Towards atomic-scale memories

(final report on the NKFI K 119797 project)

Our central research objective was to establish memory operation in novel device structures, where the characteristic size of the active region is close to atomic dimensions. To this end, we have explored various material systems, including atomic-sized metallic nanowires, single-molecule structures, graphene nanogaps and various solid-state systems with resistive switching (a.k.a. memristive) characteristics. The improved understanding of the physical mechanisms behind the memory operation was a primary goal of the project. In the following we summarize the results of our project following the numbering of the research objectives in the research plan of the project.

1. Investigation of current driven atomic-scale switching phenomena

It was shown that resistive switching can be induced in completely pure metallic wires, lacking any embedding environment. In this case voltage-induced forces are responsible for the reversible atomic rearrangements at the wire bottleneck. We have developed a novel non-oxidizing fabrication method for lithographic break junctions of sensitive metals, and thereby we could demonstrate room temperature pure atomic switching in Ag nanowires for the first time (Fig. 1A).[1] The voltage-controlled formation and dissolution of Ag nanofilaments is a fundamental ingredient of various memristive systems as well, in these, however, electrochemical metallization (ECM) is responsible for the switching process. We have shown, that in atomic-sized memristive filaments the ECM-based switching may coexist with pure atomic switching. These results (Fig. 1B,C,D) were demonstrated on three international conference talks, from which a manuscript will be submitted within the coming months.

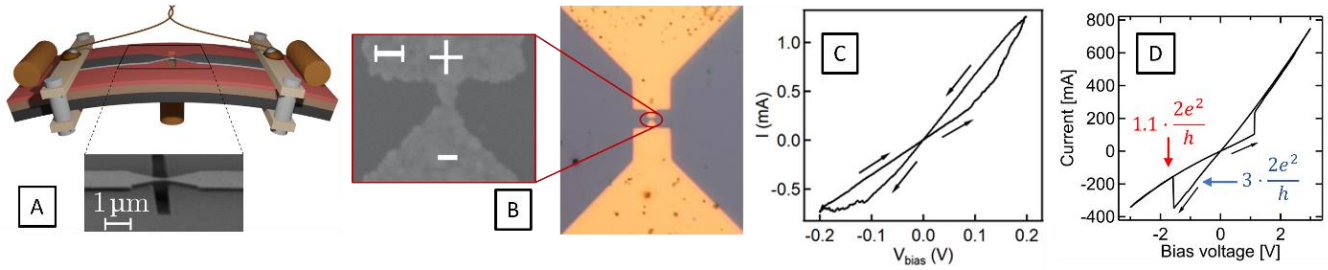

Fig. 1. Pure atomic switching phenomenon. *(A) Nanofabricated break junction device relying on a novel, non-oxidizing fabrication method.[1] (B) Nanofabricated Ag nanogap devices. This system exhibits ECM-type Ag-Ag_2S-Ag bipolar resistive switching (C) as well as room temperature pure atomic switching (D) (to be published).*

2. Resistive switching in graphene nanogaps

Within a former project, we have developed graphene nanogap devices relying on the controlled electrical breakdown of nanofabricated graphene nanowires. Along the present project we have studied the effect of the environmental conditions on the electrical breakdown mechanism, identifying burning mechanism in air and sublimation in high vacuum.[2] These experiments were mostly performed in our laboratory at BME, whereas the sample chips were fabricated at the University of Basel.

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[1] A. Nyáry, A. Gubicza, J. Overbeck, L. Pósa, P. Makk, M. Calame, A. Halbritter and M. Csontos: *A non-oxidizing fabrication method for lithographic break junctions of sensitive metals*, **NANOSCALE ADVANCES 2**, 3829-3833, 2020, IF: 4.38

[2] El Abbassi Maria, Posa Laszlo, Makk Peter, Nef Cornelia, Thodkar Kishan, Halbritter Andras, Calame Michel: *From electroburning to sublimation: substrate and environmental effects in the electrical breakdown process of monolayer graphene*, **NANOSCALE 9,** 17312, 2017, IF: 7.367

Using this electrical breakdown protocol, we have established resistive switching in graphene/silicon-oxide/graphene devices, where the switching is confined to the few nanometer-wide gap region, i.e., to a much narrower volume than in previous studies (Fig. 2).[3]

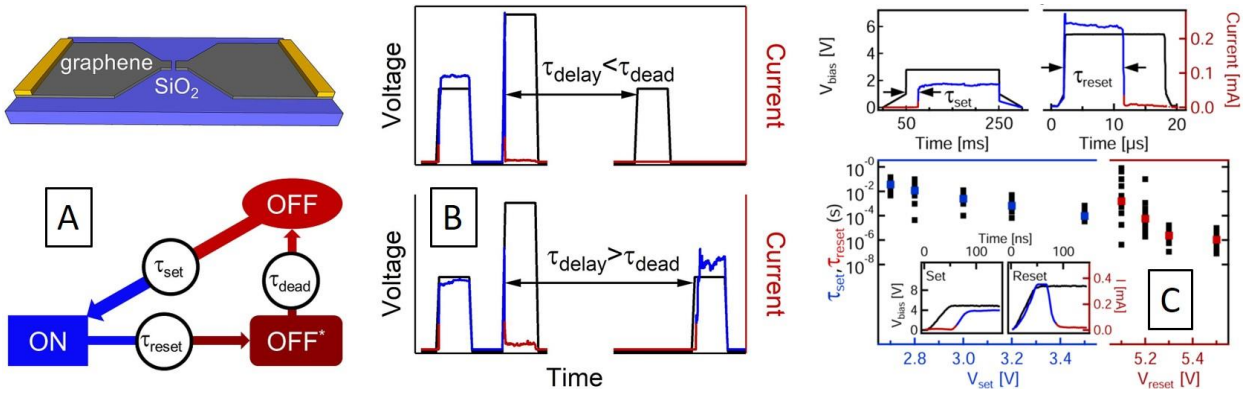

Fig. 2. Graphene -SiO_2-graphene resistive switching devices.[3] *Electrical breakdown is used to break a pre-patterned graphene nanowire (panel A top). As a result, 1-3nm wide nanogaps are established, which confine the resistive switching in the underlying SiO_2 substrate to a similarly small dimension. The intrinsic SiO_2 resistive switching is a local phase change phenomenon with unipolar switching characteristic. Both the set time and the reset time can be varied on an exponential scale upon a linear variation of driving voltage (C). Our studies revealed that the switching dynamics also relies on a further internal time scale, the dead time (panel A bottom). 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 (B).*

3. Investigation of memristive nanojunctions utilizing novel compounds in the active region, *and* 4. Development of ultra-stable on-chip memristive devices

During the project we have developed and investigated several resistive switching platforms using various device geometries. These include Ag_2S, AgI, Nb_2O_5, Ta_2O_5 and V_2O_5 scanning tunneling microscope (STM) point contact devices, vertical (crosspoint) Nb_2O_5 and Ta_2O_5 devices and lateral SiO_x and VO_2 devices (see the next section for the analysis of these devices). The extent of our device development and optimization activity exceeded the scope of the present project, and therefore a separate project was started on the *"Development of nanometer-scale resistive switching memory devices"* (NKFI K 128534, 2018-2023) with the dedicated goal of developing well-integrable on-chip resistive switching memory devices. In addition to the above memristive systems, we have also established voltage-controlled switching phenomena in single-molecule nanowires.[4]

5. Comparative study of the switching dynamics using the above-described platforms

5.1 Ultrafast, time-resolved measurements

We have developed an ultrafast measurement setup using custom build pulse generators firing pulses with 0.5ns width (Fig. 3A). Using this setup, we have studied the reversible resistive switching properties of Nb_2O_5

[3] Pósa László, El Abbassi Maria, Makk Péter, Sánta Botond, Nef Cornelia, Csontos Miklós, Calame Michel, Halbritter András: *Multiple Physical Time Scales and Dead Time Rule in Few-Nanometers Sized Graphene–SiOx-Graphene Memristors*, **NANO LETTERS 17**, 6783, 2017, IF: 12.712

[4] G. Mezei , Z. Balogh, A. Magyarkuti, and A. Halbritter: *Voltage-Controlled Binary Conductance Switching in Gold–4,4′-Bipyridine–Gold Single-Molecule Nanowires*, **THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS 11**, 8053, 2020, IF: 8.758

and AgI memristors going down to sub-nanosecond timescales (Fig. 3B,C). These results were published in NANOSCALE[5] and in the BEILSTEIN JOURNAL OF NANOTECHNOLOGY.[6]

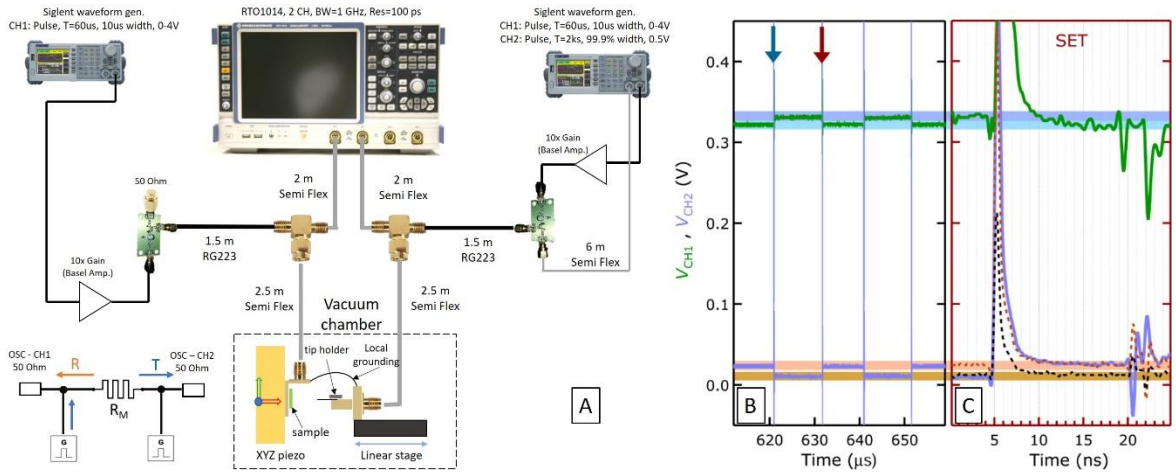

Fig. 3. Ultrafast time-resolved measurements. *(A) Our custom-built high-frequency setup. Panel (B) demonstrates reversible resistive switching in AgI junctions, which is resolved on the nanosecond-scale in panel (C). The purple curve shows a SET transition due to a 500ps FWHM pulse in comparison with the pulse response of standard SMD resistors, demonstrating the switching along the rising edge.*[6]

5.2 Superconducting subgap spectroscopy

We have studied the quantum conductance channels of Nb_2O_5 memristor junctions applying superconducting subgap spectroscopy. Close to the $2e^2/h$ quantum conductance this method is especially sensitive to the fine details of the junction's „quantum PIN code" (i.e. the set of the transmission eigenvalues), providing highly conclusive information about the nature of the conducting filaments. Our measurements provide the first direct and well-founded experimental evidence that the switching takes place due to the structural rearrangement of a truly single-atom diameter conductance channel in a transition metal oxide resistive switching device (Fig. 4).[7]

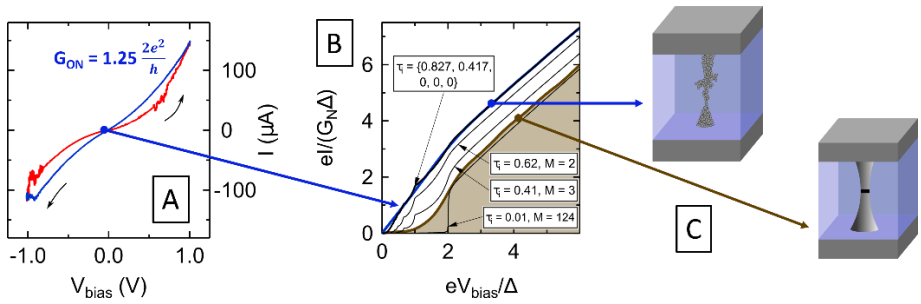

Fig. 4. Investigation of the filament diameter by superconducting subgap spectroscopy. *(A) In memristive devices the range of the analog programable filamentary conductances reaches the universal conductance quantum, which might reflect single-atom filaments. However, the conductance alone is not sufficient to prove the single-atom nature. (B,C): If the resistive switching unit is sandwiched by two superconducting electrodes, one can measure superconducting subgap structures in the voltage region of the gap. The subgap I(V) curves significantly differ for a single-atom nanowire and a broader tunnel junction even if they share the same conductance. Utilizing this principle, we have justified the single-atom nature of Ta_2O_5 resistive switching filaments.*[7]

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[5] Molnár Dániel,Török Tímea Nóra,Sánta Botond,Gubicza Agnes, Magyarkuti András, Hauert Roland, Kiss Gábor, Halbritter András, Csontos Miklós: *In situ impedance matching in Nb/Nb 2 O 5 /PtIr memristive nanojunctions for ultra-fast neuromorphic operation*, **NANOSCALE 10**, 19290, 2018, IF: 7.233

[6] Sánta, B ; Molnár, D ; Haiber, P ; Gubicza, A ; Szilágyi, E ; Zolnai, Zs ; Halbritter, A ; Csontos, M: *Nanosecond resistive switching in Ag/AgI/PtIr nanojunctions*, **BEILSTEIN JOURNAL OF NANOTECHNOLOGY 11,** 92 2020, IF: 3.65

[7] Török, Tímea Nóra ; Csontos, Miklós ; Makk, Péter ; Halbritter, András: *Breaking the Quantum PIN Code of Atomic Synapses*, **NANO LETTERS 20**, 1192, 2020, IF: 12.28

Noise measurements

We have developed a novel noise measurement system which is capable of measuring both current and voltage noise inside a Faraday cage (Fig. 5A,B). Utilizing this setup, we have investigated the noise characteristics of silver-based memristive filaments (Ag_2S and AgI) and pure silver atomic wires. This comparison revealed that the noise amplitude exhibits a very clear resistance dependence, which, however, does not depend on the fabrication method of the silver nanowires, implying that the internal dynamical fluctuations of the wires dominate the noise instead of surface effects. The resistance dependence of the noise power was successfully understood in the framework of a model considering the scattering on two level systems, and the crossover between the ballistic and diffusive transport regimes (Fig. 5F).[8]

In the field of graphene nanogaps we have obtained a detailed diagnosis on the nanogap formation process via 1/f-type noise measurements. In the nanojunction regime single-atom junction width fluctuations were identified, whereas in the nanogap regime nonlinear noise spectroscopy measurements have made clear distinction between barrier-height fluctuations and gap-size fluctuations, showing that clearly the latter are responsible for the observed noise characteristics (Fig. 5E).[9] These results facilitate the ongoing noise analysis of graphene-SiO_x resistive switching devices.

We have also demonstrated that the 1/f noise characteristics of single-molecule junctions make clear difference between monomer and dimer configurations (Fig. 5D).[10] These measurements were performed by our group member A. Magyarkuti at the Columbia University.

Relying on this broad experience in the 1/f noise analysis of various nano-scale electronic systems, we have published a review paper on the *1/f noise spectroscopy and noise tailoring of nanoelectronic devices*.[11]

[8] B. Sánta, Z. Balogh, A. Gubicza, L. Pósa, D. Krisztián, G. Mihály, M. Csontos, A. Halbritter*: Universal 1/f type current noise of Ag filaments in redox-based memristive nanojunctions,* **NANOSCALE 11**, 4719, 2019, IF: 6.97

[9] Pósa László, Balogh Zoltán, Krisztián Dávid, Balázs Péter, Sánta Botond, Furrer Roman, Csontos Miklós, Halbritter András: *Noise diagnostics of graphene interconnects for atomic-scale electronics*, **NPJ 2D MATERIALS AND APPLICATIONS 5,** 57, 2021, IF: 11.44

[10] Magyarkuti Andras, Adak Olgun, Halbritter Andras, Venkataraman Latha, *Electronic and Mechanical Characteristics of Stacked Dimer Molecular Junctions,* **NANOSCALE 10**, 3362, 2018, IF: 7.233

[11] Balogh Zoltan, Mezei Gréta, Pósa László, Sánta Botond, Magyarkuti András, Halbritter András: *1/f noise spectroscopy and noise tailoring of nanoelectronic devices*, **NANO FUTURES 5**, 042002, 2021, IF: 4.07

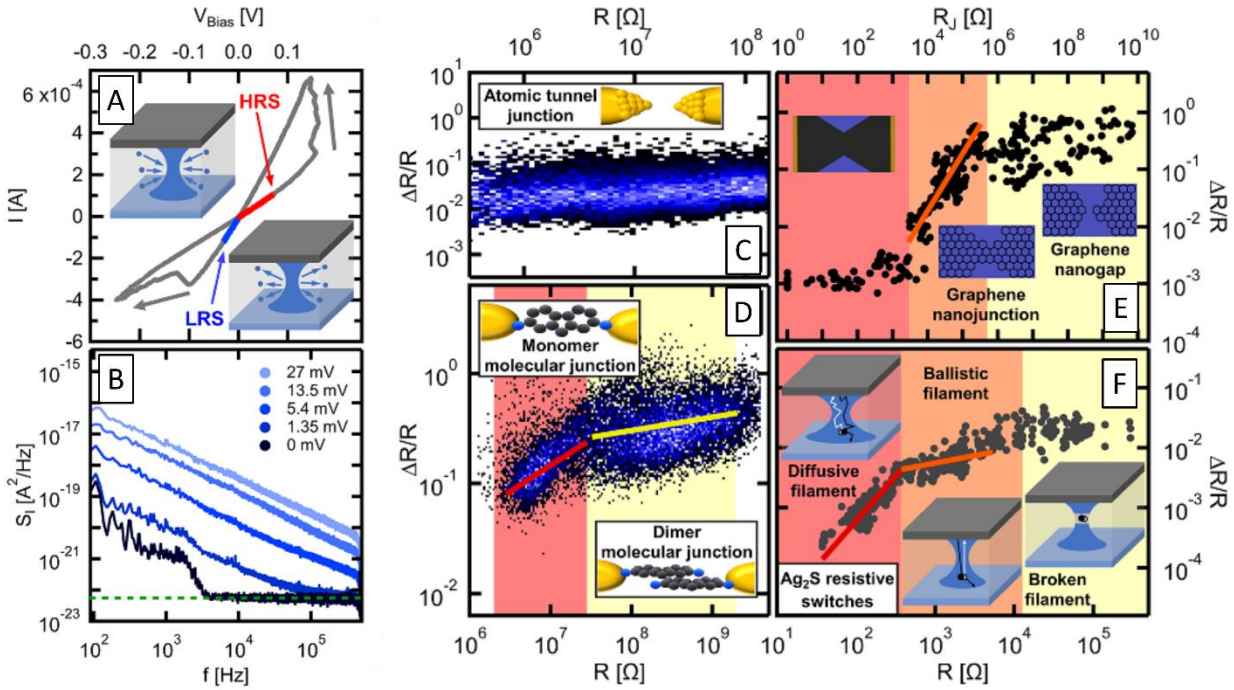

Fig. 5. 1/f-type noise measurements on nanoelectronic devices.[11] *The 1/f-type noise spectra (B) are measured in the low-bias region of resistive switching I(V) characteristics (A). The resistance dependence of the relative noise level acts as a specific device fingerprint, which was studied for atomic tunnel junctions (C), single-molecule nanowires (D), graphene nanojunctions and nanogaps (E) and Ag-based resisitive switching memories (F).*

6. Statistical analysis of large data enembles

We have continued our activity on the advanced statistical analysis of the conductance data in single-molecule structures. This relied on the introduction of novel temporal correlation analysis methods, and the investigation of structural memory effects by opening and closing correlations (Fig. 6A).[12,13] The novel, ultrasensitive measurement techniques developed by the project member Gábor Mészáros were also applied in other research groups.[14]

We have also worked on the development of novel data analysis techniques based on machine learning algorithms. In collaboration with the group of Prof. Gemma Solomon (University of Copenhagen) we have worked on the classification of experimental conductance traces using recurrent neural networks.[15] Furthermore, we have developed a novel data analysis method which is capable of a fully automatic, unsupervised classification of the single-molecule conductance traces (Fig. 6B).[16]

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[12] A Magyarkuti, K P Lauritzen, Z Balogh, A Nyáry, G Mészáros, P Makk, G C Solomon, A Halbritter: *Temporal correlations and structural memory effects in break junction measurements*, **JOURNAL OF CHEMICAL PHYSICS 146,** 092319, 2017, IF: 2.965

[13] Magyarkuti A., Balogh Z., Mezei G., Halbritter A.: *Structural Memory Effects in Gold–4,4′-Bipyridine–Gold Single-Molecule Nanowires*, **JOURNAL OF PHYSICAL CHEMISTRY LETTERS 12**, 1759, 2021, IF: 6.71

[14] Kolivoška, Viliam ; Šebera, Jakub ; Sebechlebská, Táňa ; Lindner, Marcin ; Gasior, Jindřich ; Mészáros, Gábor ; Mayor, Marcel ; Valášek, Michal ; Hromadová, Magdaléna: *Probabilistic mapping of single molecule junction configurations as a tool to achieve the desired geometry of asymmetric tripodal molecules*, **CHEMICAL COMMUNICATIONS 55**, 335,1 2019 IF: 6.16

[15] Lauritzen KP,Magyarkuti A,Balogh Z,Halbritter A,Solomon GC: *Classification of conductance traces with recurrent neural networks*, **JOURNAL OF CHEMICAL PHYSICS 148**, 084111, 2018, IF: 2.843

[16] A. Magyarkuti, N. Balogh, Z. Balogh, L. Venkataraman and A. Halbritter: *Unsupervised feature recognition in single-molecule break junction data*, **NANOSCALE 12**, 8355, 2020, IF: 6.895

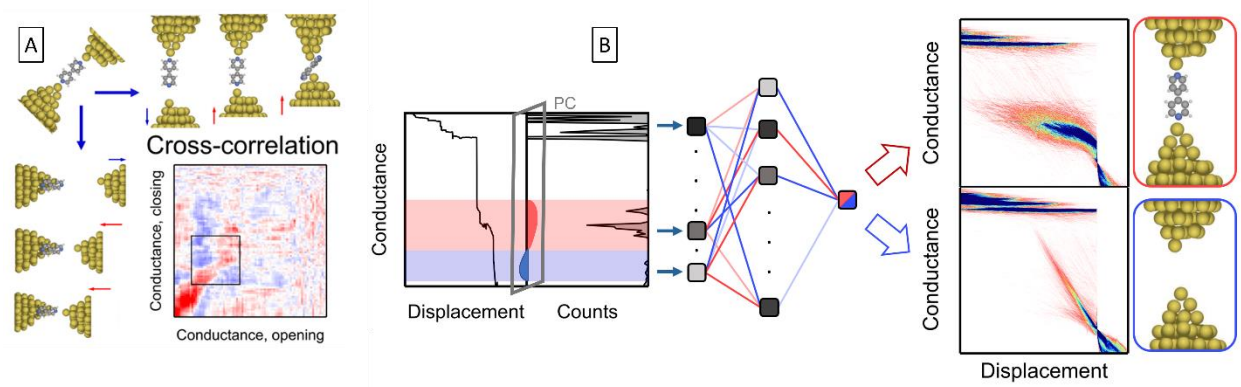

Fig. 6. Advanced statistical analysis of single molecule structures. *(A) We studied structural memory effects in gold–4,4'-bipyridine–gold single-molecule nanowires. We have demonstrated that upon a rupture the single bipyridine molecule does not flip to the side of the junction, rather it stays protruding from one apex, such that afterwards the same molecular junction can be reestablished.[13] (B) We have developed a novel unsupervised data classification method using the traces with large positive-negative principal component projections as a training data, and afterwards a simple feed-forward neural network identifies the relevant trace classes in the data.[16]*

7. Publication of the results

The results of the project were published in 16 research papers with a summed impact factor of 111, and an average impact factor of 6.9.

Along the project 4 PhD works, 5 MSc diploma works, 7 BSc theses and 7 TDK works were finalized, all being directly related to this project:

Phd works: Zoltán Balogh (2017) László Pósa (2019), András Magyarkuti (2020), Botond Sánta (2021)

MSc diploma theses: Tímea Nóra Török (2019), Dániel Molnár (2019), Dávid Krisztián (2019), Nóra Balogh (2020), Péter Balázs (2021)

BSc theses: Dávid Krisztián (2017), Noémi Vargha (2017), Patrick Haibert (2017), Nóra Balogh (2018), Csaba Sinkó (2018), Péter Balázs (2019), György Lázár (2022)

TDK works: Török Tímea Nóra (2017&2018 BME 2nd and 3rd prize, Dennis Gábor prize, OTDK 2nd prize), Nóra Balogh (2018, BME 1st prize, OTDK additional prize), Péter Balázs (2019 BME 3rd prize, National OTDK competition 1st prize), Péter Balázs (2020 BME 2nd prize, National OTDK competition 1st prize), János Gergő Fehérvári (2020 BME 1st prize, National OTDK competition 2nd prize), Roland Kövecs (2022 BME TDK, certificate of commendation)

The research results were presented on altogether 22 international oral conference talks at the leading conferences of the research field (International Workshop on "Molecular-Scale Electronics: Concepts, Contacts, and Stability", Lancaster, 2017; MEMRISYS 2019 Dresden (6 oral talks); MEMRISYS 2021 (5 online oral talks); EMRS 2022 (1 online oral talk); CIMTEC 2022, Perugia (7 oral talks); Nano2022, Sevilla (2 oral talks).