Nanocircuits beyond the resolution of electron beam lithography

(final report on the NKFI 105735 project)

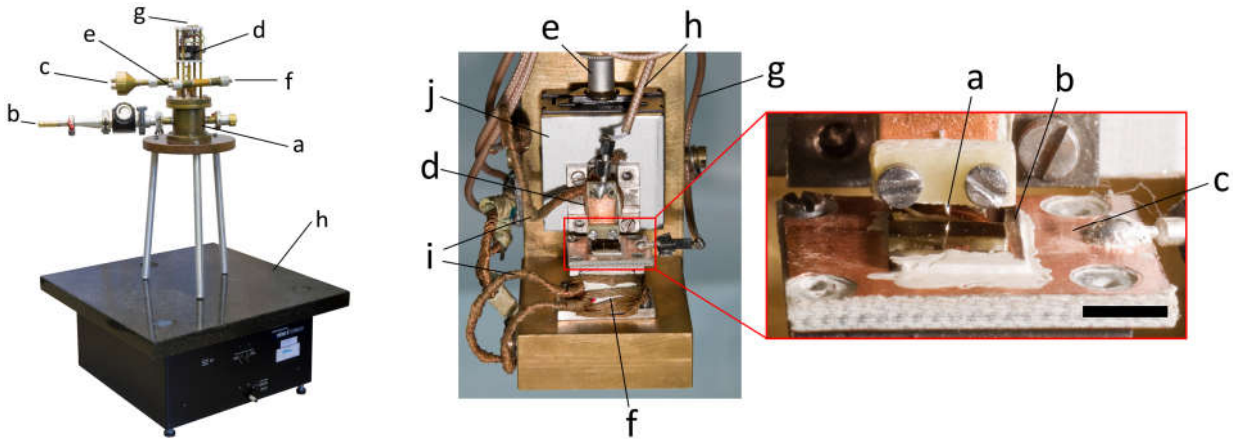
The project targeted the fabrication and characterization of nanoscale objects beyond the resolution of nanolithography, using three distinct platforms: (i) contacting single molecules by metal electrodes; (ii) fabricating graphene nanostructures; and (iii) developing atomic-scale memristors. Our experimental research was successful in all these three directions: (i) We have studied the interaction of CO molecules with metallic nanojunctions in detail; we have developed novel, advanced data analysis methods for break junction measurements; and we have observed structural memory effects and resisitve switching features in Au-bipyridine-Au break junctions. (ii) We have establidhed 1-3nm wide nanogaps by the controlled electroburning of CVD grown graphene nanoribbons, and demonstrated resisitive switching in graphene-SiOx-graphene nanogaps. (iii) We studied the switching dynamics, the transmission properties, and self-heating properties of Ag-Ag2S-PtIr memristors, and have demonstrated a proof of principle planar on-chip memristor device based on a highly simplified fabrication procedure with asymmetric all-Ag electrodes. To perform these measurements, several novel measurement setups were developed along the project including 6 new STM and 2 new MCBJ sample holders. These studies have resulted in 13 publications in prestigious international journals, 1 PhD thesis, 3 MSc theses, 1 BSc thesis and two theses for the Hungarian Scientific Students' Associations competition (TDK).

Bellow we summarize our achievements following the above three subtopics of the proposal, and first giving a summary of the technological developments along the project.

1 Development of novel measurement techniques and setups along the project

Our research group has long tradition in investigating single-atom and single-molecule conduction using the mechanically controllable break junction (MCBJ) technique. By mounting a metallic wire on the top of a bending beam and breaking the wire by the precise control of the bending one can investigate the final stage of the rupture, when the current flows through a single atom in the narrowest cross section. After the disconnection of the single-atom contact a sub-nanometer scale variable gap is established at the apex of the broken wire providing an ideal platform for contacting single molecules.

Along the project we have extended our experimental capabilities by building self-designed scanning tunneling microscope (STM) setups operating either at room temperature or at cryogenic circumstances (see an example in Fig. 1) [1-7]. Whereas the MCBJ technique has superior stability to an STM, the STM setups enable the study of atomic-scale objects between two different electrode materials. Furthermore, the possibility of surface scanning also provides an extended access to the device under study. These setups were used to study resistive switching phenomena, and single-molecule transport in an STM break-junction arrangement. Alltogether 6 STM setups were designed, manufactured and assembled, 4 for room and 2 for cryogenic temperature measurements.



(a) (b) (c)

Fig. 1. *(a) Self-designed room temperature STM setup installed on a vibration isolation platform /h/. The sample is inserted in a vacuum chamber /a/. For the rough positioning a stepper motor is used /d/. (b) Sample holder head with a linear positioner /j/, a* z *piezo positioner /d/ and an* xy *piezo positioner /f/. (c) Photo of a tip /a/ and a sample /b/ [6].*

The contacting of single organic molecules by metal electrodes was a distinguished target of the proposal. For this purpose three different experimental platforms were developed along the project: (i) we have built a room temperature MCBJ device a with liquid cell, where the studied molecules are dosed in a proper solvent; (ii) extending a low temperture MCBJ setup we have developed an in situ dosing protocol based on the local heating of the molecules in a small quartz tube with the tungsten spiral of a light bulb; (iii) we have implemented the STM break junction technique, where a self-assembled molecular monolayer is established on a thin metallic film sample, and the break junction measurement is performed by the repeated indentation of the STM tip to the sample. It is to be emphasized, that the OFF-feedback STM break junction measurements require significantly better mechanical stability than the conventional topographic imaging with feedback control, therefore special care was taken to ensure the proper mechanical stability. It was a challenging, longer than expected task to avoid unwanted contaminations in break-junction measurements on single organic molecules. Finally, a proper protocol could be worked out for the chemical handling of the samples. Another bottleneck of break junction measurements on single organic molecules is the need for ultra low level current measurement with a broad dynamic range (a current change from 10^{-4}A down to 10^{-12}A should be followed). For this purpuse, our group member, G. Mészáros has developed a custom built logarithmic current amplifier.

We have also developed a new measurement setup for electrobreakdown measurements on nanofabricated metallic and graphene samples. The sample chip is installed in high vacuum (10^{-7}mbar), and the electrical measurements are performed by the control software developed by our group member, L. Pósa, and the multiple gain linear current amplifier developed by G. Mészáros. The electrobreakdown procedure is performed by a software feedback control applying increasing amplitude ultrashort (down to 100ns) voltage pulses on the sample. After the electrobreakdown a few nm wide nanogap is established, on wich I(V) curve measurements and pulsed measurements can be performed.

It is noted, that the novel ultra-low level electronic devices developed by our group member, G. Mészáros are not only used in our group, but several international molecular electronics groups also apply them [8-11].

In summary the following measurement setups were developed along the project:

- Room temperature MCBJ device with liquid cell
- Extension of a low temperature MCBJ device with in situ dosing of organic molecules from a heated quartz tube [5]
- Custom built, ultra low noise logarithmic current amplifiers and multiple gain linear current amplifiers for break junction and electrobreakdown measurements
- 2 low temperature STM setups for STM break junction and Andreev spectroscopy measurements [4,5]
- 2 room temperature STM setups optimized for high mechanical stability [1,6]
- A room temperature STM setup optimized for pulsed measurements down to the ns timescale [2,7]
- 1 STM and 8 MCBJ setups for demonstraion purposes, and for a special laboratory exercise for high school students [4,12]
- A high vacuum electrobreakdown measurement system with pulsed feedback control [18-20]
- Sample preparation environment (chemical consumables, microscope, sample cleaning facilities)

For these developments the following most important investments were made from the project:

- PiezoMechanik SVR 150/1 piezo amplifier to drive the STM piezo actuators
- High speed digital oscilloscope card for pulsed resistive switching experiments
- Nikon microscope for sample preparation
- SoftdB STM controller dsp card
- Novascan UV ozone cleaner for sample cleaning
- MinusK vibration isolation platform for the MCBJ and STM setups

We can state, that all these developments have significantly broadened the measurement capabilities of our research group. Utilizing this experimental environment, we have achieved the following scientific results.

2 Contacting single molecules by metal electrodes

Using a heated capillary based molecule dosing system developed in a previous project (OTKA76010) we have further studied the interaction of CO molecules with atomic contacts and chains.

By the combination of the correlation analysis of break junction data and first-principles simulations we have probed the structure and evolution of **Ag–CO–Ag single-molecule junctions** both before the formation and after the rupture of the junctions (see Fig. 2a). It was demonstrated that prior to the single-molecule bridge configuration the CO molecule is already bound parallel to the Ag single-atom contact. This molecular *precursor configuration* is accompanied by the opening of additional conductance channels compared to the single-channel transport in pure Ag monoatomic junctions. To investigate the post-rupture evolution of the junction we have introduced a novel cross-correlation analysis between the opening and the subsequent closing conductance traces, which has shown that the molecule is bound rigidly to the apex of one electrode after rupture, and so the same single-molecule configuration is re-established as the junction is closed. In collaboration with the theory group of Prof. Colin Lambert (Lancaster University) the experimental results were confirmed by the simulated contact geometries, transmission eigenvalues and scattering wavefunctions. These results were published in NANOSCALE [14].

Using the novel correlation analysis techniques developed in our group, we have contributed to the analysis of combined force and conductance data on Ag-O-Ag break junctions, measured in the group of Prof. Latha Venkataraman at the Columbia University. Correlating force and conductance features we could distinguish various different atomic-scale structural motifs, including Ag-O-Ag junctions ($G=0.4G_0$) and Ag-Ag single-atom contacts with an oxygen atom in parallel ($G=1.3G_0$) (see Fig. 2b). These results were published in ACS NANO [13].

We have also investigated the formation and evolution of **Au–CO-Au single-molecule break junctions** (Fig. 2c). According to the detailed plateaus' length analysis of the conductance traces we have found that two distinct types of molecule-affected chain-formation processes are observed, which are attributed to bridge and atop type molecular configurations, where the latter has reduced conductance due to destructive Fano interference. These results are published in BEILSTEIN JOURNAL OF NANOTECHNOLOGY [15].

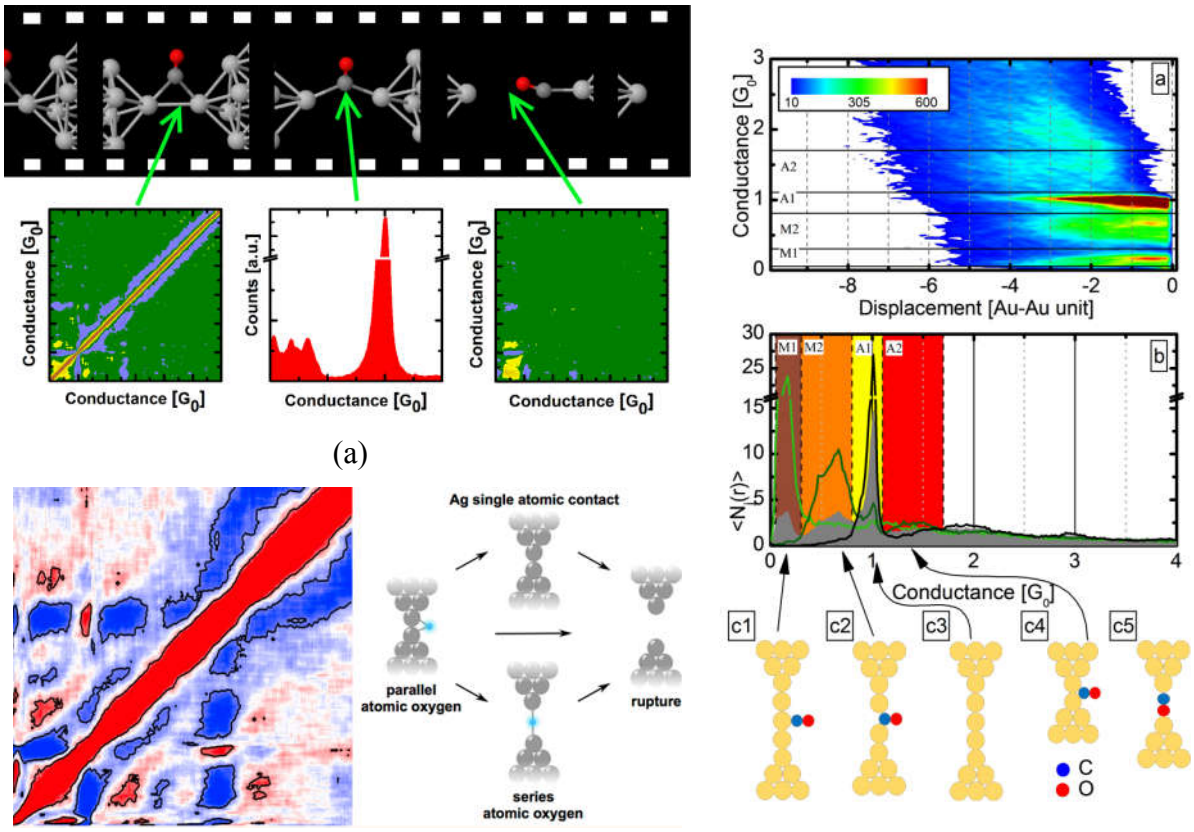
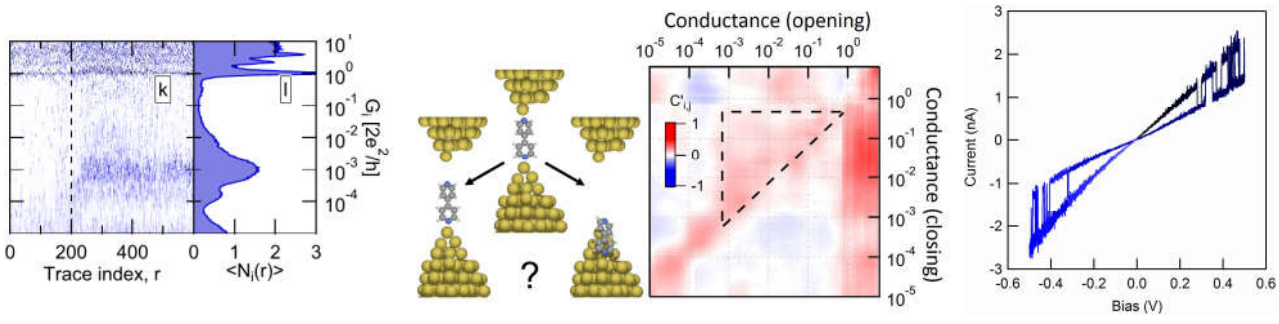


Fig. 2. *(a) Study of Ag-CO-Ag single molecule break junctions [14]. Whereas conductance histograms (bottom middle) could only detect single molecule conductance, based on the correlation analysis of the conductance traces (bottom left) and a novel cross-correlation study of the opening and closing traces (bottom right) we could follow the timelime of what happens before the formation and after the rupture of the single-molecule junction (top). (b) Study of Ag-O-Ag junctions [13]. Based on the correlation analysis of the conductance traces (left) and correlating force and conductance data different structural motifs could be identified (right). (c) Study of Au-CO-Au single-molecule junctions and molecule decorated atomic chains [15]. Two alternative chain formation processes were identified, one with an atop molecular configuration (c1) and one with a molecular bridge (c2).*

We have also studied **temporal correlations and structural memory effects** in break junction measurements by novel statistical analysis methods. We have shown that temporal histograms

are a simple, but efficient tool to check the temporal homogeneity of the conductance traces, or to follow spontaneous or triggered temporal variations, like structural modifications in trained contacts, or the emergence of single-molecule signatures after molecule dosing. To statistically analyze the presence and the decay time of temporal correlations, we have introduced shifted correlation plots. Applying these methods on gold metallic contacts as a test system, we have shown that the surface diffusion induced flattening of the broken junctions helps to produce statistically independent conductance traces at room temperature, whereas at low temperature repeating tendencies are observed as long as the contacts are not closed to sufficiently high conductance setpoints. Applying opening-closing correlation analysis on Pt-CO-Pt single-molecule junctions, we have demonstrated pronounced contact memory effects and recovery of the molecule for junctions breaking before atomic chains are formed. However, if chains are pulled the random relaxation of the chain and molecule after rupture prevents opening-closing correlations. These results are accepted for publication in THE JOURNAL OF CHEMICAL PHYSICS, Special Topic on Frontiers in Molecular Electronics [16].

The heated cappillary based molecule dosing system is not appropriate to dose larger organic molecules to low temperature break junction devices, therefore we have developed novel dosing strategies (Fig. 3a). This development, especially the warranted elimination of contaminating molecules took longer time than expected. In the last year of the project we have succeeded with this goal as well, and **we have successfully dosed organic molecules, like 4,4' bipyridine to low temperature MCBJ samples** from a locally heated quartz tube. Whereas similar molecules are readily investigeted in room temperature break junction setups, low temperature break junction measurements are not common worldwide. Our measurements have immediately demonstrated the obvious advantage of low temperature conditions: due to the frozen surface diffusion of the electrode atoms the molecular junctions stay stable for more detailed characterization. Applying opening-closing correlation analysis on Au-4,4'-bipyridine-Au single-molecule junctions, we have demonstrated that after rupture the molecule does not rearrange significantly, rather **it remains protruding from one electrode** (Fig. 3b). Investigating the I(V) characteristics of these junctions we could show **bistable electrical switching** (Fig. 3c), which is promising for single-molecule memory architectures. The finalization and the publication of these results is in progress [17].



(a) (b) (c)

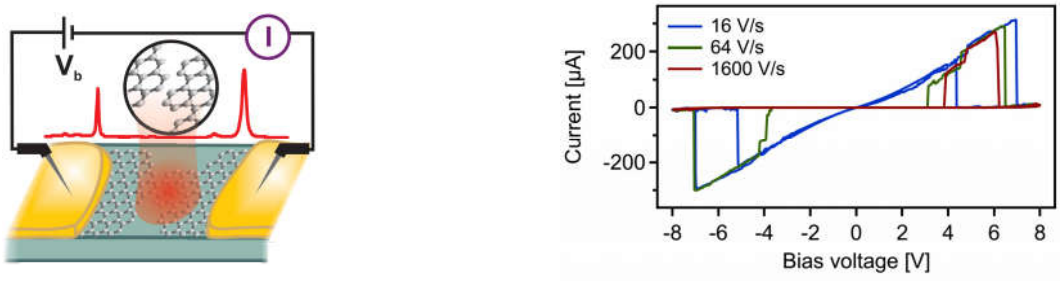
Fig. 3. *(a) In situ dosing of bipyridine molecules to Au break junctions from a heated quartz tube. On the temporal histogram (left) it is clearly seen how the molecular features appear after the heating of the qurtz tube (dashed line) [16]. (b) Correlation analysis of low temperature Au-bipyridine-Au single molecule break junction data clearly shows that after rupture the molecule does not rearrange significantly, rather it remains protruding from one electrode [17]. (c) The I(V) curves of low temperature Au-bipyridine-Au single molecule junctions exhibit bistable conductance switching [17].*

3 Graphene nanostructures

As a second platform, we have established nanogaps by the controlled electrobreakdown of graphene nanoribbon samples.

After pioneering results on exfoliated, and mostly multilayer graphene electroburning experiments in other research groups, our joint project with Prof. Michel Calame from the University of Basel was the **first to demonstrate few-nanometer wide graphene nanogaps in samples fabricated by chemical vapor deposition** (CVD) (see Fig. 4a). The CVD procedure provides a great opportunity for the simplified fabrication of hundreds of devices on a single chip, and so to perform experiments on a statistically relevant, large ensemble. Additionally, we have achieved a close to 100% yield in establishing few nanometer wide graphene nanogaps. Applying Raman microscopy we have also studied the variation of the local junction temperature along the electrobreakdown process. These results are published in NANOSCALE [18].

Using the optimized graphene nanogaps, we have studied the details of the electrobreakdown process focusing on temperature and environmental effects. Using SiO_2 substrate under the graphene samples we could observe **highly reproducible resistive switching** phenomena inside the 1-3nm wide graphene nanogaps (see Fig. 4b). The publication of these results is in progress [19-20].



(a) (b)

Fig. 4. *(a) Schematic illustration of the graphene nanogaps established by electroburning, and in situ Raman spectroscopy measurements [18]. (b) Resistive switching in graphene nanogaps at different voltage ramp rates [20].*

4 Resistive switching in atomic-scale memristor junctions

Using the self-designed scanning tunneling microscope setups we have joined another hot research topic, the study of "memristive" devices utilizing voltage controlled electrochemical switching at the nanoscale.

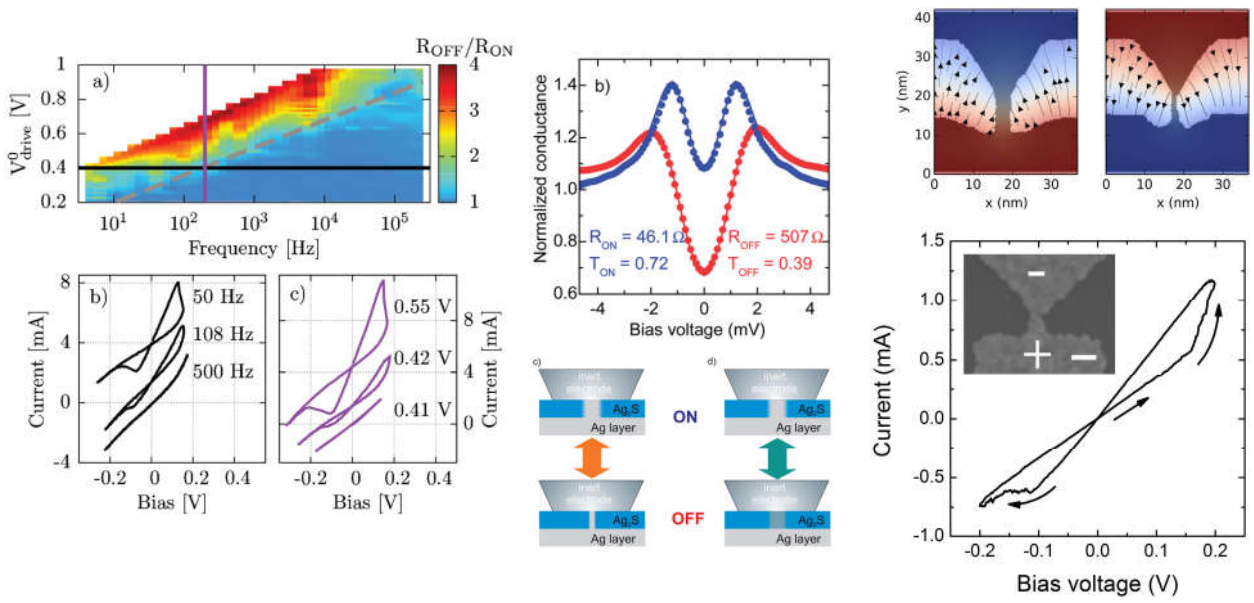
By optimizing the preparation of Ag/Ag_2S samples we have established memristor junctions exhibiting a relatively low resistance metallic character both in the ON and the OFF state. This represents a novel regime compared to the commonly studied device concepts, where the high resistance (>1MΩ) OFF state hinders fast operation due to RC time constant limitations. With our optimized devices we have demonstrated **switching by sub-nanosecond pulses.** In such devices the determination of the active device area is not evident, as the same device resistance may either correspond to a large area tunnel junction with small transmission probability or to a highly transmissive atomic-scale device. **Utilizing superconducting Andreev spectroscopy** we were the first to directly **study the transmission probability of the junction** (Fig. 5b) demonstrating that our devices are not only fast, but the **junction diameter is truly in the nanometer scale**. These results are published in NANOSCALE [21].

We have also shown that while **the switching can be ultrafast depending on the amplitude** of the driving voltage signal, **it slows down exponentially as the driving amplitude linearly decreases** (Fig. 5a). This strongly nonlinear response function is a key issue in designing devices with stable resistance states against low-level read-out signals and, at the same time, with a fast response to write operations carried out at higher bias levels. These results are published in NANOSCALE [22].

Whereas prototype Ag_2S solid electrolyte memristor chips are already available commercially, the understanding of the operation mechanism is still far from being complete. We have come closer to this by **clarifying the key role of the junction's self-heating upon resistive switching**. These results are published in NANOSCALE [23].

Conventionally resistive switching is established in Ag-Ag_2S-(electrochemically inert electrode) structures, where the asymmetric electrode material arrangement determines the direction of the bipolar switching. We demonstrated **stable resistive switchings in Ag-Ag_2S-Ag nanojunctions lacking the inert electrode**. In this architecture the **direction of the set/reset transitions** is exclusively determined by the strong inhomogeneity of the electric field at the apex of the junction **arising from the asymmetrical design** of the electrode surfaces (Fig. 5c). Based on this idea we have fabricated a **proof of principle planar on-chip memristor device** utilizing a highly **simplified fabrication procedure** compared to conventional multi-material structures (Fig. 5c). These results are published in SCIENTIFIC REPORTS [24].

Recently, we have extended our studies to novel material systems, and investigated resistive switching in **Nb-Nb2O5-PtIr memristor junctions**, where the switching is attributed to the voltage controlled migration of oxygen vacancies. These results were awarded the first prize, and the Rector's distinguished prize at the Hungarian Scientific Students' Associations competition (TDK) [6], the publication is in progress.



(a) (b) (c)

Fig. 5. *(a) The bottom panels demonstrate typical resisitive switching I(V) curves in Ag-Ag_2S-(inert electrode) structures at different driving amplitudes and frequencies. Above a positive threshold voltage on the planar Ag electrode the metallic nanowire between the two sides grows and thus the device jumps to a low resistance ON state, whereas at opposite polarity the nanowire is dissolved and the junction switches back to the OFF state. The top panel demostrates, that the switching exponentially speeds up as the driving amplitude is linearly increased [22]. (b) Applying a superconducting Nb tip as the inert electrode the transmission probability of the junction can be determined by fitting the differential conductance curves to the theory of Andreev reflections. Based on such measurements we have shown that mainly the diameter of the junction, and not its transparency changes along the switching (bottom panel) [21]. (c) The top panel shows numerical simulation utilizing asymmetric all-Ag electrodes: at a positive/negative bias on the planar bottom electrode the nanowire grows / narrows. The bottom panel demonstrates a proof of principle resisitive switching measurement in an asymmetric all-Ag planar device fabricated by single-step e-beam lithography, disconnection of the wire by electromigration, and subsequent sulfurization [24].*

5 Parallel projects

The total cost of all these developments and scientific results highly exceeds the budget of the present project. We also acknowledge the support of personal costs from the *MTA-BME Condensed Matter Research Group*, and a partial support for the memristor research from the OTKA K112918 grant (*Charge Dynamics in Nanostructures*, 2015-2017). (A part of the OTKA K112918 grant is devoted to the detailed investigation of memristive functionalities, whereas the present project targeted more the development of novel memristor structures including nanofabricated ones, and the measurement systems required for that). The molecular electronics and the graphene nanogap topics are distinct from the OTKA K112918 project.

6 Publication of the results

Theses:

[1] András Magyarkuti: *Design and development of a combined scanning tunneling and atomic force microscope*, master thesis (2013)

[2] Ágnes Gubicza: *Switching phenomena in nanoscale Ag2S memristors*, master thesis (2013)

[3] Botond Sánta: *Presenting the unseen: the implementation of two Nobel Prize-winning experiment for demonstration purposes* (STM and Cloud chamber)*, TDK thesis (2014)*

[4] Botond Sánta: *Design and development of a low temperature scanning probe miscroscope,* master thesis (2015)

[5] Anna Nyáry: *Conductance measurements on individual organic molecules*, bachelor thesis (2016)

[6] Tímea Török and Dániel Molnár: *Experimental investigation of ultrafast memristive switching in Nb2O5 nanojunctins,* TDK thesis (2016)

[7] Ágnes Gubicza: *Resistive switching phenomena in Ag2S based nanojunctions,* PhD thesis (2016)

Publications in international journals, and manuscripts under preparation:

Development of utrasensitive electronic measurements in break junction experiments

[8] Mohos Miklós, Pobelov Ilya V, Kolivoška Viliam, Mészáros Gábor, Broekmann Peter, Wandlowski Thomas, *Breaking Force and Conductance of Gold Nanojunctions: Effect of Humidity,* JOURNAL OF PHYSICAL CHEMISTRY LETTERS 5:(20) pp. 3560-3564. (2014)

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Development of a break junction device and a scanning tunneling microscope for demonstration purposes

[12] Sánta Botond, Magyarkuti András, Halbritter András, *Egy demonstrációs kísérlet, amelyben az áram egyetlen atomon keresztül folyik,* FIZIKAI SZEMLE 66:(5) pp. 154-160. (2016)

Conductance measurements on single molecules, development of novel statistical data analysis techniques

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[17] Z. Balogh, A. Magyarkuti, G. Meszaros, A. Halbritter et al, *Bistable electrical switching in low temperature Au-4,4' bipyridine-Au junctions* (under preparation)

Investigation of graphene nanogaps

[18] Cornelia Nef, László Pósa, Péter Makk, Wangyang Fu, András Halbritter, Christian Schönenberger, Michel Calame, High-yield fabrication of nm-size gaps in monolayer CVD graphene, NANOSCALE 6:(13) pp. 7249-7254. (2014)

[19] Maria El Abbassi, László Pósa, Péter Makk, Cornelia Nef, Kishan Thodkar, András Halbritter and Michel Calame, *Electrobreakdown of monolayer graphene : Substrate and environmental effects* (under preparation)

[20] L. Pósa, M. El Abbassi, P. Makk, C. Nef, M. Calame, A Halbritter, *Multiple physical timescales in few-nm sized graphene-SiOx-graphene memristors* (under preparation)

Study of resisitve switching phenomena in memristor junctions

[21] A Geresdi, M Csontos, Á Gubicza, A Halbritter, G Mihály, Fast operation of nanometer-scale metallic memristors: highly transparent conductance channels in Ag2S devices, NANOSCALE 6:(5) pp. 2613-2617. (2014)

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