Charge dynamics in nanostructures

(final report on the NKFI K112918 project)

This project targeted the continuation of an experimental scientific school previously funded by consecutive OTKA scientific school grants. The study of two novel material systems -graphene and memristive materials – was chosen as the central focus of the project. Bellow we summarize the main scietific achievements of the project relying on 14 international scientific publications with an average impact factor above 6. Additionally to the scientific achivements, we find that the project was successful in maintaining and further strengthening the scientific school. A senior researcher of the project (Szabolcs Csonka) has received a *Momentum research group* grant from the Hungarian Academy of sciences starting from September 2017, whereas the principle investigatior of this project has received an MTA-BME research group grant starting from June 2017. The other senior researcher of the project (András Halbritter) is a co-supervisor of the latter research group, and has recently started two OTKA research projects (December 2016, September 2018). In addition, recently European research network grants were started by the coordination of the participants of this project. The support of the NKFI K112918 project had crucial role in all these achievements. Additionally, this project has supported the scientific work of many students: alltogether 3 PhD, 9 BSc and 4 TDK theses were prepared along the project, and further 3 PhD and 7 MSc works are presently in progress.

Bellow we summarize the main technological achivements of the project (1), the scientific results in the fields of memristor and graphene research (2, 3), the publications including the theses of the students (4) and our recent granted projects ensuring the further progress of our research activities in the field of the present final report.

1 Main technological achievements

Here, we would like to highlight some selected technological achievements along the project.

(i) Previously our studies on resistive switching phenomena were relying on mechanically adjustable junctions using the tip of a scanning tunneling microscope to touch the sample under study. In the fremwork of the present project we have published our **first results on on-chip, nanofabricated devices** [9,10]. These results, and further studies on on-chip devices highly rely on the active collaboration with the group of János Volk at the Microtechnology Department of the Institute of Technical Physics and Materials Science (MFA), and the electron beam lithography facility at MFA.

(ii) We have further improved our high frequency setup to study resistive switching with nanosecond resolution. We have designed and assembled a **new high frequency** and high vacuum **scanning tunneling microscope** setup, using 500ps pulsing sources from both sides of the junction, 20GHz bandwidth semirigid coaxial cables and a robust piezo positioning system to withstand forces from the rigid coaxial cables (see Fig 1a).

(iii) Our earlier high quality graphene devices were based on suspending the graphene layer and cleaning the one-atomic-thin conductor by high current density. Although this fabrication scheme allows exceptionally high mobility, it places various limitations on the contacting materials and geometry of the device. hBN stacked graphene provides a much more versatile platform for high quality graphene devices, where e.g. even combination of Hall-bars, superconducting electrodes are feasible. In the framework of this project we set up a new **transfer microscope system** (see Fig. 1b), which is capable to create Van der Waals heterostructures by dry stacking method. The different layers are stamped by PDMS based holder. The fine positioning is achieved by 3 micropositioners and layers are released by local heating. The microscope is also equipped with a glass tip based additional micromanipulator. Tip with a typical end diameter of 50-100nm allows local manipulation on the surface, which was e.g. used to create combined 2D crystal / 1D nanowire hybrid devices [15].

(iv) Using closed cycle cryogenic cooling system fast magnetic field sweeps are challenging due to the limited cooling power of the pulse tube precooler. In order to carry out magnetic field sweeps in our dry delution refrigerator system, we developed a **new cold finger**. It required elimination of all magnetic components, which were – surprisingly - present in the standard chip carriers, commercial electrical sockets, standard metalized pcbs etc. Direct mounting and bonding of the silicon chip to a copper pc board provided a solution (see Fig. 1c), which allows sweep rate of 35mT/min with temperature increase lower than 15mK.

(a) (b) (c)

Fig. 1. *(a) The piezo positioning head of our new high frequency STM setup. (b) Transfer microscope setup, which allows to fabricate Van der Waals heterostructures with dry stacking technique, and equipped with glass tip (<100nm) micromanipulator. (c) New cold finger design, which eliminates all magnetic parts and thereby allows to carry out fast magnetic transport characterization in dry dilution fridge.*

2 Investigation of resistive switching junctions

Along the project we have investigated several different resistive switching material systems. We have continued our previous studies on Ag_2S based memristors [2,3,9,18,19,27], we have studied SiO_2 resistive switches contacted by graphene electrodes [10,11], and we have started to investigate AgI [28], Nb_2O_5 [16,22-25] and Ta_2O_5 [26] resistive switching junctions.

Our experimental approach partly relied on scanning tunneling microscope based point contact technique, where the tip of the STM is brougth into contact with the memristive material on the top of a metallic layer. This arrangement provides a high degree of versatility which also helps to optimize the design principles of future on-chip device architectures. Sample I(V) traces on Nb_2O_5 and Ta_2O_5 are presented in Fig. 2a,b. With this technique we have investigated the temporal dynamics of the switching in Ag_2S [2], Nb_2O_5 [22,24] and Ta_2O_5 [26] junctions. We have highlighted the role of the self-heating [3] and the local geometrical asymmetry [9] of the junction in the switching process, we have studied the atomic-scale conductance channels of the memristor junction by superconducting subgap spectroscopy [25], and we have started to study novel neuromorphic functionalities, like tunable long-term/short term memory operation [27].

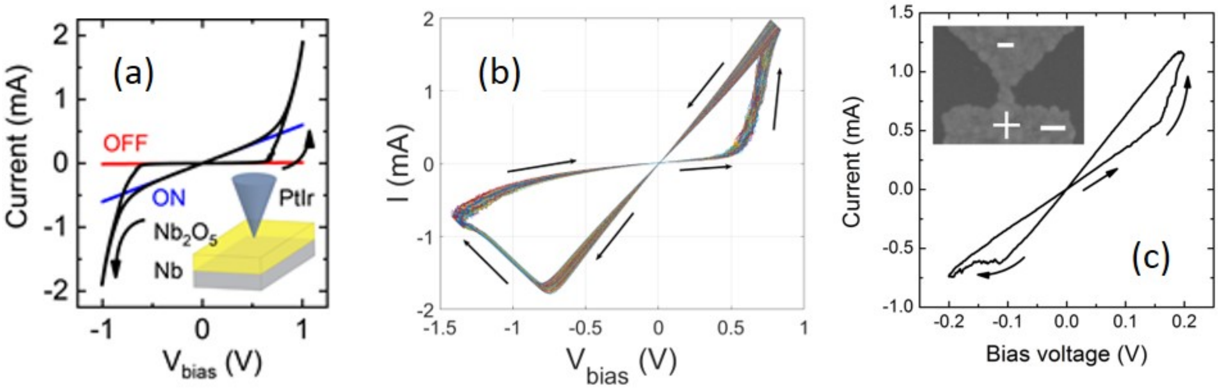

Fig. 2. *Resistive switching in Nb_2O_5 (a) and Ta_2O_5 (b) memristor junctions [16, 22-26]. The inset in (a) demonstrates the STM-based experimental arrangement. (c) Resistive switching in a nanofabricated planar Ag device prepared by electromigration and in-situ sulfurization [9].*

To step further towards integrable on-chip devices, recently we started a collaboration with the group of János Volk at the Microtechnology Department of the Institute of Technical Physics and Materials Science (MFA), and the group of Prof. Michel Calame at the Swiss Federal Laboratories for Materials Science and Technology (EMPA). Relying on the state of the art electron beam lithography infrastructures at these partner institutions, we have successfully studied [9,10] two types of nanofabricated resistive switching units.

(i) Starting from a lithographically defined silver nanowire engineered at MFA we have established a nanogap by the controlled electrical breakdown of the Ag wire. Afterwards the Ag_2S active medium was established by the in-situ sulphurization of the nanogap, and finally reproducible resistive switching was detected (Fig. 2c). The novelty of this structure lies in the simple design: prior studies have always used two different metals (Ag and an electrochemically inert metal) to establish resistive switching. Our results demonstrated that the deposition of a single metal – and thus a single lithographic step – is sufficient for the preparation of a memristor, and the geometrical asymmetry of the structure grants the well-defined direction of the switching [9].

(ii) In collaboration with EMPA we have shaped macroscopic scale (1cm^2) chemical vapor deposited single layer graphene sheets into graphene nanowires contacted by graphene electrodes (Fig. 3a), producing hundreds of devices on a single chip. Again 1-3nm wide gaps were formed by a controlled electrical breakdown method (which is attributed to burning in air and to sublimation in vacuum (Fig. 3b) [11]). Using these ultrasmall gaps we could confine the resistive switching of the underlying silicon-oxide layer to an order of magnitude smaller extension than prior studies. It was already known that SiO_x exhibits a unipolar resistive switching, where the “set” transition is attributed to an electric field driven crystallization, whereas the “reset” transition occurs at larger voltage due to a Joule-heating driven amorphization. In this scenario only the ON state is expected to be available at zero voltage, as the falling edge of the reset pulse would switch ON the device again below the set threshold. This is clearly impractical from the application point of view. However, our studies revealed that the switching dynamics also relies on a further internal time scale, the “dead time” (Fig. 3c-e) [10]. Physically, the “set” transition is found to occur only after the completion of a thermally assisted structural rearrangement of the as-quenched OFF state which takes place within the dead time after a reset operation. Thank to this a reset pulse shorter than the dead time drives the device to its OFF zero voltage state, i.e. both zero voltage states can be established by a unipolar pulse train. Our ultrasmall graphene-SiOx-graphene ReRAM units exhibit an OFF/ON resistance ratio of 10^4, endurance of $>10^3$, switching cycles and speed bellow 50ns [10].

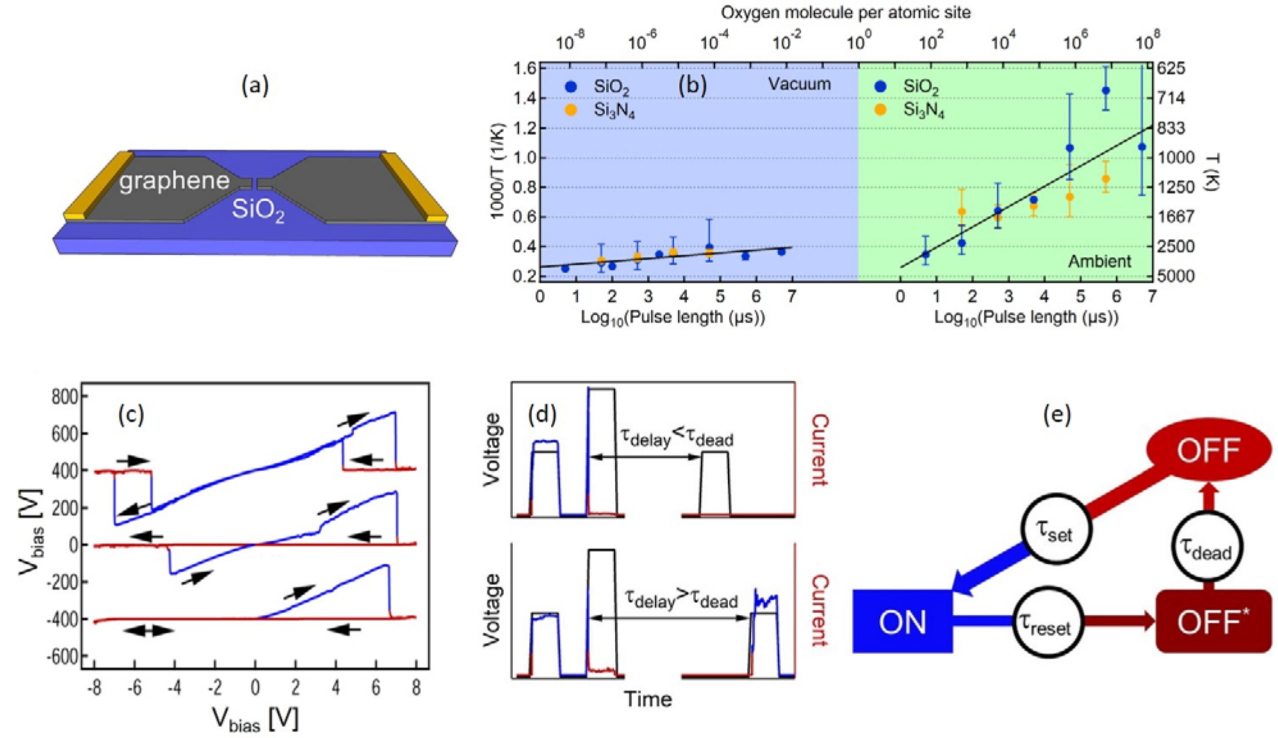

Fig. 3. *(a) A graphene nanowire is patterned on the top of the SiO_2 layer. A controlled electrical breakdown protocol is used to establish a few nm wide gap between the two graphene electrodes. (b) In order to understand the breakdown process we have studied the breakdown power in air and in high vacuum as a function of breakdown pulse length. Our results indicate two distinct breakdown mechanisms: burning in air, and sublimation in vacuum [11]. Once the graphene nanogap is established, highly reproducible resistive switching takes place in a small volume of the SiO_2 layer confined in the nanogap. Increasing the speed of the driving signal a crossover from unipolar to bipolar switching can be observed (top two curves in panel c). Our pulsed measurements demonstrate that after the reset operation the device can only be switched ON again once the so-called dead time has passed (see panel d and the flow diagram in panel e) [10].*

3 Investigation of quantum electronic devices using graphene and other 2D materials

Graphene is an ideal platform for spintronics and quantum computing applications. However, the lack of a band gap hinders electrostatic confinement, which is essential for the creation of quantum dots, the building blocks of spin-based quantum architectures. Great effort has been expended in search of a reproducible way to effectively confine electrons in graphene, but with limited success. We have found periodic conductance oscillations near quantum Hall plateaus in suspended graphene nanoribbons. They are attributed to single quantum dots that form in the narrowest part of the ribbon, in the valleys and hills of a disorder potential. In a wide flake with two gates, we have observed the signature of a double-dot system.

Our experiments serve as a proof of principle for a mechanism enabling electrostatic confinement, which exploits the gaps opening in graphene's band structure in magnetic fields. This method makes possible the realisation of highly desired graphene building blocks, such as quantum point contacts and spin quantum bits and opens new possibilities in graphene-based ballistic electronics [4].

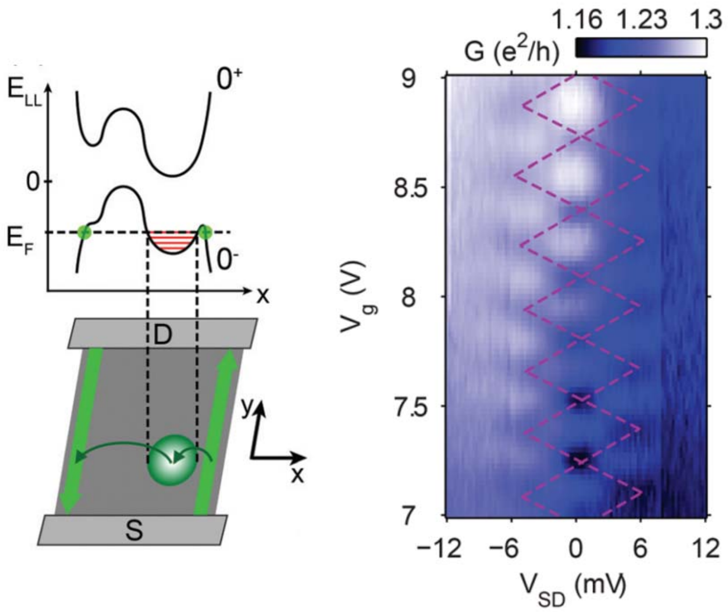

Fig. 4 Quantum dots coupled to quantum Hall edge channels: *When a confinement potential is formed inside the insulator bulk region of the quantum Hall state (left panel) and it is coupled to the edge states in the opposite side of the sample, the quantum dot generates backscattering. It induces conductance suppression when the dot levels are in resonance (right panel). See more details in Ref. [4].*

Besides fabricating and characterizing suspended graphene devices, we started to develop graphene circuits encapsulated between hBN (hexagonal boron nitride) layers. hBN has the same crystal structure as graphene, it can also be mechanically exfoliated in the same way, however it is an insulator material. With such hBN-graphene stacks also high mobility devices can be created, since hBN is a defect free insulator layer, furthermore during stacking graphene and hBN could form atomically clean interface. We present a novel method to establish inner point contacts on hBN encapsulated graphene stacks with dimensions as small as 100 nm by pre-patterning the top-hBN in a separate step prior to dry-stacking. 2 and 4-terminal field effect measurements between different lead combinations are in qualitative agreement with an electrostatic model assuming point-like contacts. The measured contact resistances are 0.5-1.5 kΩ per contact, which is quite low for such small contacts. By applying a perpendicular magnetic field, an insulating behavior in the quantum Hall regime was observed as expected for inner contacts. The fabricated contacts are compatible with high mobility graphene structures and open up the field for the realization of several electron optical proposals [1].

Graphene is a potentially interesting 2D system in the quantum Hall regime. Besides the half-integer quantum Hall effect or fractional quantum Hall effect, exotic physics such as quantum valley Hall effect may also take place. Atomic scale disorder at the edges of a flake causes intervalley scattering in the quantized edge channels, presenting an experimental platform where momentum-scattering is reduced. If doping of the flake is non-uniform, conductance channels may appear e.g. at the border of a p- or n-doped regions. Such quantum Hall edge channels (QHC) propagate in the nearly disorder-free environment of the bulk. In this direction we prepared and investigated three novel types of device geometries which provide direct information on the conductance of QHCs in the bulk. Measurements on two and four-terminal configurations prove that quantum Hall channels propagating along a p–n junction can be fully absorbed in a contact despite its screening and doping level, and contribute to the conductance in a quantized way. Our results show that p–n junctions can serve as high-efficiency current guides, and indicate that different Landau levels' co-propagating edge states can be detached from the edges by local gating [5].

In order to study supercurrent in high mobility graphene devices we investigated various superconductors as a side contact to graphene/hBN stacks. The few atomic wide overlap between the graphene layer and the superconducting metal makes the good transparency challenging. Beside the fact that some groups reported on good contacts with NbTiN and Nb, we did not observe superconducting features in graphene with these materials. MoRe gave a reliable superconducting interface, which allowed to study supercurrent in high mobility graphene device, where even the hBN substrate induced Moire effect was resolved (see Fig. 5b-c). Since NbTiN has much higher critical field (>10T), we are still testing different interface treatments, like surface cleanings, using different wetting layer etc. to create high quality NbTiN contacts.

The high mobility of hBN stacked graphene proves that hBN is an ideal insulator substrate, since it has atomically flat surface without dangling bonds. Based on these experiences we also tested hBN as a substrate for sensitive nanowire circuits. As Fig. 5a shows quantum dots were formed in InAs nanowires by local bottom gates (g1, g2 etc.) with a periodicity of 100nm, which are isolated from the nanowire (gray) by ~20nm thin hBN layer (blue). Comparing the device performance with earlier used HfOx and SiNx insulator layers, hBN based device had a very stable, silent dots, which was essential to carry out detailed magnetic characterization of double dot system. Exploring the ground state degeneracies we detected new magnetic Weyl-points in the presence of strong spin-orbit coupling [15].

Besides hBN, there are other layered materials which are non-conducting (insulator or semiconductor) and could serve as a substrate for high mobility graphene devices. The advantage of WSe_2 as substrate that it has spin-orbit interaction, which could penetrate into the graphene layer as well. The combination of graphene with spin-orbit interaction and superconducting contact could lead to exotic topological superconducting state. Graphene stacks with WSe_2 substrate (see Fig. 5d-e) showed high mobility and the presence of spin-orbit interaction in magnetotransport data [13]. For the robustness of topological superconductivity large spin-orbit interaction is essential. Considering the layered materials BiTeI has a remarkable high spin-orbit interaction, it is designed to have a giant Rashba spin-orbit interaction. As a first step to combine with graphene, we studied the exfoliation of BiTeI. Using a special exfoliation protocol we managed to create single layer of BiTeI for the first time (in collab. with group of L. Tapasztó MTA EK MFA) [12].

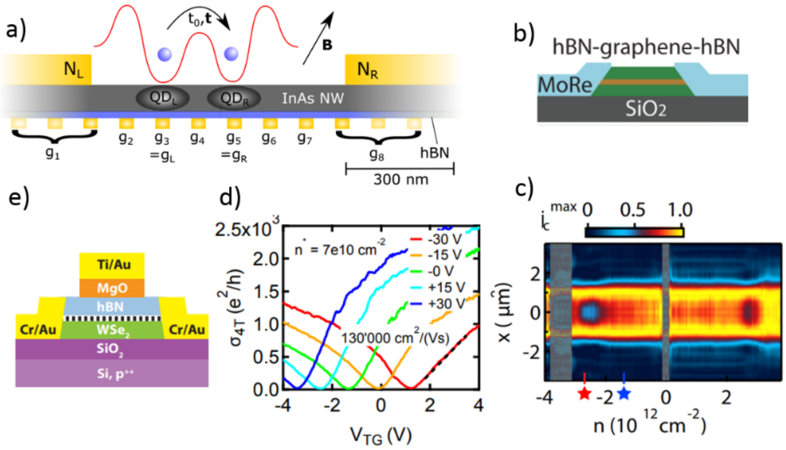

Fig. 5 Various Van der Waals heterostructures *a) Using hBN as a silent insulator in nanowire based device. b-c) hBN stacked graphene with MoRe super-conducting contact, and the spatial distribution of super-current. d-e)* WSe_2 *as silent substrate (mobility >100 kcm²/Vs) and source of proximity spin-orbit interaction.*

4 Publication of the results

Publications in international journals announcing the financial support of the present proposal:

[1] Handschin Clevin, Fülöp Bálint, Makk Péter, Blanter Sofya, Weiss Markus, Watanabe Kenji, Taniguchi Takashi, Csonka Szabolcs, Schönenberger Christian, *Point contacts in encapsulated graphene*, APPLIED PHYSICS LETTERS 107:(18) Paper 183108. (2015)

[2] Ágnes Gubicza, Miklós Csontos, András Halbritter, György Mihály, *Non-exponential resistive switching in Ag2S memristors: a key to nanometer-scale non-volatile memory devices,* NANOSCALE 7:(10) pp. 4394-4399. (2015)

[3] Ágnes Gubicza, Miklós Csontos, András Halbritter, György Mihály, *Resistive switching in metallic Ag2S memristors due to a local overheating induced phase transition,* NANOSCALE 7: pp. 11248-11254. (2015)

[4] E. Tovari, P. Makk, P. Rickhaus, C. Schonenberger, and S. Csonka *Signatures of single quantum dots in graphene nanoribbons within the Quantum Hall regime,* NANOSCALE 8: pp. 11480-11486. (2016)

[5] E. Tóvári, P. Makk, M.-H. Liu, P. Rickhaus, Z. Kovács-Krausz, K. Richter, C. Schönenberger, S. Csonka *Gate-controlled conductance enhancement from quantum Hall channels along graphene p-n junctions,* NANOSCALE 8, 19910 (2016)

[6] Z. Scherübl, G. Fülöp, M. H. Madsen, J. Nygård, S. Csonka, *Electrical tuning of Rashba spin-orbit interaction in multigated InAs nanowires,* Phys. Rev. B 94, 035444 (2016)

[7] G. Fülöp, S. d'Hollosy, L. Hofstetter, A. Baumgartner, J. Nygård, C. Schönenberger, S. Csonka *Wet etch methods for InAs nanowire patterning and self-aligned electrical contacts,* NANOTECHNOLOGY 27, Paper 195302 (2016)

[8] Halbritter A, Geresdi A, Mihaly G, *Spin polarized transport as measured by superconducting Andreev spectroscopy,* FRONTIERS IN NANOSCIENCE AND NANOTECHNOLOGY (FNN) 2:(6) pp. 1-8. (2016)

[9] Gubicza, D Zs Manrique, L Pósa, C J Lambert, G Mihály, M Csontos, A Halbritter *Asymmetry-induced resistive switching in Ag-Ag2S-Ag memristors enabling a simplified atomic-scale memory design,* SCIENTIFIC REPORTS 6: Paper 30775. 9 p. (2016)

[10] Pósa L, El Abbassi M, Makk P, Sánta B, Nef C, Csontos M, Calame M, and Halbritter A *Multiple Physical Time Scales and Dead Time Rule in Few-Nanometers Sized Graphene–SiOx-Graphene Memristor,* Nano Lett. 17: pp. 6783-6789 (2017)

[11] El Abbassi M, Pósa L, Makk P, Nef C, Thodkar K, Halbritter A, and Calame M *From electroburning to sublimation: substrate and environmental effects in the electrical breakdown process of monolayer graphene* NANOSCALE 9: pp. 17312-17317 (2017)

[12] B. Fülöp, Z. Tajkov, J. Pető, P. Kun, J. Koltai, L. Oroszlány, E. Tóvári, H. Murakawa, Y. Tokura, S. Bordács, L. Tapasztó, S. Csonka, *Exfoliation of single layer BiTeI flakes*, 2D Materials 5, 031013 (2018)

[13] S. Zihlmann, A.W. Cummings, J. H. Garcia, M. Kedves, K. Watanabe, T. Taniguchi, C. Schönenberger, and P. Makk: *Large spin relaxation anisotropy and valley-Zeeman spin-orbit coupling in WSe2/graphene/h-BN heterostructures* Phys. Rev. B 97, 075434 (2018).

[14] D.I. Indolese, R. Delagrange, P. Makk, J.R. Wallbank, K. Wanatabe, T. Taniguchi, C. Schönenberger: Signatures of van Hove singularities probed by the supercurrent in a graphene - hBN superlattice accepted in Phys. Rev. Lett. 121, 137701 (2018).

Publications in progress (closely related to the present proposal):

[15] Scherübl Z, Pályi A, Frank G, Lukács I, Fülöp G, Fülöp B, Nygård J, Watanabe K, Taniguchi T, Zaránd G, Csonka S: *Observation of spin-orbit coupling induced Weyl points and topologically protected Kondo effect in a two-electron double quantum dot*, submitted to Nature Physics, arXiv:1804.06447 (2018).

[16] Dániel Molnár, Tímea Nóra Török, Botond Sánta, Agnes Gubicza, András Magyarkuti, Roland Hauert, Gábor Kiss, András Halbritter, and Miklós Csontos*, In-situ impedance matching in Nb/Nb2O5/PtIr memristive nanojunctions for ultra-fast neuromorphic operation (*submitted to Nanoscale)

[17] D. I. Indolese, S. Zihlmann, P. Makk, C. Jünger, K. Thodkar, C. Schönenberger: Wideband and on-chip excitation for dynamical spin injection into graphene (submitted)

Science propagation:

[18] Gubicza Ágnes, Geresdi Attila, Csontos Miklós, Halbritter András, Mihály György A mesterséges intelligencia építőeleme - az Ag2S memrisztor FIZIKAI SZEMLE 67:(9) pp. 302-307. (2017)

PhD theses:

[19] Ágnes Gubicza, *Resistive switching phenomena in Ag2S based nanojunctions* (2016)

[20] Endre Tóvári, *Conducting channels and localization in graphene in a magnetic field* (2017)

[21] Gergő Fülöp, Cooper pair splitting in indium arsenide nanowires (2016)

MSc, BSc and TDK theses:

[22] Török Tímea Nóra, Molnár Dániel, *Ultragyors memrisztív kapcsolások kísérleti vizsgálata Nb2O5 nanokontaktusokban* (TDK thesis, 2016, 1st prize award at BME)

[23] Tímea Nóra Török, Experimental investigation of resistive switching phenomena in Nb2O5 memristors (BSc thesis, 2017)

[24] Molnár Dániel, Experimental investigation of the switching dynamics in Nb2O5 memristor junctions (BSc thesis, 2017)

[25] Tímea Nóra Török, Investigation of the conductance channels in atomic-sized Nb2O5 memristors (TDK thesis, 2017, 3rd prize award at BME)

[26] Csaba Sinkó, *Átmenetifém-oxid memrisztorok kísérleti vizsgálata pont-kontaktus technikával* (BSC thesis, 2018)

[27] Nóra Balogh, *Atomi méretű memóriák, mint mesterséges szinapszisok* (BSc thesis, 2018)

[28] Patrick Haiber, Resistive switching phenomena in silver iodide nano-junction devices (BSc thesis, 2017)

[29] Frank György, *HBN-InAs hibrid nanoáramkörök vizsgálata* (BSc thesis, 2017)

[30] Szentpéteri Bálint, *BiTeI/grafén hibrid nanoáramkörök készítése és vizsgálata* (BSc thesis, 2017)

[31] Kedves Máté, *Lokálisan hangolható hBN/grafén szendvicsszerkezetek készítése és vizsgálata* (BSc thesis, 2017)

[32] Kocsis Mátyás, *BiTeI nanoáramkörök készítése és vizsgálata* (BSc thesis, 2017)

[33] Szentpéteri Bálint, *Spin – pálya kölcsönhatás vizsgálata grafén/BiTeBr/hBN heteroszerkezetekben* (TDK thesis, 2017)

[34] Frank György, *Topologikusan védett alapállapoti degenerációk két spin rendszerben*, (TDK thesis, 2017, 1st prize award at BME)

5 Succesful applications for grants by the participants of the present proposal:

MTA-BME Condensed Matter Research Group
Hungarian Academy of Sciences (2017.07.01-)
Principal investigator: G. Mihály

Towards atomic-scale memories
NKFI 119797 (2016.12.01-)
rincipal investigator: A. Halbritter

Development of nanometer scale resistive switching memory devices
NKFI 128534, (2018.09.01-)
Principal investigator: A. Halbritter

Spin Physics in Low Dimensional Nanostructures
Momentum Research Grant (2017.09.01-)
Principal investigator: Sz. Csonka

Engineering Topological Superconductivity in Graphene
EU Network FLAG ERA (2018. 06.01-)
Principal investigator: P. Makk

Topologically protected states in double nanowire superconductor hybrids
EU Network QuantERA (2018. 04. 01-)
Principal investigator: Sz. Csonka