Electric field modulation of spin and charge transport in two dimensional materials and complex oxide hybrids
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EXPERIMENTAL CONCEPTS

ABSTRACT

This chapter introduces most of the experimental methods used for the research in this thesis. First the exfoliation and transfer of 2D materials on different substrates will be treated. Then the preparation procedure for SrTiO$_3$ (STO) substrates is explained. This is followed by the fabrication procedure of the electrical contacts on the 2D material based and the three terminal samples. Finally the details of the setup for electrical measurements is discussed together with the measurement circuits which were used.
3.1 EXFOLIATION

Ever since the first isolation of and measurements on a two-dimensional (2D) material in 2004 [1], there has been a major growth in research on 2D materials. The graph displays the amount of Google Scholar results for a certain material per year. Notice the increase in results around 2000 for graphene and around 2010 for MoS$_2$ and hexagonal boron nitride (h-BN).

A major reason for the popularity of graphene and other 2D material research is the accessibility of the method which was used to isolate a single layer. The only tools which are needed are: an oxidised Si wafer, a microscope, patience and some Scotch tape. The method is therefore also known as the Scotch tape method.

The basis of the method relies on the fact that the bulk materials are build up from single layers stacked on top of each other and held together by relatively weak van der Waals bonds. Since the atoms in a layer are bonded by, much stronger, covalent bonds, several layers can be peeled off. Repeating this process a few times eventually can result in a single layer.

In practise we applied some Nitto semiconductor wafer tape (which has less glue than regular tape) to a bulk crystal and removed it. This usually peals off thick layers from the bulk crystal. These thick layers could be thinned further, by placing another tape on the first piece and removing it. Usually this process was repeated 2-3 times, until transparent areas could be seen on the tape, signifying very thin regions.

Then the tape was placed on a piece Si wafer with an SiO$_2$ thickness of 300 nm. The SiO$_2$ thickness is actually of great importance, since it determines the contrast of the material on top [2]. Furthermore the substrate could be heated before or after the tape was applied and optionally combined with an oxygen plasma cleaning step, in order to increase the yield of large single layer flakes [3].

After removing the tape an optical microscope was used to find suitable flakes. The thickness could be very well estimated by measuring the contrast of a flake, since this increases in a fixed stepwise fashion, as shown in a redrawn image from reference [4].
Additionally the thickness can be verified using an atomic force microscope (AFM) [5] or Raman spectroscopy [6]. Although with AFM it can be difficult to judge the height, due to possible polymer remains on the flake and/or different interactions between the AFM tip and the substrate versus the tip and the flake [7].

3.1.1 Exfoliation on PDMS

Another possibility is to exfoliate on a piece of transparent polydimethylsiloxane (PDMS) [8]. The advantages of this method is that once a flake is found, it can easily be transferred on top of another flake. This enables more complex device geometries, as many 2D materials have different electrical properties. Also for some materials, such as MoS$_2$, it is easier to get relatively large and thin flakes on PDMS.

Exfoliation on PDMS is slightly different than on SiO$_2$. When exfoliating on PDMS it is important that the tape, containing the bulk material, is quickly pulled off. This is because flakes do not stick very well to PDMS upon slow movements, but do stick when the tape is quickly removed. Because of the low adhesion of flakes on PDMS for slow movements, they could later easily be transferred on top of another flake and/or on a different substrate.

Once exfoliated, it turns out that some materials such as graphene are very hard to see due to limited contrast, but a transition metal dichalcogenide (TMD) such as MoS$_2$ has a better contrast on PDMS. An example of MoS$_2$ contrast increment on PDMS and SiO$_2$ is shown. On PDMS the flake seems brighter the thicker it gets, because its brightness is solely determined by the reflected light off the flake. On the other hand, when it is on 300 nm SiO$_2$, it also starts changing colour after a few layers, because the colour is determined by the reflected light of the flake plus the reflected light which also went through the SiO$_2$. This makes it harder to judge the layer thickness.

After locating a proper flake it could be transferred to another substrate or on top of another 2D material as follows: 1. The PDMS stamp was on a supporting glass slide and was mounted in a modified UV mask aligner. Using the micro manipulators the flakes were aligned. 2. After adjusting, the glass slide with PDMS stamp was lowered until contact was made with the target substrate. Preferably the initial contact point was some distance away from the flake which should be transferred. Then the contact pressure is increased slightly so the fringes (who outline the contact area) move slowly past the flake. 3. Once passed the flake, the pressure was decreased so the fringes move back. Because flakes do not stick well to PDMS upon slow movements and do stick to the target substrate, it transfers to the substrate [8].
3.2 PICK-UP AND TRANSFER OF FLAKES

Another method of stacking flakes on top of each other is the so called pick-up method [9]. Using this, flakes can be picked up from a substrate and if desired be used as a base to pick up more flakes. Afterwards, the stack or flake can be deposited onto another substrate. This method is also convenient when the contrast of the 2D material is very low on the target substrate (such as graphene on SrTiO$_3$ (STO)).

In short, this method relies on a sticky film of polycarbonate (PC) (Sigma Aldrich), which was made from solution of 6 wt.% PC dissolved in chloroform. 1) The PC film was spanned across a PDMS stamp, which was mounted on a glass slide. After aligning the PDMS stamp with the target flake, it was slowly lowered onto the flake. The substrate was then heated to \(~70^\circ C\) in order to adhere the PC film to the flake. Once cooled down, the stamp was retraced taking the flake with it. 2) The first substrate was swapped for a new one and the stamp is lowered once again. 3) However, now the substrate was heated to \(~170^\circ C\), which melted the PC film. When the stamp was retracted, the flake and the film were left on the substrate [9].

1. Pick-up \((\sim 70^\circ C)\)

Glass slide

\[ \downarrow \]

PDMS

PC

\[ \downarrow \]

target flake

Substrate #1

2. Transfer

\[ \uparrow \]

Substrate #2

3. Release \((\sim 170^\circ C)\)

The PC film was removed by placing the substrate in 50°C chloroform for a few hours up to overnight. In between the chloroform was refreshed. Before the sample was taken out of the chloroform, it was refreshed three times; then replaced by isopropyl alcohol (IPA), which was also refreshed three times. During this procedure the sample stayed submerged in fluid the entire time. After drying the sample, an AFM was used to verify whether most of the PC had been rinsed off.

3.3 TITANIUM DIOXIDE TERMINATION OF STRONTIUM TITANATE

SrTiO$_3$ (STO) \((100)\) consists of alternating planes of SrO and TiO$_2$. The layer which is at the surface of the substrate is referred to as the terminating layer. When substrates are bought, they usually contain a mixed termination. It is usually preferred to have a single TiO$_2$ terminating layer across the entire surface, because it is chemically more stable.
In order to get a TiO₂ terminated surface a standard procedure was followed [10, 11]. First the sample was ultrasonicated for 30 minutes in de-ionised (DI) water to remove SrO through hydrolyses, where \( \text{H}_2\text{O} + \text{SrO} \rightarrow \text{Sr(OH)}_2 \). Next the \( \text{Sr(OH)}_2 \) was removed by ultrasonication for 30 s in buffered hydrofluoric acid (BHF). Finally the substrate was ultrasonically rinsed for 20 minutes in DI water. The surface then had terraces with rough edges, as shown on the AFM height scan. In order to get straight terraces, the sample was annealed at 960 °C for 1.5-2 hours, depending on the width of the terraces. The width of the terraces are determined by the miscut angle of the substrate.

3.4 CONTACT FABRICATION

The samples which were made for this thesis can be divided into two classes: the 2D material based samples of chapters 4 and 6 and the three terminal devices of chapter 5. Both of which had slightly different contact fabrication procedures and therefore will be treated separately.

3.4.1 Two dimensional material based samples

The contact fabrication procedure was as follows:

1. A layer of AR-P 679.04 EBL resist from AllResist was spin coated at 4000 rpm. For STO substrates, an additional layer of conductive Aquasave was spin coated, to prevent charge accumulation during electron beam lithography (EBL).

2. After baking, a scratch was made in the polymer. This was then used as a reference to position the markers around the flake.

3. Using EBL, alignment markers were written in the resist at 10 kV, with an 10 µm aperture and a dose of 150 µC cm⁻².

4. After developing for 60 seconds in methyl isobutyl ketone (MIBK):IPA 1:3 mixture, the markers were visible. The large (2 mm) markers can be seen in the corners of the image and the small (200 µm) markers are in the corners of the central rectangle.
5. A contact design was made, where the makers were used for alignment w.r.t. the flake. If magnetic contacts were used, several things had to be taken into account for the design of the contacts on the flake. First the width of the contacts was varied in a pattern of \((1, 3, 5, 2, 4, 6) \times 100\) nm, to prevent neighbouring contacts from having similar switching fields. Secondly, the last stretch of the contact had two 90° angles, to prevent domain propagation.

6. Using a second EBL step, small contacts (in a 200 by 200 \(\mu\)m\(^2\) area) were exposed at 10 kV with an 10 \(\mu\)m aperture. Large contacts (in the 2 by 2 mm\(^2\) area), were exposed at 10 kV with an 120 or 60 \(\mu\)m aperture. All contacts were exposed with a dose of 150 \(\mu\)C cm\(^{-2}\), except for structures with a dimension \(\leq 100\) nm, for which the dose was increased with a factor 1.3-1.5.

7. After development of the exposed areas, the sample was loaded into an electron beam evaporator. When the system reached a pressure \(p < 3 \times 10^{-6}\) mbar, most depositions could start. Only for tunnel barriers and Co contacts the pressure was lowered to \(p \approx 8 \times 10^{-7}\) mbar by evaporating Ti.

8. For non magnetic contacts 5 nm of Ti was evaporated as a sticking layer, followed by 40 nm of Au. For magnetic contacts first an Al tunnel barrier was evaporated in two 0.4 nm steps. After each layer, the Al was oxidised by flushing the chamber with \(O_2\) for \(\sim 10\) mins (up to a pressure of \(\sim 10\) mbar). This was followed by evaporation of 35 nm Co and 5 nm of Au or Al, to prevent the Co from oxidising.

9. Lift-off was done in 45°C acetone for \(\sim 10\) mins and rinsed with IPA.

10. The back of the sample was glued to a chip carrier using silver paste, which functioned as the back gate. In case of magnetic contacts, the direction of the small contacts on the flake w.r.t. the chip carrier (and thus the magnetic field) was important. The large bar indicates the direction of the small FM contacts, which are shown on the right. Finally, Al wire bonds connect the contacts on the sample with the chip carrier.
3.4.2 *Three terminal devices*

The device fabrication of the three terminal devices was as follows:

1. A Nb:STO substrate was chemically treated to obtain a fully TiO$_2$ terminated surface.

2. The sample was loaded into a deposition system and pumped down to a pressure $p < 10^{-5}$ mbar. Then O$_2$ gas was introduced in the load lock three times and pumped again, in order to clean all the lines from any non-oxygen gasses. Next an oxygen plasma was ignited to remove organic residues from the surface. This was done for 2 minutes at a oxygen pressure of 0.1 mbar and a power of 60 W. The plasma was at some distance away from the substrate, to prevent energetic oxygen ions from damaging the substrate.

3. After the cleaning, the chamber was pumped down to $p < 10^{-6}$ mbar. A thin layer ($\sim 1$ nm) of Al was evaporated and oxidised to form Al$_2$O$_3$ using the same O$_2$ plasma as before.

4. After pumping the chamber down to $p < 10^{-6}$ mbar, 20 nm of Co and 20 nm of Au were evaporated.

5. A photo resist (PR) was spin coated on the sample and with UV-lithography contacts were defined over the entire sample. Using Ar ion beam etching (IBE) pillar structures were etched. The central pillars have dimensions ranging from $50 \times 100$ up to $200 \times 400 \mu$m$^2$. The outer reference contacts are several times larger, so the central contact always has the highest resistance.
6. Next the etched trenches around the pillars were filled up with 150 nm of AlO<sub>x</sub> by e-beam evaporation. Then a new UV-lithography step was used to define the contact pads which consist of Ti(5 nm) and Au(150 nm). Next the sample was wire bonded onto a chip carrier. The bonds on the sample were placed directly on the Ti/Au above the AlO<sub>x</sub>, to prevent bond wires piercing into the pillars or making direct contact with the semiconducting Nb:STO substrate.

3.5 ELECTRICAL MEASUREMENTS

Most electrical measurement setups at the Physics of Nanodevices group were very similar, except for some small details. In all setups the sample could be loaded into a vacuum can ($p < 10^{-5}$ mbar), to prevent samples from oxidising. Around the vacuum can was an electromagnet, which could generate magnetic fields up to ±1.5 T, depending on the setup and pole separation. Additionally, some setups had a cryostat for temperature dependent measurements between 4 and 400 K.

The measurements were controlled via a computer which was running either LabView or (Python based) QT lab measurement software. The computer was connected to either a lock-in amplifier (SR830) for AC measurements, or to a Keithley 2400 for DC measurements. The output of these went to an IV measurement box. Although this was optional for the Keithleys, which could be connected directly to the switch box. The IV measurement box converted $V_{\text{out}}$ to a current, in a range from 1 pA/V to 100 mA/V.

The signals from the Keithley or the IV measurement box were sent to a switch box, which was used to make a physical connection to the contacts on the sample. There were different switch boxes in use, but most contain a filter to reduce noise and which adds 1 kΩ and a capacitance of 10 nF to each contact.

The return signals from the switch box either went directly to the Keithley or went via the IV measurement box. The IV measurement box could amplify the return signal with a factor 1 to $10^5$. Then the signals were sent to the lock-in or Keithley, which could be read out by the computer.

Additionally a second Keithley could be connected to the back of the substrate, in order to gate the channel of the device.
3.6 Measurement Circuits

Using the switch box three different circuits could be set up, where each measured a different part of the device and/or parts of the setup.

First of all the 2 probe geometry measured all the resistances in the circuit: the leads and filters \( R_f \) (where usually the filters have a larger resistance than the leads), the resistance of the contacts/interface/area below the contact \( R_c \) (where usually the interface dominates) and finally the resistance of the channel \( R_{\text{channel}} \).

Secondly in a 3 probe geometry we could single out \( R_f + R_c \), because the voltage probes only measure a potential difference in parts where a current was running. As mentioned, \( R_f \) is usually dominated by the filters with a known resistance, thus \( R_c \) was easily deduced. Finally the resistance of the channel could be measured in a 4 probe geometry.

3.6.1 Lock-in amplifiers

For some measurements the signals were very small compared to the noise. In order to recover the signal, a lock-in amplifier was used. A lock-in sends out a sinusoidal reference signal \( V_{\text{out}} = V_L \sin(\omega_L t + \theta_L) \). This signal was converted to a current in our lab using the IV measurement box and sent to the sample. The return signal from the sample was also a sinusoidal signal \( V_{\text{in}} = V_{\text{sig}} \sin(\omega_r t + \theta_{\text{sig}}) \), which again went the IV measurement box.

Both signals were then multiplied in the lock-in by the phase-sensitive detector:

\[
V_{\text{psd}} = V_{\text{out}} V_{\text{in}} = \frac{V_L V_{\text{sig}}}{2} \left[ \cos \left( [\omega_r - \omega_L] t + \theta_{\text{sig}} - \theta_{\text{ref}} \right) - \cos \left( [\omega_r + \omega_L] t + \theta_{\text{sig}} + \theta_{\text{ref}} \right) \right].
\]

After passing the signal through a low pass filter, in order to remove all AC signals, only a DC signal was left if \( \omega_L = \omega_r \):

\[
V_{\text{psd}} = \frac{V_L V_{\text{sig}}}{2} \cos \left( \theta_{\text{sig}} - \theta_{\text{ref}} \right).
\]

The result is a DC signal which is proportional with the signal amplitude \( V_{\text{sig}} \).

REFERENCES

3. EXPERIMENTAL CONCEPTS