Development of nanometer scale resistive switching memory devices

(final report on the NKFI K 128534 project)

As indicated by its title, the project focused on the development of various on-chip resistive switching (RS) devices. These plans aimed at a significant step forward compared to the previous activity of our group, where we investigated resistive switches using point-contact techniques, mainly in Scanning Tunneling Microscope STM layouts. The latter is a versatile tool for fundamental research purposes but does not allow integration and application in more complex neuromorphic circuits. This broad device development activity is only partially included in the scientific publications of our project, therefore *part I* of the final report is devoted to the more detailed summary of this development activity, whereas *part II* briefly overviews our scientific achievements, which are underpinned by 11 scientific publications acknowledging the K128534 project with an average impact factor of 6.35. As detailed in the footnote references altogether 3 BSc thesis works and 5 MSc diploma works were finalized closely related to the project, and our students participated with 5 works at the national TDK conference (a countrywide competition on student research) taking a 2^{nd} prize twice, and 1^{st} prize three times. Along the project 4 Ph.D. works were finalized, all giving important contribution to the achievements summarized here. The scientific results were presented at 7 leading international conferences of the field giving 22 oral and several poster presentations. Among the participants, László Pósa received a Bolyai Scholarship along the project, whereas Tímea Nóra Török successfully applied for the Cooperative Doctoral Program project (Development and investigation of ultra-small on-chip resistive switching memory devices). Based on the achievements of this project, the PI and László Pósa successfully applied for consortial follow-up NKFI K project entitled *Information Processing with Resisitive Switching Memories* (NKFI K143169&K 143282, 2022 December – 2026 November).

I. Summary of our device development activity

We have developed and optimized several on-chip RS devices. These include planar devices, where a pair of metallic electrodes with a nanogap in-between is fabricated on the top of the active resistive switching medium (Fig. 1a), and vertical crosspoint devices (Fig. 1b), where the active medium is sandwiched between two perpendicularly aligned metallic nanowires. In both cases the devices were prepared by electron beam lithography in the Nanosensors Laboratory of the Institute of Technical Physics and Materials Science at the Centre for Energy Research. Vanadium oxide, silicon oxide, tantalum oxide and niobium oxide were applied as the active medium, whereas the contacting electrodes were fabricated from various metals also including graphene in the case of lateral devices. Additionally, we have also developed nanofabricated mechanically controllable break junction (MCBJ) devices, where the electrical manipulation (switching) is extended by the possibility of mechanical stretching.

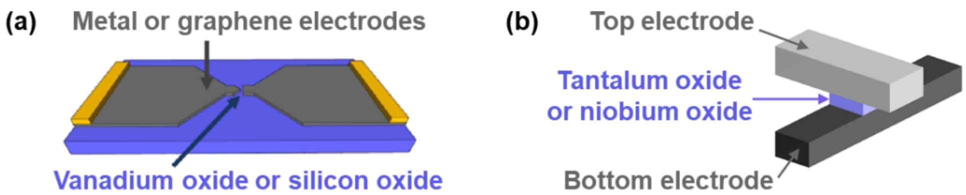

Fig. 1. *Schematics show (a) planar-type and (b) vertical crosspoint device geometries.*

I.1. SiO_2 planar resistive switching devices

In graphene-silicon-oxide-graphene resistive switching devices the switching characteristics were well-known from our previous studies. Within this project we have further optimized the device structure using a bowtie geometry,[1] which enabled a better control over the electrical breakdown of the graphene nanowire, i.e. the establishment of a graphene nanogap for contacting the SiO_2 resistive switch underneath. In these devices a so-called dead-time restricts the fast, repeated operation. We attempted the decrease of the deadtime by the treatment of the SiO_2 layer (Ar plasma treatment, and the replacement of thermally oxidized SiO_2 layer by chemical vapor deposited SiO_2 layer), but these attempts were only partially successful, the dead-time could not be reduced, but the electro-formation voltage significantly decreased (from 8-9V to 3-5V). Furthermore, we have contacted SiO_2 resistive switches by various metallic electrodes, including Pt and Nb (see Fig. 2). Devices with Pt electrodes exhibited similar characteristics to the graphene SiO_2-graphene devices, offering a much simpler fabrication procedure compared to the graphene structures, promoting applications, where transparency and/or flexibility is not required. Nb-SiO_2-Nb devices also exhibited resistive switching, but the switching characteristics of SiO_2 were sometimes replaced by I(V) curves characteristic to Nb_2O_5 or NbO_2 switching, which hinders the reliable application. The produced SiO_2 devices were investigated in our publication on the set time analysis[2] (see part II.1.), and in various diploma, TDK and PhD works.[1,3,4,5,6,7,8]

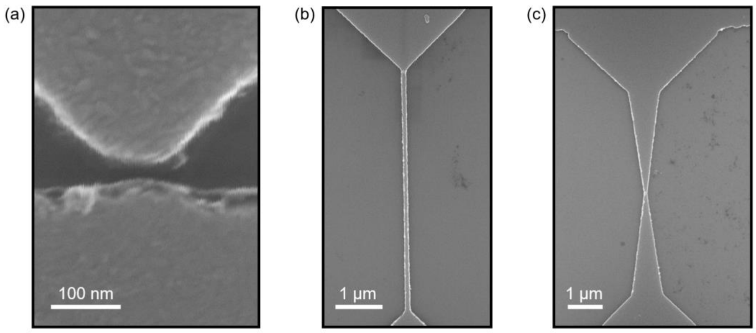

Fig. 2. *Representative SiO_2 devices with metallic electrodes (SEM images) (a) Asymmetric gap-type, (b) line and (c) bowtie geometries. The latter two types need to undergo an electrobreakdown process to establish a gap.*

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[1] László Pósa, Resistive switching in ultrasmall nanogap devices, **Ph.D. thesis**, 2019

[2] Török, T. N.; Fehérvári, J. G.; Mészáros, G.; Pósa, L.; Halbritter, A., Tunable, Nucleation-Driven Stochasticity in Nanoscale Silicon Oxide Resistive Switching Memory Devices, **ACS APPLIED NANO MATERIALS 5**, 6691 (2022)

[3] Dávid Krisztián, Zajmérés SiOx-grafén memrisztív rendszeren (Noise measurement on SiO_2-graphene memristive system), **Diploma thesis**, 2019

[4] Péter Balázs, SiO_2 rezisztív kapcsolók vezetési mechanizmusának vizsgálata zajjelenségeken keresztül (Conduction properties of SiO2 resistive switches – a noise analysis), **TDK work**, 2020 (BME TDK 2nd prize, **National TDK 1st prize**)

[5] Péter Balázs, SiO_2 fázisváltó memóriák zajjelenségeinek és hőmérsékletfüggő transzportjelenségeinek vizsgálata (Investigation of noise and temperature-dependent transport phenomena in SiOx phase-change memories), **Diploma thesis**, 2021

[6] János Gergő Fehérvári, Nanoméretű fázisváltó memóriák időskáláinak kísérleti vizsgálata (Experimental investigation of time scales for nanoscale phase-change memories), **TDK work**, 2020 (BME TDK 1st prize, **National TDK 2nd prize**)

[7] János Gergő Fehérvári, Sztochasztikus jelenségek rezisztív kapcsoló memóriákban (Stochastic phenomena is resistive switching memories), **BSc thesis**, 2021

[8] Török Tímea Nóra, Development and investigation of ultra-small on-chip resistive switching memory devices, **Ph.D. thesis** (submitted in January, 2024)

I.2. Nb_2O_5 and Ta_2O_5 crosspoint RS devices

Transition metal oxide RS devices are key ingredients of our research and development activities. First, we have successfully developed Nb_2O_5 and Ta_2O_5 resistive switching layers turning from the method of anodic oxidation to reactive sputtering. These layers were characterized by XPS (X-ray photoelectron spectroscopy) measurements[10] at our collaborating partner (EMPA, Switzerland), and by STM point-contact RS experiments in our labs. Afterwards, we have successfully developed Nb_2O_5 and Ta_2O_5 on-chip crosspoint RS devices (see Fig.3). These devices enable reliable switching characteristics with up to 10^5 reproducible switching cycles, analog tunable conductance weights, and an exponential speed-up of the switching upon a linear increase of the driving voltage (Fig. 3c). All these characteristics make these devices ideal for applications in neuromorphic computing schemes. These devices were studied and applied in our publications[9,10] related to the project, and in various TDK, BSc thesis, MSc diploma and PhD works.[11,12,13,14]

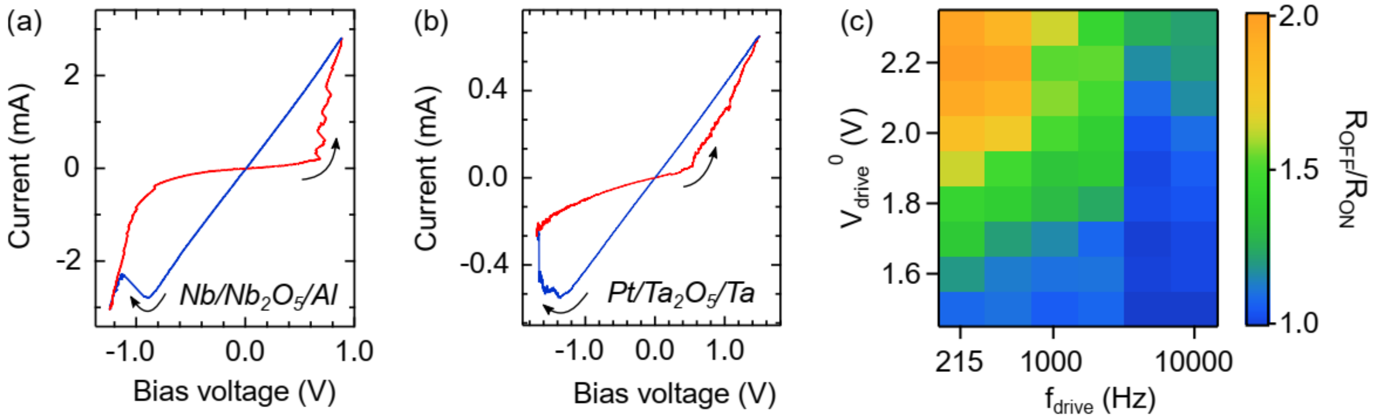

Fig. 3. *Typical RS characteristics of (a) Pt/Nb_2O_5/Al crosspoint devices and (b) Pt/Ta_2O_5/Ta crosspoint devices. (c) Time-voltage dilemma of Pt/Nb_2O_5/Al devices: at linearly increasing driving voltage amplitudes the same resistance ratio is obtained at exponentially increasing frequencies.*

I.3 Vanadium-oxide planar resistive switching devices

The non-volatile transition metal oxide RS devices in the previous section act as artificial synapses in neuromorphic applications. Another important type of RS devices include volatile threshold switches, which are ideal candidates to reproduce various neural spiking functionalities. We have invested strong efforts to include such volatile RS devices in our device pool. We have successfully developed VO_2 layers[15] and RS devices, where the RS phenomenon relies on a Mott-type metal-to-insulator transition. The specialty of our

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[9] T. N. Török, M. Csontos, P. Makk, A. Halbritter, Breaking the Quantum PIN Code of Atomic Synapses, **NANO LETTERS 20**, 1192 (2020)

[10] Sánta, B.; Balogh, Z.; Pósa, L.; Krisztián, D.; Török, T. N.; Molnár, D.; Sinkó, Cs.; Hauert, R.; Csontos, M.; Halbritter, A., Noise Tailoring in Memristive Filaments, **ACS APPLIED MATERIALS & INTERFACES** 13, 7453 (2021)

[11] György Lázár, Filamentáris rezisztív kapcsoló memóriák zajjelenségeinek vizsgálata (Investigation of the noise properties of filamentary resistive switching memories), **BSc thesis**, 2022

[12] Anna Nyáry, Atomic processes in resistive switching devices: from fluctuations to reversible atomic rearrangements, **Ph.D. thesis** (submitted in February, 2024)

[13] Botond Sánta, Rezisztív kapcsoló memóriák dinamikai vizsgálata (Investigation of the dynamics of resistive switching memories), **Ph.D. thesis**, 2021

[14] Tímea Nóra Török, Rezisztív kapcsolási jelenség vizsgálata Nb_2O_5 pontkontaktusokban, (Study of resistive switching phenomenon in Nb2O5 point contacts), **Diploma thesis**, 2019

[15] Pósa, L.; Molnár, Gy.; Kalas, B.; Baji, Zs.; Czigány, Zs.; Petrik, P.; Volk, J., A Rational Fabrication Method for Low Switching-Temperature VO2, **NANOMATERIALS 11,** 212 (2021)

devices is the ultrasmall device structure: we were the first to apply a special device geometry, where a V-shaped electrode on one side focuses the switching to an ultra-small volume[16] (Fig. 4b). We have performed detailed characterization measurements on these devices, including electron energy loss spectroscopy, Transmission electron microscopy (Fig. 4e), as well as temperature and voltage dependent characterization of the switching. These devices were studied in two publications and in several TDK, BSc thesis, MSc diploma and PhD works.[8,17,18,19]

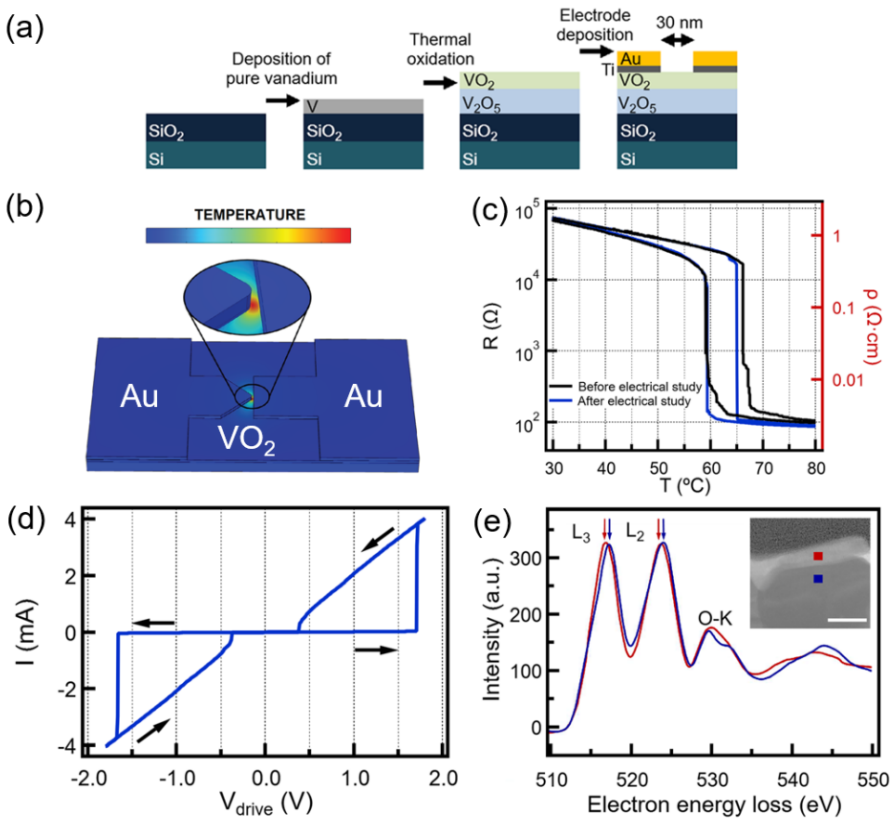

Fig. 4. *General characteristics of VO_2 nanogap memristors developed by our group. (a) Deposition steps of the devices illustrated schematically. (b) Structure of the planar-type device, also illustrating the local temperature in the device (finite element simulations). (c) Resistance – temperature dependences, exhibiting drastic resistance change with hysteresis, indicative of Mott phase transition. (d) Typical driving voltage-dependent RS I(V) characteristics. (e) EELS spectra recorded at the top (red line) and bottom (blue line) layers identifed by cross-sectional TEM imaging (inset).[16]*

I.4. Development of nanofabricated MCBJ devices using air-sensitive metals

MCBJ devices have crucial importance in investigations, where electrical manipulation is extended by mechanical stressing. The traditional fabrication recipe, however, includes an undercutting step, where oxygen plasma treatment is applied, which would however, destroy air sensitive metals. For instance, the traditional method was improper to produce silver MCBJ devices. We have developed a novel fabrication

[16] Pósa, L.; Hornung, P. ; Török, T. N.; Schmid, S. W.; Arjmandabasi, S.; Molnár, Gy.; Baji, Zs.; Dražić, G.; Halbritter, A.; Volk, J., Interplay of Thermal and Electronic Effects in the Mott Transition of Nanosized VO2 Phase Change Memory Devices, **ACS APPLIED NANO MATERIALS 6**, 9137 (2023)

[17] Axel Katona, Katona Axel Attila, VO2 fázisváltó memóriák dinamikai jelenségeinek vizsgálata, (Investigation of the dynamic phenomena of VO2 phase-change memories), **BSc Thesis**, 2022

[18] Sadaf Arjmandabasi, Development and characterization of phase change resistive switching memories, **Diploma thesis**, 2022

[19] Hornung Péter, Nanoméretű VO2 fázisváltó memória kapcsolásának vizsgálata végeselem szimulációval (Investigation of nanometer-sized VO2 phase change memory using finite element model), **TDK work**, 2022 (BME TDK 1st prize, **National TDK 2nd prize**)

scheme, which is appropriate to produce nanofabricated MCBJ devices from air sensitive metals (Fig. 5). We have successfully fabricated Ag MCBJ devices and demonstrated room temperature pure atomic switching phenomenon in these (Fig. 5j). These results are published[20] and included in a PhD thesis.[12]

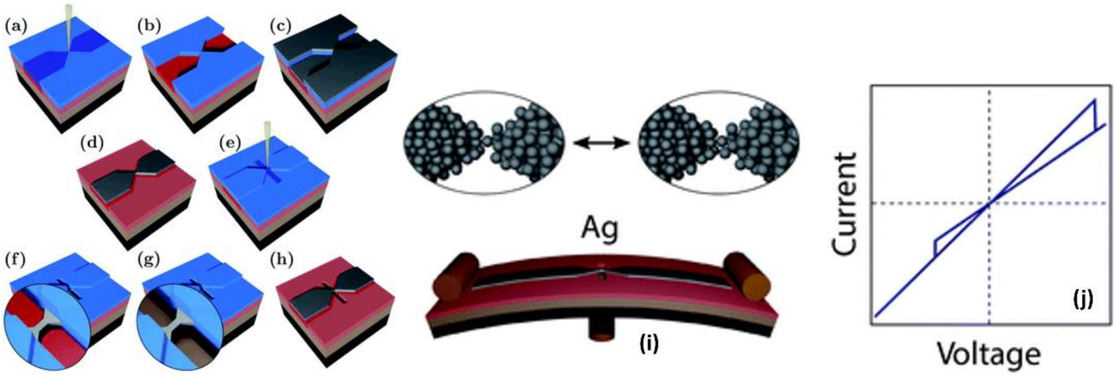

Fig. 5. *Nanofabricated Ag MCBJ devices. Panels (a-h) demonstrate the fabrication steps, (i) illustrates the device geometry, where the Ag nanowire can be thinned and broken by mechanical stretching in a three-point bending geometry, and panel (j) is an example pure atomic switching I(V) curve.*[20]

II.1 Understanding the switching mechanism.

Relying on the developed on-chip RS devices we have performed several studies with the goal of understanding some important aspects of the switching phenomenon in various material systems.

We have investigated the cycle-to-cycle variation of the set-time (i.e. the time-delay of switching ON the device after the rising edge of the programming pulse) in graphene-SiO_2-graphene RS devices[2,6] (Fig. 6a-d). Going beyond the investigation of average set time characteristics and studying the entire distribution in the framework of nucleation theory, we have gained fundamental information about the nanocrystal formation mechanism. We identified a nucleation-driven set process instead of a growth driven process. Furthermore, we demonstrated that the set time is sensitive to the nanostructure of the initial high-resistance state, which is intentionally tunable by the amplitude of the reset operation.

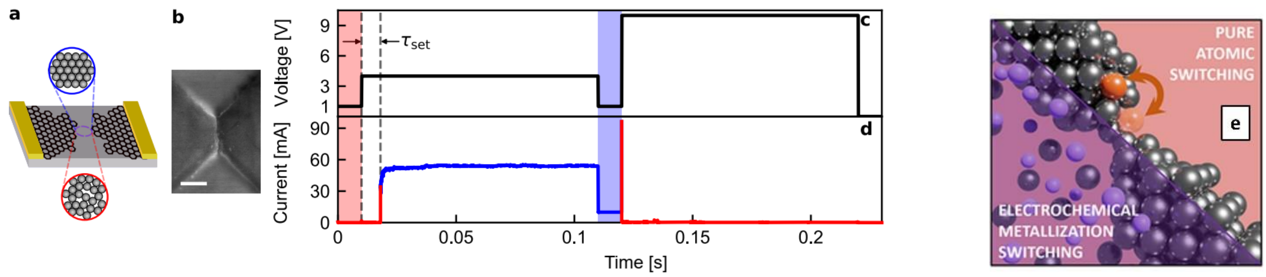

Fig. 6. *(a) Illustration of a planar graphene/SiO_2/graphene nanogap device with gold electrodes. The crystalline structure of the ON state and the amorphous structure of the OFF state are depicted. (b) Scanning electron microscopy image of a graphene/SiO_2/graphene nanogap device with a scalebar of 200 nm. (c) Rectangular switching pulse scheme for studying set time dynamics and (d) typical current response of the device demonstrating the τ_{set} set time. (e) Illustration of our study investigating the differences between pure atomic switching and electrochemical metallization resistive switching.*[21]

In our VO_2 devices we have investigated the interplay of nanoscale thermal and nonlinear electronic phenomena.[16,19] The well-focused voltage profile in our V-shaped nanoscale devices facilitated the device modeling and the identification of physical mechanisms behind the phase transition (Fig. 4b). We have found that purely thermal or electronic effects fail to describe the device operation, however, according to our

[20] Nyáry, Anna ; Gubicza, Agnes ; Overbeck, Jan ; Pósa, László ; Makk, Péter ; Calame, Michel ; Halbritter, András ; Csontos, Miklós, A non-oxidizing fabrication method for lithographic break junctions of sensitive metals, **NANOSCALE ADVANCES 2**, 3829 (2020)

finite element simulations, a combined electronic and thermal model provides a precise description of the device characteristics. These results facilitate the understanding as well as the thermal and electronic design of novel VO_2-based neuronal devices.

As a third topic we investigated Ag-based RS devices. Silver plays a prominent role as an active material in resistive-switching memory devices based on electrochemical metallization. Such a structure contains in its active volume nanoscale Ag filaments. Meanwhile, a fundamentally different type of resistive switching occurs in an atomic wire of pure Ag, where an embedding, ion-hosting environment is absent. Our comparative study clarified the characteristics and origins of the latter, purely atomic switching phenomenon, highlighting its importance in silver-based memristive devices as the active volume approaches truly atomic dimensions (Fig. 6e). This project was initiated along the NKFI K119797 project (*Towards atomic-scale memories*), but the results were finalized and published within this project.[12,21]

II.2. Ultrafast measurements

We have developed a high-frequency memristor characterization setup which is capable of investigating sub-nanosecond resistive switching.[22, 23] As a goal of another NKFI project (119797) this setup was used to study the switching properties of AgI point contact memristors, but it also serves as an important characterization tool for the characterization of novel on-chip devices in the framework of the present project. Utilizing this knowledge on ultrafast switching experiments, we have investigated RS in tantalum pentoxide on-chip memristors with picosecond time resolution. These measurements were performed by Miklós Csontos (a former member of this research project) at ETH Zürich, where the picosecond resolution measurement systems are available, whereas the PI of the present project gave relevant contribution to the design and understanding of the measurements. The 10 second switching time reported in this paper is the current world record, the fastest RS process ever resolved (Fig. 7).[24]

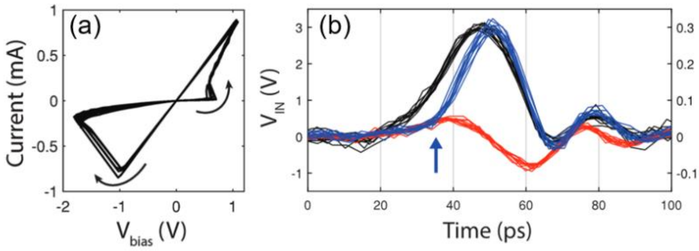

Fig. 7. *(a-c) Picosecond-resolution electrical studies of Pt/Ta_2O_5/Ta/Pt devices, showing (a) low frequency I(V) characteristics and (b) ultra-fast, ~10ps set process.*[24]

II.3. Noise analyis

We have developed a versatile measurement system to investigate the noise properties of RS devices.[3,4,5,10,11,12,13] This system was first used to study Ag-based point-contact resistive switches, and on-chip pure Ag electromigrated nanowires [25] and was later applied to Nb_2O_5,[10] SiO_2[3,4,5] and Ta_2O_5[11,12] on-chip

[21] Nyáry, A. ; Balogh, Z. ; Vigh, M. ; Sánta, B. ; Pósa, L. ; Halbritter, A., Voltage-time dilemma and stochastic threshold-voltage variation in pure-silver atomic switches, **PHYSICAL REVIEW APPLIED 21**, 014027 (2024)

[22] Dániel Molnár, Kapcsolások dinamikájának vizsgálata, Nb2O5 memrisztív nanokontaktusokban (Investigating the switching dynamics of Nb2O5 memristive nanojunctions) **Diploma thesis**, 2019

[23] 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)

[24] Csontos, M. ; Horst, Y. ; Olalla, N.J. ; Koch, U. ; Shorubalko, I. ; Halbritter, A. ; Leuthold, J., Picosecond Time-Scale Resistive Switching Monitored in Real-Time, **ADVANCED ELECTRONIC MATERIALS 9**, 2201104 (2023)

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

devices. Our broad experience on 1/f-type measurements was also summarized in a review paper.[26] Our comparative noise analysis[10] demonstrated that the transition metal oxide RS devices (Ta_2O_5 and Nb_2O_5) exhibit almost two orders of magnitude smaller overall noise level than the Ag based systems due to disorder-induced noise suppression. Based on this experience we are setting up a noise map (Fig. 8a) including a very broad range of RS material systems, demonstrating the dependence of the noise level on the chosen material system as well as the analog tunable conductance state of the devices. This comparative information is essential for RS device development, as in some applications the smallest possible noise levels are desired, whereas in probabilistic optimization applications tunable noise can be harvested as a computational resource.

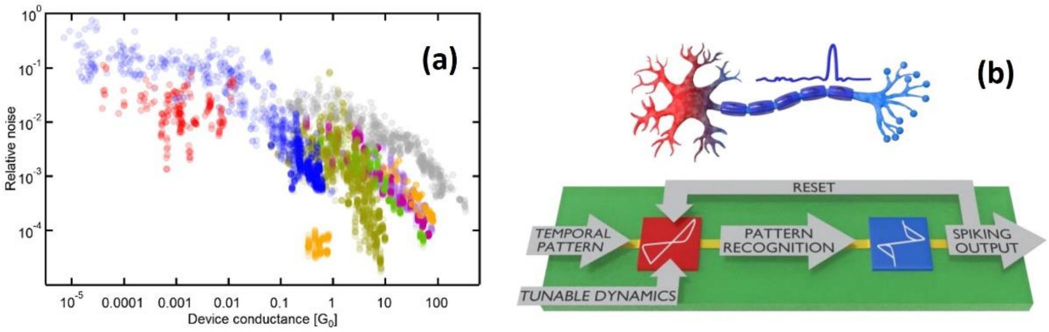

Fig. 8. *(a) Relative noise level in various RS material systems (different colors) at various device conductances (partly unpublished data). (b) Scheme of our neural information processing circuit.*[27,32]

II.4. Neuromorphic information processing

Driving our research activity towards the application of the developed on-chip RS devices, we have simulated more complex neuromorphic circuits relying on the realistic device characteristics of our chips. One study utilized the complex dynamical properties of the RS devices, demonstrating that the proper adjustment of the device dynamics can be utilized to recognize complex temporal patterns.[27] This scheme was further extended by VO_2 artificial neuron, which emits a neural spike once the first Ta_2O_5 input device recognizes the temporal pattern (Fig. 8b).[28] Another study simulated large-scale so-called Hopfield neural networks, which can be used to solve complex computational problems (like max-cut graph segmentation). We have demonstrated, how the proper tuning of internal noise level aids the convergence of the algorithm.[29,30]

III. Links to other projects

The present project, i.e. an extended activity on the development of on-chip resistive switching devices was inspired by a previous NKFI grant (K119797, *Towards atomic-scale memories, 2016-2021).* The latter project focused on the physical understanding of single-atom, single-molecule and resistive switching junctions mostly established in an STM point-contact arrangement. In the starting years of the present project the

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[26] Balogh, Z.; Mezei, G.; Pósa, L.; Sánta, B.; Magyarkuti, A.; Halbritter, A., 1/f noise spectroscopy and noise tailoring of nanoelectronic devices, **NANO FUTURES 5**, 042002 (2021)

[27] P. Balázs, Processing complex signals with simulations of single memristors and small memristor networks, **TDK thesis**, 2019 (**1st prize at the National TDK conference in 2021**)

[28] A.R. Kövecs, Neurális dinamikával rendelkező memrisztor alapú detektoráramkör megvalósítása (Implementation of a neural-dynamics-based memristive detector circuit), **TDK work**, 2022

[29] János Gergő Fehérvári, Sztochasztikus Optimalizáció Hangolható Zajforrásként Működő Memrisztorok Segítségével (Stochastic Optimization Using Tunable Memristors as Noise Sources), **TDK work**, 2023 (BME TDK 2nd prize, **National TDK 1st prize**)

[30] János Gergő Fehérvári, Exploring the Operation of Memristive Netvorks Relying on the Realistic Noise Characteristics of Silicon Dioxide Phase Change Memories, **Diploma thesis**, 2023

publications were shared with the K119797 project, where the fundamental research results[9,23,25] are dedicated to the K119797 project, but these publications already include important material and device preparation aspects, as well as the development of novel characterization techniques that laid the foundations for the present project. On the other hand, the present project inspired a follow-up NKFI grant (K143169&K143282 *Information Processing with Resisitive Switching Memories, 2022-2026*). The experimental realization and publication of the neuromorphic information processing schemes prepared in TDK and diploma works, and summarized in II.4. is a specific goal of the above follow-up grant, already delivering the first publication,[31] and a preprint paper.[32]

[31] J. G. Fehérvári, Z. Balogh, T. N. Török, A. Halbritter, Noise tailoring, noise annealing, and external perturbation injection strategies in memristive Hopfield neural networks, Journal: **APL MACHINE LEARNING**, 2, 016107 (2024)

[32] D. Molnár, T. N. Török, R. Kövecs, L. Pósa, P. Balázs, Gy. Molnár, N. Jimenez Olalla, J. Leuthold, J. Volk, M. Csontos, A. Halbritter, Autonomous neural information processing by a dynamical memristor circuit,
https://doi.org/10.48550/arXiv.2307.13320