

FANCY MASTERARBEIT OF DEATH

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1 INTRODUCTION

2 PHYSICAL PROPERTIES OF TRANSITION METAL DICALCOGENIDE MONOLAYERS

2.1 CRYSTAL STRUCTURE AND SYMMETRIES

Like to all layered materials, TMDs consist of large covalently bound sheets, that are held together by the weak van-der-Waals force. And similar to graphite these sheets have a hexagonal lattice structure and form layers of only one unit-cell in the out-of-plane axis. It is the details of these unit-cells that distinguish TMDs from graphite and other layered materials. The fundamental building block of the bulk crystal is a single sheet, the monolayer that consists of three atomic layers – A layer of transition metal atoms like tungsten (W) or molybdenum (Mo) sandwiched between two layers of chalcogen atoms like sulfur (S), selenium (Se) or tellurium (Te). This thesis is primarily concerned with tungsten-based TMDs : WSe_2 and WS_2 . TMDs can be in different phases, that have a different crystal structure as well as different electronic properties. The semiconducting phase is called 2H. In this configuration every transition-metal atom has six neighbouring chalcogen atoms and forms a trigonal prismatic unit-cell, with the transition-metal in the center as depicted in Figure (Figure). A TMD monolayer exhibits a D_{3h}^1 -symmetry. The unit-cell is invariant under 3-fold rotation as well as in-plane reflection. In the top-view (Figure) this looks similar to the hexagonal lattice structure of graphene, but with the key difference of a broken inversion symmetry. When the unit-cell is inverted with the transition metal atom as its inversion center, the chalcogen atoms wind up in empty locations and so they to with any possible inversion point.

2.2 CRYSTAL STRUCTURE AND SYMMETRIES

2.3 ELECTRONIC BANDSTRUCTURE AND SPIN ORBIT COUPLING

2.4 EXCITONS IN TMDS

2.4.1 BINDING ENERGY

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3 FABRICATION OF FIELD EFFECT STRUCTURES

The fabrication of a functioning field effect structure of TMD mono- or bilayers roughly consists of three different procedures. The production of suitable flakes of TMD's, the preparation of an electrode both on the sample and in the substrate and the assembly of the full device on top of it.

3.1 MECHANICAL EXFOLIATION

Thin films of layered materials like TMD's, like many nanomaterials, can be fabricated using a top-down or bottom-up approach. The bottom-up approach for these particular materials is called chemical-vapor deposition (CVD) (Reference). Because of its scalability it is the leading candidate that could be used in an industrial fabrication pipeline. However, the top-down approach of mechanical exfoliation (Reference) has become the first choice for a lot of projects to build high quality model systems, that can be used to study physics in low dimensions. The reason is the so far superior quality of few-layer flakes in terms of defects and contaminants as well as the synergy with dry transfer methods (Reference (Later chapter)).

The mechanical exfoliation process – often referred to as the “scotch tape method” – is based on the fact, that the van-der-Waals forces between adjacent layers in TMD's are much weaker, than the lateral covalent bonds inside them. In fact, they are weak enough, that they can be easily broken apart by adhesive tape.

The starting point is a solid crystal of TMD-material, that can be produced either naturally or synthetically with high purity (supplied by hq-graphene). When a stripe of adhesive tape is brought in contact with it, a small amount can be peeled off. With a second stripe, that is put on the first one, the process is repeated multiple times. Each time, the fresh tape is peeled off its parent, the strong adhesion between tape and TMD ensures a clean interface. Three to four repetitions are an optimum to produce monolayers of a useful size. More repetitions further thin the material but heighten the risk of these thin films to break to smaller pieces, which complicates processing the flakes later on and build larger devices.

To prepare monolayer flakes for the assembly of more complex devices, they first have to be transferred onto a suitable substrate. In this work, this substrate is silicon with a layer of thermal oxide that is between 50 and 90 nm thick. Before wafers of this material are brought in contact with the exfoliation tapes they are cleaned both in acetone and isopropanol before being exposed to oxygen plasma for 180 s. This ensures a clean surface and maximizes the material that sticks to the wafer (Reference). After the tape is in contact, the wafer is heated to 90°C. After cooling down the tape can be peeled off and the wafer is inspected for monolayers. As seen in [Figure], during this process a large number of flakes of different sizes and thicknesses are transferred and it is uncommon to find more than one monolayer of suitable size on a wafer of 10 by 10 mm.

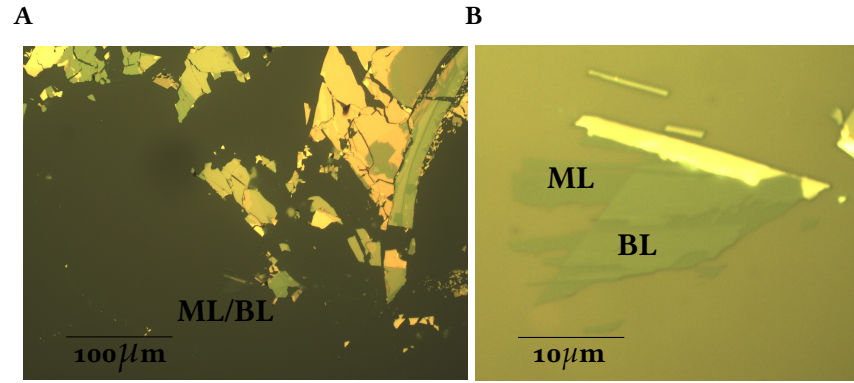


Figure 3.1: **A** During the exfoliation process a lot of flakes of different size and thickness are scattered over the substrate. Interesting specimen have to be searched for by hand. **B** Flake consting of mono- and bilayer regions that can be identified by their optical contrast.

3.1.1 LAYER NUMBER

Under an optical microscope monolayers can be identified using the optical contrast and the color. It is possible to verify the layer number by this criteria alone using a camera and image analysis software(Reference/Victor?), however this is much more reliable on transparent substrates, since the optical contrast is higher and the lighting conditions can be controlled more precisely. With our optical microscope and Si/SiO_2 substrates, monolayer candidates where instead verified using photoluminescence (PL) imaging(Referenz Andre). Because of the direct band-gap, monolayers of TMD's are much more efficient emitters than even bilayers with almost an order of magnitude difference in PL-intensity. The result can be seen in Figure 3.2. The sample is excited with a laser with a wavelength above the A-exciton resonance and only the PL is collected on the chip of a USB-camera. A detailed description of the optical setup can be found in (Optical Setup). As can be seen, the PL-image clearly identifies the monolayer-regions through bright intensity, while the bilayer region of the flake is not visible at all. On the microscope picture on the other hand, both regions do not differ much in color and reflectance and can be tricky to tell appart, especially when the lighting is inhomogenous or changes over time.

Other methods to idetify monolayers inlcude both photoluminescence and Raman spectroscopy(Reference). However, for assembling devices and verifying the quality of exfoliated flakes, PL-imaging proved to be the fastest and most versatile method.

3.2 HEXAGONAL BORON NITRIDE

For spectroscopic studies of TMD's the right substrate plays one of the most crucial parts. Hexagonal boron nitride (hBN) has proven to be the suppperior choice to observe narrow linewidth spectra in TMD's. On substrates like SiO_2 dangling bonds and strain due to surface roughness

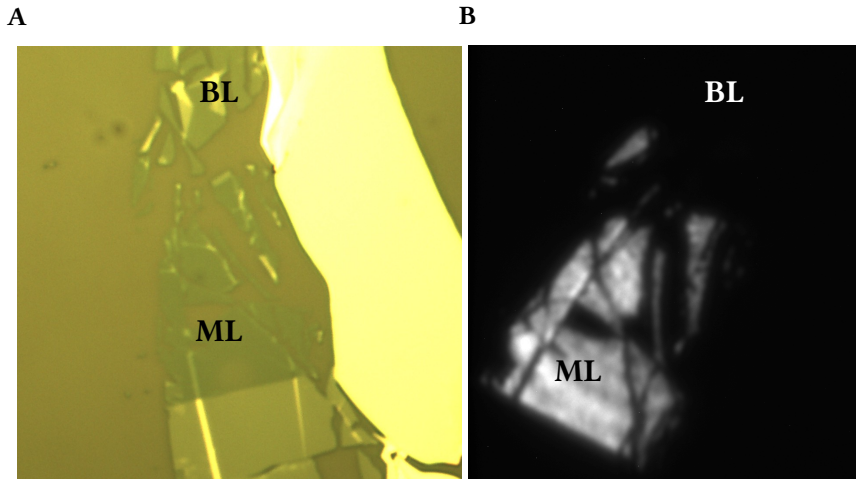


Figure 3.2: Comparison of mono- and bilayers of WSe_2 . **A** The reflectance contrast of mono- and bilayers can be used to measure the layer number. The difference is however small enough to misidentify them under changing or inhomogeneous lighting conditions. **B** The monolayer shows much higher PL-intensity than the bilayer and can therefore be identified very easily.

can induce scattering of excitons, that reduce the lifetime and induce inhomogeneous broadening. This effects are strong enough make many different spectral features indistinguishable. hBN is an has a large indirect band-gap in the UV-range, and acts like a transparent insulator. Furthermore, its graphene-like crystal structure allows the exfoliation of atomically flat terraces, that can be used as a dielectrically calm substrate, not only for optical measurements on TMDs but for other areas of layered materials as well. The best results have been obtained by not only placing flakes on hBN but to fully encapsulate them. Since hBN , much like TMDs is a layered material, flakes of it can be exfoliated in the same manner and TMD-monolayers can be fully encapsulated by “sandwiching” them between two flakes of hBN .

3.3 ELECTRODE FABRICATION

The goal of this thesis was, to fabricate high quality TMD-monolayer samples that are gate-tunable, meaning control over the charge density inside the monolayer flake leveraging the field effect. The problem of designing such a device can be understood as using the 2D-material as one plate of a capacitor, and charging it, by applying a voltage. The other plate or “back-gate” in this analogy is the conducting boron-doped silicon substrate. Flake and substrate are separated by a 50nm layer of thermal silicon-dioxide, that functions as the dielectric of the gate-structure. Both the sample on top and the back-gate have to be contacted to allow the application of a voltage.

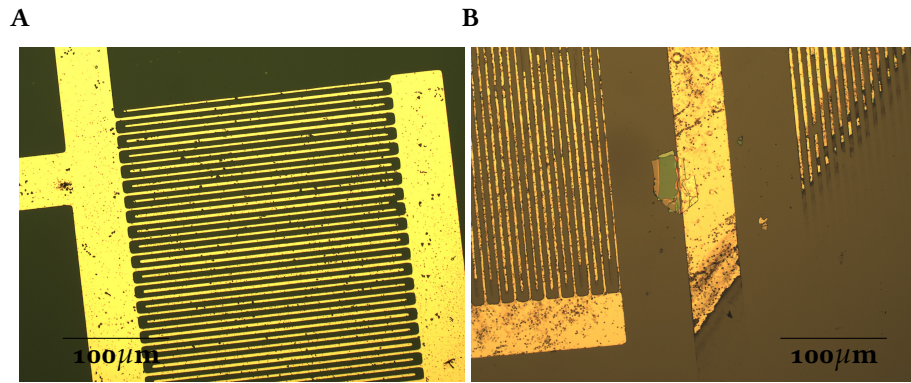


Figure 3.3: **A** Electrodes are written onto the substrate prior to the assembly of the hBN-TMD heterostructure. A preused chromium mask of an interdigital structure is used for the gold pattern. **B** As long the heterostructure is dropped in contact with a thick line of the gold pattern, minor defects in the electrode structure do not affect the functionality of the device.

3.3.1 UV-LITHOGRAPHY

In many gated devices, that incorporate TMD-monolayers, the gate electrodes are actually fabricated directly onto the sample as a last step(Referenzen). While the fabrication of contacts can be more precisely tailored in this way, the big drawback is the exposure of the monolayers to a lot of chemicals like photoresist and developer, that can contaminate the sample and lower its quality. Therefore in this work a more simple approach was chosen. Instead of writing contacts after transfer, contacts are fabricated beforehand. The encapsulated hBN-TMD-heterostructure can be contacted by dropping it on the edge of the gold structure.

The gold patterns are created using contact lithography using a chromium mask, deposited on glass. Because the heterostructure can be dropped at any point on the substrate, the precise shape of the gold structure is unimportant. Therefore no new lithographic mask had to be fabricated. Instead a suitable mask was chosen from old preused structures. The downside is, that these masks can deteriorate over time and over many uses, but because of the low requirements for the electrodes all its defects manifest themselves in a purely aesthetic manner and do not affect its functionality.

The process starts with spin coating blabla-photoresist on a Si/SiO_2 wafer. Using the blabla-Maskaligner, the wafer is brought in contact with the mask before exposing it to uv-light for 18 seconds. After that, the pattern is developed using blabla-developer, that washes out the exposed photoresist.

In the next step, the sample is coated in an X-ray evaporation system. First, a 1-5nm film of titanium is deposited on the substrate, that acts as a bonding agent. Subsequently a 50nm film of gold is deposited ontop, that forms the actual top-gate electrode. After removing the sample from the high-vacuum chamber the undevelopped photoresist is removed in the so called “lift-off”. The substrate is simply bathed in acetone, that desolves the resist below most of the deposited gold and only the structures in the developed areas remain. To speed up the

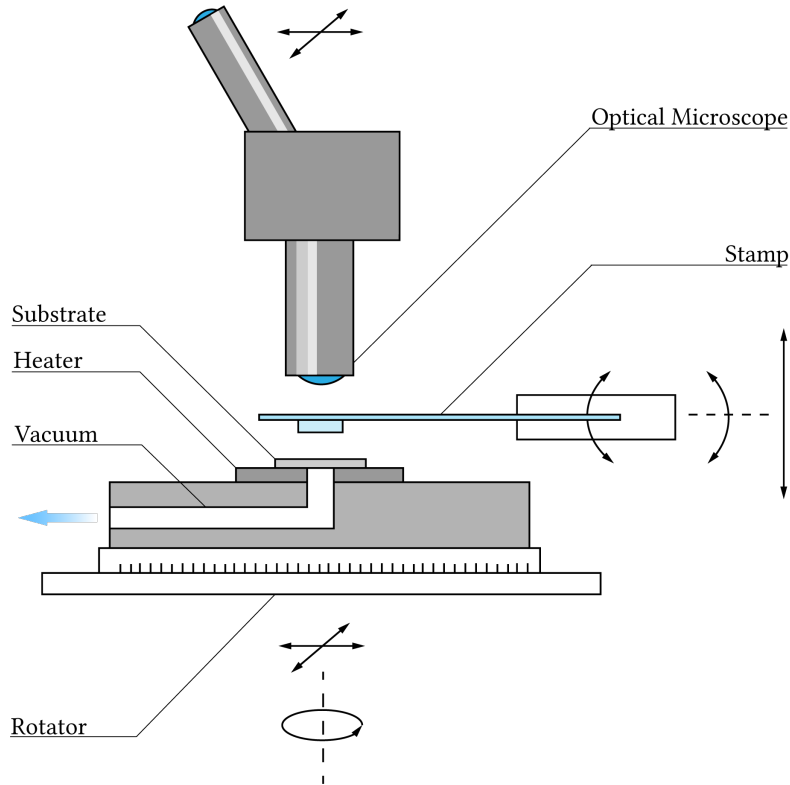


Figure 3.4: Setup for hot pick-up and stamping. The substrate is placed on a small, round **ceramic heater** with a 3mm whole in the center(Referenz Thorlabs), that is PID-controlled and can reach temperatures up to 200°C. It is mounted airtight onto the massive sample holder, that is connected to a **vacuum pump** to hold the **substrate** in place. It is **fully rotatable** and can be moved in plane. The PDMS/PPC **stamp** is mounted to a z-translator and can be tilted with respect to both in-plane axes. The OPTICAL MICROSCOPE can also be moved in-plane.

lift-off process, the sample can be placed in an ultrasonic cleaner at a low power.

The resulting structure can be seen in Figure 3.3.

3.4 HOT PICK-UP AND TRANSFER

The mechanical exfoliation method is popular also for its synergy with dry transfer methods. CVD-grown TMD-flakes are grown on suitable substrates and can be transferred to target substrate using a variation of wet methods, that involve powerful solvents or a combination of solvents and polymer films to lift the grown flakes off their initial substrate(Referenz PMMA method etc.). The advantage of the exfoliation method in this regard is that flakes can be put on any substrate directly from the adhesive tape. That led to the invention of “viscoelastic stamping”, where the TMD-material is exfoliated on a substrate of viscoelastic polymer called polydimethylsiloxane (PDMS)(Reference). This so called “stamp” could then be brought in contact

with the target substrate and peeled off carefully to drop down the flake at a desired condition opening up the possibility of producing carefully designed heterostructures deterministically.

The requirement to sandwich samples in hBN opened up the possibility of using the van-der-Waals forces between hBN and 2D-materials not only to drop down exfoliated layers, flake by flake but to pick up 2D-materials with hBN-flakes, increasing the yield as well as ensuring very clean interfaces, free of contaminants of the polymer stamp.

The method used for this work is called “hot pick-up and stamping” (Reference). The stamp used in this process is a block of PDMS, mounted on a glass slide with transparent adhesive tape. This block is spin-coated with a polymer polypropylene carbonate (PPC). To make sure, that the polar PPC sticks to the stamp while being heated to high temperatures it is treated in oxygen plasma for at least 20 minutes before the spin coating.

The TMD-flake is exfoliated on a Si/SiO₂ substrate and so are suitable bottom and top hBN flakes. The primary criteria for finding the right hBN-flakes is the flatness of its surface, so that the TMD-flake can be encapsulated between two large terraces without cracks or steps. To allow a fast fabrication process, this flatness is only judged with help of an optical microscope. More sophisticated methods like atomic force microscopy can be used to verify the flatness more accurately, however this not only extends the fabrication process but does not help determining the quality of the top hBN flake, since its interface is facing down after being exfoliated on the parent substrate.

The goal of the hot pick-up is now to use a hot-plate to control the van-der-Waals forces between hBN, TMDs and the substrate to ensure adhesion between the parts of the heterostructure as well as to reduce contamination with water molecules from the ambient air.

After all precursors are prepared on Si/SiO₂ substrates, the actual pick-up and stamping process can be carried out. The fabrication setup can be seen in (Figure whatever). The first step is the pick-up of the top hBN flake. At 40°C the van-der-Waals forces between hBN and PPC are already strong enough to lift the flake off the silicon substrate. In the next step the hBN is dropped on the TMD-flake. To make the interface as clean as possible the temperature for this drop is raised to 110°C. This ensures a stronger van-der-Waals force between hBN and TMD than between TMD and silicon-dioxide but more importantly contamination through droplets of water from the ambient air is minimized above its boiling point and other contaminants are more mobile as well. By slowly pressing the stamp against the substrate, this dirt can leave the interface of the two flakes and fewer blisters form (hotpickupper). The stack of TMD and hBN can then be picked up again following the same procedure that was used for the bare hBN flake. Afterwards it is dropped down on the bottom hBN flake. To contact the TMD flake to gold part of it has to remain outside the hBN encapsulation. This part does not necessarily have to be a monolayer but can also be any form of TMD, that is in contact with it so charges can be transported. The hBN on the other hand is elastic enough so that thicker material does not affect the encapsulation of mono- or bilayer regions.

The last step is to transfer the whole stack to its final position in contact with the electrodes. This is accomplished by repeating the pick-up process once again and dropping the stack in contact with the gold structure.

Despite the strong plasma treatment of the PDMS-stamp in some cases the PPC can peel off during the drop down part of the transfer due to high heat as the polymer becomes ever more liquid. In this case the sample can be carefully treated with acetone, which dissolves the poly-

mer rapidly. The sample subsequently has to be cleaned in isopropanole and blown dry with nitrogen gas.

3.4.1 ANNEALING

While the hot pick-up should in theory ensure a hBN-TMD interface free of contamination, especially contamination due to humidity in the ambient air can remain between the layers and seriously lower the quality of the sample. To remove this pollution, the sample can be annealed(Referenz). During annealing, the sample is placed in an annealing oven. While maintaining a high vacuum of 10^{-3} mbar, the oven heats the sample up to 250°C for around three hours. Other recipes, that use higher or lower temperatures or longer annealing times can work just as well as long as they ensure the complete evaporation of residual water.

Different groups report different recipes for this procedure(Referenzen). During the hot pick-up method the TMD-flakes are never in contact with anything but ambient air and cleanly cleaved hBN-interfaces. More aggressive recipes, that work at higher temperatures or for longer times to remove also contaminations that arise from the stamp therefore have a limited advantage over milder annealing conditions.

4 SAMPLE CHARACTERIZATION

4.1 OPTICAL SETUP

The optical setup is a confocal microscope. In contrast to a “conventional” microscope, the sample is placed in the focal plane of a low temperature objective. The focal point is the same for excitation of the sample and the detection of the reflection or photoluminescence signal, hence the name. A scheme of the complete setup can be seen in Figure 4.1. The excitation beam from a laser is guided to the so called excitation arm with a single mode optical fibre. It passes through a linear polarizer to define a polarization axis and is reflected to the objective by a beam-sampler. To analyze the mostly circularly polarized light of the detection beam, it passes through a quarter waveplate and another linear polarizer and is focussed into another optical fibre, that is connected to a spectrometer. The sample is mounted on a piezo nanopositioner inside a cryostat or can of liquid helium and connected to a voltage source, to tune the charge density in the TMD flake. A strong, homogenous magnetic field can be supplied by a superconducting magnet.

For photoluminescence spectroscopy, the sample is excited with a laserbeam with a narrow frequency profile and a higher intensity. Because this beam has a much higher intensity, than the collected PL it is tuned to a higher frequency than the main exciton resonance. A shortpass filter in the excitation arm makes sure, no Raman modes from the optical fibre pollute the spectrum. A longpass filter, right before the optical fibre of the detection arm blocks the laser, so that only PL reaches the spectrometer. To obtain a reflection spectrum, these filters are omitted. Instead, the sample is illuminated with a broad band light source at a low power. To find the signal, a background spectrum, recorded in absence of the TMD flake is subtracted from the main spectrum.

$$S_R = \frac{\Delta R}{R} = \frac{R_{\text{flake}} - R_{\text{background}}}{R_{\text{background}}} \quad (4.1)$$

The signal S_R is the difference of the Reflection signals of TMD flake and background. The division by the background reflection is made to normalize the signal. The resulting reflection spectrum should show only features, of the flake. In practice, the obtained data has to be evaluated with some precautions in mind, to avoid misidentifying for example interference effects due to differences in hBN thickness as features of the absorption behaviour of the sample.

4.2 SAMPLE CHARACTERIZATION

There are two dimensions to characterize the quality of a sample. Its optical properties must include narrow linewidths, to identify different features of the spectrum and it has to be gate-

4 Sample characterization

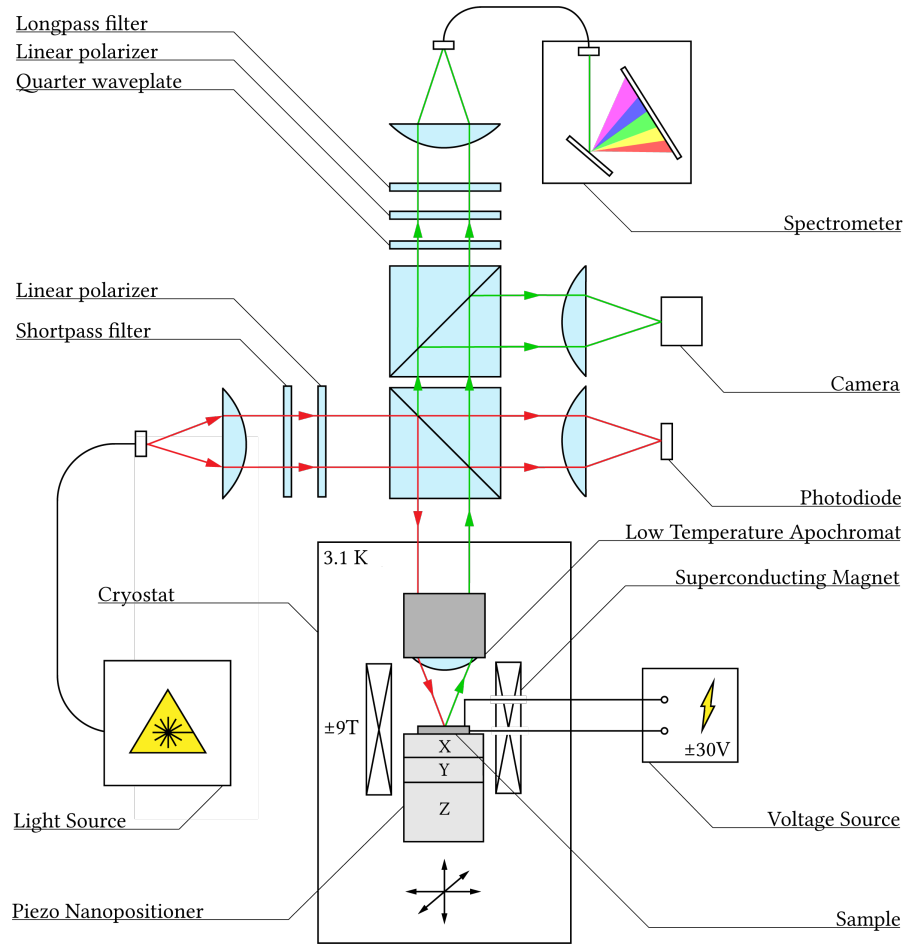


Figure 4.1: Optical setup for confocal spectroscopy: Light from a **laser**-source is guided to the setup in a single mode optical fibre and collimated. To cut off raman-modes, that are created in the fibre a **shortpass** filter is installed behind the collimator. A **linear polarizer** defines a polarization axis. A **beam-sampler** is reflecting the excitation beam into a **low temperature apochromat**, whose focus lies on the sample, with a spotsizes of $\sim 0.5\mu\text{m}$. The sample is mounted on a **piezo nanopositioner**, that is placed inside a **cryostat** at a temperature of up to 3.1 K or in a container of liquid helium at 4.2 K. The cryostat is equipped with a **superconducting magnet** that can supply a homogenous magnetic field up to 9T. The sample electrodes are connected to a **voltage source** (Yokogawa) that supplies $\pm 32\text{V}$. The detection spot is identical with the excitation. The reflection or photoluminescence is collimated again in the objective and passes through a σ^+/σ^- -analyzer consisting of a **quarter waveplate** and a **linear polarizer**, before being focussed in the detection fibre that connects to a **spectrometer**. A **camera** can be used to monitor the spot and image the sample, if it is brought out of focus.

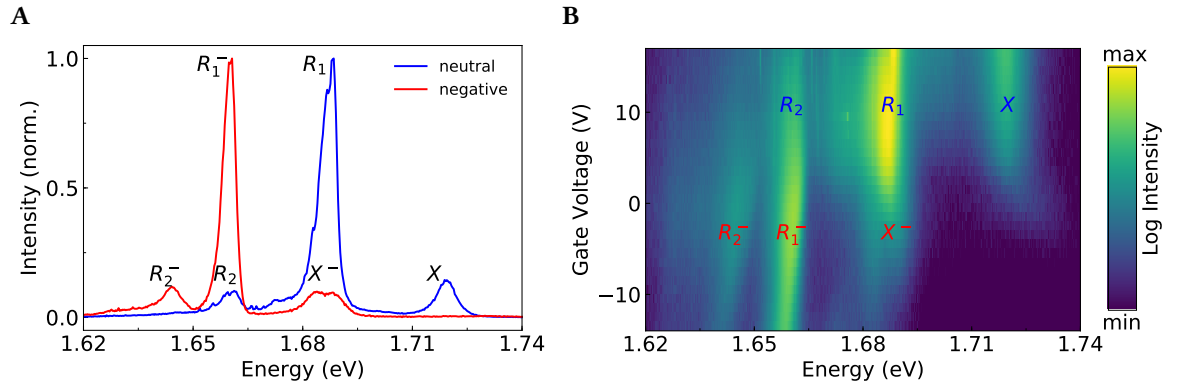
tunable, which means the contact of TMD flake to the electrode as well as the backgate have to function and the SiO_2 layer has to sustain enough voltage to tune in and out of neutral and charged regimes.

4.3 ELECTRICAL CHARACTERIZATION

To function of a gate-tunable TMD-device is threefold. The top-gate electrode has to be in contact with the flake of interest, the contacts to the backgate have to function, especially at low temperature and the dielectric has to hold enough voltage to see effects in the optical spectrum. Because the flake has only one contact, no transport measurement is possible. Hence the quality of the top-gate contact can only be assessed by seeing its effects in the optical spectrum. The other two criteria can be checked and quantified without any optical means. As mentioned in (Section 1 fabrication) the p-doped silicon bulk material, that is used as the back-gate electrode is prepared with two contacts. Both of these contacts can be connected to a simple multimeter, to measure the resistance between them. For this particular material a resistance of 5-6 Ω means, the contacts function as planned. If there is no contact or a high resistance, one of the contacts might still be functional. This can be assessed by observing the spectrum for different voltages, just like the top-gate. Nevertheless, having an additional check by using two back-gate contacts, helps troubleshooting in case of issues with the device.

The quality of the dielectric is quantified by measuring the capacity of the device for different voltages and monitoring the leak current (see Figure CV). A constant voltage across the desired range of operation ($\pm 30\text{V}$) is added to a small alternating current of small amplitude ($U_0 = 10 \text{ mV}_{pp}$, $f = 77.1 \text{ Hz}$). The real part of the resulting current is the resistive current, or leakage and the imaginary part is proportional to the capacity. Both parts can be measured in a lock-in amplifier. For our devices, the leakage current at low voltages should not exceed the pico-ampere range. For characterizing the dielectric the constant voltage can be raised until the resistive current starts rising exponentially. The corresponding voltage is the maximum, that should be applied in the particular sample, because a higher voltage can result in charges breaking through the dielectric and forming conducting channels, thus disabling the gate-tunability permanently. This sensitivity is the reason to use this more complicated characterization method instead of simply monitoring the current while applying voltages directly. Because very low currents can be measured with the lock-in amplifier, the boundary of safe operation can be approached very carefully.

4 Sample characterization



4.4 SPECTRAL RESOLUTION

4.4.1 SPECTRAL FEATURES AT DIFFERENT DOPING LEVELS

4.5 OPTICAL SETUP

4.5.1 PHOTOLUMINESCENCE SPECTROSCOPY

4.5.2 ABSORPTION SPECTROSCOPY

4.6 SAMPLE CHARACTERIZATION

4.6.1 ELECTRICAL PROPERTIES

4.6.2 NARROW LINEWIDTH

4.7 GATE SWEEP IN MAGNETIC FIELD # FULL CONTROL

4.7.1 DOPING REGIMES

4.7.2 G-FACTORS

Appendices

A LINESHAPES AND FITTING PROCEDURES

A.1 ASYMMETRIC LORENTZIAN

A.2 FANO RESONANCE LINESHAPE