ACTA IMEKO
ISSN: 2221-870X
September 2023, Volume 12, Number 3, 1 - 5

Memristive devices for metrological applications

Vitor Cabral[1], Alessandro Cultrera[2], Shaochuan Chen[4], João Pereira[6], Luis Ribeiro[1], Isabel Godinho[1], Luca Boarino[3], Natascia De Leo[3], Luca Callegaro[2], Susana Cardoso[6], Ilia Valov[4,5], Gianluca Milano[3]

[1] *Instituto Português da Qualidade, Rua António Gião 2, 2829-513 Caparica, Portugal*
[2] *Istituto Nazionale di Ricerca Metrologica- Quantum Metrology and Nanotechnologies, Strada delle Cacce 91, 10135 Torino, Turin, Italy*
[3] *Istituto Nazionale di Ricerca Metrologica- Advanced Materials and Life Sciences Division, Strada delle Cacce 91, 10135 Torino, Turin, Italy*
[4] *RWTH-Aachen university, IWE2, Sommerfeldstr. 24, 52074 Aachen, Germany*
[5] *Research Centre Juelich, PGI-7, Wilhelm Johnen-Str, 52425 Juelich, Germany*
[6] *INESC Microsistemas e Nanotecnologias, Rua Alves Redol 9, 1000-029 Lisboa, Portugal*

ABSTRACT
The EMPIR project 20FUN06 MEMQuD - "Memristive devices as quantum standard for nanometrology" has as one of its fundamental goals the development of technical capability and scientific knowledge for the implementation of a quantum resistance standard based on memristive devices characterized by high scalability down to the nanometer scale, compatibility with CMOS, complementary metal-oxide semiconductor, and working in air at room temperature. In this work it is presented an overview of the project, highlighted relevant characteristics and working principles of memristive devices and potential applications with focus on metrological application with framing allowed by the last revision of the International System of Units SI that is the motivation and background for the aim of this project.

Section: RESEARCH PAPER

Keywords: Memristive; quantum conductance; quantum resistance; nanometrology

Citation: Vitor Cabral, Alessandro Cultrera, Shaochuan Chen, João Pereira, Luis Ribeiro, Isabel Godinho, Luca Boarino, Natascia De Leo, Luca Callegaro, Susana Cardoso, Ilia Valov, Gianluca Milano, Memristive devices for metrological applications, Acta IMEKO, vol. 12, no. 3, article 25, September 2023, identifier: IMEKO-ACTA-12 (2023)-03-25

Section Editor: Jan Saliga, Technical university of Kosice, Slovakia, Jakub Svatos, CVUT Prague, Czech Republic, Platon Sovilj, University of Novi Sad, Serbia

Received January 23, 2023; **In final form** May 2, 2023; **Published** September 2023

Funding: This work was supported by the European project MEMQuD, code 20FUN06. This project (EMPIR 20FUN06 MEMQuD) has received funding from the EMPIR programme co-financed by the Participating States and from European Union's Horizon 2020 research and innovation programme.

Corresponding author: Vitor Cabral, e-mail: vcabral@ipq.pt

1. INTRODUCTION

The revision of the International System on Units (SI) by the General Conference on Weights and Measures (CGPM), at its 26th meeting, in 2019 [1] redefined the base units through fixed values of fundamental physical constants, and represented a significant and historic step forward where, since for the first time all the 7 base units of the SI do not rely on any artefact, material property or measurement descriptions. Concerning the electrical units, the redefinition of the base unit ampere (A) in terms the exact value of the elementary charge e, and the definition of the exact value of the Plank constant h, allowed the harmonization of the realization of electrical units with the already established realizations of the conventional units Ω_{90} and V_{90}, realized and disseminated via the Quantum Hall Resistance Standard (QHRS) and the Josephson Voltage Standard [2]. Even though these realizations are much more reliable than the previous, the required systems for the implementation of a QHRS are still rather complex and time consuming to operate, demanding high magnetic fields and low temperature values, near 1 K.

Memristive devices, or memristors (from the contraction of memory + resistor), are a new class of nanoscale devices where ionics is coupled with electronics and where device functionalities rely on nanoionic effects. Initially theorized in 1971 from Prof. Chua [3], the ideal concept of memristor, was associated with the so-called resistive switching devices in 2008 by the group of Stanley Williams at HP labs [4]. These are two terminal devices where a switching film (usually a metal-oxide) is sandwiched in between two metal electrodes in a metal-insulator-metal (MIM) structure (Figure 1.I) [5].

In these devices, the internal state of resistance depends on the history of the applied voltage and current exhibiting the

I

II

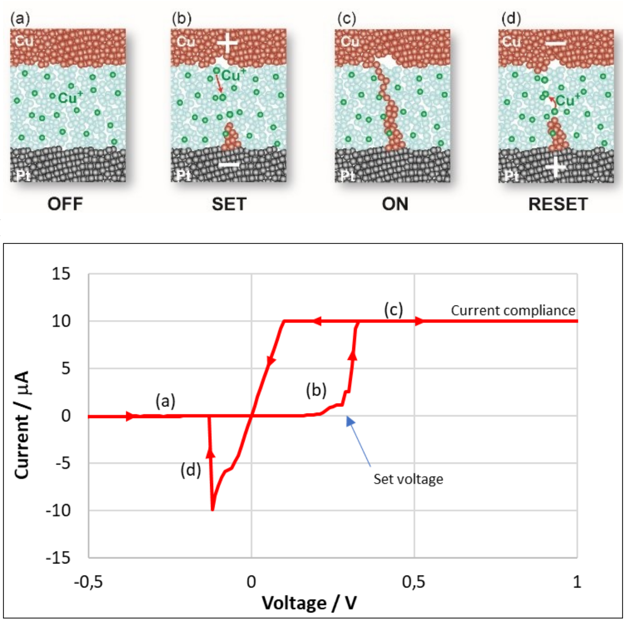

Figure 1. **(I)** Schematic presentation of the operation principles of cation based ReRAM memory cells with a Cu active electrode and Pt counter electrode. (a) depicts the initial or OFF state. (b) shows the dissolution of metallic Cu to Cu+ ions and the formation of the metallic filament in the 'program' or 'set'operation. (c) is the short-circuited ON state. (d) shows the dissolution of the filament in the 'erase' or 'reset' step under reverse bias and the return to the OFF state [8]. **(II)** I-V characteristic curve of a crossbar cell based on Pt/Cu/SiO2/Cu/Pt (30nm/30nm/50nm/30nm) obtained for a sweep voltage signal and a current compliance of 10 µA. Cell fabricated and experimental data obtained in exploratory measurements done in the framework of the EMPIR MEMQud project.

typical hysteretic loop in the *I-V* plane showed in Figure 1.II and Figure 2. By exploiting these characteristics, it was demonstrated that memristive devices can have applications in next-generation memories, in-memory computing architectures and neuromorphic architectures. Particularly, memristive devices under specific conditions of operation can show low resistance states activated in the device corresponding to values multiple (or half-integer multiples) of the fundamental conductance value, $G_0 = 2\,e^2/h$. This means that these devices offer a promising platform to observe and generate quantum resistance values in air, at room temperature, and without the need of any applied magnetic field as it is needed for the QHRS. Moreover, they also can work in harsh conditions such as low/high temperatures, exposure to electromagnetic waves and X-ray, and are resistant to high-energy particles.

These quantum values of resistance are therefore in line with the spirit and fundamental characteristic of the revision of the SI electrical units, depending on the fixed values of the fundamental constants e and h.

The EMPIR [6] project MEMQuD - "Memristive devices as quantum standard for nanometrology" [7] aims to study in detail the quantum effects in memristive devices and to investigate fundamental aspects underpinning memristive technology. The simpler way to operate this new device, its high scalability down to the nanometre scale and on-chip integration open the possibility of new applications with relevant impact on metrology and industry, meeting the challenges opened by the revised SI where new experiments and devices can be explored, enabling the on-chip integration of quantum reference standards.

In Section 2 we will present an overview of the MEMQuD project describing its technical activity's structure and objectives. In Section 3, fundamentals of memristive devices are described focusing on their mode of operation and specific electrical behaviour. Relevant metrological characteristics and a model to estimate a combined uncertainty that could be assigned to the quantum resistance values generated by these devices are also detailed. In Section 4 metrological and other applications are identified. Finally, in the concluding section the guidelines to the research work needed are identified and summarized.

2. OVERVIEW OF THE MEMQUD PROJECT

The three-year duration (2021-2024) MEMQud project is run by a consortium of 15 European participants [7]: 6 National (or Designated) Metrology Institutes and 9 among research institutes and universities with broad technical and scientific expertise that provide to the project the needed interdisciplinary skills to implement and underpin the project activities and goals.

The project activities are grouped in three work packages: 1) Memristive device fabrication and characterisation, 2) Nanoelectrical and nanodimensional characterisation of memristive devices and 3) Development of a quantum-based standard of resistance based on memristive devices.

The first group of activities is focused on manufacturing of memristive cells by the combination of depositing functional layers, structuring methods, surface treatment and engineering supported by traceable analytical and dimensional characterisation techniques.

The second workpackage investigates nanoionic processes by advancing reliable nanoelectrical and nanodimensional characterisation at near atomic scale of the physical mechanism of the memristive, including the development of a traceable quantification of chemical, structural and ionic/electronic properties of memristive devices through microscopy techniques such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Secondary Ion Mass Spectroscopy (SIMS), X-ray Spectrometry including X-ray Diffract (XRD) and Energy Dispersive X-ray Spectroscopy (EDS).

The third group of activities is focused on the metrological electrical characterisation of quantized conductance levels in memristive devices including the investigation of quantized state stability, and the influence of ambient conditions and noise analysis. Also, a statistical approach and protocols for analysing quantum conductance phenomena, modelling and experimental evaluation of uncertainty associated with quantized states, device-to-device variability and inter laboratories variability will be addressed. Finally, it will be assessed the possibility to develop and test a resistance standard demonstrator in a CMOS circuit, meeting the challenges opened by the revised SI where new experiments and devices can be explored for allowing integration of fundamental units as on-chip standard references.

3. CHARACTERISTICS AND OPERATION OF MEMRISTIVE DEVICES

The operation of memristive devices (Figure 1 and Figure 2) [5] is achieved through an electrical stimulus applied to its terminals that is responsible for the transition between a high resistive state (HRS) or OFF state and a low resistive state (LRS) or ON state. This resistive switching mechanism is related to the formation/dissolution of a conductive path (filament) bridging the two electrodes that is responsible for an increase/decrease of the device conductivity.

Among several different types memristors redox-based memory cells (ReRAMs) show particular promises. Depending on the materials, mobile ions and redox reactions one can distinguish between electrochemical metallization cells ECM (also called CBRAM or PMC); valence change memories VCM or OxRAM and thermochemical memories (TCM). In the case of ECM, the formation of the conductive filament under the action of the applied electric field corresponding to a SET process has been shown to be related to redox reactions. These reactions involve the dissolution of metal atoms from electrochemically active electrode (Ag, Cu, Ni, Fe etc.) to form metal ions that migrate in the insulating matrix (e.g., an oxide) with the capability to conduct ions. The process will continue with the nucleation (growth) at the counter electrode made by an inert material (e.g., Pt, Ir, TiN, etc.). Once the filament is completely formed, the device reaches the LRS or ON state. When the applied voltage is reversed, the reduction reactions and consequent dissolution of the conductive filament are promoted, and a RESET process occurs bringing the device to an HRS or OFF state.

In the case of VCM cells, the variation of the internal state of resistance is related to reactions and transport of oxygen-related defects such as oxygen vacancies.

A relevant characteristic of this mechanism is observed when the size of filament is reduced to the atomic scale. In this case, the conductive filament that connects the two electrodes consists in a ballistic conduction path for electrons involving discrete conductive channels [9], [10]. Each of these conductive channels contributes with a maximum amount of one fundamental quantum of conductance G_0 ($G_0^{-1} \approx 12.9$ kΩ) to the total conductance, G:

$$G = T\, n\, G_o\,, \qquad (1)$$

where T is the transmission coefficient representing the probability of electron tunnelling (with a value between 0 and 1) and n is an integer number representing the number of conductive channels. However, half-integer multiples of G_0 were also observed for certain types of memristive devices configuration.

It is possible to control the conductance states with different types of external electrical stimulation: voltage and current sweeps, pulse or constant voltage or current signals. By properly defining the external electrical stimulation signal it is possible to control the filament formation/dissolution and the related quantum conductance states activated in that process [9], [10].

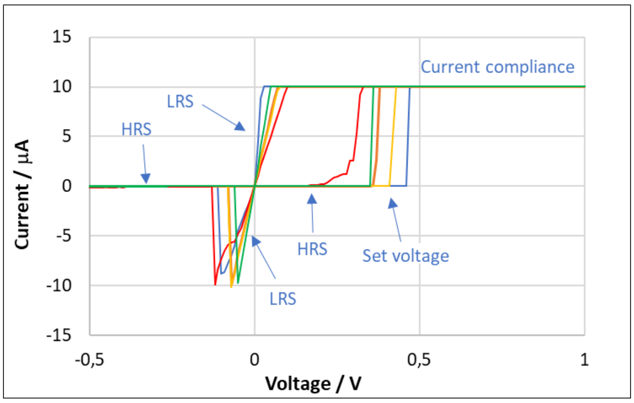

Figure 2. I-V characteristic curve of a crossbar cell based on Pt/SiO2/Cu/Pt (30 nm/30 nm/50 nm/30 nm) obtained for a sweep voltage signal and a current compliance of 10 µA. The different curves correspond to several consequent set/reset cycles. Cell fabricated and experimental data obtained in exploratory measurements done in the framework of the MEMQud project.

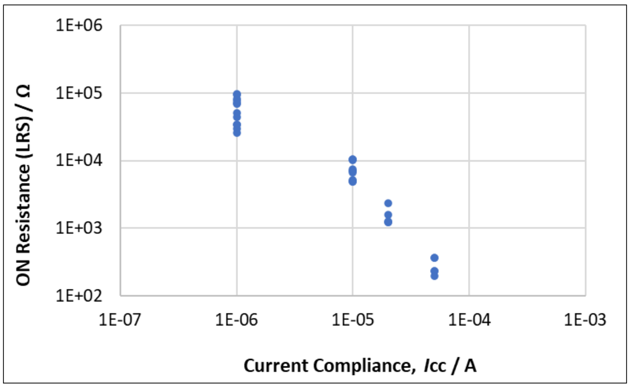

Figure 3. Value of the ON Resistance obtained as function of the current compliance (*I*cc) applied in the activation of the low resistve state (LRS) of the device. Crossbar cell fabricated and experimental data obtained in exploratory measurements done in the framework of the MEMQud project.

The current compliance value of the electrical signal applied to the device (in a triangular sweep voltage signal) to define the transition of the resistive state of the device from the HRS to the LRS will prevent the irreversible break down of the device and will determine the obtained ON resistance value corresponding to the LRS. Experimental data obtained in exploratory measurements made within the scope of this project and presented in Figure 3, for a crossbar cell of Pt/SiO_2/Cu/Pt (here the active electrode, Cu, is covered with a capping layer of Pt), show that the value of the ON resistance decreases with the value of the applied current compliance. This shows that current compliance determines the size of the conducting filament in the switching layer and the corresponding conductance (or resistance) of the device in the LRS. Current compliance adjustment will therefore be one of the external electrical signal parameters to be controlled to induce resistive states corresponding to multiples of G_0.

In this framework, the materials and thickness of the electrodes, of the active electrode capping layers (when used) as well as the switching layers play an important role in the electrochemistry of the cell and ionic transport properties and, therefore, in the functionality characteristics of these devices as, for example, the achievable resistance value and its stability in the HSR [8].

3.1. Relevant metrological characteristics

Figures of merits and recommended evaluation methods are being discussed at the scientific level in ref. [11], [12]. Already identified figures of merit in the scientific community include device reliability (memristive endurance), state retention (time that device remains in a conductive state after being programmed), switching time, energy consumption, variability and scalability to cite a few. These figures of merit could be in the future recognised as key control characteristics for industrial electrotechnical products based on, or involving, memristive devices.

From the point of view of a potential metrological application, for example as a quantum standard of resistance, retention times of the order of some seconds or minutes (conductive filaments can spontaneously dissolve over time) as has already been demonstrated are sufficient to access and transfer (e.g., by potentiometric method) the quantum resistance value. Recent exploratory measurements performed on

Pt/SiO_2/Ag/Pt based cell show stable quantum conductance states maintained with a "read voltage signal" (constant voltage signal applied to the cell terminals with a value lower than the "Set voltage" with the purpose to "read" the conductance state without disturbing the conductive filament) for tens of minutes.

More relevant and challenging is the intrinsic stochasticity process associated with the filament formation/dissolution and dynamics due to the atomic rearrangement. Another source of variability is observed as electronic noise due atomic fluctuations near the point contact. Incomplete dissolution of the filament during the RESET process with ions specimens remaining in the insulating matrix and interactions of these ions with local environment conditions (O_2, H_2O) will change the initial conditions of the ion concentration in the insulating matrix in subsequent SET processes as well as promote oxidative/corrosive process of the formed filament, respectively. The oxidative/corrosive effect is responsible for the removal of atoms and/or formation of localized corrosive elements that affect the stability of the filament [9]. After the applied electric field, these supportive or destructive forces can influence the stability/reproducibility of the conductive filament.

The combination of the sources of variability affects the repeatability and the reproducibility of these devices as can be seen in Figure 2 where we have different slopes for the *I-V* curves in the LRS and in Figure 3 with the dispersion of the values obtained for the ON resistance corresponding to each current compliance value and resulting from several activations of the device.

Besides these relevant sources of uncertainty associated to random effects, the presence of parasitic resistances [10] should also be considered in the assessment of the quantum resistance value. Figure 4 [5] schematically shows an equivalent electrical circuit for memristive cell where the quantized resistance R_c due to the filament constriction is associated to parasitic resistances. The resistance of the insulating material, R_i, associated in parallel with the R_c in series with the bulk filament resistance R_f has a value much larger than $R_c + R_f$ and corresponds to the value found for the HRS of the device. The minimization of this systematic effect is promoted by devices of the type where the difference between the resistance values of HRS and LRS are maximized. On the other hand, it is expected that usually $R_e \ll R_f \ll R_c$. In this case, the minimization of the effect of these parasitic resistances in series with R_c is favoured where their values are minimized related to R_c which means that $R_c = 1/G_0$ is a preferable quantized state to metrological applications.

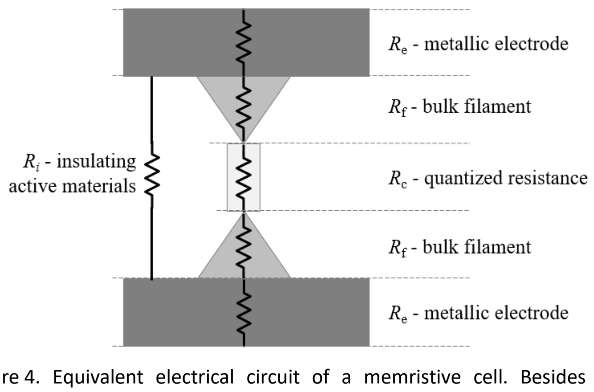

Figure 4. Equivalent electrical circuit of a memristive cell. Besides the quantized contact resistance R_c, the equivalent circuit is composed of the bulk filament resistance R_f, the resistance of the insulating active materials R_i and the resistance of the metallic electrodes R_e.

It was demonstrated [8] that HRS and LRS values and their stability depends on the materials and thickness used for the electrodes, capping layer of the active electrode and switching film. These parameters will determine the number of metal cations generated by oxidation in the active electrode, diffused in the switching film and nucleation and growth in the counter electrode in the SET process. Higher concentration of cations in the SET process allows the formation of larger conductive filaments corresponding to lower values of resistance in the LRS. Incomplete dissolution of the conductive filament in the RESET process implies the accumulation of cations in the switching layer and hence i) lower values of the resistance in the HRS and ii) lower stability of this values during cycling. As a consequence, selection criteria for materials and thickness in devices for metrological applications should target LRS with quantum resistive values equal to $1/G_0$ and with the highest possible resistance value in the HRS.

3.2. Uncertainty expression

The estimation of the overall or combined uncertainty assigned to a quantum value of conductance or resistance generated by these devices, will have to take into account all the contributions from systematic and random effects identified above in 3.1. [13] [14]. The systematic error of parasitic resistances should be quantified and corrected (the uncertainty of this correction will be accounted for as one of the uncertainty components of the combined uncertainty). The variability corresponding to the resistance value obtained at each activation of the device and associated to the stochastic behaviour of these devices could be first reduced with programming techniques to validate the desired quantum level of resistance before accessing it. Cycle-to-cycle and device-to-device variability will determine the reproducibility of the generated quantized resistance R_c through the measurement of the memrisitive cell resistance R (2) and could be estimated from the fluctuations of the mean values of R observed during a selected stable quantum state. Repeatability will be limited by the measurement noise and could be quantified by the experimental standard deviation of R of a stable quantum state. Auxiliar variables, δx, could be defined to take into account these systematic and random effects and introduced in the inverse of equation (1) to stablish a base measurement model to the measurand R:

$$R = \frac{1}{T\,n\,G_0} + \delta R_{\mathrm{p}} + \delta R_{\mathrm{re}} + \delta R_{\mathrm{rr}}\,, \tag{2}$$

where δR_{p} is the correction of the equivalent parasitic resistance associated with the quantized resistance ($1/(T\,n\,G_0)$); δR_{re} and δR_{rr} represent repeatability and reproducibility effects respectively.

A combined uncertainty of R, could be expressed by the propagation of uncertainties to equation (2), resulting in the following equation:

$$u_c^2(R) = u^2(\delta R_{\mathrm{p}}) + u^2(\delta R_{\mathrm{re}}) + u^2(\delta R_{\mathrm{rr}})\,, \tag{3}$$

where $u(x)$ is the uncertainty associated with the estimation of each one of the related random input variables, x.

4. METROLOGICAL AND OTHER APPLICATIONS

The properties of memrisitve devices as scalability, high operational speed, compatibility with CMOS technology (both in terms of materials and processes) have been exploited and demonstrated in applications as a new generation of non-volatile memories as well as in the emulation of neural and synaptic processes.

The integration of memrisitve devices in CMOS circuits also opens the possibility of obtaining a "zero chain traceability" resistance standard available *in situ* and with the possibility to be integrated in any type of electronic measurement instrumentation to support auto-adjustment and auto-calibration process. The covered metrological range of applications will depend on the uncertainty that could be attributed to the generated reference quantity of resistance generated by these devices.

Other specific relevant applications are being identified with the help of the stakeholders of this project. In sensors networks, the calibration of each sensor is usually difficult and a distributed and statistical approach is exploited, where the traceability is propagated among sensors. In this context, the traceability of each sensor can be achieved by integrating memristive devices.

The use of devices in harsh environments (ionizing environments and cosmic rays can strongly affect not only active components such as transistors but also passive components, including resistors. As an example, neutron irradiation damages the material crystallinity (embrittlement effect), thus strongly modifying its resistance. This strongly affects the functionalities of integrated circuits and sensors. The nature of the memristive devices and its application as resistance standard is promising to overcome these effects and to be stable in ionizing environments and under cosmic ray irradiation.

In certain kind of programmable gain amplifiers, its gain (or also the cut-off frequency of a filter) can be modified by changing the value of an associated resistor. The internal programmable resistance state of the memristive devices can also be exploited for programming the gain of amplifiers in analogue circuits.

5. CONCLUSIONS

The potential of the quantum conductance effect in memrisitve devices is for the first time explored to be applied in the metrology field as a quantum resistor standard. This specific application highlights the need to improve the control and domination of quantum conductance levels to obtain stable and reproducible steps (plateaux) of resistance. To achieve that, the proper operation parameters (voltage/current stimulation modes) related to the materials used (for electrodes and switching films), the effects of temperature and moisture and device engineering must have to be investigated and tested.

Improving the understanding of the relationship between this quantum phenomenon and the discrete atomic structures of the conductive filaments also need further investigation.

All these aspects will be investigated throughout the activities planned in the MEMQuD project in an integrated multidisciplinary technical and scientific approach.

ACKNOWLEDGEMENT

This work was supported by the European project MEMQuD, code 20FUN06, funded by the EMPIR programme co-financed by the Participating States and from European Union's Horizon 2020 research and innovation programme.

REFERENCES

[1] BIPM, The International System of Units (SI Brochure). Bureau International des Poids et Mesures, ISBN 978-92-822-2272-0, 2022. Online [Accessed 06 January 2023] https://www.bipm.org/en/publications/si-brochure/

[2] BIPM, Mise en pratique for the definition of the ampere and other electric units in the SI, in SI Brochure. Bureau International des Poids et Mesures, 2019, Appendix 2. Online [Accessed 06 January 2023] https://www.bipm.org/en/publications/mises-en-pratique.

[3] Leon Chua, Memristor - the missing circuit element, IEEE Transactions on circuit theory, 18.5, 1971, pp. 517-518. DOI: 10.1109/TCT.1971.1083337

[4] Dmitri B. Strukov, G. S. Snyder, D. R. Stewart, R. S. Williams, The missing memristor found, Nature 453.7191, 2008, pp. 80-83. DOI: 10.1038/nature06932

[5] Vitor Cabral, A. Cultrera, S. Chen, João Pereira, Luís Ribeiro, Isabel Godinho, Luca. Boarino, N. De Leo, Luca Callegaro, Susna Cardoso, Ilia Valov, Gianluca Milano, Memristive devices as a potential resistance standard, Proc. of the 25th IMEKO TC4 Int. Symp. on Measurement of Electrical Quantities, Brescia, Italy, 2022, pp. 13-17. DOI: 10.21014/tc4-2022.03

[6] EURAMET, European Metrology Programme for Innovation and Research. Online [Accessed 06 January 2023] https://www.euramet.org/research-innovation/research-empir/

[7] INRiM, 20FUN06 MEMQUD, Memristive devices as quantum standard for nanometrology. Online [Accessed 06 January 2023] https://memqud.inrim.it/

[8] Shaochuan Chen, Ilia Valov, Design of materials configuration for optimizing redox-based resistive switching memories, Advanced Materials 34.3, 2022. Online [Accessed 06 January 2023] DOI: 10.1002/adma.202105022

[9] G. Milano, M. Aono, L. Boarino, U. Celano, T. Hasegawa (+ 8 more authors), Quantum conductance in memristive devices: fundamentals, developments, and applications, Advanced Materials 34, 2022. DOI: 10.1002/adma.202201248

[10] G. Milano, F. Ferrarese Lupi, M. Fretto, C. Ricciardi, N. De Leo, L. Boarino, Memristive Devices for Quantum Metrology, Adv. Quantum Technol, 5, 2020. DOI: 10.1002/qute.202070051

[11] Mario Lanza, H.-S. Philip Wong, Eric Pop, Daniele Ielmini, Dimitri Strukov (+ 49 more authors), Recommended methods to study resistive switching devices, Advanced Electronic Materials, vol. 5, issue1, January 2019, 1800143. DOI: 10.1002/aelm.201800143

[12] M. Lanza, R. Waser, D. Ielmini, J. J. Yang, L. Goux (+ 31 more authors), Standards for the characterization of endurance in resistive switching devices, ACS nano, 15.11, 202, 17214-17231. Online [Accessed 06 January 2023] https://pubs.acs.org/doi/pdf/10.1021/acsnano.1c06980

[13] BIPM, JCGM 100:2008, Evaluation of measurement data - Guide to the expression of uncertainty in measurement. Bureau International des Poids et Mesures, 2028. Online [Accessed 06 January 2023] https://www.bipm.org/en/committees/jc/jcgm/publications

[14] BIPM, JCGM GUM-6:2020, Guide to the expression of uncertainty in measurement - Part 6: Developing and using measurement models. Bureau International des Poids et Mesures, 2028. Online [Accessed 06 January 2023] https://www.bipm.org/en/committees/jc/jcgm/publications