### *Towards Spin Injection in Graphene by the Use of an MoS*<sub>2</sub> *Tunnel Barrier*

a thesis presented by Firoz Reinders to The Faculty of Mathematics and Natural Sciences

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE IN THE SUBJECT OF PHYSICS

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#### Abstract

In this thesis, we focused on a novel device that uses materials beyond those conventionally used to study spin transport in graphene.

For this, we used two dimensional materials that are structurally compatible with graphene and have tunable electronic transport properties. The basic objective was to tune the contacts so as to achieve efficient tunneling transport into graphene.

One key material used in this direction is the metal transition dichalcogenide  $MoS_2$ , due its relative ease in preparation and characterisation. In this work we describe the design and fabrication of a multilayer stack that uses  $MoS_2$  as a tunnel barrier for injecting spins into graphene from a ferromagnetic electrode such as cobalt. Tuning of the electronic properties is done by the application of a back gate.

Ultimately, however, spin injection was not found, and results showed that the MoS<sub>2</sub> functioned as transport channel instead of tunnel barrier.

Our recommendations for further research would be to bring additional contacts directly onto the graphene channel, whereas our devices had only contacts directly on  $MoS_2$ . This could promote the use of  $MoS_2$  as a tunnel barrier instead of lateral transport through the  $MoS_2$ .

# Contents

1	Тне	ORY	4
	1.1	Two current model	4
	1.2	Spin injection, relaxation and conductivity mismatch	6
	1.3	Non Local Measurements	9
	1.4	Two Dimensional Materials	11
	1.5	Device design	14
2	Dev	ice Fabrication Methods	15
	2.1	Exfoliation of two dimensional materials	15
	2.2	Optical Characterisation of Two Dimensional Materials	16
	2.3	Stacking of two dimensional materials	17
	2.4	Atomic Force Microscopy	19
	2.5	Device fabrication	22
3	Mea	SUREMENT METHODS	27
	3.1	Characterisation of resistances	28
	3.2	Application of a gate voltage	29
	3.3	Spin transport measurements	30
4	Resu	JLTS AND DATA ANALYSIS	31
	4.1	Stack characterisation	31
	4.2	Electrical measurements	34

4.3	Spin measurements	37
4.4	Conclusion and Outlook	38

42

#### References

# List of Figures

1.1.1	Circuit representation of (a) parallel and (b) anti parallel aligned ferromagnets separated	
	by a non-magnetic metal and a schematic representation of what happens to either up	
	and down electrons travelling through this stack	5
1.2.1	Spin injection from a ferromagnetic (FM) material (left) into a material (M) (right).	
	(a) Spin imbalance in the ferromagnet (left) its density of states. Due to an electrical	
	current, the spin imbalance of the FM is reflected in the density of states of the M close	
	to the interface (middle). Further away from the interface, the equilibrium of the M	
	is restored. (b) Schematic representation of the interface between FM and M and the	
	chemical potential of the spins which decay exponentially from the interface. Adapted	
	from [2]	7
1.2.2	Normalized non local resistance as a dependence on applied back gate. We notice three	
	different contact "behaviours": transparent (top), pinhole (middle) and tunneling (bot-	
	tom). Adapated from $[17]$ The definition of the non-local resistance is explained in 1.3.	8
1.3.1	(a) Schematic representation of a non-local spinvalve. (b) The density of spins at the	
	position of each contact. Notice the difference between parallel and anti-parallel mag-	
	netisations of the different contacts.(c) Non-local resistance of the device - note the	
	switching of resistance depending on the relative magnetisation of the contacts. Every	
	additional ferromagnetic contact adds a "jump" at its own switching point. (b) and (c)	
	are adapted from [28]	10

1.4.1	(a) Graphene lattice. One white and black carbon atom together form a single unit cell.	
	(b) Square resistance of graphene as dependent on the carrier density. This can exper-	
	imentally controlled by application gating. At zero density, the resistance is highest, as	
	there are no free states available. When going to positive (negative) densities, more elec-	
	trons (holes) become available for transport, decreasing the resistance. This peak can be	
	referred to as Dirac peak	12
1.4.2	(a) Schematic representation of $MoS_2$ layers. The yellow and black spheres represent	
	sulphur and molybdenum respectively. (b) Band diagram of $MoS_2$ . Note that the indi-	
	rect band gap is for multilayer MoS <sub>2</sub> , whilst the direct band gap is for single layer MoS <sub>2</sub> .	
	Adapted from [22]	13
1.5.1	Schematic representation of the band bending of $MoS_2$ and the Schottky barrier formed	
	at the contact/MoS_2/graphene interface for the device used in this thesis	14
2.1.1	(a) We take two scotch tapes (blue rectangular shapes) and bulk of our two dimensional	
	material. (b) We encapsulate the bulk material by tape. (c) We pull off the tapes gently.	
	Due to weak van der Waals forces binding the layers of the two dimensional material,	
	the tape will pull some layers with it from the bulk. (c) We press the tape onto a clean	
	substrate. (d) A substrate with flakes of our two dimensional material	16
2.2.1	Color plot of the contrast as a function of wavelength and $SiO_2$ thickness. The color	
	scale on the right shows the expected contrast. Adapted from [7]	17
2.3.1	Schematic representation of flake transferring by a PDMS stamp with a thin polycar-	
	bonate film. (a) The glass slide with PDMS stamp covered by polycarbonate is put onto	
	the mask aligner. (b) The stamp is aligned with the selected flake by optical microscopy,	
	and subsequently pressed onto the substrate. When in contact, the substrate is heated	
	to $\sim$ 60 $^{\circ}\text{C}.$ The mask aligner and microscope are left out in this representation. (c) Af-	
	ter cooling, the stamp is pulled off from the substrate, taking the flake with it. (d) The	
	picked up flake is aligned with a different one and the stamp is pressed down onto the	
	substrate. The substrate is heated such that the polycarbonate melts. (e) After melting,	
	the stamp is taken off the substrate, leaving the polycarbonate and the stack of flakes. $(f)$	
	No polycarbonate is covering the stamp anymore.	19
2.4.1	Schematic model of a reactive ion etching chamber.	20

2.4.2	Schematic model of an evaporation chamber.	22
2.5.1	(a) Exfoliation of hBN, $MoS_2$ or Graphene onto a Si/SiO <sub>2</sub> wafer. (*Possible thinning of	
	flakes by RIE.) (b) Optical characterisation and selection flakes of two-dimensional ma-	
	terials. (c) Transferring of selected flakes onto one another. (e) Sideview after transfers	
	of all flakes (except for the multilayer graphene). (d) Spin coating of samples. (e) Pat-	
	tern writing onto samples and development of written patterns. (g) Metal deposition.	
	(h) Lift off. Some flexibility can occur in this schematic. For some samples - and addi-	
	tional multilayer of graphene was transferred on top of the $MoS_2$ . This layer was etched	
	into strips by RIE. Furthermore, the layer thinning of $MoS_2$ has for some samples been	
	done after deposition onto the stack	23
2.5.2	(a) A single layer graphene flake. (b) A multilayer graphene flake. (c) A few layer $MoS_2$	
	flake. (d) A flake of hexagonal boron nitride	24
2.5.3	(a) A stack with no multilayer graphene after lift-off. This device is finalized. (b) Schematic	
	overview of the device.	26
3.0.1	Schematic of the measurement setup	28
3.1.1	(a)-(c) are circuit representations of devices with four contacts. The grey, purple and	
	brown resistors represent the wiring, contact and sheet resistances respectively. (a) A	
	two probe measurement on the device measures the addition of all resistances. (b) A	
	three probe measurement will take only the wiring and the contacts in account. (c) A	
	four probe will measure only the sheet resistance.	29
4.1.1	Microscopic images of a hBN/SLG/MoS $_2$ /MLG stack on silicon substrate with 300 nm	
	SiO <sub>2</sub> . This particular sample is labeled RR2D1. Left (a) a falsely colored AFM image.	
	Here, the purple color signifies the $SiO_2$ substrate. The green color shows the still ex-	
	posed parts of the hBN flake, whereas the blue color does the same for the $MoS_2$ . The	
	single layer graphene is masked by the other flakes, but positioned by the red outline.	
	The top strips of multilayer graphene is shown by the grey color. Note the many bubles	
	and polymer residues. Right (b) A 100x zoom of the sample by optical microscopy.	
	Note again the bubbles and polymer residues show up as light yellow and brown spots	32

4.1.2	(a) Atomic force image of the stack before etching was initiated. The height of the $MoS_2$	
	flake is determined to be 4.4 nm (Profile 2: red line), whilst that of the hBN is 5.7 nm	
	(Profile 1: black line). (b) After 120 seconds of etching, the height of the hBN that is	
	not covered by $MoS_2$ is 1.1 nm (Profile 1: black line), whilst the height of the $MoS_2$ with	
	the covered hBN is 8.4 nm. As such, 0.6 nm (Profile 2: red line) should be etched from	
	the $MoS_2$	33
4.2.1	(a) Light microscopic photo of a device at 100x magnifaction. Broken contacts are de-	
	picted with a cross. Working contacts are labeled by a number. Note the top contacts	
	running over the flake are simply test contacts, they are not taken into consideration for	
	any measurements. (b) Schematic overview of the device with only the working con-	
	tacts depicted	34
4.2.2	(a) Voltage-current dependence of the contacts. Note the kink in the line of contact	
	43, this is due to incorrect sensitivity at those points of the measurement setup. (b)	
	Schematic representation of the three probe circuit used for measuring the contact re-	
	sistance of contact 4	35
4.2.3	(a) Sheet resistance as dependent on back gate. Despite the nonlinear dependence, no	
	Dirac curve is seen. (b) Schematic representation of the four probe circuit to measure	
	the sheet resistance	36
4.2.4	(a) Current path when the $MoS_2$ is acting as a tunnel barrier for spin injection into	
	graphene. (b) Current path when transport goes laterally through $MoS_2$	36
4.2.5	(a) Dependence of the contact resistance and the sheet resistance on the back gate. (b)	
	Schematic representation of the circuit for measuring the contact resistance (using $V_{\scriptscriptstyle 1})$	
	and the contact resistance and sheet resistance together (using $V_{\scriptscriptstyle 2}).$	37
4.2.6	In the case of $V_g < 0$ : Strongly bent $MoS_2$ band. This bending gets stronger when a neg-	
	ative back gate is applied. The electrons traveling through the $MoS_2$ experience a rela-	
	tively high barrier, increasing the resistance for the lateral direction of $MoS_2$ . In the case	
	of $V_g > o$ Weakly bent MoS <sub>2</sub> band. This bending gets less when a positive back gate is	
	applied. In this case, the electrons traveling laterally through the $MoS_2$ experience less	
	resistance, as it is easier for them to hop over the barrier	38

4.3.1	Attempt at measuring the spin valve effect by sweeping the magnetic field whilst measur-	
	ing the resistances. Note that there is no switching behaviour as is seen in the spin valve	
	in Figure 1.3.1. (a) Measurement data obtained. (b) Four probe setup used to measure a	
	spin-valve effect.	38
4.4.1	Schematic of an iter ation of used devices. One contact is now positioned directly onto	
	the single layer graphene, possible promoting the function of ${ m MoS}_2$ as a tunnel barrier	39

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### Introduction

SMALLER, FASTER AND MORE. These comparatives are the leading motives for the development of new devices. It is Moore's law that drives this development in the integrated electronics industry: the number of transistors per chip area will approximately be doubled every twenty four months [23], [24]. However, when we keep downscaling, new effects related to change in physical properties, will start to play larger roles. An example would be leakage currents by quantum tunneling. The challenge is to use such properties to our advantage. Alternative technologies have emerged in the past two decades to address these challenges and *Spintronics* is one of them [9]. In spintronics the spin of an electron is used, in addition to the classical concept of the electron charge, for both storage, transport and manipulation of information.

Spins can take one of two orientations, up or down. However, a distinct property associated with the electron spin is the length and time over which they can preserve their information before relaxing. As such, the information linked to spin is lost when it relaxes. Our goal is then to find materials with long spin life times.

Since its discovery in 2004, Graphene has shown to be an extremely suitable material for both electronic and spintronic applications [26]. It brings many properties with it that are useful for several applications, such as thermal stability, chemical inertness, and excellent electronic properties. More importantly, it is shown that the experimental spin relaxation length of graphene can be as large as 12 µm [14].

Whereas theoretically spin information in graphene should be preserved over longer times, many external factors have to be taken into account, such as the interfaces between graphene and the rest of the device for this to be clearly discernible. It has been shown that the use of a tunnel barrier leads to a huge improvement of spin relaxation times [17]. Whereas metal oxides are often used as these barriers, the uprising of two dimensional materials, partially due to the explosive popularity of graphene, showed that two dimensional

materials are also excellent candidates for tunnel barriers, such as hexagonal boron nitride [8]. This is primarily because of their ease of stacking and lattice matching with other two dimensional materials, thereby assisting easier device fabrication protocols.

In this bachelor thesis, we treat the use of the transition metal dichalcogenide  $MoS_2$  as a tunnel barrier. Its thickness dependent band gap and easy optical characterisation makes the material very suitable for its integration as a tunnel barrier. Some theory is treated about the basics of spintronics, spin injection and detection and two dimensional materials. This is followed up by a list of methods used in the fabrication of our device, and their application. Thereafter the methods for measurements are discussed, linking theory and experiment. Finally, the measurements are analysed, with recommendations for further research.

It is the theory that decides what can be observed.

Albert Einstein

# Theory

SPINTRONICS REQUIRES, in addition to the understanding of charge transport, the physical principles that governs the transport of electron spins. An introduction of these novel concepts is given in this chapter. In combination with the device fabrication, the justification and clarification of why measurements are as they are (see Chapter 3) follows directly from the theory.

#### 1.1 TWO CURRENT MODEL

Perhaps the easiest way to get a grasp of spintronics is to start with an explanation of the Giant Magnetoresistance (GMR) principle [5], [6], an effect used in many of today's hard drives. Briefly, the GMR effect can be said to be a change in the resistance due to the influence of a nearby magnetic field. The total current through a ferromagnetic metal can be split into two separate currents. In this *two current model*, proposed by Valet and Fert [29], the current where the electron spins are aligned parallel to the



**Figure 1.1.1:** Circuit representation of (a) parallel and (b) anti parallel aligned ferromagnets separated by a non-magnetic metal and a schematic representation of what happens to either up and down electrons travelling through this stack.

magnetisation, the spins are said to be up ( $\uparrow$ ). When they are, on the other hand, anti-parallel aligned, we say the spins to be down ( $\downarrow$ ). Usually, a spin up electron travelling from one ferromagnet to the other, is less scattered than a spin down electron. This is mathematically described by the Einstein relation:

$$\sigma_{\uparrow(\downarrow)} = D(E)_{\uparrow(\downarrow)} e^2 \nu(E_f)_{\uparrow(\downarrow)},\tag{1.1}$$

where  $\sigma$  is the conductivity, D(E) is the diffusion constant, *e* is the electron charge and  $v(E_f)$  stands for the density of states at the energy  $E_f$ . The  $\uparrow (\downarrow)$  subscript notifies the up (down) state of the current.

#### 1.1.1 GIANT MAGNETO-RESISTANCE OR GMR

Imagine two ferromagnets (F) separated from one another by a non-magnetic metal (M) layer. The difference in conductivity, as we discussed in 1.1, is then described by the circuits in Figure 1.1.1 depending on the relative magnetisation of the ferromagnets.

For the parallel case we can express the resistance as:

$$R_p = rac{2R_\uparrow R_\downarrow}{R_\downarrow + R_\uparrow}.$$
 (1.2)

Similarly, for the anti-parallel case we have that

$$R_{ap} = \frac{R_{\uparrow} + R_{\downarrow}}{2}.$$
 (1.3)

As such, when we define the difference of the resistances:

$$\Delta R = \frac{(R_{\downarrow} - R_{\uparrow})^2}{2(R_{\downarrow} + R_{\uparrow})}.$$
(1.4)

#### 1.2 Spin injection, relaxation and conductivity mismatch

To study spin transport characteristics, we need to design devices that include materials from which we inject spins, such as ferromagnet (FM), to the material (M) where we want to transport them in; such as metals, semiconductors, graphene etc.

When the FM and the M are connected, the spin imbalance in the FM needs to be efficiently transported into the M. The destruction of the injected spin imbalance happens over a characteristic length scale away from the interface, into which the spin diffuse. This is because there is no natural spin imbalance in the M, and since the spins relax in the M, we will find the M to be in equilibrium again far from the FM/M interface. This process is schematically shown in Figure 1.2.1.

We describe this by the electrochemical potential of the up and down spins,  $\mu_{\uparrow}$  and  $\mu_{\downarrow}$  respectively. As such, our electrochemical potential is given by  $\mu_{\circ} = \frac{\mu_{\uparrow} + \mu_{\downarrow}}{2}$  and our spin electrochemical potential by  $\mu_{\circ} = \frac{\mu_{\uparrow} - \mu_{\downarrow}}{2}$ . Furthermore, we define a current density and a spin current density as  $J_c = J_{\uparrow} + J_{\downarrow}$  and  $J_s = J_{\uparrow} - J_{\downarrow}$  respectively, where

$$J_{\uparrow(\downarrow)} = -\frac{\sigma_{\uparrow(\downarrow)}}{e} \nabla \mu_{\uparrow(\downarrow)}.$$
(1.5)

Since we have a spin imbalance in the FM,  $J_{\uparrow} \neq J_{\downarrow}$  and for the equilibrium state of the M  $J_{\uparrow} = J_{\downarrow}$ . This means that there must be a spin build up, or spin accumulation, at the FM/M interface. This accumulation can be described by the Bloch equation [12]:

$$\frac{\mathrm{d}\vec{\mu}_s}{\mathrm{d}t} = D\nabla^2\vec{\mu}_s - \frac{\vec{\mu}_s}{\tau} + \vec{\omega}_L \times \vec{\mu}_s, \qquad (1.6)$$



**Figure 1.2.1:** Spin injection from a ferromagnetic (FM) material (left) into a material (M) (right). (a) Spin imbalance in the ferromagnet (left) its density of states. Due to an electrical current, the spin imbalance of the FM is reflected in the density of states of the M close to the interface (middle). Further away from the interface, the equilibrium of the M is restored. (b) Schematic representation of the interface between FM and M and the chemical potential of the spins which decay exponentially from the interface. Adapted from [2].

with spin relaxation time  $\tau$  and the Larmor frequency  $\vec{\omega_L} = g \frac{\mu_B}{\hbar} \vec{B}$ . The gyromagnetic factor g is approximated to be g = 2 [10],  $\vec{B}$  is the magnetic field and  $\vec{\mu}_B$  is the Bohr magneton. The steady state solution at zero magnetic field gives a clear exponential decay of the spin accumulation:

$$\mu_{s} = \exp\left(\frac{-x}{\sqrt{D\tau}}\right) = \exp\left(\frac{-x}{\lambda}\right), \qquad (1.7)$$

where  $\lambda = \sqrt{D\tau}$  is the spin relaxation length of the material in which the spins are injected.

#### 1.2.1 CONDUCTIVITY MISMATCH

A reoccurring problem for spin injection is the conductivity mismatch. When the conductivities of the FM and M differ greatly  $\left(\frac{\sigma_M}{\sigma_{FM}} \ll 1\right)$ , only a small spin polarized current can be injected. Furthermore, a large

polarisation of the injector ferromagnet is desirable to enhance device performance [27].

The conductivity mismatch is very influential at low contact resistances (transparent contacts). On the other hand, when we go to higher contact resistances, we can circumvent the conductivity mismatch by using a tunnel barrier [17]. Introducing a tunnel barrier will increase the spin imbalance in the semiconductor, and has proven to be effective in graphene. In general, we discriminate between three types of contacts: transparent, pinhole and tunneling. These type of contacts roughly correspond to low contact resistances, intermediate contacts resistances (tunneling with "pinholes") and high contact resistances respectively, and their behaviour is shown in Figure 1.2.2



**Figure 1.2.2:** Normalized non local resistance as a dependence on applied back gate. We notice three different contact "behaviours": transparent (top), pinhole (middle) and tunneling (bottom). Adapated from [17] The definition of the non-local resistance is explained in 1.3.

#### 1.2.2 SPIN RELAXATION

After injection into the transport channel, there are a handful of mechanisms that cause spin relaxation. When thinking of spin relaxation, it is important to understand the difference between the spin relaxation time  $T_r$  and the spin dephasing time  $T_p$ . For the first, the spins exchange energy with the crystal lattice they travel through, eventually losing their ordering. The latter, however, conserves the spins themselves, but loses the phase a spin has when precessing around an external magnetic field [34]. The times in which either one of these processes happens, determine the spin diffusion length  $\lambda$ . The major offenders for spin relaxation are named below.

#### Elliot Yafet (EY)

Scattering of charge carriers causes the spins to flip, reducing the average spin lifetime. Simultaneously, spin-orbit coupling causes dephasing of the spin. It is found that the spin lifetime varies linearly with the momentum scattering time [16]. The source of these scattering events can be found in the existence of defects.

#### D'YAKONOV PEREL (DP)

It is most evident in materials that exhibit intrinsic magnetic fields coming from spin orbit coupling. Thus when scattering changes this intrinsic field due to a change in the spin orbit coupling, we get less dephasing of said spins. There is an inversely linear dependence of the spin relaxation time on the spin dephasing time.

#### BIR-ARONOV-PIKUS (BAP)

This mechanism causes electron spin relaxation by local fluctuating magnetic fields caused by electron-hole exchange scattering [34].

#### Hyperfine interaction

Hyperfine interaction with the nuclear spins of the crystal lattice can cause spin relaxation.

#### **1.3** Non Local Measurements

To inject and detect spins efficiently, a non local spin valve geometry can be used [15]. A stack of semiconductor/tunnel barrier/injector is made as is schematically shown in Figure 1.3.1.a. This high resistant tunnel barrier serves to reduce the conductivity mismatch as said in 1.2.1. The polarised charge current is injected into electrode  $I_-$  and flows to  $I_+$ . The nature of these spins (up or down) is dependent on the magnetisation of the injecting electrode. Below the injecting electrode, a spin accumulation can be found that diffuses through the injected material, leading to a pure spin-current. Due to the different relaxation mechanisms mentioned in the previous section, these spins relax when diffusing. Using electrodes  $V_+$  and  $V_-$ , it is possible to measure the spin concentration of this non equilibrium state as a so called non-local voltage  $V_{nl} = V_{+,\uparrow(\downarrow)} - V_-$ . The nature of the probed spins is dependent on the magnetisation of the probing electrode. if the probing electrode  $V_+$  is parallel aligned to  $I_+$ , it will probe the same type of spins as are



**Figure 1.3.1:** (a) Schematic representation of a non-local spinvalve. (b) The density of spins at the position of each contact. Notice the difference between parallel and anti-parallel magnetisations of the different contacts.(c) Non-local resistance of the device - note the switching of resistance depending on the relative magnetisation of the contacts. Every additional ferromagnetic contact adds a "jump" at its own switching point. (b) and (c) are adapted from [28].

injected, resulting in a positive non local voltage. If, on the other hand, aligned in an anti-parallel fashion, then the opposite happens and a negative non-local voltage is measured. This non-local voltage reflects the spin-dependent chemical potential difference due to relaxation of the injected spins.

The nature of the non local voltage signal can be controlled precisely by the switching of the magnetisation of the electrodes by the use of an external magnetic field *B*, parallel to the long sides of the electrodes. When the electrodes are appropriately distanced and differ in spatial dimensions, especially thickness, switching of their magnetisation will occur at different magnetic fields. This is due to the difference in coercivity of the electrodes caused by the shape anisotropy.

Using the injected spin current and the measured non-local voltage, we define a non-local resistance  $R_{nl}$ :

$$R_{nl} = \frac{V_{nl}}{I_{inj}} \tag{1.8}$$

When the probing electrode  $V_{nl}$  is parallel aligned to the injecting electrode it probes the parallel aligned spins and vice versa. Thus, we can safely say that  $\delta R_{nl} = R_{nl,p} - R_{nl,ap} = 2R_{nl,p}$ . Some terms and conditions apply to these measurements however. The probing electrode  $V_+$  will have to be within the distance of the relaxation length  $\lambda$  to measure a sensible signal.  $V_-$ , our reference electrode, however, will have to be far enough away from the probing contact, at least a distance  $d = \lambda$ . If this is not done,  $V_-$  probes a nonequilibrium spin distribution, as not all spins will be relaxed yet.

#### 1.4 Two Dimensional Materials

The hype for two dimensional materials is far too exciting to not be involved with. Many show interesting electrical and chemical properties, they are easily acquired and application is often cheap and reproducible (see Section 2.1). Furthermore, applications of two dimensional materials truly shine when they are used in tandem. This is because, although their structure is often similar, their properties can be widely different.

#### 1.4.1 GRAPHENE

Graphene consists of a so called honeycomb lattice of carbon atoms as seen in Figure 1.4.1.a. The distance between two neighbouring atoms is a = 1.42 Å. Furthermore, it is a two-dimensional half metal with high mobility charge carriers [3]. Moreover, two dimensional graphene has no band gap and has a linear dispersion relation around its Dirac point [4], as seen in the hourglass-like figures in Figure 1.4.1.b. This is in contrast with most two-dimensional materials, that show parabolic dispersion relations. Although this vanishing of the density of states near the Dirac point make graphene not so feasible for traditional transistors, its strength lies in the fact that control over the Fermi level becomes much easier. The carrier density of graphene is easily tuned by using electrical gating. Applying a gate voltage gives electron transport or hole transport by bringing the Fermi level above or below the Dirac point respectively. This gives tunability of the resistance of our graphene, as seen in Figure 1.4.1.b, as more carriers imply a lower resistance. The shown square resistance is a normalization of the channel resistance that can be measured through graphene:  $R_{sq} = R_{channel} \frac{L}{W}$ .

The feasibility of graphene for spin transport is found when we relate its properties to the spin relaxation mechanisms in Section 1.2.2. Firstly, carbon (Z=6) has a very low atomic weight. As such, relaxation by spin orbit coupling (the DP mechanism) will be minimal. Secondly, a low contribution of the hyperfine



**Figure 1.4.1:** (a) Graphene lattice. One white and black carbon atom together form a single unit cell. (b) Square resistance of graphene as dependent on the carrier density. This can experimentally controlled by application gating. At zero density, the resistance is highest, as there are no free states available. When going to positive (negative) densities, more electrons (holes) become available for transport, decreasing the resistance. This peak can be referred to as Dirac peak.

coupling to the spin relaxation can be found due to the zero nuclear spin of the <sup>12</sup>C Isotope. As about 1% of all carbon atoms are different isotopes, we can say that graphene will not be influenced relaxation by hyperfine interaction. Furthermore, it is shown that the BAP mechanism is not the major offender for the spin relaxation in two dimensional materials as graphene, and the defect induced scattering (EY mechanism) is often the major culprit [16]. As such, theoretically, graphene seems to be an excellent material candidate for spin transport, with possible spin relaxation times of even microseconds [11]. However, some practical problems occur, as the spin transport is not only influenced by intrinsic properties of graphene. The influence of the substrate [11] and the contacts on the spin relaxation times in graphene is critical. As such, it is shown that single layer graphene shows much better spin transport when it is on top of a hexagonal boron nitride (hBN) layer. Since the hBN lattice closely resembles that of graphene, using a thin layer beneath graphene will reduce defects, and thus spin scattering. Furthermore, the effect of contact resistances and benefits of a tunnel barrier was shown in Section 1.2.1.

#### 1.4.2 Two Dimensional Tunnel Barriers

Traditional tunnel barriers for spin injections are often metal-oxides. However, precise control over their growth is limited and problems such as pin-holes often occur. As the type of contact resistance is essential

to the quality of the device, two dimensional materials offer a solution. Small crystal flakes with different thicknesses are relatively easy to obtain due to being bound by weak van der Waals forces. Thus, thicknesses (and with it resistance) of the tunnel barriers can be easily tuned, especially with methods for further thinning down the crystals such as is mentioned in Section 2.3.1.



**Figure 1.4.2:** (a) Schematic representation of  $MoS_2$  layers. The yellow and black spheres represent sulphur and molybdenum respectively. (b) Band diagram of  $MoS_2$ . Note that the indirect band gap is for multilayer  $MoS_2$ , whilst the direct band gap is for single layer  $MoS_2$ . Adapted from [22].

It was already stated that hBN serves very well as a substrate for graphene due to its matching lattice. Spin injection through a hBN tunnel barrier has also been reported [31]. The problem, however, with hBN is that optical characterisation of thin flakes becomes quite hard. Furthermore, tunneling is suppressed for barrier thicker than 6 layers hBN [8]. Thus, fabrication of these devices can be very complex. Transition metal dichalcogenides are a group of materials, which consist of a transition metal (elements of group III to XII) and two chalcogenide atoms, such as sulphur (S), selenium (Se) or tellurium (Te). They are two dimensional materials for which thin layers can be easily obtained.

We focused on using the metal transition dichalcogenide  $MoS_2$  as a tunnel barrier. In contrast to hBN, optical characterisation of few layer  $MoS_2$  is fairly easy.  $MoS_2$  is a tri-layered material (see Figure 1.4.2.a) where the interlayer forces are, just as with graphene, weak van der Waals forces. The thickness of a single layer  $MoS_2$  is 6.5 Å [19]. A peculiar property of  $MoS_2$  lies in the fact that multilayer  $MoS_2$  is an indirect semiconductor with a band gap up  $E_g = 1.29$  eV in bulk, whilst single layer  $MoS_2$  is an indirect semiconductor with a band gap of  $E_g = 1.8$  eV [22], see also Figure 1.4.2.b.

When looking at its function as tunnel barrier, the high atomic weight of the molybdenum is a key property. Its high atomic weight promotes tunneling of spins through the layers, as they would relax easily within MoS<sub>2</sub> itself. Furthermore, the Schottky barrier formed at the interface of the FM/MoS<sub>2</sub>/graphene device



**Figure 1.5.1:** Schematic representation of the band bending of  $MoS_2$  and the Schottky barrier formed at the contact/ $MoS_2$ /graphene interface for the device used in this thesis.

(Figure 1.5.1) will determine the type of transport. Applying a gate voltage will change the Schottky barrier height. As such, tunneling through the barrier can be either suppressed or promoted.

#### 1.5 DEVICE DESIGN

For spin transport, the devices in this thesis make use of a single layer graphene with a two dimensional material,  $MoS_2$ , as tunnel barrier. Ferromagnetic cobalt contacts are used to polarise and inject spins. Due to reducing the contact resistance, a multilayer graphene can be incorporated in between the ferromagnetic contacts and the  $MoS_2$ . Due to this multilayer graphene acting as a metal contact with a semiconductor  $(MoS_2)$ , the Shottky barrier schematically shown in Figure 1.5.1 is expected to form.

For efficient spin injection in the devices used in this thesis, a hexagonal boron nitride flake is used as substrate for the graphene. This should reduce strain in the graphene due to its lattice matching [33]. Often, it may be said that the interface is the device.

Herbert Kroemer

# 2

## Device Fabrication Methods

A STEP-BY-STEP FABRICATION GUIDE is given before we dive into the methods of measurements. Preparation of the samples is of high importance, as simple mistakes can reduce the quality of the device fairly easily. As such, not only the raw fabrication steps are treated in this chapter, but methods of analysis of the samples by for example AFM and optical microscopy will make their appearance as well. After treating the production methods, their application in the fabrication of the device will be given in a schematic overview.

#### 2.1 Exfoliation of two dimensional materials

Silicon wafers with a controlled grown top layer of SiO<sub>2</sub> were used as the substrate for all different exfoliation steps. However, the thickness of this top layer differed, depending on what it was used for (i.e. different type of substrates for the optical characterisation of flakes and the use of a thick SiO<sub>2</sub> layer for back gating). Throughout the experiment, three different thicknesses were used: silicon with either 90, 300 or a 500 nm

#### thick layer of SiO<sub>2</sub>.

Narrow strips were diced out of an 4 inch Si wafer using a wafer cutter. Before exfoliation, the strips were thoroughly cleaned in acetone for ten minutes in an ultrasonic bath at power 4, followed by a rinse with isopropyl alcohol (IPA). A dry blow with nitrogen is used to evaporate the remaining liquid.

The two dimensional layered materials - graphene, MoS<sub>2</sub> and hBN - of the final device were obtained by means of mechanical exfoliation. Due to the weak van der Waals interaction that bonds the layers together, mechanical cleaving is possible. Using Nitto tape, exfoliation of these materials is an highly effective and low cost method of obtaining few layers [13]. See Figure 2.1.1 for a schematic of this so called Scotch tape method. Different results are expected when changing the applied force, number of exfoliations before pressing the material on a substrate, the quality of the tape and similar factors. As such, a downside of exfoliation is its low reproducibility and uncertainty. However, its low cost effectiveness towers over this relatively small downside.



**Figure 2.1.1:** (a) We take two scotch tapes (blue rectangular shapes) and bulk of our two dimensional material. (b) We encapsulate the bulk material by tape. (c) We pull off the tapes gently. Due to weak van der Waals forces binding the layers of the two dimensional material, the tape will pull some layers with it from the bulk. (c) We press the tape onto a clean substrate. (d) A substrate with flakes of our two dimensional material.

#### 2.2 Optical Characterisation of Two Dimensional Materials

Characterisation of exfoliated flakes is done mainly by optical microscopy. Using the optical properties of the materials, the thickness of the exfoliated materials on the  $SiO_2$  can be determined with high precision [25], [30]. Depending on the thickness of the  $SiO_2$  layer the materials are exfoliated on, the optical contrast

changes for the same material, i.e. the contrast of a single layer graphene on a substrate with a 90 nm thick SiO<sub>2</sub> layer is much higher than for a single layer graphene on a substrate with a 300 nm thick SiO<sub>2</sub> layer. Figure 2.2.1 shows the contrast of graphene flakes at different thicknesses of SiO<sub>2</sub> and different wavelengths as an example for the optical characterisation of two dimensional materials. Note that on a 300nm layered SiO<sub>2</sub> substrate, the best optical contast (15%) is given by light with a wavelength  $\lambda = 600$  nm. Similarly, thinner layer MoS<sub>2</sub> are also characterised more easily on substrates with a 90 nm SiO<sub>2</sub> layer. However, as the thickness of the hBN flakes was much less important - the hBN only served as an anti-strain layer for the graphene - and it is safer to use a thicker layer of SiO<sub>2</sub> when back-gating is applied, the eventual stacks were deposited on either 300 nm or 500 nm layered SiO<sub>2</sub> on silicon substrates.



**Figure 2.2.1:** Color plot of the contrast as a function of wavelength and  $SiO_2$  thickness. The color scale on the right shows the expected contrast. Adapted from [7].

#### 2.3 STACKING OF TWO DIMENSIONAL MATERIALS

As the different materials are all exfoliated on their own substrates, stacking them will require a method of transferring the selected flakes on one another. This section will treat the method used for stacking, which is schematically shown in Figure 2.3.1. For this, a small Polydimethylsiloxane (PDMS) stamp on a glass slide is used and covered by a thin layer of polycarbonate (PC, Sigma Aldrich) [32].

The thin film of polycarbonate is acquired by pipetting a solution of 6% polycarbonate dissolved in chloroform on a glass slide. Using a second glass slide to gently squish the liquid gives a fairly uniform layer of polycarbonate after the second glass slide is slid off. A small piece of tape containing a slightly larger hole than the size of the PDMS stamp is then used to pick up some polycarbonate, with which the PDMS stamp is then covered.

Following this, the slide containing the PDMS is then put into a customised mask aligner (Figure 2.3.1.(a)). The PDMS stamp is aligned with the selected flake and it is gently pressed downwards until there is contact between the substrate and the stamp (Figure 2.3.1.(b)), but the stamp is yet to cover the selected flake. Consecutively, the substrate is heated to  $\sim 60$  °C, thus slightly melting and expanding the polycarbonate layer until it covers the flake. Directly after, we let the sample cool down. Due to this, the polycarbonate pulls back and - when done right - takes the selected flake with it when the stamp is gently pulled off the substrate (Figure 2.3.1.c).

By aligning the then picked up flakes with others, it is possible to stack several flakes, in order to make hetero structures, or transfer them to different substrates (Figure 2.3.1.d). When the final transfer is done, the PDMS stamp is once again gently pressed on the substrate. Now, however, the substrate is heated to  $\sim$  150 °C - causing the polycarbonate to melt onto the substrate after the PDMS stamp is retracted (Figure 2.3.1.e and 2.3.1.f). This polycarbonate is then removed by a 5 hour bath of chloroform heated to 50 °C.

#### 2.3.1 Reactive Ion Etching

Reactive Ion Etching, or RIE, can be used for both patterning and thinning down of exfoliated materials. The etching method uses atoms from which electrons have been ionized by an oscillating electromagnetic field to bombard a sample. The ions react with matter on the substrate and a leftover non-volatile product is easily swept away - effectively removing parts of the sample. A schematic of the setup for such a system can be found in Figure 2.4.1.

The electrons can be removed by the oscillating magnetic field due to the difference in weight of the electrons and the atoms they are bound to. The much more massive atomic cores react only slightly to the oscillating field - and are then separated from their active electrons, creating an ion plasma. Any electrons absorbed by the walls of the RIE system do not alter the electronic state of the system as they are simply taken to the ground. However, electrons absorbed on the wafer platter create a large electric imbalance. This charge imbalance attracts the now positive ions, bombarding them onto the substrate. The ions can either react with the material on the substrates, or knock individual atoms or molecules out of the crystals. The benefits of RIE is it's high anisotropy and the low redeposition due to volatile products after chemical reactions of the plasma and the etched materials.



**Figure 2.3.1:** Schematic representation of flake transferring by a PDMS stamp with a thin polycarbonate film. (a) The glass slide with PDMS stamp covered by polycarbonate is put onto the mask aligner. (b) The stamp is aligned with the selected flake by optical microscopy, and subsequently pressed onto the substrate. When in contact, the substrate is heated to  $\sim 60$  °C. The mask aligner and microscope are left out in this representation. (c) After cooling, the stamp is pulled off from the substrate, taking the flake with it. (d) The picked up flake is aligned with a different one and the stamp is pressed down onto the substrate. The substrate is heated such that the polycarbonate melts. (e) After melting, the stamp is taken off the substrate, leaving the polycarbonate and the stack of flakes. (f) No polycarbonate is covering the stamp anymore.

#### 2.4 Atomic Force Microscopy

For the further characterisation and analysis of finalized stacks, atomic force microscopy, or AFM, was used. In AFM, a cantilever with a small sharp tip is used for imaging of the sample. A laser beam is focused on top of the cantilever and reflected towards a position detector. As such, the deflection of the cantilever is measured. There are two modes for the AFM, the contact (DC) mode, and the tapping (AC) mode. As we have only made use of the tapping mode, this will be treated a bit more in depth. In the tapping mode, we excite the cantilever close to its resonance frequency, causing it to permanently oscillate. At this frequency, little energy is necessary to maintain a strong oscillation. If the oscillating cantilever is brought close to the sample surface, the cantilever oscillation will be damped even at very small forces between sample and cantilever.

There are a few factors limiting the resolution of the AFM. The largest, and perhaps most obvious, is the tip and its bluntness. The smaller the radius of curvature of the tip, the smaller the features that can be resolved.

Secondly, the accumulation of dirt on the end of the tip can also dull the tip and result in image distortion. Furthermore, a "double tip" problem is possible, in which images are formed with a tip with more than one end point that contact the sample while imaging.

For the analysis of AFM images, the freeware program Gwyddion<sup>1</sup> is used.



Figure 2.4.1: Schematic model of a reactive ion etching chamber.

#### 2.4.1 Electron Beam Lithography or EBL

In electron beam lithography, or EBL, electrons are used to write a pattern onto the samples. By exposing the spin coated electron beam resist layer to electrons, the solubility is changed, enabling parts of the film to be washed away. The working of EBL is similar to Scanning Electron Microscopy, but its purpose is different.

The advantages of EBL are many. Firstly, due to EBL being a direct writing method, it is perfect for flexible writing of patterns. This automatically implies the redundancy of masks. Another advantage of EBL is that it enables high resolution writing due to the small wavelengths possible with electrons.

When getting to these small wavelengths, it is not diffraction that limits the smallest resolution size as is the case with photolithography. It is mainly electron-material interactions that determine the write size limit. Firstly, forward (small angle) scattered electrons, causes effective broadening of the incoming beam by secondary electrons. Secondly, we can introduce the proximity effect caused by backward (large angle) scattered electrons: backscattered electrons cause additional exposure at areas away from the incident beam.

However, back scattering is not all bad. Back scattered electrons in EBL give us this profile with just a single resist layer.

<sup>&</sup>lt;sup>1</sup>http://gwyddion.net

Furthermore, another significant disadvantage of using EBL is that it requires a vacuum to give the beam an unobstructed path and reduce scattering before the beam has even hit the sample. The higher the vacuum, the better the beam quality.

Scattered electrons can be used for imaging as in a scanning electron microscope (SEM). An image is created when the incident beam is scanned across the sample its surface. The scattered electrons are then detected for each position by an electron detector. The intensity of the scattered electrons is used to create contrast. This intensity is usually dependent on the sample material and the depth the electrons originate from (i.e. heavy metals give more scattering). Secondary electrons gives excellent information of the surface morphology, whilst back scattered electrons can escape from much deeper.

To eventually transfer a pattern onto the samples, a resist is needed. This resist is spin coated onto the sample. A pre-coating bake higher then 100 °C evaporates any water present on the surface of the substrate, whilst a pre-exposure bake (softbake) at the same temperature will evaporate any remaining solvent of the resist. Furthermore, a softbake reduces risk of adhesion to the substrate and prevents the dissolving of one layer into a second coat in multilayer coating. However, some problems that can occur with a softbake are thermal decomposure of the active compounds in positive resists and thermal cross-linking in the negative resist.

The EBL system used for pattern writing is the e-line raith GmbH<sup>2</sup>

#### 2.4.2 Thin Film Deposition

A thin film of ferromagnetic metal is grown onto the structures after the lithographic steps and their development. This is done by electron beam deposition, which is a physical vapor deposition method. In this method, an evaporant sits in a heavy water cooled copper hearth, whilst a beam of high energy electrons is emitted from a filament below the hearth. A magnetic field bends the electron beam such that it directly heats the evaporant, which then evaporates and adheres to the substrate inside the coating chamber. Due to the high energy, the crucible - or boat - in which the evaporant resides in the hearth, has to be made of inert materials with high heat resistance. Figure 2.4.2 shows a schematic model of an evaporation chamber. The system used for thin film deposition is the Temescal FC 2000<sup>3</sup>.

<sup>&</sup>lt;sup>2</sup>https://www.raith.com

<sup>&</sup>lt;sup>3</sup>https://www.temescal.net/systems/BJD-2000/



Figure 2.4.2: Schematic model of an evaporation chamber.

#### 2.5 DEVICE FABRICATION

Here, a clear overview is given of the exact fabrication of our devices. A short clarification of these steps is given in the various subsections. The steps are shown as in the overview of Figure 2.5.1. The final result of the device should be a silicon sample with a top grown layer  $SiO_2$ . Stacked on this substrate are bottom, relatively thick, layers hBN with a single layer graphene (SLG) sandwiched also by a few layers of  $MoS_2$  on top. For some devices, an additional layer of multilayer graphene is used before depositing ferromagnetic cobalt contacts. On the others, the contacts are deposited directly.

#### 2.5.1 Exfoliation, characterisation and transfer of materials

Graphene was obtained from exfoliation onto 90 nm  $SiO_2$  substrates, as their contrast seemed best on these substrates. Similarly, all used  $MoS_2$  flakes were also obtained from 90 nm substrates. The hexagonal boron nitride flakes are exfoliated onto 300 nm or 500 nm  $SiO_2$  substrates to make sure that eventual back gating would not break the device. Figure 2.5.2 gives a few examples of characterised flakes characterised by optical microscopy.

To create a stack, firstly  $MoS_2$  is picked up by the transfer method explained in 2.3. Then, after alignment with this  $MoS_2$  flake, a single layer graphene flake is picked up by the same method. The last step involves melting the polycarbonate onto a hBN flake after alignment. When a multilayer graphene contact pattern



**Figure 2.5.1:** (a) Exfoliation of hBN,  $MoS_2$  or Graphene onto a Si/SiO<sub>2</sub> wafer. (\*Possible thinning of flakes by RIE.) (b) Optical characterisation and selection flakes of two-dimensional materials. (c) Transferring of selected flakes onto one another. (e) Sideview after transfers of all flakes (except for the multilayer graphene). (d) Spin coating of samples. (e) Pattern writing onto samples and development of written patterns. (g) Metal deposition. (h) Lift off. Some flexibility can occur in this schematic. For some samples - and additional multilayer of graphene was transferred on top of the  $MoS_2$ . This layer was etched into strips by RIE. Furthermore, the layer thinning of  $MoS_2$  has for some samples been done after deposition onto the stack.

is required on the device - a multilayer graphene is picked up even before the MoS<sub>2</sub> in the same way. To end the transfers, the sample is put in a chloroform bath to dissolve the polycarbonate as is explained in Section 2.3.



**Figure 2.5.2:** (a) A single layer graphene flake. (b) A multilayer graphene flake. (c) A few layer  $MoS_2$  flake. (d) A flake of hexagonal boron nitride.

#### 2.5.2 PATTERN WRITING BY EBL

After stacking, patterns are written by EBL - be it etch channels or contacts. However, before writing, there is the need of a electron beam resist to write on. This resist is spin coated onto the sample at 4000 rpm for one minute. In our case, AR-P 950K 679.04 from allresist is used <sup>4</sup>. PMMA is an electron-sensitive polymer that gives an excellent undercut when used in EBL. The percentage implies its dissolvability, as a higher percentage of polymer will, under the same circumstances, give a thicker layer of PMMA. The 950K gives the molecular weight, and thus the chain length, of the polymer.

The written structures - marker patterns, contact patterns and etch channel patterns were designed with the software e-line<sup>5</sup>, a vector program in which the design is directly transferable to the *Raith GmbH e-Line Electron Lithography System*.

Marker patterns were transferred to the sample for alignment before writing anything else. Different marker "fields" were created for alignment at different scales. A field of 2000 by 2000 mm<sup>2</sup> was used for course

<sup>&</sup>lt;sup>4</sup>http://www.allresist.de/ebeamresists-ar-p-630-670/

<sup>&</sup>lt;sup>5</sup>https://www.raith.com

alignment, one for 200 by 200  $\mu$ m<sup>2</sup> for precise alignment, and in the case of the pattern writing onto the multilayer graphene contacts, an additional 100 by 100  $\mu$ m<sup>2</sup> field with markers was used for high precision alignment.

Etch channels are written to etch the multilayer graphene on some stacks - the distance between these channels differed depending on the dimensions of the whole stack.

After a pattern is written onto the PMMA, it is needed to develop these exposed areas. A 60 second exposure by a solution of (1:3) Methyl isobutyl ketone (MIBK):IPA washes off the exposed polymer. Due to MIBK being highly aggressive against PMMA, a short IPA bath of around 30 seconds is used to stop the development. The residues of IPA is subsequently taken off with a nitrogen blowdry.

#### 2.5.3 Reactive Ion Etching of Materials

#### Layer thinning of $MoS_2$

For some samples with the  $MoS_2$ , this tunnel barrier is etched by an argon plasma to thin it down. Initially, an oxygen plasma was used for the etching of  $MoS_2$ . However, we stepped back from using oxygen plasma for a few reasons. Firstly, the etching rate of the oxygen plasma at low power for  $MoS_2$  is low and inefficient. To add onto that, using high power also affects the  $SiO_2$  layer, thus changing the optical contrast. Moreover, there is the possibility of the oxygen reacting with the  $MoS_2$ . Argon plasma is, on the other hand, shown to be effective for the etching of  $MoS_2$ , having a reported etching rate of 115 s per layer [20]. The etching was done by an argon plasma at a power of 50 W and a pressure of 0.01 mbar. Beforehand, an argon flush was performed.

#### PATTERNING OF MULTILAYER GRAPHENE

The multilayer graphene that is used for electrical contact with MoS<sub>2</sub> will have to be etched to obtain electrically isolated ferromagnetic contacts for spin injection. Due to the relatively high etch rates for graphene, an oxygen plasma serves well for the controlled patterning of graphene. The etching was initiated after writing an etch channel pattern was written by EBL. How the exact patterning is done is treated in more depth 2.4.1. Etching times depended on the thickness of the used graphene multilayer flakes. Etching was done by an oxygen plasma at 50 W and at 0.01 mbar. Beforehand, an oxygen flush was performed.



**Figure 2.5.3:** (a) A stack with no multilayer graphene after lift-off. This device is finalized. (b) Schematic overview of the device.

#### 2.5.4 Deposition of Ferromagnetic Cobalt Contacts

The final step requires getting the ferromagnetic contacts onto the stack. This is done by electron beam evaporation as is explained in 2.4.2. The thicknesses differed depending on the thickness of the used hBN. For thicker hBN, a rotational deposition was done with an angle of 20. Furthermore, the sample was rotated around its own central axis for a uniform deposition. A 40 nm film of cobalt was deposited on thin hBN ( $\sim$ 10 nm), whilst for thicker hBN ( $\sim$ 150 nm) a 60 nm cobalt film was used. This was done under a deposition rate of 1 Å s<sup>-1</sup>. However, the cobalt deposition rate was very unstable, deviating with approximately 0.3 Å s<sup>-1</sup>.

To minimize oxidation of the cobalt contacts, a thin additional film of gold was deposited. For thin hBN flakes this additional gold layer was  $\sim$ 40 nm thick, for thinner hBN the thickness for the gold layer was  $\sim$ 10 nm.

#### LIFT OFF

After the deposition, the unexposed PMMA layer is taken off by lift off. This is done by a 10 minute bath in acetone heated to  $50 \,^{\circ}$ C on a hot plate. As such the residue PMMA with the thin metal films on top is taken off, and all we are left with is our final device. After lift-off, the device should look similar to the one shown in 2.5.3.

Through measurement to knowledge.

Heike Kamerlingh Onnes

# **3** Measurement methods

DEPENDING ON THE AMOUNT OF CONTACTS CONNECTED, it is possible to measure different properties of the device. From two connections up to four, this chapter treats the different electrical circuits used to characterise transport in our devices.

Firstly, the sample is stuck to a sample holder and wirebonded. It is then loaded into a vacuum tube in between two magnetic poles. Via the sample holder, the sample its contacts are connected to a switch-box, which can electrically connect, ground or float every contact individually. The switch-box itself is connected to a lock-in amplifier through an IV-measurement box. Lastly, a computer running LabView is connected to the lock-in amplifier. A random lock-in frequency below 20 Hz is used to filter out any noise frequencies. This setup is schematically shown in Figure 3.0.1



Figure 3.0.1: Schematic of the measurement setup.

#### 3.1 CHARACTERISATION OF RESISTANCES

#### 3.1.1 Two probe measurements

With two probe measurements, the voltage drop is measured over the same contacts through which the current is sent. As such, we measure the addition of the wiring resistance  $R_w$ , contact barrier resistance  $R_c$  and the resistance of our channel or sheet of two dimensional material  $R_s$ . This is schematically shown in Figure 3.1.1.a. With this, we can characterise the type of contacts we have, as is discussed in Section 1.2.1. High lock-in phase shifts and high resistances often signify broken and badly working electrodes.

#### 3.1.2 THREE PROBE MEASUREMENTS

With three probe measurements, only the resistances for which the current is enclosed by the voltage probing electrodes is taken into account. Thus we get a contribution of only the contact barrier resistance and the wiring resistance,  $R_c$  and  $R_w$  respectively, giving even more details for the characterisation of the contacts. Figure 3.1.1.b schematically shows a three probe measurement.

#### 3.1.3 Four probe measurements

Connecting all electrodes separately to the voltage and current terminals gives us the possibility of electrical characterisation of the transporting sheet. The current is sent through the most outer contacts, whilst the voltage drop is measured over the contacts in between. Thus, only the resistance of the transporting channel, the sheet resistance  $R_s$ , and not that of the contacts,  $R_c$ , is measured (Figure 3.1.1.c). The sheet resistance can be normalized to the square resistance,  $R_{sq}$ , by multiplying it with the ratio of the length and

the width of the transporting flake.



**Figure 3.1.1:** (a)-(c) are circuit representations of devices with four contacts. The grey, purple and brown resistors represent the wiring, contact and sheet resistances respectively. (a) A two probe measurement on the device measures the addition of all resistances. (b) A three probe measurement will take only the wiring and the contacts in account. (c) A four probe will measure only the sheet resistance.

#### 3.2 Application of a gate voltage

Using a back gate, a gate voltage can change the Fermi level of the transport channel. As such, we can tune the resistances by sweeping the back gate voltage. With this, further characterisation of the contacts can be done. When measuring the sheet resistance of graphene, a Dirac curve will be shown with variation of the back gate, such as in Figure 1.4.1. The back gate voltage is applied by using a Keithley 2410<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup>http://www.keithley.com/products

#### 3.3 Spin transport measurements

Spin transport measurements are done with non-local four probe measurements as was explained in Section 1.3. These measurements have also been performed under application of a back gate.

In God we trust. All others must bring data.

W. Edwards Deming

# **4** Results and data analysis

BEFORE ANYTHING, we look at some data acquired for the characterisation of the stacked devices. Then we will treat the data for electrical and spin measurements, such as the non local measurements treated in Section 1.3.

#### 4.1 STACK CHARACTERISATION

After fabrication of a complete stack by transfering, the first thing done is a height and thickness analysis by AFM. A few reoccuring problems became clear with this.

Firstly, as seen in the transparent to white spots of Figure 4.1.1, there is a big problem of bubbles potentially forming. These bubbles form directly when stacking  $MoS_2$  onto the single layer of Graphene. Furthermore, when stacking everything onto the hBN flakes, more bubbles can be observed. As both  $MoS_2$  and hBN are hydrophobic by nature, they effectively trap any residing water the moment they are stacked onto differ-

ent materials. Reducing the amount of bubbles formed is possible by shortly heating the sample before stacking. As such some water will evaporate and escape from the surface, causing less trapping of water. Furthermore, several steps in the process cover the whole stack by polymers.

Whereas first the polycarbonate used for the stacking of the materials is used, every stack is spin coated by PMMA before any lithograpy is performed. This implies that the surfaces of the materials can still have polymer residues, even after the removal of the covering layer by chloroform or acetone. An additional cleaning step might remove some of the residues.

AFM measurements showed that the thicknesses of all used  $MoS_2$  flakes were around 3 nm to 4.5 nm thick, corresponding to 4 to 7 layers of  $MoS_2$ .



**Figure 4.1.1:** Microscopic images of a hBN/SLG/MoS<sub>2</sub>/MLG stack on silicon substrate with 300 nm  $SiO_2$ . This particular sample is labeled RR2D1. Left (a) a falsely colored AFM image. Here, the purple color signifies the  $SiO_2$  substrate. The green color shows the still exposed parts of the hBN flake, whereas the blue color does the same for the  $MoS_2$ . The single layer graphene is masked by the other flakes, but positioned by the red outline. The top strips of multilayer graphene is shown by the grey color. Note the many bubles and polymer residues. Right (b) A 100x zoom of the sample by optical microscopy. Note again the bubbles and polymer residues show up as light yellow and brown spots.

Using the AFM image shown in Figure 4.1.1.a, we substracted some height profiles of the device. The multilayer strips of graphene have a thickness of 1.2 nm, whereas the  $MoS_2$  has a thickness of 4.2 nm. The hBN is relatively thick, showing a thickness of 165 nm. Whereas the  $MoS_2$  might be too thick for efficient tunneling, electrical characterisation of transport through underlying SLG is shown for  $MoS_2$  up to 10 layers thick [1].

#### 4.1.1 LAYER THINNING MEASUREMENTS

As thin MoS<sub>2</sub> flakes werer hard to acquire, some layer thinning by RIE was done for samples with no top multilayer graphene. Characterisation of this thinning was hard to do, since etching was initiated after the flakes were stacked. Thus, not only the thickness of the MoS<sub>2</sub> was changing, but the thickness of the exposed hBN flake as well. Figure 4.1.2.a shows a difference in contrast after thinning down the MoS<sub>2</sub> and hBN of device RR2D3. In Figure 4.1.2.b, AFM images are shown before and after etching for 120 seconds. Assuming that there is no change in the thickness of substrate its SiO<sub>2</sub>, it can be determined that around 0.6 nm is etched from the MoS<sub>2</sub> flake - corresponding to approximately one layer. This is in agreement with what is found by *Liu et al.* [21].



**Figure 4.1.2:** (a) Atomic force image of the stack before etching was initiated. The height of the  $MoS_2$  flake is determined to be 4.4 nm (Profile 2: red line), whilst that of the hBN is 5.7 nm (Profile 1: black line). (b) After 120 seconds of etching, the height of the hBN that is not covered by  $MoS_2$  is 1.1 nm (Profile 1: black line), whilst the height of the  $MoS_2$  with the covered hBN is 8.4 nm. As such, 0.6 nm (Profile 2: red line) should be etched from the  $MoS_2$ .

Furthermore, for extremely long etching times ( $\sim 600 \text{ s}$ ), it can be noted that even a change in the substrate its SiO<sub>2</sub> can be found. In addition to the difficulty in characterising the change in thickness, etching of stacks showed possible bursting of bubbles.

#### 4.2 Electrical measurements

By electrical measurements we can determine the nature of contacts we have (i.e. transparent, pinhole or tunneling contacts). Furthermore, it should enable us to get an electrical characterisation of the device and its components.

Using the same device (RR<sub>2</sub>D<sub>1</sub>) as depicted in Figure 4.1.1, electrical characterisation and spin valve measurements were performed. Figure 4.2.1 shows device RR<sub>2</sub>D<sub>1</sub> with its contact pattern and a schematic overview. Working contacts are labeled with a number - broken contacts are, on the other hand, depicted with a cross.



**Figure 4.2.1:** (a) Light microscopic photo of a device at 100x magnifaction. Broken contacts are depicted with a cross. Working contacts are labeled by a number. Note the top contacts running over the flake are simply test contacts, they are not taken into consideration for any measurements. (b) Schematic overview of the device with only the working contacts depicted.

Three terminal measurements as shown in Figure 4.2.2(a) for the contact resistances wielded unexpected results - giving a large difference between the different contact resistances of different contacts. Their linear behaviour suggests that the contacts are not of tunneling nature. The resistance of contact 4  $R_{c,4}$  was determined to be 375  $\Omega$ , whereas the contact resistance of contact 43  $R_{c,43}$  is determined to be 6520  $\Omega$  by taking the slopes in Figure 4.2.2.a.



**Figure 4.2.2:** (a) Voltage-current dependence of the contacts. Note the kink in the line of contact 43, this is due to incorrect sensitivity at those points of the measurement setup. (b) Schematic representation of the three probe circuit used for measuring the contact resistance of contact 4.

#### 4.2.1 INFLUENCES OF THE GATE VOLTAGE

The low resistance of contact four is expected to be due to interference of the bubble with the contact. This is because contact 4 showed a strange dependence on both back gate and temperatures, which both influences the bubble [1].

The dependence of the sheet resistance on an applied back-gate voltage was done by a four probe measurement as depicted in (4.2.3.b) When measuring the sheet resistance of graphene, the result should yield a Dirac curve as dependence on the applied back gate voltage, similar to the one seen in 1.4.1.b. Furthermore, the maximum square resistance for a single layer graphene should be around  $6 \text{ k}\Omega$ .

Whereas the measured sheet resistance does show a nonlinear decay (Figure 4.2.3.a), there is no dirac peak even at high gate voltages. In addition to that, the square resistance  $(R_{square} = R_{sheet} \frac{L}{W})$  would be even



**Figure 4.2.3:** (a) Sheet resistance as dependent on back gate. Despite the nonlinear dependence, no Dirac curve is seen. (b) Schematic representation of the four probe circuit to measure the sheet resistance.



**Figure 4.2.4:** (a) Current path when the  $MoS_2$  is acting as a tunnel barrier for spin injection into graphene. (b) Current path when transport goes laterally through  $MoS_2$ .

higher, as the single layer graphene flake is longer than it is wide.

Figure 4.2.5.a shows measurements where the resistance of contact 43 and the transport channel are taken simultaneously and where only the resistance of contact 43 is taken. We note that the behaviour of the contact resistance as dependent on back gate is similar to that of the sheet resistance. The decreasing resistance with more positive backgate is to our expectations when the transport goes laterally through  $MoS_{27}$ , as is schematically shown in Figure 4.2.4.b.



**Figure 4.2.5:** (a) Dependence of the contact resistance and the sheet resistance on the back gate. (b) Schematic representation of the circuit for measuring the contact resistance (using  $V_1$ ) and the contact resistance and sheet resistance together (using  $V_2$ ).

This can be understood by the Shottky barrier that forms between the contact/MoS<sub>2</sub> interface. The bending of the MoS<sub>2</sub> band is directly influenced by the applied back gate, where a higher gating voltage corresponds to less bending. This is conceptually explained in Figure 4.2.6. Reducing the bending would imply that electrons hop over more easily, which in turn decreases the resistance. This works the other way around as well: a decreasing gate voltage corresponds to a higher stronger bending, which corresponds to a higher resistance. This is in agreement with the MoS<sub>2</sub> being an n-type semiconductor for which an applied positive gate voltage induces an accumulation of electrons [18], and the fact that a positive (negative) back gate causes an increasing Fermi level for the contacts as it directly induces electrons (holes).

#### 4.3 SPIN MEASUREMENTS

High contact resistances are essential to acquire tunneling nature of contacts. However, in the used geometry it seems that spins cannot be forced to tunnel through the  $MoS_2$ . Instead of obtaining the switching character of the resistance when changing the relative magnetisation of the contacts, as was seen in Figure 1.3.1, a flat, constant resistance was obtained as seen Figure 4.3.1.

This leads us to believe even further that the  $MoS_2$  does not function as a tunnel barrier, but as a transport channel instead.



**Figure 4.2.6:** In the case of  $V_g < 0$ : Strongly bent MoS<sub>2</sub> band. This bending gets stronger when a negative back gate is applied. The electrons traveling through the MoS<sub>2</sub> experience a relatively high barrier, increasing the resistance for the lateral direction of MoS<sub>2</sub>.

In the case of  $V_g > 0$  Weakly bent MoS<sub>2</sub> band. This bending gets less when a positive back gate is applied. In this case, the electrons traveling laterally through the MoS<sub>2</sub> experience less resistance, as it is easier for them to hop over the barrier.



**Figure 4.3.1:** Attempt at measuring the spin valve effect by sweeping the magnetic field whilst measuring the resistances. Note that there is no switching behaviour as is seen in the spin valve in Figure 1.3.1. (a) Measurement data obtained. (b) Four probe setup used to measure a spin-valve effect.

#### 4.4 CONCLUSION AND OUTLOOK

Electrical characterisation measurements performed on our Co/multilayer

graphene/MoS<sub>2</sub>/single layer graphene device showed high contact resistances.

Four probe measurements with applied back gating indicated that the MoS<sub>2</sub> did not function as a tunnel barrier for spin injection, but rather as conducting channel itself. This can be said because no Dirac curve

appeared, indicating no transport through single layer graphene. An attempt at spin transport measurements strongly supports the idea of our  $MoS_2$  sheet functioning as an electrical transport channel, as no switching spin valve behaviour could be seen when sweeping the magnetic field.

Using the current geometry, it is shown that there is electrical tunability of the contacts, even when the transport is laterally through the  $MoS_2$ . Applying a positive back gate should decrease the bending of the  $MoS_2$  band. Therefore, there is a decrease of the resistance. This also works the other way around, where a decrease of gate voltage should increase the bending, and as a result increase the resistance.

To gain vertical transport through the  $MoS_2$  layer instead of lateral transport, a direct contact on the single layer graphene can be introduced. As such, this contact can promote tunneling through the  $MoS_2$ , as it will actively drain the current through our graphene. Figure 4.4.1 schematically shows the design of such a device, and is an iteration of the used device design in this thesis.



**Figure 4.4.1:** Schematic of an iter ation of used devices. One contact is now positioned directly onto the single layer graphene, possible promoting the function of  $MoS_2$  as a tunnel barrier.

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