Publishable Summary for 20FUN06 MEMQuD
Memristive devices as quantum standard for nanometrology

Overview

Memristive devices are electrical resistance switches that couple ionics (i.e., dynamics of ions) with electronics. These devices offer a promising platform to observe quantum effects in air, at room temperature, and without an applied magnetic field. For this reason, they can be traced to fundamental physics constants fixed in the revised SI for the realisation of a standard of resistance. However, as an emerging technology, memristive devices lack standardisation and insights in the fundamental physics underlying their working principles, hindering their use. The overall aim of the project is to investigate and exploit quantum conductance effects in memristive devices i) for the realisation of quantum-based standards of resistance that operate reliably, in air and at room temperature with scalability down to nanometre precision and ii) for neuromorphic applications. In particular, the project will focus on the development of memristive model systems and nanometrological characterisation techniques at the nanoscale level in memristive devices, in order to better understand and control the quantised effects in memristive devices. Such an outcome will seek the possibility for the realisation of a standard of resistance implementable on-chip for self-calibrating systems with zero-chain traceability in accordance with the revised SI. In addition, a detailed knowledge and understanding of quantum conductance effects and device kinetics will boost the realisation of neuromorphic systems and new hardware platforms for computing.

Need

Over the past decade, the rapid development of information and communication technologies opened new horizons for artificial intelligence and green technologies. These developments challenge the state-of-the-art of nanoelectronics in demanding new hardware architectures to overcome von Neumann computing by implementing neuromorphic-type of data processing. Memristive devices have recently gained tremendous interest not only in the scientific community but also in the semiconductor industry as building blocks for hardware implementation of in-memory computing and artificial intelligence, due to their ability to emulate neuromorphic type of data processing combined with high scalability down to almost atomic scale, low power consumption (<pJ for operation) and high operational speed (ps).

The revision of the SI in 2019 represents an historic change of paradigm for metrology, defining all the SI units in terms of fundamental constants of nature. The development of new experiments and devices are now needed for correlating physical observables to the fixed defining constants, paving the way for the realisation of self-calibrating systems that can independently refer to the fundamental constants of nature with zero-chain traceability. In accordance with the revised SI, memristive devices exhibiting quantised conductance levels represent promising platforms for on-chip integrated and complementary metal-oxide-semiconductor (CMOS) compatible standard of resistance, which work in air and at room temperature.

While novel materials and devices for nanoelectronics indeed offer many potential benefits, they also bring challenges for testing and characterisation. As an emerging technology, memristive devices lack standardisation and insights in the fundamental physics underpinning their technology, hindering their further development. Understanding and controlling resistive switching behaviour at the nanoscale is therefore highly challenging and high throughput metrology is urgently required. The development of new technologies for nanoelectronics, including quantum technologies, neuromorphic computing and related metrology, is in line with the European R&D programmes “Quantum Technologies Flagship” and the “Human Brain Flagship”. For this purpose, memristive model systems need to be developed, to establish a relationship in between material properties and device functionalities. The understanding of nanoionic processes involved in memristive devices requires i) advancements in nanoelectrical characterisation techniques, ii) the development of a traceable quantification of chemical, structural and ionic/electronic properties of memristive devices and iii) the development of metrological cross-platforms measurement techniques. These are the key requirements for understanding and controlling quantised conductance effects in such devices for the realisation of the standard of resistance.

Objectives

The overall objective and technological target of this project is to provide, in a metrological framework, technical capability and scientific knowledge for the *mise en pratique* of a resistance standard based on memristive devices characterised by high scalability down to the nanometre scale, CMOS compatibility and working in air at room temperature.

The specific objectives of the project are:

1. To **develop well-controlled memristive model systems** for establishing a relationship between the revealed material properties and actual device functionalities. This should include the 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.
2. To **investigate nanoionic processes by advancing reliable nanoelectrical characterisation of memristive devices** by using metrological scanning probe microscopies (SPMs) for probing its local electrical properties by means of traceable conductive AFM (C-AFM), scalpel C-AFM for 3D reconstruction of the memristive cells and Scanning Tunnelling Microscopy (STM).
3. To **develop a traceable quantification of chemical, structural and ionic/electronic properties of memristive devices** through scanning microscopy (AFM, SEM), Secondary Ion Mass Spectroscopy (SIMS), X-ray Spectrometry including X-ray Diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDS) in order to achieve nanodimensional characterisation at near atomic scale of the physical mechanism of the memristive cell.
4. To **develop metrological cross-platforms measurement techniques** with high resolution in space (< 10 nm) and time (< ms) for investigating device dynamics by correlating the variation of chemical/structural properties to the electrical response of memristive devices *in operando*. To also develop a quantum-based standard of resistance for nano applications including CMOS compatible and on-chip implementable resistance standards.
5. To **facilitate the take up of the technology and measurement infrastructure developed in the project** by the measurement supply chain (nanometrology), standards developing organisations (IEC TC 113, Versailles Project on Advanced Materials and Standards (VAMAS) TWA 2) and end users (nanoelectronics).

Progress beyond the state of the art

A set of memristive devices exhibiting quantum conductance phenomena has been developed and characterised through the combination of deposition of functional layers, structuring methods, and surface treatment and engineering. Memristive model systems exhibiting quantised conductance phenomena has been developed through surface/interface modifications and device structuring, providing suitable platforms for the investigation of ionic processes underlying resistive switching effects and Quantum Point Contact (QPC) phenomena.

The project will go beyond the state of art by advancing the metrological electrical characterisation of quantised conductance phenomena in memristive cells by analysing time stability, device-to-device variability, dependence on temperature and environment and noise of quantised states. A statistical approach to analyse experimental data has been developed, while the uncertainties associated with quantum conductance levels in memristive devices will be analysed. Proper guidelines for the fabrication of memristive cells with quantised conductance phenomena are under establishment.

Improvement of dimensional traceability of operando SPM techniques including C-AFM, scalpel AFM and STM will allow the investigation of local electrical properties of memristive cells and QPC constructions while a new high throughput and reference-free XRF technique will be used for unveiling the influence of doping and impurities on memristive and quantised conductance phenomena. As a result, the development and the complementarity of the operando and cross-platforms measurement techniques will provide a detailed understanding of the resistive switching mechanism of memristive cells working in quantised conductance regime as well as make significant advances in the development of metrology at nanoscale.

New theoretical and compact models including variability and fluctuations effects in memristive devices in the QPC regime are under development and their consistency will be validated on experimental data from the project.

As a result of this project, the project will investigate the possibility of realising a resistance standard demonstrator based on memristive devices working at room temperature, in air and without an applied magnetic field. Its performance will be evaluated in terms of accuracy, time stability and reproducibility.

Results

Development of well-controlled memristive model systems

Vertically stacked and lateral memristive devices by combination of functional layers and structuring methods have been fabricated and electrically characterised. This includes the fabrication of memristive cells with different functional layer oxides including SiO_2 (with different impurities and doping levels), TaO_x, HfO_2 and NbO_x with different thicknesses (in the range 10 - 90 nm), different combination of metal electrodes including Ag, Cu, Ag:Cu alloys, Nb, Au, Ag, Pt, TiN, Ir, Ni and Fe, and different capping layers including TiN and Pt. Also, memristive cells based on low dimensional systems have been realised, including memristive cells based on single nanowires, single nanowire junctions and nanowire networks. Also, memristive cells based on single layer MoS_2 2D materials have been fabricated. Device interface engineering included the fabrication of memristive cells with the insertion of a graphene layer in between the functional layer and the electrodes.

Fabricated memristive cells have been electrically characterised to evaluate their resistive switching performances and their capabilities for showing quantum conductance levels. Device performances including endurance, retention, operating voltages (i.e. electroforming voltage, SET and RESET voltages) and neuromorphic functionalities have been evaluated. Results on the effects of a combination of factors such as electrodes, electrolytes, capping layer materials and their thicknesses on the electrical response of devices have been achieved. Different measurement strategies including voltage sweeps and current sweeps for observing quantum conductance levels in fabricated devices have been explored. Further materials and interfaces will be investigated for further improving switching properties and quantum conductance effects.

Investigation of nanoionic processes by advancing reliable nanoelectrical characterisation

The process for spatial calibration of Scanning Probe Microscopy (SPM) tools has been performed through length standards at the nanoscale based on self-assembled nanostructures based on deblock copolymers that allows nanopatterning of a substrate over large scale, where the period (in the range between 20 and 50 nm) of the nanostructures represents the measurand (note that in this range no commercial transfer standards are available). For increasing the stability of the measurand, nanostructures have been transferred to a SiO_2 substrate by reactive ion etching. After GISAXS analysis that provided traceable measurements of the periods, these calibration samples have been disseminated among partners for calibration of their AFM setups. Memristive devices have been investigated by direct probe switching using conductive atomic force microscopy. First, the technique has been optimised to induce forming, set and rest inside the AFM tool. Later, a Diamond probe has been used to remove the top electrode in the active devices and investigate the type of filament induced under the Au electrode. Multiple devices are inspected, and an average equivalent disc radius of 55 nm is found for NbOX-based cells. Selected memristive devices have been investigated with Scalpel SPM. First, the technique has been optimised to work with the devices from the project, here a specific type of diamond probe was selected and worked in an air environment by means of a DT-NDT AFM system. More specifically, devices with different top-electrode sizes, namely 500 and 1000 nm have been studied for each sample. Segmentation, analysis and 3D interpolation of the scalpel SPM data have been performed. Thus, generating tomographic observation of the filaments responsible for the switching of NbOx-devices. High-resolution scalpel SPM has been obtained with a combination of multi-probe and adaptive scanning conditions. This is providing an improved resolution in the filament reconstruction improving the signal to noise ratio of scalpel SPM data set of a factor 2.

Development of a traceable quantification of chemical, structural and ionic/electronic properties of memristive devices

The development and refinement of advanced traceable quantification strategies for nano- and micro- beam based XRF analysis using suitable benchmark systems has been performed. An initial set of experiments with respect to fundamental parameters and mass attenuation coefficients on selected materials involved for the fabrication of memristive devices have been performed. Traceable XRF measurements on oxide switching layers to evaluate doping levels and impurities in oxide layers employed for the realisation of memristive devices are a prerequisite for investigating switching mechanism in memristive cells, have been performed on selected materials. Additional experiments and analyses on other materials have been planned. In operando TEM analyses have been performed to correlate the electrical response of the device with morphological changes. These preliminary experiments have been performed on nanowire-based device and additional measurements are planned in other devices. The refinement of traceable quantification strategies will enable traceable quantification of chemical, structural and ionic/electronic properties of fabricated memristive devices.

Development of cross-platforms measurement techniques and a quantum-based standard of resistance

Possible applications of memristive-based resistance standards have been discussed among partners, identifying key performance characteristics, such as stability of the quantum point contact, device endurance and operational conditions in terms of applied voltage/current to evaluate in memristive devices working in the quantum conductance regime. The draft of a guide on metrological electrical characterisation of memristive cells have been further developed and shared among partners, including a draft of main aspects of a protocol for the characterisation of memristive cells, for data processing and result reporting. Based on the developed measurement protocol, an interlaboratory comparison on memristive behavior of memristive cells working in the quantum conductance regime has been conducted and aggregated data analysis have been performed. Concerning modeling activities, the model for resistive switching devices working in the quantum regime able to reproduce multiple quantum steps and memory effects has been further developed. Modelling activities will support the evaluation of uncertainty on quantum levels in memristive devices and, at the same time, will provide a tool for simulating the implementation of computing paradigms in memristive-based architectures. The discussion on key performance characteristics required will guide further development of memristive cells working in the quantum regime.

Impact

The project partners have been engaging in a significant number of dissemination and communication activities aimed at scientific, metrological and industrial end-user communities. The impact on the scientific community is testified by a total of 23 open access peer-reviewed publication in high impact scientific journals, including Nature Materials, Advanced Materials, ACS Applied Materials and Interfaces, Neural Networks and others. The target audience of these works ranges the physical, electrochemical, chemical, electronic engineering and neuromorphic computing engineering communities. Project-related works have been presented in a total of 40 conferences including MEMRISYS 2021, MEMRISYS 2022 Nanoinnovation, and the Spring and Fall 2021 meetings of the European Materials Research Society (additional conference presentations are planned in late 2023 and in 2024), with several invited talks to well-established conferences in the field of memristive devices. In addition, project partners have organised the EMRS ALTECH symposium together with PTB, CEA and NPL in June 2021, on the Analytical techniques for precise characterisation of nanomaterials. This symposium was the 3rd most attended symposium from EMRS Spring Meeting 2021 (from a total of 19 symposia). During 4 days of conference, 150 papers were presented (6 invited, 70 oral, 74 posters), with contributions from 21 different countries. Also, a project partner was involved in the International Steering Committee of MEMRISYS 2022, a worldwide recognised conference in the field of memristive devices, with participation in the organisation of a session focused on quantum effects in memristors. Project partners are also involved in the organisation of the upcoming MEMRISYS 2023. Two invited lectures have been given to the Photonics for Security, Reliability and Safety, Erasmus Mundus Joint Master’s Degree students on neuromorphic computing with memristive devices and memristive devices for quantum metrology. To promote the exchange of skills between project partners and to complement project activities, two Research Mobility Grants (RMGs) have been funded in the project framework and a visiting period for a PhD student at a partner premises has been organised. In addition, training courses for consortium and for audience have been organised. Project outputs and related events are promoted on the project website and posts regularly on social media through Facebook, Instagram and LinkedIn. The first stakeholder meeting was held in September 2021 with 33 attendees representing academia, metrological organisations, and industrial end-users.

Impact on industrial and other user communities

The development of metrological nanoelectrical and nanodimensional characterisation tools and techniques represents a breakthrough in the detailed understanding of the physical mechanism underlying memristive phenomena, paving the way for the realisation of design rules and roadmaps for rational design and ultimate scaling of memristive devices not only for metrological applications but also for next-generation devices and hardware architectures for neuromorphic computing and AI applications. The development of methods and best-practices to extract meaningful and quantitative information of electrical and chemical properties at the nanoscale can impact the entire sector of nanoelectronics and nanotechnology.

The developed spatial calibration standards in the range 20-50 nm will enable calibration of nanodimensional characterisation tools. Also, the ongoing development of multiprobe and scalpel SPM will lead to an increase in the resolution of commercially available nanoelectrical and nanodimensional characterisation tools.

Impact on the metrology and scientific communities

The scientific community will benefit from this project through the advancement in understanding of fundamental physical and nanoscale electrochemical processes to regulate resistive switching and quantised conductance phenomena in memristive devices. Due to the multidisciplinary interest in memristive devices, the project will have an impact not only on the metrology and physics community but also on the chemistry, electronic engineering, computer science and biology communities, facilitating the further development of quantum technologies and artificial intelligence in diverse directions. To maximise the uptake of the project outputs, the project plan includes convening special sessions at international conferences and specific training courses.

Impact on relevant standards

As part of the impact in the metrological community, project partners presented project activities and results to 13 international and national standardisation technical committees. Among them project partners provided input to four subcommittees of ISO TC 201 (Surface chemical analysis), including subcommittees SC6 (SIMS), SC7 (XPS), SC9 (SPM) and SC10 (XRR and XRF) with respect to improved traceability and uncertainties by means of the qualification of appropriate nanoscale calibration samples as well as mutual validation procedures. Moreover, outputs have been presented at the steering committee Versailles Project on Advanced Materials and Standards (VAMAS) on the closer Technical Working Areas (TWA) including the "Surface and Chemical Analysis (TWA 2)". In this framework, the possibility of developing of inter-laboratory studies for reproducibility and to assess new protocols for incrementing measure expertise have been discussed. Also, the project has engaged with technical committees and metrology organisations such as the EURAMET TC-EM and its subcommittee for Electricity and Magnetism, the COOMET TC 1.3 Electricity Magnetism, IEC TC 113: Nanotechnology standardisation for electrical and electronic products and systems. At the national level, results have been disseminated through standardisation technical committee such as the CT 194 - Nanotechnologies and DIN NA 062-08-17 and at the Technical Committee for nanotechnologies of the Portuguese standardisation body. Also, the project will seek the opportunity to present project outputs at the GULFMET TC-EMFT.

Longer-term economic, social and environmental impacts

The outcomes of this project will contribute to the development of new technologies and advancement of nanoelectronics and nanotechnology, including new hardware for brain-inspired neuromorphic computing and quantum technologies for development of artificial intelligence, autonomous systems and Internet of Things (IoT).

The metrology developed within the framework of this project will contribute to the development of nanoelectronics devices for the realisation of new hardware architectures, capable of tackling societal challenges such as the development of artificial intelligence. The development of new computing paradigms could reduce power consumption by orders of magnitude compared to conventional computing technologies, helping Europe to reduce the impact of information technology on carbon emission and to reach net-zero energy targets to combat climate change.

List of publications

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This list is also available here*:* https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	01 June 2021, 36 Months	
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Internal Funded Partners: 1. INRiM, Italy 2. CEA, France 3. IPQ, Portugal 4. PTB, Germany 5. TUBITAK, Türkiye 6. VTT, Finland	External Funded Partners: 7. CPI, United Kingdom 8. FZ-Juelich, Germany 9. IMDEA, Spain 10. IMEC, Belgium 11. POLITO, Italy 12. TOBB, Türkiye 13. UAB, Spain	Unfunded Partners: 14. INESC MN, Portugal 15. TUDO, Germany
RMG1: TUBITAK, Türkiye (Employing organisation); INRIM, Italy (Guestworking organisation) RMG2: INRIM, Italy (Employing organisation); PTB, Germany (Guestworking organisation)		