambient conditions, the surface of GeSe is remarkably stable and defect-free, making this material very appealing for device applications.

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6.1 Introduction

SPARKED by the discovery of graphene,^{1,2} a single layer of sp^2 carbon atoms arranged in a honeycomb structure, tremendous attention has been paid to other two-dimensional materials, such as the elemental group IV materials³⁻⁹ and the transition metal dichalcogenides.¹⁰⁻¹² More recently also, black phosphorene, a monolayer material composed of phosphorus atoms with a puckered structure, attracted much attention because of its extraordinary properties. Black phosphorene is a semiconductor with a direct band gap of 1.5 eV and a high hole mobility.^{13,14} Unfortunately, black phosphorus is very susceptible to the adsorption of oxygen and water,^{15,16} which can severely degrade the performance of black phosphorus based electronic devices. Although different passivation methods have been developed to protect the surface, the intrinsic properties of black phosphorus are also affected by the protection.

New air-stable two-dimensional materials with a "phosphorene-analog" puckered structure, such as GeS, GeSe, SnS and SnSe, have been predicted to possess properties very comparable to black phosphorus.¹⁷⁻²¹ The very good performance of these materials, including ultrahigh charge carrier mobility with strong anisotropy,²²⁻²⁴ high thermoelectric ZT value,^{25,26} giant piezoelectricity,²⁷ high photo responsivity,²⁸ and sensitivity for various gases²⁹ make these class of materials of great potential interest for a broad range of applications.

In this chapter, we will study GeSe, a material which occurs in two polymorphs, α -GeSe and β -GeSe, respectively. GeSe consist of six-membered rings of 3 Ge atoms and 3 Se atoms. The six-membered ring of α -GeSe has a chair configuration, which makes the structure α -GeSe very comparable to black phosphorene. The six-membered ring of β -GeSe exhibits a boat configuration.³⁰ α -GeSe is the most abundant polymorph, whereas β -GeSe is only found at high pressures and high temperatures. Both GeSe polymorphs are semiconductors. Bulk GeSe is a p-type semiconductor with a rather complicated electronic band structure revealing closely placed direct and indirect band gaps.³¹⁻³⁵ A monolayer of α -GeSe is predicted to have a direct band gap of ~ 1.1 - 1.2 eV,^{32,36} which makes this material an appealing candidate for optoelectronic applications, such as near-infrared photodetectors. Density functional theory calculations revealed that there no imaginary phonon modes, implying that a monolayer of α -GeSe is stable.³² The band gap of

other polymorph, i.e. β -GeSe, is substantially smaller and amounts about 0.5 eV for the bulk phase and 0.9 eV for a monolayer.

The orthorhombic unit cell of α -GeSe involves two atomic layers. Each of these layers consists of four three-fold coordinated atoms, which form zig-zag chains (see Figure 6.1(d)). The bond between these Ge-Se atoms has a polar-covalent character. The layers are held together by weak Van der Waals interaction and therefore the material can easily be mechanically exfoliated.

Figure 6.1: (a) Atomic Force Microscopy (AFM) image of an α -GeSe surface. Scanning size: $20\mu\text{m} \times 20\mu\text{m}$. (b) Height profile of the inserted AFM image. (c) Atomically resolved scanning tunneling microscopy image of α -GeSe. Sample bias is -0.8 V and tunneling current is 0.5 nA. (d) The schematic structure model of α -GeSe, with the top and side views.

Here we will study the structural and electronic properties of α -GeSe surfaces using scanning tunneling microscopy and atomic force microscopy. Our experimental study is inspired by a recent density functional theory study by Hu et al.,³² which revealed that the electron density is very high at the Se atoms and very low at the Ge atoms. α -GeSe has a centered rectangular surface unit cell, but in the scanning tunneling microscopy images only a primitive cell is resolved. This experimental finding is in excellent agreement with the aforementioned density functional theory calculations. In addition, the α -GeSe surface, which is prepared by exfoliation under ambient conditions, is remarkably defect- and impurity free. This is in marked contrast to black phosphorus, which is very susceptible to the adsorption of water and oxygen. The outstanding properties of α -GeSe make this material a very appealing candidate for future electronic, optoelectronic, thermoelectronic devices.

6.2 Experimental detail

THE α -GeSe crystal was purchased from HQ Graphene (Groningen, The Netherlands). The lattice parameters of GeSe have been determined by X-ray diffraction measurements and are given by $a=3.8$ Å, $b=4.4$ Å and $c=10.8$ Å (a, b are in-plane and c is out-of-plane). Before the GeSe samples were transferred into the load-lock of our ultra-high vacuum system, a few layers of the GeSe crystal were peeled off using mechanical exfoliation. The main chamber of our ultra-high vacuum system is equipped with a room temperature Omicron scanning tunneling microscope (STM) and has a pressure of $\sim 3 \times 10^{-11}$ mbar. The topographic STM images were recorded in the constant current mode using electrochemically etched Pt/Ir STM tips. The dI/dV and dI/dz signals were obtained by a lock-in amplifier. The sample bias (dI/dV) or the z -piezo (dI/dz) were modulated with a small high frequency (1.89 kHz) sinusoidal signal with an amplitude of 18 mV and 10 mV, respectively. After the STM measurements, the sample was taken out of the ultra-high vacuum system and transferred to an ambient Bruker atomic force microscope (AFM). Kelvin probe force microscopy was used to determine the work function of GeSe. In order to obtain an accurate absolute value for the work function of GeSe we have used several reference materials (Si, Au and Al) with well-defined work functions. We have used silicon tips with a force constant of 0.4 N/m, a resonance frequency of 70 kHz and a tip radius

of about 2 nm.

The calculations in this research were performed using the first-principles calculation method based on density function theory (DFT) implemented in the CASTEP (Cambridge Serial Total Energy Package) code.^{37,38} The electron-core interaction and exchange-correlation potentials were treated using ultrasoft pseudo-potentials and the generalized gradient approximation (GGA) using the PW91 formula,^{39,40} respectively. The valence electrons of Ge and Se are given by $4s^2 4p^2$ and $4s^2 4p^4$, respectively. The k-point meshes in Brillouin zone were obtained using the special k-point sampling of the Monkhorst-Pack scheme. Furthermore, the thresholds for energy change per atom, maximum force, maximum displacement and maximum stress of converged structures were less than 5×10^{-6} eV/atom, 0.01 eV/Å, 5×10^{-4} Å and 0.02 GPa, respectively. To model the surface structures of GeSe, we have used the plane slabs method, in which periodic boundary conditions are applied to the surface supercell including a 10 Å thick vacuum region and a slab consisting of several atomic layers.⁴¹

6.3 Results and discussion

6.3.1 The structure of GeSe

IN Figure 6.1(a) a large scale AFM image of an α -GeSe surface is shown. Several step edges, which mainly run from the top of the image to the bottom of the image, can be discerned. The heights of these steps are ~ 0.5 nm, or multiples thereof. In Figure 6.1(b) a line profile across a single layer GeSe step with a height of 0.5 nm is shown.³⁶ A small scale atomically resolved STM image recorded at room temperature is displayed in Figure 6.1(c). A rectangular unit cell with dimensions 3.8 Å by 4.4 Å is clearly visible. A schematic model of the surface of α -GeSe is shown in Figure 6.1(d).

Since we do not observe a centered rectangular unit cell, but only a primitive rectangular unit cell in our filled-state STM images we conclude that only Se (or Ge) atoms are resolved. In order to determine which of the two types of atoms shows up in the filled-state STM images we first have a look at the electronic configurations of both atoms. Ge atoms and Se atoms have electronic configurations given by $[\text{Ar}]3d^{10}4s^24p^2$ and $[\text{Ar}]3d^{10}4s^24p^4$, respectively. Since (1) Se atoms have more valence electrons than Ge atoms and (2)

Se is more electronegative than Ge, we anticipate that the Se atoms appear more prominent in filled-state STM images than Ge atoms. Therefore, we arrive at the tentative conclusion that the observed primitive rectangular cell reflects the positions of the Se atoms. This finding is in excellent agreement with our density functional theory calculations (see Figure 6.2). In Figure 6.2 a simulated scanning tunneling microscopy image at a sample bias voltage of -1 V using the CASTEP code is displayed. As shown in Figure 6.2 the electron density at the Se atoms is very high, whereas the electron density at the Ge atoms is much lower. Figure 6.1(d) illustrates the structure model of α -GeSe, including a top view and a side view. The surface unit cells is outlined by the red dotted line. The primitive unit cell is comprised of two puckered layers, which are stacked on top of each other. The yellow and blue circles refer to the Se and Ge atoms, respectively. In the inset of Figure 6.1(c) a fast Fourier transfer pattern of the topographic STM data is shown. The surface lattice constants are $a=3.8$ Å and $b=4.4$ Å, respectively, which is in good agreement with experimental X-ray data.⁴²

In Figure 6.3(a) an atomically resolved filled-state STM image of an area of 40 nm by 25 nm is shown. The sample bias is -0.7 V and the tunneling current is 400 pA. The α -GeSe surface is remarkably free of defects and impurities. Moreover, it should be emphasized here that the α -GeSe surface is remarkably stable against oxidation and water adsorption since even after being exposed to ambient conditions for three weeks the surface is still defect- and impurity free. The small amplitude large scale waviness that is present in Figure 6.3(a) is very common for exfoliated two-dimensional materials. Simultaneously with the topography we also recorded the differential conductivity by modulating the sample bias with a small sinusoidal voltage (18 mV). The differential conductivity, dI/dV , image exhibits a slightly lower resolution than the topographic image. It is worthwhile to note that protrusions (depressions) in the topographic image show up as depressions (protrusions) in the differential conductivity. The reason for this inversion effect has to do with the apparent barrier height, which is larger at a protrusion than at a depression resulting in a smaller effective decay length at a protrusion. The spatial variation of the apparent height will show up in the differential conductivity as a background that is proportional to the inverted topographic image.

Figure 6.4(a) shows a large-scale STM topographic image. A dim, bright and flat region on the crystal surface are labeled by black, red and blue dashed

Figure 6.2: Simulated filled-state scanning tunneling microscopy image of the α -GeSe surface. The electron density at the Se atoms is substantially higher than that at the Ge atoms.

contours, respectively. The scanning tunneling spectra recorded at these regions are displayed in Figure 6.4(b). All three regions are semiconducting with a band gap of about 1 eV, which agrees pretty well a gap of 0.88 eV that we obtained by density functional theory calculations (see Figure 6.5). The differential conductivity curves of the three regions are shown in Figure 6.4(c). As noted before the dim regions exhibit a higher differential conductivity, i.e. higher local density of states, than the bright regions at the set point voltage (-0.7 V), which can be explained by the aforementioned inversion effect.

Figure 6.3: (a) STM topographic image of α -GeSe surface. Sample bias is -0.7 V and tunneling current is 0.4 nA. (b) Simultaneously recorded the dI/dV map using a lock-in amplifier (modulation voltage 18 mV and oscillation frequency 1.89 kHz).

Figure 6.4: (a) STM topographic image of an α -GeSe surface. Scanning size: $50\text{nm} \times 50\text{nm}$. (b) STS spectra of a dim, bright and flat region. All spectra were averaged over 200 spectra (c) Differential conductivities of the dim, bright and flat regions.

6.3.2 The work function and defects

THE work function of the α -GeSe substrate has been determined by Kelvin probe force microscopy. In order to determine the absolute value of the work function of α -GeSe we have first measured the contact potential difference between the AFM tip and three reference samples, (Si, Al and Au), which have well-defined work functions.⁴³ We found a work function of 4.7 eV for α -GeSe, which agrees well with earlier measurements by Song et al.⁴⁴

Although the α -GeSe surface is surprisingly defect- and impurity free we occasionally observe tiny depressions (see Figure 6.6(a), where two of these tiny depressions are outlined by a blue circle). These tiny depressions are located in the center of the rectangular unit cells, i.e. at the location of a top layer Ge atom. In Figure 6.6(b) a spatial map of dI/dz of the same area as depicted in Figure 6.6(a) is shown. Following the theory from Tersoff and Hamann,⁴⁵ the tunneling current I and probability $T(V, E, z)$ are given by,

$$I = C \int_0^{eV} \rho_t(E - eV) \rho_s(E) T(V, E, z) dE \quad (6.1)$$

Figure 6.5: Electronic band structure of bulk GeSe.

and

$$T(V, E, z) = \exp\left(-2\frac{\sqrt{2m}}{\hbar}z\sqrt{\phi_A + \frac{eV}{2} - E}\right) \quad (6.2)$$

respectively. C is a proportionality constant, e is the elementary charge and V is the applied voltage between the tip and sample. ρ_t and ρ_s are the density of states of the tip and sample, respectively. E and z are the electron energy and the tip-sample distance, respectively. m is the electron mass and ϕ_A is the local apparent barrier height. Using equations (6.1) and (6.2) it is straightforward to derive an expression for dI/dz ,

$$\frac{dI}{dz} = C \int_0^{eV} \rho_t(E - eV) \rho_s(E) \frac{T(V, E, z)}{dz} dE \approx \frac{2\sqrt{2m}}{\hbar} I \sqrt{\phi_A} \quad (6.3)$$

where, $\phi_A = (\phi_s + \phi_t)/2$, ϕ_s and ϕ_t are the work functions of the sample and tip, respectively. Since the tunneling current is kept constant the dI/dz signal is directly proportional to the local work function, i.e. the apparent barrier height. Interestingly, the two tiny defects do not show up in the dI/dz map. Based on these observations, we arrive at the conclusion that the tiny depressions are caused by missing Ge atoms in the top layer. This invisibility

Figure 6.6: (a) Atomically resolved STM topographic image of an α -GeSe surface with two vacancies. Scanning size: $9\text{ nm} \times 9\text{ nm}$. (b) dI/dz map of the same area as in panel (a) with a modulation voltage of 10 mV. Sample bias is -0.8 V and tunneling current is 0.5 nA.

of the Ge atoms in the scanning tunneling microscopy measurements is in line with the density functional theory calculations of Hu et al..³²

6.4 Conclusions

THE structural and electronic properties of the α -GeSe surface has been investigated with atomic force microscopy, scanning tunneling microscopy and spectroscopy. Filled-state scanning tunneling microscopy images only reveal the Se atoms in the top layer resulting in a primitive rectangular surface unit cell with lattice constants of 3.8 Å and 4.4 Å, respectively. Scanning probe spectroscopy measurements reveal that α -GeSe is a p -type semiconductor with a band gap and work function of 1.0 eV and 4.7 eV, respectively,. The surface of α -GeSe is surprisingly defect and impurity free. The most abundant defect that we found is a missing Ge atom in the top layer. The moderated band gap, the high quality of the α -GeSe surface and stability in air makes this two-dimensional material an appealing candidate for technological applications.

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Determination of the Fermi velocity of graphene on MoS₂ using dual mode scanning tunneling spectroscopy

In this chapter, the Fermi velocity of graphene on MoS₂ is measured by dual mode scanning tunneling spectroscopy. In this method, the tunnel current (I) and the derivative of the current to the gap width (dI/dz) are measured simultaneously as a function of sample bias (V) at constant tip-substrate distance. Owing to the difference in lattice constants between graphene (2.461 Å) and MoS₂ (3.161 Å), a moiré structure is found with a periodicity of 1.07 nm and a twist angle of 4°. These experiments reveal that the electronic band structure of graphene remains intact in the band gap region of MoS₂. The Fermi velocity of graphene on MoS₂ is determined to be $1.2 \pm 0.1 \times 10^6 \text{ m/s}$.

This chapter is based on Jiao, Z. and Zandvliet, H. J. W. Applied Physics Letters, 118(16), 163103 (2021).

7.1 Introduction

THE successful isolation of a single layer graphene, the first two-dimensional material, has led to a true revolution in contemporary condensed matter physics.^{1,2} In the wake of the success of graphene there have been many efforts to synthesize other elemental two-dimensional materials that have properties similar to graphene.³⁻⁵ One of the most eye-catching properties of graphene is its linear dispersion relation. Owing to this linear dispersion relation, the electrons behave as massless realistic particles. The Fermi velocity, is, however, only a small fraction of the speed of light. The Fermi velocity, which can be extracted from angle-resolved photoemission or quasi particle interference experiments, is one of the key parameters of graphene as it bears information on a broad range of fundamental properties. One of the intriguing properties of graphene is that the Fermi velocity increases with increasing electron-electron interaction.⁶ The latter is in marked contrast with conventional Fermi liquids, where the Fermi velocity decreases with increasing electron-electron interactions. The Fermi velocity of graphene can in principle be tuned by varying the charge carrier concentration. Owing to the logarithmic dependence of the Fermi velocity on the charge carrier concentration the Fermi velocity can, unfortunately, only be varied over a small range. There are however other ways to tailor the Fermi velocity of graphene, such as introducing a periodic potential,⁷ coupling to a dielectric substrate⁸⁻¹⁰ and twisting and/or bending of the graphene sheet.^{11,12}

The graphene revolution is not only accompanied by many exciting and intriguing scientific discoveries, but it has also led to numerous proposals for potential applications of graphene.¹³ As an application or device that is based on a single layer free-standing of graphene is not very tractable, graphene has to be placed on a support. During the past decade many substrates for graphene have been scrutinized. Metal substrates are not a good choice as the electronic states of the metal can hybridize with the electronic states of graphene near the Fermi level. This hybridization will, most likely, destroy the unique electronic properties of graphene. In order to decouple the key electronic states of graphene from its underlying substrate, a material with a band gap is required. A frequently used substrate for graphene is SiO₂. However, even this band gap material can have detrimental effects on the electronic properties of graphene. Due to the roughness of SiO₂ also the graphene sheet becomes corrugated. The local curvature effects in graphene

can lead to large pseudo magnetic fields, as high as 100 Tesla.¹⁴ In addition, charged defects and impurities in the SiO₂ layer lead to charge puddles, which results in a decrease of the charge carrier mobility. A substrate that is completely flat, possesses a large band gap (6 eV) and has the same honeycomb structure as graphene, is hexagonal boron nitride (*h*-BN).¹⁵ *h*-BN seems to be the ideal substrate for graphene as it also belongs to the class of two-dimensional Van der Waals materials. There is, however, a downside of using *h*-BN as a substrate for graphene. The lattice constants of graphene and *h*-BN differ only by 1.8%, which results in the formation of relatively large moiré patterns. The periodicity of these moiré patterns depends on the exact twist angle between graphene and *h*-BN and can be large as 13.9 nm. The moiré structure results in a weak periodic potential in the graphene layer. In the case of massless Dirac fermions the chirality of the charge carriers prevents the opening of a band gap, but instead the moiré structure gives rise to the development of additional Dirac cones in the electronic band structure.¹⁵ The larger the moiré periodicity, the closer the new Dirac cones move towards the Fermi level of the graphene and the more they affect the properties of the low energy electrons of graphene. It would therefore be very beneficial to search for other Van der Waals band gap materials that have a larger mismatch with graphene as this results in smaller moiré structures. The transition metal chalcogenides is a class of two-dimensional materials that can be considered as an appealing substrate for graphene.^{16–20} The interaction between graphene and transition metal chalcogenides is expected to be very weak as both materials belong to the class of two-dimensional Van der Waals materials. In addition, transition metal chalcogenides can be exfoliated and are therefore usually extremely flat. The graphene/MoS₂ Van der Waals heterostructure exhibits a high charge carrier mobility²¹ and the MoS₂ substrate is gapped.^{22,23} The combination of these properties makes the graphene/MoS₂ system very appealing for technological applications, such as field-effect based devices,^{24,25} memory cells^{26,27} and energy harvesting.²⁸

In this chapter, we will scrutinize the structural and electronic properties of graphene on MoS₂. We will first demonstrate that the linear band structure of graphene remains intact in the band gap region of the MoS₂ substrate. Subsequently, we will determine the Fermi velocity of graphene using dual mode scanning tunneling spectroscopy. Our method has a spatial resolution down to the atomic scale and does not require the presence of scattering centers, as is needed for quasi particle interference measurements.

7.2 Experimental and theory details

THE experiments were performed in an ultra-high vacuum system with a base pressure below 3×10^{-11} mbar that is equipped with a scanning tunneling microscope (Omicron STM-1). The MoS₂ samples were purchased from HQ graphene and the graphene samples were obtained from Graphenea, respectively. Prior to the transfer of a monolayer of graphene to the MoS₂ substrate, we peeled off a few layers from the MoS₂ substrate by mechanical exfoliation. Electrochemically etched Pt/Ir tips were used for the scanning tunneling microscopy and scanning tunneling spectroscopy measurements. Graphene monolayers were transferred to MoS₂ via the solvent transfer technique (the detail can be seen in Chapter 2.4). In order to measure the $dI(V)/dz$ signal during the conventional open-feedback loop $I(V)$ measurements we have applied a small sinusoidal signal with an amplitude of 30 mV and a frequency of 543 Hz to the z-piezo.²⁹ The $dI(V)/dz$ signal was measured with a Stanford Research Systems SR830 lock-in amplifier. The dI/dV signal was obtained by taking the numerical derivative of the $I(V)$ curve.

7.3 Results and discussion

7.3.1 Moiré pattern

As a 2D material, MoS₂ consists of trilayers, i.e. one layer of Mo atoms sandwiched between two S layers. In nature, MoS₂ occurs in two phases the so-called 2H and 3R phases. The 2H phase, which we consider here, has a hexagonal symmetry, whereas the 3R phase exhibits a rhombohedral symmetry. There is a third, metastable, phase which is referred to as the 1T-MoS₂ phase. This phase is metallic and has a tetragonal symmetry.

In Figure 7.1 an empty state scanning tunneling microscopy image of the bare MoS₂ substrate is shown. The MoS₂ surface is quite defect and impurity free. The most abundant defects are missing S atoms with a typical density of about 3×10^{-3} nm⁻². A fast Fourier transform of the scanning tunneling microscopy image (see inset) shows the hexagonal symmetry of the MoS₂ substrate.

Since graphene and MoS₂ are both very flat and have a honeycomb structure. The lattice constant of MoS₂ is 3.161 Å, which is substantially larger

than the lattice constant of graphene (2.461 Å). Owing to this relatively large lattice mismatch, the predicted maximum moiré periodicity is only several times of lattice constant and therefore the new Dirac cones are located far away from the Fermi level. Before discussion the structural model, we first elaborate on the moiré periodicity for graphene on MoS₂. The periodicity of the moiré structure, λ , can be determined using,¹⁵

Figure 7.1: Scanning tunneling microscopy image (15 nm by 15 nm) of the pristine MoS₂ substrate. Sample bias is 1.5 V and tunnel current is 1.1 nA. The inset shows the fast Fourier transform.

$$\lambda = \frac{a(1 + \delta)}{\sqrt{\delta^2 + 2(1 + \delta)(1 - \cos \theta)}} \quad (7.1)$$

where $a=2.46$ Å is the lattice constant of graphene, $b=3.161$ Å the lattice constant of MoS₂, $\delta = \frac{b-a}{a}$ the lattice mismatch and θ the rotation angle between the graphene and MoS₂ honeycomb lattices.

According to the equation (7.1), the wavelength of moiré pattern decrease with increasing rotation angle. The maximum moiré periodicity, which occurs at a rotation angle of 0°, is 1.107 nm. Interestingly, the moiré pattern for hexagonal-hexagonal heterostructure include three different positions, which

named AA, AB and BA, respectively. Especially for twist bilayer graphene, the domain walls between AB and BA regions exhibit topologically protected states.^{30,31} In this case, MoS₂ substrate consists of trilayers, i.e. one layer of Mo atoms sandwiched between two S layers. Hence, the AB_S and BA_{Mo} regions in Figure 7.2(d) can clearly observe the contrasting color, corresponding to black and green, respectively. This can be further demonstrated by the red rhombus frame drawn in Figure 7.2(b). Here the four vertices of the rhombus represent to AA points, and the remaining two triangular areas with different brightness are AB_S and BA_{Mo}, respectively.

In Figure 7.2 a filled state (a) and empty state (b) scanning tunneling microscopy image of graphene on MoS₂ is shown. Both images show a moiré superstructure with a periodicity of 1.07 nm. Interestingly, as shown by the blue dotted line in Figure 7.2 (b), the orientation of moiré pattern with 4 rotation angle is different from the orientation of the carbon atoms. This results appear to make sense and to be compatible with our theoretical expectations. In Figure 7.2(c) a fast Fourier transform of panel (b) is shown. The spots of the hexagonal (1×1) unit cell of graphene are highlighted by green circles, whereas the spots belonging to the moiré superstructure are highlighted by white circles. The white and green lines in Figure 7.2(c) reveal that there is a rotation angle of about 4° between the graphene and the moiré unit cells. Replicas of the moiré spots are also visible around the spots of the (1×1) graphene unit cells. In addition, other examples shown in Figure 7.3 and 7.4 are consistent with previous result. According to the wavelength, their rotation angle correspond to 5° and 2.5° , respectively. Among them, STM topography images of graphene on MoS₂ under different bias voltage shows the same rhombus moiré pattern. The difference is that the moiré pattern under different bias voltage shows empty or filled states.

7.3.2 Determination of the Fermi velocity

IN order to obtain more information on the electronic structure we have recorded $I(V)$ curves on the bare MoS₂ substrate as well as on the graphene/MoS₂ regions. As shown in Figure 7.5(a), the MoS₂ is n -type semiconductor and has a band gap of about 1.1 eV. The density of states of the graphene layer reveals a V -shaped density of states, which is one of the hallmarks of a two-dimensional Dirac materials. The Dirac point is located at -0.08 eV. Since the scanning tunneling spectra are recorded at room temperature the V -shaped dI/dV curve is a bit rounded near the Dirac point. In addition,

Figure 7.2: (a)-(b) Scanning tunneling microscopy of graphene on MoS₂ recorded at a sample bias of -0.8 V (a) and 0.8 V (b). A moiré superstructure with a periodicity of 1.07 nm is observed. The unit cell is outlined by the red lines in (b). The rotation angle between the graphene and MoS₂ substrate is 4°. (c) Fast Fourier transform of image (b). The spots in the green circles corresponds to the (1 × 1) unit cell of graphene. The spots in the white circles are due to the moiré superstructure. The two hexagonal set of spots are rotated by 4°. (d) Ball-and-stick model of the moiré pattern. The unit cell (red lines) and alignment along one of the high symmetry directions of graphene (dotted blue line) are highlighted in panels (b) and (d).

Figure 7.3: STM and FFT images of the graphene on MoS₂ substrate with a 5 degree rotation angle. The set point parameters are: $V = -0.4\text{V}$, $I = 1.0\text{ nA}$ (a),(c); $V = 0.4\text{V}$, $I = 1.0\text{ nA}$ (b),(d).

Figure 7.4: STM images of the graphene on MoS₂ substrate with a 2.5 degree rotation angle. The set point parameters are: $V = -0.6\text{V}$, $I = 1.0\text{ nA}$ (a), $V = -0.3\text{V}$, $I = 1.0\text{ nA}$ (b); $V = 0.3\text{V}$, $I = 1.0\text{ nA}$ (c); $V = 0.6\text{V}$, $I = 1.0\text{ nA}$ (d).

near the valence and conduction band edges of the MoS₂ substrate the slope of the dI/dV signal of graphene gradually increases.

Figure 7.5: (a) Differential conductivity (dI/dV) of the bare MoS₂ substrate (blue curve) and graphene of MoS₂ (red curve) versus sample bias (V). The inset point of the IV curves are MoS₂ 1 V and 400 pA, graphene -0.8 V and 1 nA. Inset $(dI/dV)/(I/V)$ of graphene versus V. (b) Schematic representation of electronic band structure of graphene on MoS₂ in reciprocal space. The blue lines correspond to the maximum of the valence band and minimum of the conduction band of MoS₂. The red lines represent the Dirac cone of graphene. The grey area corresponds to the region where E_q (6) is applicable. The Dirac point is located at -0.08 ± 0.02 eV. (c) squared normalized inverse decay length, $\kappa^2/\kappa^2(-0.35V)$, versus V. The dotted lines are fits using equation (7.9) with $\nu_F = 1.1 \times 10^6$ m/s (blue curve) $\nu_F = 1.2 \times 10^6$ m/s (red curve) and $\nu_F = 1.3 \times 10^6$ m/s (green curve).

In Figure 7.5(b) a schematic representation of the band structure of graphene and MoS₂ is given. The blue lines corresponds to the minimum of the conduction band and the maximum of the valence band of bulk MoS₂. The Dirac point of graphene is located at the *K* point at an energy of -0.08 V. The Dirac points falls in the band gap of the MoS₂ substrate. In order to obtain more information on the electronic band structure of graphene on MoS₂ we recorded dual $I(V)$ and $dI(V)/dz$ spectra. As mentioned before the $I(V)$ spectrum provides information on the density of states. The $dI(V)/dz$ spectrum provides information on the band structure, particularly on the dispersion of the energy bands. In principle the dispersion relation of the low-energy electrons can also be determined by angle-resolved photo-emission or quasi-particle interference, a scanning tunneling microscopy technique that measures the electron standing wave patterns in the vicinity of scattering centers such as

defects, impurities and step edges. Our method relies on dI/dz spectroscopy, a technique that has been introduced more than three decades ago by Feenstra, Stroscio and Fein.^{32,33} These authors have shown that the inverse decay length, which can be extracted from the dI/dz signal, bears information on the parallel momentum of the electrons that are involved in the tunneling process.

Before elaborating on experimental results we will first introduce the method we have used to extract information of the dispersion relation of the low-energy electrons in graphene. The tunneling current as a function of applied bias voltage V and tip-sample separation z can be approximated by a simple one-dimensional model of the tunnel barrier. In this simple model the tunnel current is given by,

$$I(z, V) = \int_0^{eV} \rho_s(E) \rho_t(E - eV) e^{-2\kappa z} dE \quad (7.2)$$

where E is the energy of the electrons and $\rho_{s,t}$ the density of states of substrate and tip, respectively. The inverse decay length, κ , is given by,

$$\kappa = \sqrt{\frac{2m^*}{\hbar^2}(\bar{\phi} + \frac{eV}{2} - E) + k_{//}^2} \quad (7.3)$$

where m^* is the effective mass of the electron, $\hbar$ the reduced Planck constant, $\bar{\phi} = \frac{\phi_s + \phi_t}{2}$ the average work function of substrate and tip and $k_{//}$ the shift in parallel momentum that the electrons encounter when they tunnel from tip to substrate or vice versa. For small sample biases, i.e. $eV \ll \bar{\phi}$, the derivative of the tunnel current to the gap width is given by,

$$\left(\frac{dI}{dz}\right)_V = \int_0^{eV} \rho_s(E) \rho_t(E - eV) \frac{d}{dz} e^{-2\kappa z} dE = -2\kappa I \quad (7.4)$$

In the band gap region of MoS₂, the parallel momentum of the low energy electrons of graphene is given by,

$$k_{//} = \Gamma K - K = \frac{4\pi}{3a} - k \quad (7.5)$$

where the length of the ΓK vector is $4\pi/3a$, where $a=0.2461$ nm is the lattice constant of graphene and k the wave vector of the Dirac electrons with respect to K . The dispersion relation of the low-energy electrons in graphene is given by,

$$E - E_D = \hbar\nu_F k \quad (7.6)$$

where E_D is the Dirac point of graphene and ν_F is the Fermi velocity. By inserting Equation (7.4)-(7.5) in Equation (7.2) we find,

$$\kappa(V) = \sqrt{\left[\frac{2m^*}{\hbar^2} (\bar{\phi} + \frac{eV}{2} - E) + \left(\frac{4\pi}{3a} - k \right)^2 \right]} \quad (7.7)$$

By inserting $E = eV$ and $k = \frac{E - E_D}{\hbar\nu_F}$ we finally find,

$$\kappa^2(V) = \left[\frac{2m^*}{\hbar^2} (\bar{\phi} - \frac{|eV|}{2}) + \left(\frac{4\pi}{3a} - \frac{(|eV| - E_D)}{\hbar\nu_F} \right)^2 \right] \quad (7.8)$$

Since in our case $V < 0, E_D < 0$ and $|V| > |E_D|$ we finally find,

$$\begin{aligned} \kappa^2(V) = \frac{2m^*}{\hbar^2} \bar{\phi} + \left(\frac{4\pi}{3a} \right)^2 + \left(\frac{E_D}{\hbar\nu_F} \right)^2 - \left(\frac{m^*}{\hbar^2} + \frac{8\pi}{3a\hbar\nu_F} + \frac{2|E_D|}{\hbar^2\nu_F^2} \right) |eV| \\ + \frac{8\pi|E_D|}{3a\hbar\nu_F} + \left(\frac{eV}{\hbar\nu_F} \right)^2 \end{aligned} \quad (7.9)$$

In Figure 7.5(c) the squared normalized inverse decay length, $\kappa^2(V)/\kappa^2(V_0)$, is plotted versus the sample bias V . As a reference we have used the inverse decay length at $V_0 = -0.35V$. The experimental $\kappa^2(V)/\kappa^2(V_0)$ is fitted model by equation (7.9). The Dirac point is located to -0.08 V, see Figure 7.2a. In the range of voltages that we consider here ($[-0.35 \text{ V}, -0.8 \text{ V}]$) the term proportional to V^2 is much smaller than the term proportional to V and therefore the fitted curve is almost linear. The term that is linear in V is dominated by the $\frac{8\pi}{3a\hbar\nu_F}$ term. The other two terms, i.e. the $\frac{m^*}{\hbar^2}$ and $\frac{2E_D}{(\hbar\nu_F)^2}$ terms are, of course, included in the fitting, but their contribution to the fitting of the Fermi velocity is negligible.

The Fermi velocity is predicted to be inversely proportional to the relative dielectric constant.⁸ The relative dielectric constant for graphene on a MoS₂ substrate can be approximated by the average dielectric constants of the media at both sides of the graphene sheet, i.e. $\epsilon_{Gr} = \frac{\epsilon_{MoS_2} + \epsilon_{vac}}{2}$ ($= 2.5$). The Fermi velocity that we extracted from our fit ($1.2 \pm 0.1 \times 10^6 \text{ m/s}$) agrees very well with available experimental data and theoretical calculations.^{34,35}

The energy dispersion can also be measured with other techniques, such as angle-resolved photoemission spectroscopy and quasi particle interference.

Angle-resolved photoemission spectroscopy can only probe filled-states and does not exhibit the high spatial and energy resolution that our technique offers. Quasi particle interference has the same spatial and energy resolution, but this technique needs the presence of defects, impurities and/or steps, which can affect the local electronic structure.

7.4 Conclusion

IN conclusion, we have presented a method that allows to determine the Fermi velocity of graphene on a band gap substrate. The method relies on a measurement of the sample bias dependent inverse decay length in a tunneling junction. The method provides an accurate estimate of the Fermi velocity because it is rather insensitive to the key tunneling parameters, such as the effective mass and the work function of tip and substrate. We have found a Fermi velocity of $1.2 \pm 0.1 \times 10^6$ m/s for graphene on MoS₂. The Fermi velocity we have extracted is higher than that of free-standing graphene owing to the dielectric screening of the MoS₂ substrate and agrees very well with available experimental data. Our method is also applicable to single component crystalline substrates as well as systems where a single or bilayer of a material is placed on a substrate.

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Summary and Outlook

IN this thesis we have studied several 2D materials as well as a few Van der Waals heterostructures. The most famous and probably also most promising 2D material is graphene. Graphene can be found in Nature and the material is stable against ambient conditions, which is extremely beneficial for technological applications. Unfortunately, graphene also has one severe drawback: it is gapless and therefore pristine graphene cannot be used for field-effect based device applications. Owing to its flat honeycomb lattice the application of a transversal electric field does not result in the opening of a bandgap. There have been several successful attempts to open a bandgap in graphene, however this bandgap opening often goes at the expense of the high charge carrier mobilities in graphene. As an alternative for graphene we have studied in this project germanene. Germanene, the germanium analogue of graphene, is also a 2D Dirac material that hosts Dirac fermions, but the honeycomb lattice is buckled. This buckling allows the opening of bandgap by applying an external transversal electric field. This electric field results in a shift of charge from one triangular sub-lattice to the other sub-lattice. Compared to graphene, germanene also suffers from two major drawbacks. The first, and major, drawback of germanene is that the material does not occur in Nature and therefore it has to be grown or synthesized on a suitable substrate. As has been pointed out in this thesis it is of key importance to select a suitable substrate. The ideal substrate for germanene is a 2D Van der Waals material with a substantial bandgap. This bandgap leaves the key electronic states of germanene, which are located in the vicinity of the Fermi level, intact as there are no electronic states from the substrate to hybridize with. In this thesis we show that molybdenum disulfide is a suitable substrate for germanene. The second drawback of germanene is that the material is not stable under ambient conditions. Exposure of germanene to air will lead to oxidation of the material. In order to protect germanene against oxidation the material can be capped or encapsulated by another material. The ideal capping or encapsulating material is hexagonal boron nitride. Hexagonal

boron nitride is a 2D Van der Waals material with a bandgap of about 6 eV. Owing to time constraints we were, unfortunately, not able to study the encapsulation of germanene in this project.

In the first part of the thesis we have scrutinized the growth of germanium on molybdenum disulfide in order to resolve the still outstanding question whether the Ge atoms prefer to intercalate between the MoS₂ layers or rather form Ge islands on-top of the MoS₂ substrate. Based on our scanning tunneling microscopy study we arrive at the conclusion that there are three key factors that govern the growth of this system: (1) the defect concentration of the MoS₂ substrate, (2) the growth temperature and (3) the deposition rate. For a low defect concentration, a low deposition rate and a high growth temperature the Ge atoms have a high probability to find an intercalation portal in the molybdenum disulfide substrate and intercalate before meeting another Ge atom or a defect. For a high defect concentration, a high deposition rate and a low temperature there is fair change that the deposited Ge atoms find a defect or another Ge atom and nucleate on the molybdenum disulfide substrate before they find an intercalation portal in the MoS₂ substrate. In a series of experiments we show that both cases, i.e. intercalation and growth on-top, do indeed occur. In addition, we have investigated the electronic inhomogeneity of germanene grown on molybdenum disulfide. Using scanning tunneling spectroscopy we have recorded spatial maps of the Dirac point of germanene. We observed charge puddles in the germanene sheet. The Dirac point varies from -30 meV to +15 meV, corresponding to a charge density in the puddles in the range of 2.6×10^{-3} electrons to 6.6×10^{-4} holes per nm². The radius of these puddles is about 10-20 nm, resulting in a total charge of the order of one charge carrier per puddle. We found that the defect concentration in the top layer of the molybdenum disulfide substrate is very comparable to the density of charge puddles. These findings show that, despite the weak Van der Waals interaction between germanene and molybdenum disulfide, even a single charged defect in the molybdenum disulfide substrate can have a substantial effect on the electronic properties of germanene.

The first part of the thesis is completed with a theoretical study of the effect of an external transversal electric field on the quantum state of matter of 2D Dirac material with a buckled honeycomb structure. Due to the broken symmetry of the buckled honeycomb lattice charge can be shifted from one triangular sub-lattice to the other triangular sub-lattice. This charge shift

results in a change of the bandgap of the 2D Dirac material. In the absence of an electric field the material has a spin-orbit gap. With increasing electric field this bandgap first closes and then reopens again. For small electric fields the 2D Dirac material is a 2D topological insulator, but beyond the critical electric field where the gap closes the material becomes a regular band insulator.

In the second part of the thesis we studied germanium selenide (GeSe). GeSe, which is a semiconductor that belongs to the group-VI transition metal monochalcogenides. GeSe has never been imaged with atomic resolution and therefore our study provides the first atomically resolved real-space images. We found that the GeSe surface has a centered rectangular unit cell with dimensions $a=3.8 \text{ \AA}$ and $b=4.4 \text{ \AA}$, respectively. Filled-state scanning tunneling microscopy images only reveal the positions of the Se atoms, whilst the Ge atoms cannot be resolved. The GeSe surface is remarkably defect-free, apart from some missing Ge atoms in the top layer. Scanning tunneling spectroscopy show that the semiconducting GeSe surface is *p*-type with a band gap of about 1 eV. We have managed to put single graphene layers on the GeSe substrate, but unfortunately the heterostructure was not clean enough for the development of moiré patterns. Owing to these difficulties we have decided not to present these results in this thesis.

In the last chapter of this these we have studied the properties of a single layer of graphene on a molybdenum disulfide substrate. Both materials have a honeycomb lattice, but the lattice constant differs substantially (0.316 nm for molybdenum disulfide versus 0.246 nm for graphene). The relatively large difference in lattice constants results in relatively small moiré unit cells that do not exceed 1.2 nm. Despite the fact that (1) molybdenum disulfide is a band gap material and (2) molybdenum disulfide graphene only weakly interact with each other, we found that the low-energy bands of graphene are affected by the molybdenum disulfide. In order to study the electronic band structure of the graphene on the MoS₂ we have developed a novel spectroscopic scanning tunneling technique. Using this novel scanning tunneling technique we found that the Fermi velocity of graphene is about $1.3 \times 10^6 \text{ m/s}$, which is about 20% higher than the Fermi velocity of pristine graphene. The increase in the Fermi velocity is explained by the dielectric screening of the molybdenum disulfide. This is interesting as electron-electron interactions in conventional 2D electron gases result in a decrease of the Fermi velocity. We believe our newly developed technique is also applicable to many other 2D

Van der Waals heterostructure systems.

Samenvatting

HET proefschrift dat nu voor u ligt heeft betrekking op een studie van een aantal tweedimensionale materialen en Van der Waals heterostructuren. Het meest bekende tweedimensionale materiaal is zonder twijfel grafeen. Grafeen komt in de Natuur voor en is stabiel in de open lucht, hetgeen zeer prettig is voor technologische toepassingen. Helaas heeft grafeen ook een groot nadeel: het materiaal heeft geen band gap, waardoor het niet geschikt is voor veld-effect gerelateerde toepassingen. Vanwege de vlakke honingraatstructuur leidt een aangelegd elektrisch veld niet tot de opening van een band gap. Er zijn meerdere succesvolle pogingen gedaan om een band gap in grafeen in te openen, maar de opening van een band gap in grafeen ging altijd ten koste van de hoge mobiliteit van de ladingsdragers. In dit project hebben we o.a. germaneene bestudeerd. Germaneene, de germanium versie van grafeen, is een ook een tweedimensionaal Dirac materiaal, maar het honingraatrooster is niet vlak, maar gerimpeld. Deze gerimpelde structuur maakt het mogelijk om met een uitwendig elektrisch veld een band gap te openen. Het elektrische veld zorgt voor een ladingsverschuiving van het ene hexagonale sub-rooster naar het andere hexagonale sub-rooster. Helaas heeft ook germaneene een paar nadelen. Ten eerste, germaneene komt niet in de Natuur voor en daarom dient dit materiaal gesynthetiseerd te worden. Het vinden van een geschikt substraat voor de synthese is de grote uitdaging. Een geschikt substraat voor germaneene is een Van der Waals materiaal met een band gap. Deze band gap is nodig om de elektronische toestanden in de buurt van het Fermi niveau van het germaneene te ontkoppelen van het onderliggende substraat. In dit proefschrift tonen we aan dat molybdenum disulfide een geschikt substraat is voor germaneene. Een tweede nadeel van germaneene is dat het niet stabiel is in de open lucht. Germaneene oxideert zeer snel en daarom is het belangrijk het germaneene te bedekken met een ander materiaal zodat het germaneene beschermd wordt tegen oxidatie. Een geschikt materiaal hiervoor is hexagonaal boron nitride. Hexagonaal boron nitride is een Van der Waals materiaal met een band gap van ongeveer 6

eV. Helaas hebben wij in dit project de bescherming van het germaneene niet kunnen onderzoeken.

In het eerste gedeelte van dit proefschrift hebben we de groei van germaneene op molybdenum disulfide (MoS_2) onderzocht. De centrale vraag is of het germanium op het MoS_2 substraat groeit, of liever onder een MoS_2 laag kruipt. Wij hebben laten zien dat beide scenario's in principe mogelijk zijn. Welk scenario optreedt hangt af van: (1) de defectconcentratie in het MoS_2 substraat, (2) de groei temperatuur en (3) de depositiesnelheid. Voor een hoge defectconcentratie, een hoge depositiesnelheid en een lage temperatuur bestaat er een grote kans dat germaniumatomen elkaar treffen en een groeikern vormen op het oppervlak, voordat ze de kans krijgen om onder een MoS_2 laag te kruipen. We hebben daarnaast ook gekeken naar de vorming van ladingspoelen in het germaneene. Deze ladingspoelen hebben een typische grootte van 10-20 nanometer en kunnen zowel elektronen als gaten bevatten. Het totaal aantal ladingsdragers per poel is ongeveer 1. We vonden dat de defectconcentratie in het MoS_2 substraat erg vergelijkbaar is met de concentratie van ladingspoelen. Dit laatste versterkt de aanname dat de ladingspoelen in het germaneene veroorzaakt worden door de defecten in het MoS_2 substraat. In het eerste gedeelte van het proefschrift hebben we ook gekeken naar het effect van een extern elektrisch veld op de elektronische eigenschappen van een tweedimensionaal Dirac materiaal met een gerimpelde honingraatstructuur. Door de gebroken symmetrie van het gerimpelde honingraatstructuur wordt lading van het ene hexagonale sub-rooster naar het andere hexagonale sub-rooster verschoven. Vanwege spin-orbit koppeling heeft het materiaal bij afwezigheid van een elektrisch veld een kleine band gap. Bij toenemende elektrisch veldsterkte sluit deze band gap eerst om vervolgens weer te openen. Bij de heropening van de band gap ondergaat het materiaal een topologische faseovergang van een tweedimensionaal Dirac materiaal naar een normaal band gap materiaal.

In het tweede gedeelte van proefschrift hebben het materiaal germanium selenide (GeSe) bestudeerd. GeSe is een halfgeleider die behoort tot de groep van VI transition metal monochalcogeniden. Dit materiaal is nog nooit eerder met atomaire resolutie afgebeeld. We laten zien dat GeSe een gecentreerde rechthoekige eenheidscel heeft met afmetingen van 3.8 Ångström bij 4.4 Ångström. Scanning tunneling microscopy afbeeldingen van de gevulde toestanden laten alleen de Se atomen zien. Het GeSe is opmerkelijk defect-vrij afgezien van enkele missende Se atomen. Scanning tunneling spectroscopie

metingen tonen aan dat GeSe een *p*-type halfgeleider met een band gap van ongeveer 1 eV. Vervolgens hebben we een grafeen laag op het GeSe substraat gedeponneerd. Vanwege de vele verontreinigen is het ons niet gelukt om een moiré structuren te realiseren. In het laatste hoofdstuk van dit proefschrift hebben we de structurele en elektronische eigenschappen van een grafeen laag op een MoS₂ substraat bestudeerd. Beide materialen hebben een honingraatstructuur, maar de roosterconstanten zijn substantieel anders (2.46 Ångström voor grafeen en 3.16 Ångström voor MoS₂). Ten gevolge van dit grote verschil in roosterconstanten kunnen de moiré eenheidscellen niet groter worden dan 1.2 nm. Ondanks het feit dat (1) MoS₂ een band gap materiaal is en (2) MoS₂ en grafeen een zwakke interactie vertonen, vonden we dat de elektronische toestanden van grafeen toch werden beïnvloed. Door gebruik te maken van een nieuw ontwikkelde spectroscopische techniek vonden we dat de Fermi snelheid van de elektronen in grafeen op MoS₂ ongeveer 20% hoger is dan voor puur grafeen. De toename van de Fermi snelheid wordt veroorzaakt door de dielektrische screening van MoS₂. Dit is een interessant omdat elektron-elektron interacties in conventionele tweedimensionale elektron gassen aanleiding geven tot een reductie van de Fermi snelheid. We zijn er van overtuigd dat onze nieuw ontwikkelde techniek ook toegepast kan worden op andere tweedimensionale Van der Waals heterostructuren.

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