EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

Investigation of Metal Ions Drift in Memristive Devices using Perturbed Angular Correlation (PAC) method

[11th of January 2023]

A. Mokhles Gerami[1,2], P. Schaaf[3], J. H.-Schell[2,4], M. Blum[3], B. Mohammadi[1], T. T. Dang[4], I. C. J. Yap[4], K. Johnston[2], A. W. Carbonari[5], B. S. Correa[5], N. P. Lima[5], A. P. dos S. Souza[5], A. A. M. Filho[5], L. S. Maciel[5]

1 School of Particles and Accelerators, Institute for Research in Fundamental Sciences (IPM), Tehran P.O. Box 19395-5531, Iran
2 European Organization for Nuclear Research (CERN), CH-1211 Geneva, Switzerland
3 Chair Materials for Electrical Engineering and Electronics, Institute of Materials Science and Engineering, Institute of Micro and Nanotechnologies MacroNano, TU Ilmenau, Gustav-Kirchhoff-Strasse 5, 98693 Ilmenau, Germany
4 Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45141 Essen, Germany
5 Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP, São Paulo 05508-000, Brazil

Spokesperson(s): [Peter Schaaf] [peter.schaaf@tu-ilmenau.de], [Adeleh Mokhles Gerami] [adeleh.mokhles.gerami@cern.ch]
Technical coordinator: [Juliana H-Schell] [juliana.schell@cern.ch]

CERN-INTC-2023-013 / INTC-I-250
11/01/2023

Abstract

Although memristive devices, thanks to their unique current-voltage properties, can be a very efficient choice in the development of high speed and low-cost computing hardware, such devices are not commercialized mainly due to the construction issues. Among these technical issues, the lack of a reliable model to explain the physics of switching mechanism is the main problem, since the resistance switching mechanism is based on the drift of metal ion atoms into the active insulator layer as a function of the applied voltage. In this research work, we focus on the study of the local configurations of the metal ion atoms and the nature of the defects around the ions in different type of active insulator layer in memristive devices. This purpose are driven with special techniques based on the comparison of PAC spectroscopy results with DFT calculations. The results of this research are useful for understanding the operation mechanism of memristive devices and pave the way for their use in a wide range of applications.

Requested protons: 8 shifts protons on target, (split into 3 runs over one years)
Experimental Area: [GLM, ISOLDE hall or offline laboratories at 508 building]

Introduction:

Nowadays, nanoscale resistive switching devices are increasingly used in semiconductor industry, so that artificial intelligence (AI) is becoming part of quotidian life. AI has a wide range of applications such as autonomous vehicles, robotics, medicine, image recognition for security, marketing, business risk analysis, machine learning, and many other applications [1]. Therefore, any technological advancement related to the production of faster computing resources affects these AI-based technologies and applications. Until now, the most cases of devices are built based on complementary metal–oxide–semiconductor (CMOS) [2]. Although in the CMOS technology, computing performance has increased drastically based on Moore's law [3] and Dennard's law [4] but there are still some challenging mainly due to leakage current, power consumption, switching speed, and complicated geometry as it is presented in Fig.1 Left. Another reason is originated from the architecture of existing hardware for computational resources, which is based on von-Neumann architecture [5]. The memory and processing unit are physically separated in von-Neumann architecture, as is shown in Fig. 1 Right. A drawback with this architecture is that the interaction of different units reduces the speed of calculations, consumes more electrical power. In order to solve these problems, the current technology needs to be replaced with suitable and novel technology. Memristor technology, because of its simple structure, is a potentially powerful candidate to overcome the current limitations of CMOS devices.

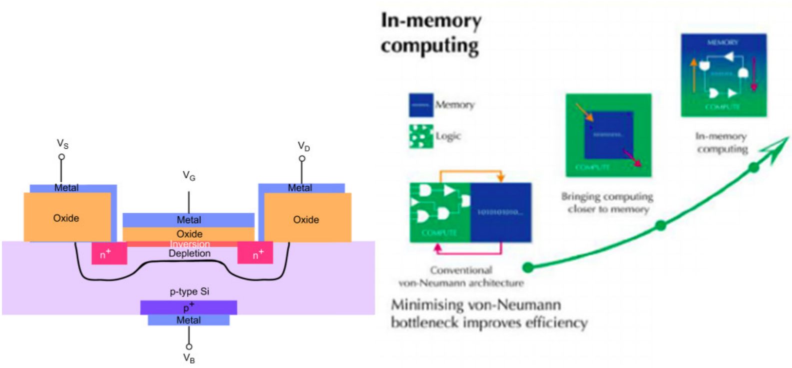

Fig. 1: Left): A schematic of the complementary metal-oxide-semiconductor (CMOS) devices [2]. Right): The predicted evolution of computing processing units by memristive device technology [5].

Literatures review and state-of-arts:

The memristive devices are fabricated by growing a semiconductor layer, called an active insulator layer, between two different metal electrodes such as silver (Ag) and platinum (Pt) [6]. In 1971, this new generation of electrical elements was conceptually introduced by Chua [7] as the fourth fundamental electrical circuit element based on symmetry arguments. Chau proved theoretically that memristive devices do not behave like conventional resistors and their voltage-current relationship depends on the history of the applied current or voltage. Memristive devices are classified according to the switching trajectory of their current-voltage (I(t)-V(t)). Generally, there are two types of resistive switching: volatile and non-volatile switching states [8]. The resistive switching phenomenon refers to the abrupt change in the resistance of devices due to the application of an alternating current pulse. In the volatile switching mechanism, the resistance of the material changes when a high enough voltage is applied, but the resistance returns to its initial value when the voltage source has been switched off. In contrast, the resistance in devices with non-volatile resistive switching mechanisms remains unchanged even after eliminating the external voltage source [9]. Recently, it is observed that the resistance switching mechanism of non-volatile memristive devices depends on the type of material used as an active insulator layer. For example, memristive devices made by binary transition metal oxide semiconductors [8, 10] are exhibited unipolar I-V characteristics (Fig. 2 Left). In another research, it is shown that the bipolar I-V characteristic (Fig. 2 Right) can be achieved by using complex oxides compounds [8, 11] such as $YBa_2Cu_3O_{7-x}$ (YBCO), $SrTiO_3$ (STO), Zn-doped amorphous SiO_x (SZO), and also off-stoichiometry binary oxide.

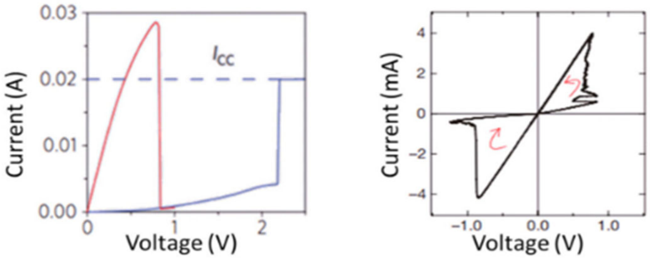

Fig. 2: the current vs voltage characteristics of resistive switching in the type of left) unipolar [10] , right) bipolar [11].

Selection of the active insulator layer and optimization of the device design are critical to improve switching performance and reduce the parameter variability to a level sufficient for large-scale commercialization. This requires a detailed understanding of ion channel migration and its coupling with electron transport - the dominant dynamics in the memristive mechanism - during the switching process. In 2008, Yang and co-workers [12] succeeded in presenting a premier model for switching behaviour in $Ag/TiO_2/Pt$ devices. According to this model, applying a positive voltage to the metal electrodes (Ag) leads to the formation of an ion channel (conductance filament) by drifting the positively charged Ag through the electric field within the active insulator layer, that is corresponding to the low resistance (ON) state. When the Ag+ ions reach the opposite electrode, a sudden drop in resistance will take place. In contrast, if a reverse voltage is applied, Ag will be oxidized at the inert electrode interface and move it back in the active insulator layer, which is corresponding to the high resistance (OFF) state as shown in Fig. 3. The results shows that the ON/OFF conductance ratio is 1000 for a 50 nm TiO_2 layer. In this research [12], the authors concluded that the location, concentration, and distribution of the forming oxygen vacancies around Ag^+ in the TiO_2 layer control the conductance, rectification, and polarity switching in the memristive device.

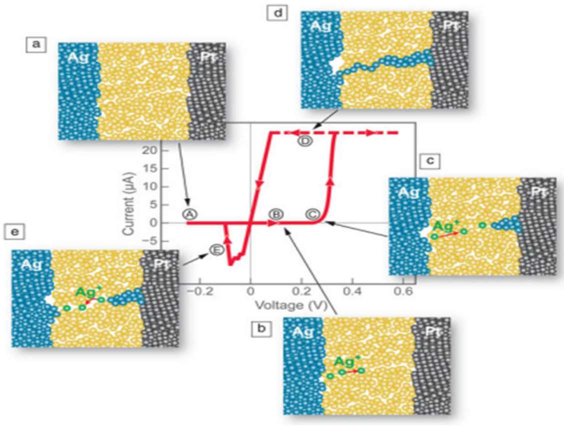

Fig. 3: Schematic representation of ion channel formation and bipolar resistive switching in $Ag/TiO_2/Pt$ memristive devices, the image was adapted from reference [8].

For a detailed study of the migration of ion channels into the active insulator layer, several researchers have presented different theoretical models, including Molecular Dynamics

(MD) [13] and Kinetic Monte Carlo (KMD) [14]. The research group of Sun et al. [15] can simulate the electrical switching behavior based on electron transport modeling using MD and KMD methods. Also N. Ghenzi present a model based on density functional theory (DFT) to calculate the relative probability of a conductive filament on the Au/TiO_2/Cu memristor. They explained that the ion channel is originated by the drift of interstitial Cu^+ ions with oxygen vacancies [16] because, when the Cu atom is in the interstitial position, they obtained the lowest energy which is corresponded to the stable point. However, this result has not been verified experimentally.

Research Objective:

Up to now, the physical mechanism of memristor-based devices such as controlling ion channels with the drifting of metal ions is not fully known and yet, there are some fundamental questions about the physical mechanism of ion channel formation that need to be answered. The questions like what are the mobile species within the active insulator layer and where are they located and how do they move under electrical excitations? Which defects arise around metallic ions at different applied voltages? How does the device transit from the high resistance state (HRS) to the low resistance state (LRS)? As a consequence of this research, a comprehensive study will be used to address these fundamental questions using several conventional characterization techniques including the current-voltage measurement technique (I-V curves), and the transmission electron microscope (TEM). However, these techniques cannot directly probe the local position of the metal ions in the active insulator lattice and the nature of the defects that form after the metal ions drift. To extract this information and also to determine the possibilities of a phase transition during the temperature change in different types of memristive devices, we propose a novel experimental technique using implanted radioactive ions and measurement with perturbed angular correlation (PAC) spectroscopy [17, 18]. Experimentally, it was found that the implanted ions can affect the processing of the switching mechanism and improve the stability of memristive devices operation [19, 20]. For example, the research group of Mikhaylov [19] has shown that the irradiation of the oxide surface of the Au/SiO_2/TiN memristive device with Xe^+ ions (at an energy of 5 keV) reduces the fluctuations of the electroforming voltage and increases the current ratio in the high/low resistance states. Although several experimental PAC measurements have so far been dedicated to the study of the physical properties of bulk semiconductors and metal materials [21, 22, 23, 24, 25, 26], which are briefly presented in the next section, but there are no reports on the PAC measurement for the characterization of ion channel in memristive devices. Therefore, we aim to investigate the effects of the implanted isotope on the switching mechanism by measuring the current-voltage curve. Also, we use PAC spectroscopy to study the local symmetry configuration of the implanted ions in the active insulator lattice with and without applying the voltage. For doing this research, we have selected the $^{111}In/^{111}Cd$ and $^{111m}Cd/^{111}Cd$ isotopes to implant them into memristive devices because they have sufficiently long half-life times of 2.8 days and 48.5 minutes, respectively. Since the metal ions in the ion channel are Ag^+ at the memristive device types of Ag/active insulator layer/Pt, we are also interested in using the $^{111}Ag/^{111}Cd$ probe for discovering the position of the Ag^+ ions in the active insulator layer. Considering this important point that there are challenges in understanding of the PAC experimental results, using a numerical model based on DFT calculation will help us to interpret the data.

Research Methodology:

Memristive Device Construction:

Precise fabrication of memristive chips is particularly important to achieve the research goal. However, the choice of a suitable fabrication technique as well as the production of the devices requires access to well-equipped and advanced laboratories in the fields of solid-state physics and nanoscience as well as having expertise in lithographic techniques. Technische Universität Ilmenau (TUIL) [27], as one of the leading academic centers, is well equipped in these areas and the research teams have constructed several memristive devices [28, 29] to be studied in the current research. The devices fabricated consist of 12 chips. Each chip itself consists of a 2×2 grid of memristive devices which are made of TiO_2 semiconductors between the active electrode (Ag) and the inert electrode (Pt) on insulator substrate, as shown in Fig. 4a and 4b. The topology of the electrodes is different for each chip, although the height of the semiconductor channels between electrodes is the same and is about 800 nm. In this study, three different electrode configurations of 1μm×10μm, 1μm×1μm, and 10μm×10μm are investigated to gain a better understanding about the effects of the electrode shape on the formation of the ion channel and to optimize the performance of the device. In addition, the influence the crystalline phase of active insulator material on ion channel formation will be studied. In this research, the semiconductors layers of TiO_2, VO_2 have been used in the memristive devices construction.

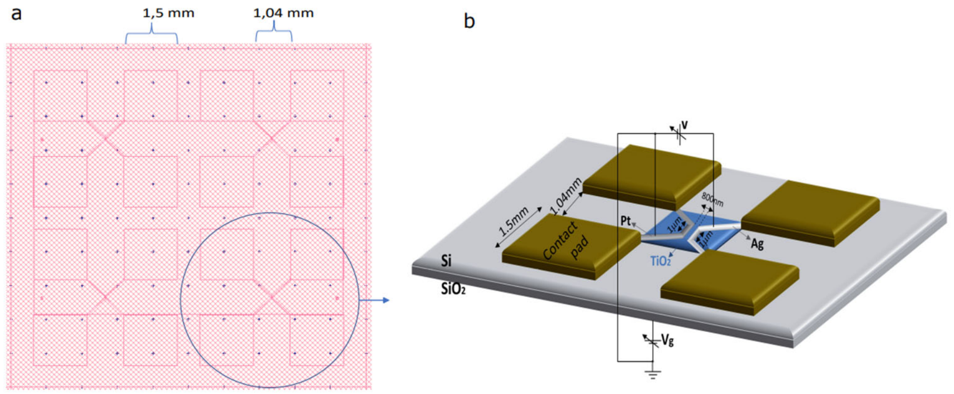

Fig. 4: a) top view of 2×2 grid of memristive devices in one chip, b) image of $Ag/TiO_2/Pt$.

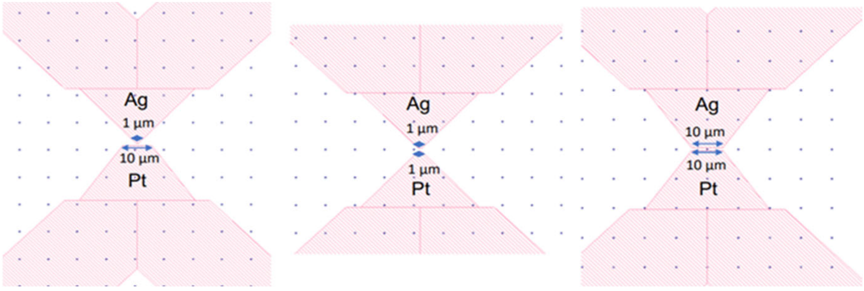

Fig. 5: Three different electrode configurations of 1μm×10μm, 1μm×1μm, and 10μm×10μm in each memristive device chips.

Measurement Technique and Simulation:

So far, the effects of implanted radioactive isotopes such as $^{111}In/^{111}Cd$, $^{111m}Cd/^{111}Cd$ and their interaction with point defects in semiconductor oxide lattices (TiO_2 [22, 23, 24], VO_2 [21]) and bulk metal materials (Pt, Ag) [25, 26] were studied by PAC measurements. For instance, the PAC experimental results of $^{111}In/^{111}Cd$ and $^{111m}Cd/^{111}Cd$ probes on TiO_2 [22] show the presence of the main clear electric quadrupole interaction that is due to the Cd atoms located on Ti sites in the rutile phase. However, it is reported that the PAC spectra of implanted In and Cd behave differently with the same implantation and annealing, this characteristic is interpreted to mean that the lattice of TiO_2 is mostly free of point defects after annealing for ^{111}In/^{111}Cd probes, and the implanted ^{111m}Cd/^{111}Cd probes acts as highly stable "trap" for defects. On the other hand, for metal materials of silver and platinum, the internal oxidation of ^{111}In and ^{111m}Cd have been recorded by PAC spectroscopy [25, 26]. It was reported [26] that the internal oxidation of very dilute cadmium and indium in silver single crystals below 700 K leads to the formation of cadmium-oxygen and indium-oxygen complexes, respectively. The use of these materials in the construction of memristive devices with implanted radioactive isotopes generate new properties in the structure of materials, which can lead to a change in the switching mechanism. Therefore, the structural characterization of the semiconductors as an active insulator layer between two electrodes is important to understand the physics of resistive switching behaviour at different temperatures and voltages. In this work, the effect of implanted ions on memristive devices in the pristine state (without applying a voltage) and in the switched state (with applying positive and negative voltage) is investigated using current-voltage (I-V) measurement. Since the origin types of non-volatile resistive switching systems (unipolar and bipolar) arise from different types of microscopic structural changes [8], the phenomena related to the position of metal ions and their surrounding defects in the ion channel must be determined as a function of parameters such as temperature and voltages, in order to improve the device operation. This information can be obtained using a local and precise experimental technique of PAC spectroscopy. Furthermore, the effect of oxidation of Ag on the formation of ion channel will be studied using the ^{111}Ag/^{111}Cd probe.

For further interpretation of the experimental results, we will use the DFT simulation that are in the framework of the WIEN2k [30] and VASP [31] codes. This can be achieved by comparing the calculation results of the electric field gradient (EFG) [32] with the experimental results from PAC. Therefore, special attention is made to the estimation of the EFG tensor, which can provide information about the ion channels that formed in the active insulator layer.

In summary, the main goals of this project are: I) Investigations the local lattice environment of metal ions and existing defects around metal ions which are formed in ion channel at memristive devices. II) Investigation the effect of implanted isotopes on switching mechanism using current-voltage measurement by applying the positive and negative voltages on metal electrodes.

Summary of requested protons:

Beam	Min. intensity	Target material	Ion source	Shifts	System
^{111}In	>1.10^{7}	UC_x	Surface or RILIS	2	Ag/TiO_2/Pt, Ag/VO_2/Pt
^{111}Ag	1.10^{8}	UC_x	RILIS	2	Ag/TiO_2/Pt, Ag/VO_2/Pt
^{111m}Cd	1.10^{8}	Molten Sn	VD7	4	Ag/TiO_2/Pt, Ag/VO_2/Pt

In the future, it is planned to build memristive devices with other semiconductor layers such as WO_3, HfO_2, V_2O_3 after the testing phase of this proposal is completed and compare the results with the results of this proposal. It is also planned to change the material of the conducting electrodes to find optimized memristive devices.

References:

[1] S. Nabwire, et al., “Application of artificial intelligence in phenomics,” Sensors , vol. 21, no. 13, p. 4363, 2021. https://doi.org/10.3390/s21134363.

[2] O. Kononchuk, B.-Y. Nguyen., Silicon-on-insulator (SOI) technology: Manufacture and applications, Elsevier, 2014.

[3] J.R. Powell, “The quantum limit to Moore's law,” Proceedings of the IEEE, vol. 96, no. 8, pp. 1247-1248, 2008. DOI: 10.1109/JPROC.2008.925411.

[4] R. H. Dennard, et al., “Design of ion-implanted MOSFET's with very small physical dimensions,” IEEE Journal of solid-state circuits, vol. 9, no. 5, pp. 256-268, 1974. DOI: 10.1109/JSSC.1974.1050511.

[5] D. Ivanov, et al., “Neuromorphic artificial intelligence systems,” arXiv preprint arXiv:2205, p. 13037, 2022. https://doi.org/10.48550/arXiv.2205.13037.

[6] B. Mohammad, et al., “State of the art of metal oxide memristor devices,” Nanotechnology Reviews, vol. 5, no. 3, pp. 311-329, 2016. https://doi.org/10.1515/ntrev-2015-0029.

[7] L. Chua., “Memristor-the missing circuit element,” IEEE Transactions on circuit theory, vol. 18, no. 5, pp. 507-519, 1971. DOI: 10.1109/TCT.1971.1083337.

[8] J. Del Valle, et al., “Challenges in materials and devices for resistive-switching-based neuromorphic computing.,” Journal of Applied Physics, vol. 124, no. 21, p. 211101, 2018. https://doi.org/10.1063/1.5047800.

[9] E. Janod, et al., “Resistive switching in Mott insulators and correlated systems,” Advanced Functional Materials, vol. 25, no. 40, pp. 6287-6305, 2015. https://doi.org/10.1002/adfm.201500823.

[10] D.-H. Kwon, et al., “Atomic structure of conducting nanofilaments in TiO2 resistive switching memory,” Nature nanotechnology, vol. 5, no. 2, pp. 148-153, 2010. https://doi.org/10.1038/nnano.2009.456.

[11] D. B. Strukov, et al., “The missing memristor found,” nature, vol. 453, no. 7191, pp. 80-83, 2008. https://doi.org/10.1038/nature06932.

[12] J. J. Yang, et al., “Memristive switching mechanism for metal/oxide/metal nanodevices,” Nature nanotechnology, vol. 3, no. 7, pp. 429-433, 2008. https://doi.org/10.1038/nnano.2008.160.

[13] S. E. Savel’ev, et al., “Molecular dynamics simulations of oxide memristors: thermal effects,” Applied Physics A, vol. 102, no. 4, pp. 891-895, 2011. https://doi.org/10.1063/1.3622665.

[14] T. Sadi, et al., "Investigation of resistance switching in SiOx RRAM cells using a 3D multi-scale kinetic Monte Carlo simulator," Journal of Physics: Condensed Matter, vol. 30, no. 8, p. 084005, 2018. DOI 10.1088/1361-648X/aaa7c1.

[15] W. Sun, et al., "Understanding memristive switching via in situ characterization and device modeling," Nature communications, vol. 10, no. 1, pp. 1-13, 2019. https://doi.org/10.1038/s41467-019-11411-6.

[16] N. Ghenzi, et al., "Tailoring conductive filaments by electroforming polarity in memristive based TiO2 junctions," Applied Physics Letters, vol. 104, no. 18, p. 183505, 2014. https://doi.org/10.1063/1.4875559.

[17] J. Schell, P. Schaaf, and D. C. Lupascu., "Perturbed angular correlations at ISOLDE: A 40 years young technique," AIP Advances, vol. 7, no. 10, p. 105017, 2017. https://doi.org/10.1063/1.4994249.

[18] H. Frauenfelder and R.M. Steffen, "Alpha-, Beta- and Gamma-Ray Spectroscopy," Angular Correlation, p. 997, 1965.

[19] A. N.Mikhaylov, et al., "Effect of ion irradiation on resistive switching in metal-oxide memristive nanostructures," Journal of Physics: Conference Series, vol. 1410, no. 1, p. IOP Publishing, 2019. DOI 10.1088/1742-6596/1410/1/012245.

[20] D. Hasina, et al., "Ion Beam-Mediated Defect Engineering in TiOx Thin Films for Controlled Resistive Switching Property and Application," ACS Applied Electronic Materials, vol. 3, no. 9, pp. 3804-3814, 2021. https://doi.org/10.1021/acsaelm.1c00417.

[21] A. Carbonari, et al., "Influence of valence of doping element on local electronic and crystal structure in vanadium oxides: Time-Differential Perturbed Angular Correlations spectroscopy at ISOLDE," No. CERN-INTC-2018-001, 2018.

[22] J. Schell, et al., "In and Cd as defect traps in titanium dioxide," Hyperfine Interactions, vol. 238, no. 1, pp. 1-9, 2017. https://doi.org/10.1007/s10751-016-1373-7.

[23] J. Schell, et al., "Ion implantation in titanium dioxide thin films studied by perturbed angular correlations," Journal of Applied Physics, vol. 121, no. 14, p. 145302, 2017. https://doi.org/10.1063/1.4980168.

[24] J. Schell, et al., "TDPAC study of Fe-implanted titanium dioxide thin films," AIP Advances, vol. 7, no. 9, p. 095010, 2017. https://doi.org/10.1063/1.4994247.

[25] W. Bolse, M. Uhrmacher, and K. P. Lieb., "Perturbed angular correlation studies of the oxidation of implanted 111In in FCC metals," Materials Science and Engineering, vol. 69, no. 2, pp. 375-379, 1985. https://doi.org/10.1016/0025-5416(85)90336-2.

[26] W. Segeth, et al., "Internal oxidation of In and Cd impurities in silver," Physical Review B, vol. 39, no. 15, p. 10725, 1989. https://doi.org/10.1103/PhysRevB.39.10725.

[27] "https://www.tu-ilmenau.de/en/university/departments/department-of-electrical-engineering-and-information-technology/profile/institutes-and-groups/micro-and-nanoelectronic-systems-group/research/neuromorphe-systeme," [Online].

[28] H. Wang, et al., "Efficient fabrication of MoS 2 nanocomposites by water-assisted exfoliation for nonvolatile memories," Green Chemistry, vol. 23, no. 10, pp. 3642-3648, 2021. DOI: 10.1039/D1GC00162K.

[29] S. Park, et al., "Engineering Method for Tailoring Electrical Characteristics in TiN/TiOx/HfOx/Au Bi-Layer Oxide Memristive Devices," Frontiers in Nanotechnology, vol. 3, p. 29, 2021. https://doi.org/10.3389/fnano.2021.670762.

[30] P. Blaha, et al., "WIEN2k: An APW+ lo program for calculating the properties of solids.," The Journal of Chemical Physics, vol. 152, no. 7, p. 074101, 2020. https://doi.org/10.1063/1.5143061.

[31] J. Hafner, "Ab-initio simulations of materials using VASP: Density-functional theory and beyond," Journal of computational chemistry, vol. 29, no. 13, pp. 2044-2078, 2008. https://doi.org/10.1002/jcc.21057.

[32] P. B. K. Schwarz, "Solid state calculations using WIEN2k," Computational Materials Science, vol. 28, no. 2, pp. 259-273, 2003. https://doi.org/10.1016/S0927-0256(03)00112-5.

Appendix

Description of the proposed experiment

Please describe here below the main parts of your experimental set-up:

Part of the experiment	Design and manufacturing
SSP-GLM Chamber	■ To be used without any modification ☐ To be modified
Annealing furnaces	■ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
Perturbed angular correlation existing in the building of 508	☐ Standard equipment supplied by a manufacturer ■ CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]	

HAZARDS GENERATED BY THE EXPERIMENT

Additional hazard from flexible or transported equipment to the CERN site:

Domain	Hazards/Hazardous Activities		Description
Mechanical Safety	Pressure	■	N2 gas
	Vacuum	■	typically 10^{-6} mbar
	Machine tools	☐	
	Mechanical energy (moving parts)	☐	
	Hot/Cold surfaces	■	RT-600 K
Cryogenic Safety	Cryogenic fluid	☐	[fluid] [m^3]
Electrical Safety	Electrical equipment and installations	■	Up to 20 [V], [current will be measured] [A]
	High Voltage equipment	■	[up to 2kV]
Chemical Safety	CMR (carcinogens, mutagens and toxic to reproduction)	☐	[fluid], [quantity]
	Toxic/Irritant	☐	[fluid], [quantity]
	Corrosive	☐	[fluid], [quantity]
	Oxidizing	☐	[fluid], [quantity]
	Flammable/Potentially explosive atmospheres	☐	[fluid], [quantity]
	Dangerous for the environment	☐	[fluid], [quantity]

Non-ionizing radiation Safety	Laser	☐	[laser], [class]
	UV light	☐	
	Magnetic field	☐	[magnetic field] [T]
Workplace	Excessive noise	☐	
	Working outside normal working hours	■	Possible, if the beam time is scheduled 24h per day
	Working at height (climbing platforms, etc.)	☐	
	Outdoor activities	☐	
Fire Safety	Ignition sources	☐	
	Combustible Materials	☐	
	Hot Work (e.g. welding, grinding)	☐	
radioactivity	Isotope		111mCd (48 min) 111In (2.8 days) 111Ag (7.45 days)
	Activity		max 3-4 MBq per sample