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PhD Thesis booklet

Van der Waals heterostructures: from fabrication to hydrostatic pressure experiments

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1 Introduction

The discovery of graphene opened a new chapter in material science in 2004,[1] which was worth the 2010 Nobel Prize.[2] Not only being the first free-standing one atomic layer thick two-dimensional (2D) material ever isolated, but graphene also exhibits unprecedented electronic and outstanding mechanical properties including the massless Dirac nature and the chirality of the charge carriers originating from the non-trivial Berry phase, the Klein tunnelling, quantum electrodinamical effects at 300 times lower speed than the speed of light, or the half integer quantum Hall effect.[3–9] Before this PhD work, experimental research activity in the BME Nanoelectronics Lab focussed on the transport properties of graphene alone, placed on Si substrate or suspended in vacuum.[10–17]

In recent years, few layer thick, single crystalline flakes were produced from other materials as well via the same micromechanical cleavage as in the case of graphene. Among them, one can find semiconductors, insulators, semimetals, superconductors or strongly correlated materials.[18, 19] In addition, stacking these layers on top of each other is also possible, where covalent bonds stabilise the atoms in the component layers, which are held together by the van der Waals (vdW) interaction.[18, 20] There are multiple techniques that can be used to make such vdW heterostructures, among which the one that yields the best quality results is the dry stacking assembly method.[21] It allows to combine single or few layer thick crystal flakes of any suitable material with an arbitrary orientation angle with respect to each other, which leads to a much larger range of possibilities than any layer-by-layer epitaxial growth process. In addition, the interaction between the component layers modifies the electronic properties of the heterostructures and results in a plethora of interesting systems, which exhibit proximity-induced spin–orbit coupling (SOC), tunnelling effects for spin valves, magnetic ordering induced by neighbouring layers, moiré effects leading to superconductivity and other exotic phenomena, and many more, which have been the subject of extensive research in recent years.[22, 23]

2 Objectives

My PhD thesis reports advancements on various parts of the fabrication and study of vdW heterostructures.

The first objective of my PhD work was to build a transfer microscope required for the dry stacking assembly method and to adapt the process to the BME Nanoelectronics Lab based on the experience of my previous visit in the group of prof. Christian Schönenberger at the University of Basel.

Possible directions in the development of vdW heterostructures include the search for new component materials, however, some of the layered crystals are challenging to use due to various reasons like chemical instability in air,[24] or the easy exfoliation of thin flakes. A remarkable example is the layered ternary compound BiTeI, which hosts giant Rashba SOC,[25] therefore, it is a candidate to be an important component in future spintronic devices. However, exfoliating single layers of BiTeI (SL BiTeI, a single triplet of Bi, Te, and I atomic layers) remained elusive, possibly because the polar structure of BiTeI leads to stronger interlayer attraction than in case of graphite or the commonly used hexagonal boron nitride (hBN). One of the objectives of this PhD work was to produce SL BiTeI flakes for the first time.

In transport experiments, an important detail of the heterostructures is the design of the electrical contacts to the conducting layer, which is graphene in the cases discussed in this thesis. Since it is usually covered with another material in a heterostructure, at least with a layer of hBN, contacting is done conventionally by etching through the stack and establishing one-dimensional (1D) contact interfaces at distinct points of the boundary of the conducting layer of the heterostructure.[26] An alternative is to fabricate hBN/graphene/hBN heterostructures with point-like contacts *inside* the graphene sheet using a pre-patterned top hBN layer at the stack assembly. These contacts, called inner point contacts (PCs), are far away from the boundary of the graphene flake; therefore, they are topologically separated from each other. My objective was to investigate this topological separation of the contacts in high out-of-plane magnetic field transport measurements, where the system is in the quantum Hall state.

Another experimental degree of freedom in studying vdW heterostructures is the interaction strength of the component layers, which depends primarily on the interlayer distance. Although the interlayer coupling is generally fixed for each device at fabrication time by rotation angle or interface contamination among others, it is possible to tune the interlayer coupling at post-fabrication time by applying hydrostatic pressure on the device. Despite its potential interest, only a few study of hydrostatic pressure experiments appeared until recently,[27–29] because the conventional way of performing transport measurements on nanocircuits is incompatible with the hydrostatic pressure environment. My objective was to develop a systematic solution to this incompatibility issue and elaborate an efficient way of performing hydrostatic pressure experiments on vdW heterostructures.

The hydrostatic pressure is expected to push the component layers closer to each other, which increases the interlayer coupling. My last objective was to demonstrate, using the new measurement setup, the effect of the changing interlayer coupling on the transport of an hBN/graphene/WSe_2 heterostructure. Known for the presence of proximity-induced SOC in the graphene layer due to its neighbour WSe_2,[30, 31] this heterostructure is expected to show enhanced spin–orbit effects on increasing pressure.

3 Thesis points

1. **I demonstrated for the first time the successful exfoliation of single layer flakes of the giant Rashba spin–orbit material BiTeI.** I showed that using a modified mechanical exfoliation carried out on stripped gold substrate, samples can be obtained up to lateral sizes between 50 and 100 µm. Using scanning tunnelling microscopy measurements, I demonstrated the presence of BiTeI on the obtained sample surface. Using atomic force microscopy measurements, I showed that the optically identified large surface areas are covered continuously with BiTeI with only small and sparse holes in the two-dimensional (2D) flake. At the boundary of such a hole, I demonstrated that the coverage consists of a single triplet of Bi–Te–I atomic layers. I proved that the flake boundary detected under optical microscope by a channel-selective contrast enhancement corresponds to the boundary of the BiTeI coverage. [T1]

2. **I showed that the quantum Hall edge states of inner point contacts of a graphene sample are topologically separated from each other and from the edge states of the sample boundary.** I performed transport experiments in magnetic field on hBN/graphene/hBN heterostructures with inner point contacts, which were created with etching holes in the top hBN layer prior to the heterostructure assembly. I showed that the transport was suppressed between the contacts at high magnetic field and certain charge carrier concentrations, which is a demonstration of the topological separation of the edge states around the contacts from each other and from the crystal boundary in the quantum Hall state. [T2]

3. **I showed that an hBN capping layer is a necessary and sufficient protection for graphene-based vdW heterostructures in a kerosene environment, under hydrostatic pressure.** I developed a new setup to conduct hydrostatic pressure transport experiments on nanocircuits based on vdW heterostructures using a dedicated sample holder head in a piston–cylinder hydrostatic pressure cell up to a maximal pressure higher than 2 GPa. I successfully carried out transport measurements on nanocircuits under pressure in the hostile environment of kerosene, which is the pressure transmitting medium. I demonstrated that the presence of kerosene strongly degrades the mobility of graphene, however, a covering hBN layer provides a good protection from this undesired effect. [T3]

4. **Using hydrostatic pressure, I enhanced the proximity-induced spin–orbit coupling in graphene.** I performed transport measurements on an hBN/graphene/WSe_2 heterostructure from ambient pressure up to 1.8 GPa at four values in increasing order. As the pressure increased, magneto-conductance measurements showed a transition from weak localisation to weak anti-localisation. Using multiple fit formulas and a novel fitting method, I analysed the measurement data along with auxiliary field effect measurements to separate the effect of chirality from that of the SOC and showed that the observed transition is the result of an increase of ca. 70% in the Rashba SOC parameter with respect to its value at ambient pressure. [T4]

Publications related to the thesis points

[T1] Bálint Fülöp, Zoltán Tajkov, János Pető, Péter Kun, János Koltai, László Oroszlány, Endre Tóvári, Hiroshi Murakawa, Yoshinori Tokura, Sándor Bordács, Levente Tapasztó, and Szabolcs Csonka. Exfoliation of single layer BiTeI flakes. *2D Materials*, 5(3):031013, June 2018. Impact factor (2018): 8.55

[T2] Clevin Handschin, Bálint Fülöp, Péter Makk, Sofya Blanter, Markus Weiss, Kenji Watanabe, Takashi Taniguchi, Szabolcs Csonka, and Christian Schönenberger. Point contacts in encapsulated graphene. *Appl. Phys. Lett.*, 107(18):183108, November 2015. Impact factor (2015): 3.53

[T3] Bálint Fülöp, Albin Márffy, Endre Tóvári, Máté Kedves, Simon Zihlmann, David Indolese, Zoltán Kovács-Krausz, Kenji Watanabe, Takashi Taniguchi, Christian Schönenberger, István Kézsmárki, Péter Makk, and Szabolcs Csonka. New method of transport measurements on van der Waals heterostructures under pressure. *Journal of Applied Physics*, 130(6):064303, August 2021. Editor's Pick. Impact factor (2020): 2.546

[T4] Bálint Fülöp, Albin Márffy, Simon Zihlmann, Martin Gmitra, Endre Tóvári, Bálint Szentpéteri, Máté Kedves, Kenji Watanabe, Takashi Taniguchi, Jaroslav Fabian, Christian Schönenberger, Péter Makk, and Szabolcs Csonka. Boosting proximity spin–orbit coupling in graphene/WSe_2 heterostructures via hydrostatic pressure. *npj 2D Materials and Applications*, 5(1):82, September 2021. Impact factor (2021): 11.44

Other publications

[T5] Zoltán Scherübl, András Pályi, György Frank, István Endre Lukács, Gergő Fülöp, Bálint Fülöp, Jesper Nygård, Kenji Watanabe, Takashi Taniguchi, Gergely Zaránd, and Szabolcs Csonka. Observation of spin–orbit coupling induced Weyl points in a two-electron double quantum dot. *Nature Communications Physics*, 2(1):108, September 2019. Impact factor (2019): 8.11

[T6] Zoltán Kovács-Krausz, Anamul Md Hoque, Péter Makk, Bálint Szentpéteri, Mátyás Kocsis, Bálint Fülöp, Michael Vasilievich Yakushev, Tatyana Vladimirovna Kuznetsova, Oleg Evgenevich Tereshchenko, Konstantin Aleksandrovich Kokh, István Endre Lukács, Takashi Taniguchi, Kenji Watanabe, Saroj Prasad Dash, and Szabolcs Csonka. Electrically controlled spin injection from giant Rashba spin–orbit conductor BiTeBr. *Nano Lett.*, 20(7):4782–4791, July 2020. Impact factor (2019): 11.238

[T7] Péter Kun, Bálint Fülöp, Gergely Dobrik, Péter Nemes-Incze, István Endre Lukács, Szabolcs Csonka, Chanyong Hwang, and Levente Tapasztó. Robust quantum point contact operation of narrow graphene constrictions patterned by AFM cleavage lithography. *npj 2D Materials and Applications*, 4(1):43, December 2020. Impact factor (2019): 11.44

[T8] Bálint Szentpéteri, Peter Rickhaus, Folkert K. de Vries, Albin Márffy, Bálint Fülöp, Endre Tóvári, Kenji Watanabe, Takashi Taniguchi, Andor Kormányos, Szabolcs Csonka, and Péter Makk. Tailoring the band structure of twisted double bilayer graphene with pressure. *Nano Lett.*, 21(20):8777–8784, October 2021. Impact factor (2021): 11.189

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