Chapter 3

# Memristive Anodic Oxides: Production, Properties and Applications in Neuromorphic Computing

Andrea Brenna, Fernando Corinto, Seyedreza Noori, Marco Ormellese, MariaPia Pedeferri and Maria Vittoria Diamanti

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http://dx.doi.org/10.5772/intechopen.79292

**Abstract**

Memristive devices generally consist of metal oxide elements with specific structure and chemical composition, which are crucial to obtain the required variability in resistance. This makes the control of oxide properties vital. While CMOS compatible production technologies for metal oxides deposition generally involve physical or chemical deposition pathways, we here describe the possibility of using an electrochemical technique, anodic oxidation, as an alternative route to produce memristive oxides. In fact, anodization allows to form a very large range of oxides on the surface of valve metals, such as titanium, hafnium, niobium and tantalum, whose thickness, structure and functional properties depend on process parameters imposed. These oxides may be of interest to build neural networks based on memristive elements produced by anodic oxidation.

**Keywords:** titanium dioxide, tantalum oxide, hafnium oxide, niobium oxide, memristor, resistive switching, anodizing

## 1. Introduction

Although still dominated by silicon technology, information storage devices—and more generally speaking nanoelectronic devices—are now facing the challenge of finding new materials and paradigms, in order to further improve features such as computation and write speed, data density, operation voltages, and fabrication costs. A variety of alternatives to traditional information processing devices have been proposed, boosting new scientific research in semiconductor principles and technologies [1]. In this frame, memristors—or resistive switching

materials, as the two terms identify the same switching behavior [2, 3]—were identified as valuable candidates for alternative nanoelectronic devices [4–7], with particular reference to nonvolatile memories and neuromorphic applications.

Indeed, several oxides are capable of resistive switching, that is, their resistance can be switched through a suitable voltage pulse between at least two different values—a high resistance state, HRS, also addressed as OFF state, and a low one, LRS, identified as ON state, by operations of "set" (OFF-ON) and "reset" (ON-OFF). Among them, $SiO_2$ [8, 9], $TiO_2$ [3], $HfO_2$ [10] and $Ta_2O_5$ [11] are the most studied.

Oxide properties—thickness, composition, stoichiometry and defectiveness—are crucial to determine whether it shows memristive properties, and the values of main switching parameters. Hence, the production technique plays a major role, as in turn it determines oxide characteristics; yet, the most commonly employed oxide synthesis/deposition techniques imply high investment costs and rather long deposition times to achieve satisfactory results.

We here present and summarize current knowledge on the growth of oxides with resistive switching capability by anodic oxidation, a low-cost electrochemical technique that may find a new niche of application in the production of memristive metal oxides. In Paragraph 2, the principles of anodic oxidation are described to highlight the typical oxide characteristics that can be achieved. The discussion will be limited to thin oxide layers, and no reference will be made to thicker ceramic oxides produced in sparking regime, as they are not pertinent to the present application [12]. Paragraph 3 provides a comparison of the characteristics of different metal oxides that show memristive properties, focusing on those that can be obtained by anodic oxidation, and then specifically focuses on anodic oxides. Finally, in Paragraph 4, the potential application of these materials in neuromorphic computing is discussed.

## 2. Anodic oxidation

Generally speaking, Ti, Hf, Ta, Zr and, valve metals are potential candidates to be anodized. Anodic oxidation is an electrochemical technique that allows to grow nanometric oxide films at a metal surface, with controlled chemical composition, structure and thickness that are defined by properly choosing the relevant electrochemical parameters—cell voltage, electrolytic solution, process time [13–15].

The technique consists of polarizing the metal by imposing a current flow between the specimen and a counterelectrode immersed in a suitable electrolyte. Metal atoms are oxidized to cations, which progressively combine with oxygen (or oxygen-containing) anions from the electrolyte to form an oxide layer that deposits on the metal surface. It is both an inward and outward growth mechanism, with a slight predominance of $O^{2-}$ charge carriers transport across the oxide to reach the metal surface where metal cations are produced, owing to the higher mobility of oxygen anions with respect to metal cations [14]. Given a determined metal or metal alloy, oxide characteristics are then determined by the set of anodizing parameters: electrolytic solution composition, concentration and temperature; feeding voltage; method of voltage application (galvanostatic, potentiostatic, potential ramp). Two main classes of anodic oxides are of interest to obtain memristive behavior and will be described in the following,

namely, compact thin films and nanotubular films; the switching behavior of anodic oxides will be addressed in Section 3.3.

### 2.1. Thin compact films

Ion migration that allows oxide growth during anodizing takes place in a solid film tens, or hundreds, of nanometers thick; therefore, it is associated with very high electric fields, in the order of $10^7$ V/cm. To achieve such conditions, current densities of some tens or hundreds of A/m$^2$ are used, and cell voltages to produce thin compact films are between 10 and 100 V [12, 16]. A very large number of electrolytes can be employed, from diluted acids to neutral salts, to alkaline solutions [17–19]. Such oxides generally show an amorphous, or predominantly amorphous, structure, especially at low voltages, where only some non-stoichiometric crystal phases like Magnéli phases may appear.

Oxide thickness increases linearly with applied cell voltage: anodizing ratios are in the range of 2 ± 0.5 nm/V depending on metal composition, electrolyte and growth mode—either galvanostatic or with potential ramp [12, 17–19]. The thicker the oxide already formed, the more onerous its further thickening: indeed, at growing voltages—and hence oxide thicknesses—other parasitic processes may kick in, consuming part of the current supplied to the electrode. As a consequence, if the amount of charge employed in the process is used to estimate oxide thickness by coulometry [20, 21], the so-calculated thickness is affected by parasitic reactions, since a portion of current is dissipated, mostly in oxygen evolution, to an increasing extent with increasing cell voltage (**Figure 1**) [19, 20]. Most of research studies on the growth of thin films by anodic oxidation refer to titanium and its alloys and to aluminum [12–14, 22–25], given their relevance in already mature industrial applications. Some works are also proposed on other metals, such as zirconium, niobium, hafnium; yet, they generally focus on the obtaining of high specific surface area morphologies, such as nanotubes [26], which are described in next paragraph.

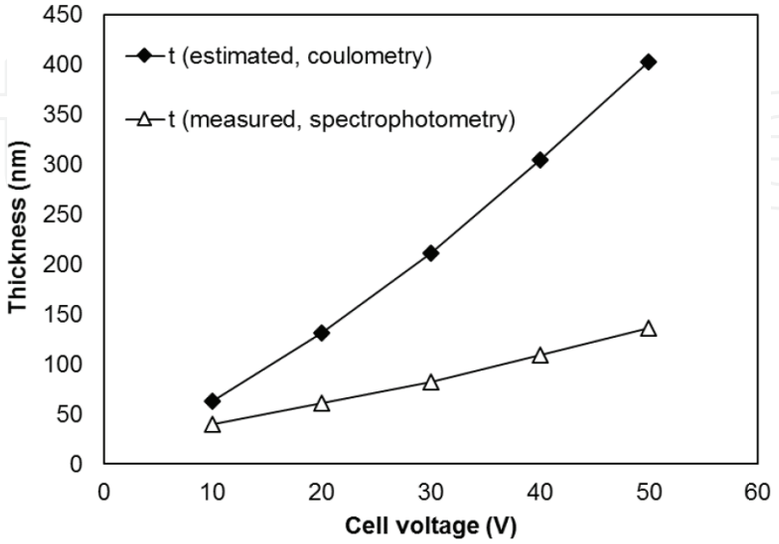


**Figure 1.** Thickness versus voltage curve of a typical galvanostatic anodic oxidation process performed in acid electrolyte: Measured oxide thickness grows linearly with voltage, while coulometry exponentially overestimates thickness due to parasitic reactions.

### 2.2. Nanotubular films

In the presence of aggressive species that are capable of localized dissolution of the growing oxide, nanotubular films can be grown, as shown in **Figure 2**. The peculiar morphology is associated with the simultaneous electrochemical growth of the oxide and its chemical dissolution operated by fluoride ions or, less frequently, other halogen ions. To achieve the formation of a nanotubular layer, a potentiostatic process is applied, where the chosen cell voltage—in the range 20–120 V—is maintained constant for various times, from few minutes to few hours [27, 28].

These nanostructures are usually developed on valve metals for applications in fields where an enhanced specific surface area is required, that is, in photocatalysis, photovoltaics, hydrogen production and sensing, where having the largest possible number of active sites of the oxide able to interact with the surrounding environment increases the material functional efficiency [27, 28]. Nevertheless, resistive switching capabilities were identified also in these nanostructures, as will be discussed in detail in Section 3.3.

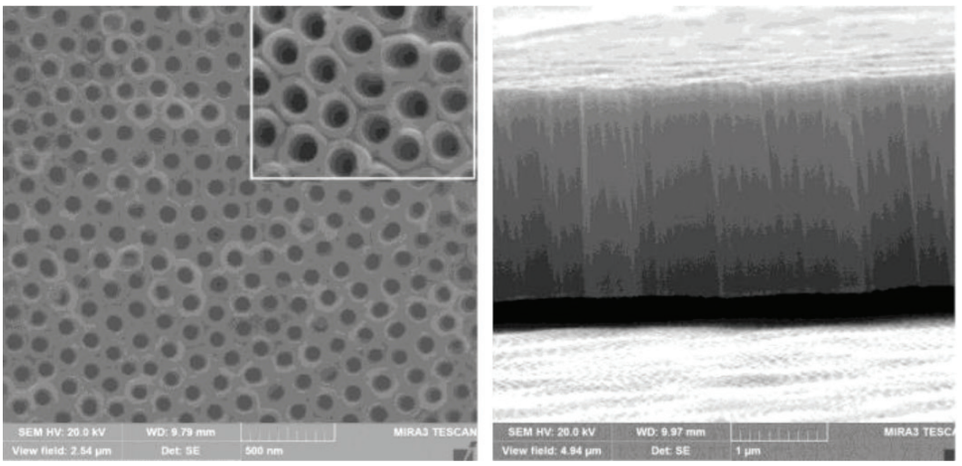


**Figure 2.** Top and cross-section view of $TiO_2$ nanotubes grown by anodic oxidation of the titanium substrate in organic electrolytes. Adapted with permission from Ref. [29].

## 3. Memristive metal oxides

### 3.1. General considerations and parameters of interest

Different switching mechanisms are observed in metal oxides—and even other mechanisms are envisioned for other materials, such as chalcogenides or polymers, which we will not refer to:

- the drift of oxide lattice defects, mostly oxygen vacancies, with consequent change in oxide valence, either localized on a restricted area called filament (**Figure 3**), or distributed over the whole area following an interface model (valence change mechanism, VCM);

- a change in stoichiometry induced by heating (thermochemical mechanism, TCM);
- the formation of conductive filaments by migration of ions from an active electrode metal and their deposition at the counterelectrode (electrochemical metallization mechanism, ECM, also called conductive bridge, CB) under the applied electrical field [4].

The most easily occurring switching mechanisms common to all metal oxides are VCM and ECM. Yet, mixed filamentary switching mechanisms, both by electrode ions migration and metal oxide reduction due to vacancies migrations, have been observed in the literature, as shown in **Figure 4**, where the two filament formation mechanisms are described [31]. Given the wide variety and complexity of switching mechanisms observed, we suggest to refer to specific reviews for a detailed explanation of the physics behind specific resistive switching mechanisms in memristive oxides [4, 32–34].

As already mentioned in the Introduction section, resistive switching implies the modification of the metal oxide of interest from a high resistance state (HRS) to a low resistance one (LRS), and vice versa (**Figure 4**). Conventionally, a set event is described as the switch from HRS to LRS, while reset, that is, restoring the initial high resistance of the oxide, causes the passage from LRS to HRS. Both events are driven by an electrical input, and more specifically by the application of a voltage. If set and reset require the application of reverse polarity, then the switching is defined bipolar, while in unipolar switching, the direction of change in resistance state depends on voltage amplitude, not on its polarity. Yet, materials usually do not show immediately a switching behavior: a first stage called electroforming is required, operated at higher voltages, which triggers the material switching ability, making subsequent cycles easier and occurring at lower voltages [35, 36]. Indeed, reset operations only allow to recover and redistribute defects (vacancies, electrode metal ions) at the oxide-electrode interface, while a conductive path remains pre-set in the inner part of the oxide [5, 37].

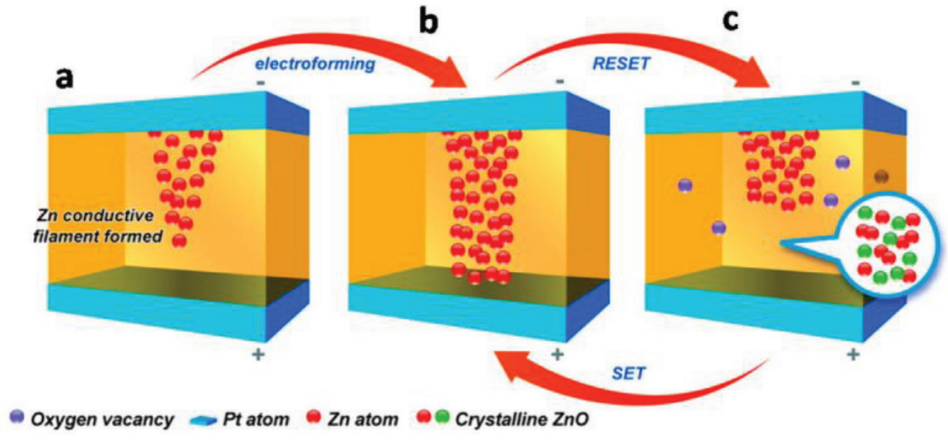


**Figure 3.** Schematic diagram for the mechanism of resistive switching in Pt/ZnO/Pt devices. (a) the migration of oxygen vacancies toward the cathode (oxygen ions ($O^{2-}$) toward the anode) and rearrangement of Zn-dominated $ZnO_{1-x}$ leads to the formation of a conductive filament (b). (c) the rupture of the filament by joule heating. Owing to the migration of oxygen ions, the ReRAM resets back to the off state. Reprinted with permission from Ref. [30].

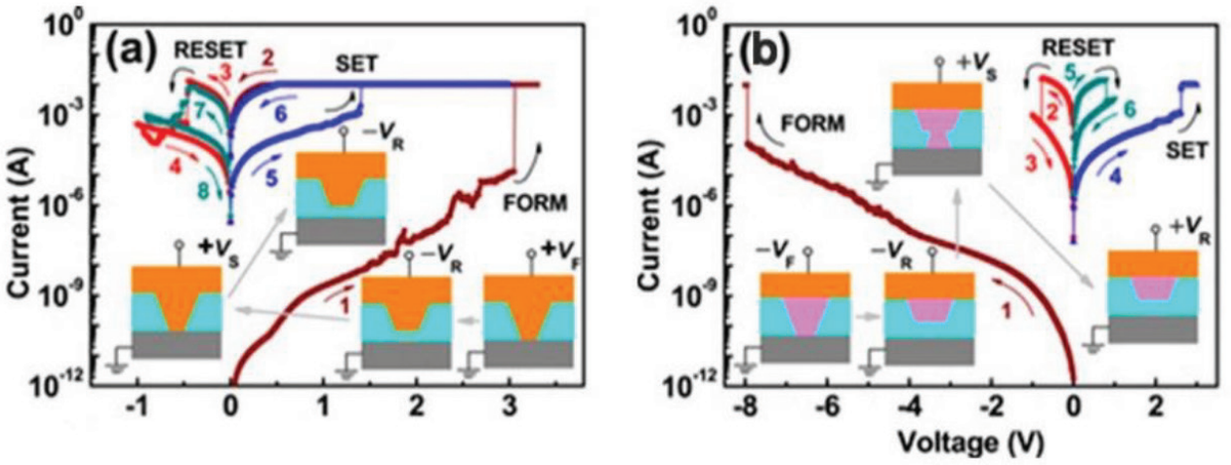


**Figure 4.** Four different operation modes for cu/ZnO/Pt in which the resistive switching originates from the formation and rupture/annihilation of (a) Cu, (b) Zn filaments. The insets schematically show filament evolution processes. Adapted with permission from Ref. [31].

The voltage applied in the electroforming step is larger than that needed in set/reset operations (**Figure 4**): the electroforming voltage in many cases is as high as a few volts and linearly dependent on oxide thickness [38–40]. Efforts are being made to produce forming-free devices; unfortunately, this is most often obtained by decreasing film thickness, which at the same time increases its defectiveness, reducing device reliability. The voltages that are required to operate the device are relevant as well: the key parameters are the write voltage, $V_{wr}$, and the read voltage, $V_{rd}$, which determine the entity of the signals required during the whole device operation. The write voltage is less dependent—in some cases even independent—on oxide thickness, as it only needs to recreate the conductive region at the oxide-electrode interface, and should be in the order or few hundred mV to allow good device efficiency and low energy consumption, while the read voltage is usually one order of magnitude lower to avoid possible undesired changes of resistance state during read operations.

When describing and comparing materials with memristive capabilities, another fundamental parameter is the $R_{off}/R_{on}$ ratio, that is, the ratio between material resistance in the HRS vs. LRS, which gives an indication on the efficiency and robustness of switching. Indeed, although ratios of few units are theoretically sufficient to operate a device, a $R_{off}/R_{on}$ ratio higher than 10 is generally recommended, to avoid uncertainties in read operations and improve reliability [4].

Another important touchstone parameter is endurance, that is, the number of cycles applicable to the material without loss of switch and no (or better, limited) decay of $R_{off}/R_{on}$ ratio.

One last characteristic can play a major role, especially in neuromorphic computing, that is, the possibility to achieve multilevel storage, which makes the difference between binary and analog switching. This can be achieved either by multiple resistance states [41–44] or by encoding information not only in the conductive filament size, which rules resistivity, but also in its orientation through complementary switching [45, 46]. These aspects will be addressed in Paragraph 4.

### 3.2. Dependence of switching behavior on metal oxide characteristics

As anticipated, this section compares the switching behavior of metal oxides that hold an interest in the frame of anodic oxidation, that is, the discussion is focused on oxides of metals that are liable to anodizing. These include titanium, niobium, tantalum, hafnium, and zirconium. Oxides are often indicated as $TiO_{2-x}$, $NbO_x$, $TaO_x$, $HfO_{2-x}$, $ZrO_{2-x}$ to take non-stoichiometry into account.

On these metal oxides, either filamentary switching or interfacial valence change has been observed, depending on oxide composition, production method, and metal electrode composition. Interestingly, a unified model was proposed: to be integrated in CMOS technology, feature size will be decreased more and more, until reaching the actual size of a filamentary conduction path—which would then occupy the whole component area [34].

When the formation of oxygen vacancies (or metal precipitates) filaments is involved, the localized current percolation path preferentially locates at grain boundaries or lattice inhomogeneities, as revealed by C-AFM and TEM measurements reported in several works (see for instance [47–49]) and represented in **Figure 5**. Moreover, multiple resistance states can be obtained and explained by considering two directional movements of vacancies: from one electrode to the other, crossing the whole oxide thickness, to generate the filament; and a lateral one, to increase filament size or create new filaments [50, 51]. From a material point of view, multiple states can be seen as a gradual increase in non-stoichiometry. As an example, for $TiO_2$, the memristive behavior is generally ascribed to the movement of vacancies that gradually create an oxygen depleted layer with composition $TiO_{2-x}$, which gains conductivity for $x > 1.5$ [52], hence the higher the quantity of vacancies formed, the wider the area that reaches low resistance conditions, which allows a gradual change in LRS that can be exploited to produce multistate devices.

Yet, grain boundaries and other structural inhomogeneities related to crystalline oxide structures may strongly affect actual device performances: in fact, grain boundaries not only make switching easier, as abovementioned, but also cause a decrease in $R_{off}/R_{on}$ ratio, plus they alter performance evaluation with respect to single crystal devices of envisioned nanometric size. Hence, amorphous layers are often preferred, given their enhanced reproducibility and

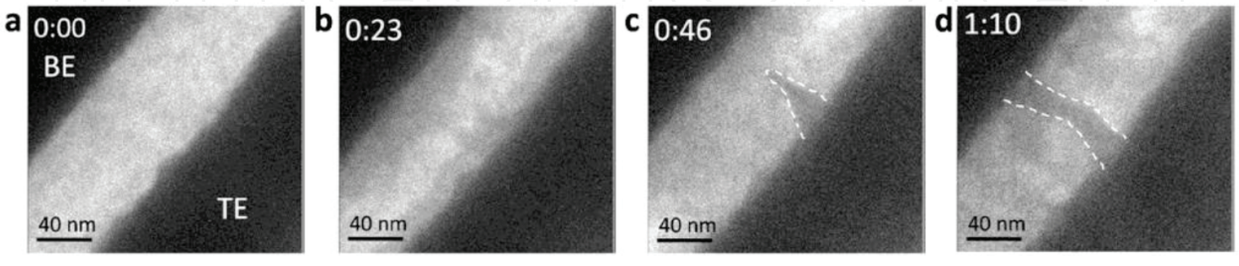


**Figure 5.** A series of in situ TEM images clipped from the video. (a) At the start of recording, the ZnO was in the initial state. (b) When voltage was applied, the contrast of ZnO enhanced near both electrodes. (c) A conical-shaped filament generated near the top electrode. The white dashed line highlights the filament. The specimen was still in the high-resistance state. (d) The columnar filament passed through the ZnO film connecting the top and bottom electrodes. Adapted with permission from Ref. [30].

better long term stability with respect to polycrystalline ones: these properties, ascribed to the material structural homogeneity, nicely match with an easier production with respect to single crystal oxides [53–55].

More recently, low-cost processes have been successfully employed to produce resistive switching oxides, including solution processing—sol-gel, hydrothermal synthesis—and electrochemical techniques, both electrodeposition and anodic oxidation. The former set of techniques has the advantage of producing oxides free of substrate, hence they can be deposited on any substrate, including flexible ones [56–58]. Production of the oxides generally involves mild temperatures and ambient pressures in case of sol-gel [57, 59–62], or the use of a pressurized vessel, specific for hydrothermal treatments [63–65], which in all cases represent low-cost alternatives to low pressure, high-temperature chemical or physical deposition processes.

On the other hand, the absence of a substrate implies an immobilization step—which can be performed by drop-coating, inkjet printing, and other methods—that may introduce a further level of inhomogeneity in the final device properties. Indeed, oxide particles need to be dispersed in a proper solvent, which must then be completely removed: defects such as porosities due to solvent removal, or even residual solvent may then arise. To improve homogeneity, often multiple deposition steps are performed, which increases overall film thickness and consequently electroforming voltage [59], while oxygen or argon plasma etching can be employed to introduce oxygen vacancies in the as-deposited materials, hence reducing electroforming voltages or even eliminating the need for this step [60, 66–68]. The possibility of applying multiple coating steps also opens the way to sol-gel processed double-layer structures [69], which brings potential benefits that span from increased endurance to reduced power consumption [44, 70–72]. For instance, in $TiO_2$-based memristors oxygen vacancies migration can lead to oxygen gas evolution at the anode, which irreversibly compromises the oxide stoichiometry: the presence of a blocking layer can act as sink of oxygen ions and limit currents involved, avoiding oxide breakdown [3, 73, 74].

Concerning the switching type, both unipolar and bipolar switching can be observed within the same material [75, 76]: which of the two is operating can be associated at a first approximation with different reset processes, being thermal dissolution the prevailing one for unipolar behavior, and ionic migration responsible for bipolar switching ([5] and references therein: [77–79]).

### 3.3. Anodic oxides showing memristive behavior

The choice of anodic oxidation to produce memristive elements is driven by a number of benefits over current technologies, first of all its low cost, non-vacuum and low-temperature characteristics. Moreover, it allows to produce amorphous oxides with nonstoichiometric composition [14, 49, 80], that is, already containing a non-negligible amount of oxygen vacancies, and characterized by higher density compared with sputtered films, where residual porosity is intrinsic to the production technique [81]. Eventually, anodizing allows fast oxide growth: to obtain a metal oxide few tens of nanometers thick, the general duration of an anodizing process is in the order of few seconds, and it can be performed with a relatively

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low power equipment (voltage scale 0–30 V, current scale 0–100 mA) in a neutral solution of non-aggressive salts [17]. Another advantage is the possibility to use the same metal substrate as a back-end material, that is, one of the two electrodes is intrinsically integrated in the component. Currently, the biggest drawback that limits applications of anodic oxidation is the minimum device size: the technique is generally employed on full surfaces, thus not allowing the growth of space-confined nanometric or sub-micrometric pads, and the only method to reduce the size of the anodized spot is to apply insulating masks that avoid electronic contact of the metal with the electrolyte.

Keeping in mind these important general features, we here summarize current research on anodic oxides showing memristive characteristics.

The first indication of anodic oxides presenting memristive behavior was recorded on titanium oxides grown in a water-glycerol-based ammonium fluoride solution at 30 V. No clear morphological characterization of the oxide is made; yet, although the presence of fluorides may indicate typical conditions of nanotubes production, the short anodizing times applied allow to presume the growth of a compact oxide, some tens of nanometers thick. Interestingly, annealing has a detrimental effect on the memristive behavior. This is ascribed to the exceeding formation of oxygen vacancies that creates ohmic contacts; in addition, annealing is known to induce crystallization in anodic oxides which—in the anodizing conditions considered—would show amorphous structure in the as-prepared state [82]. This may have as well a role in the degradation of resistive switching. Other compact oxide films showing memristive behavior were then grown on titanium as well as on niobium and tantalum: anodizing in diluted phosphoric acid at 25 V, corresponding to an oxide thickness of approximately 60 nm, was found to allow the achievement of the best switching behavior [83].

The cited works all based their considerations on macroscale samples. A nanoscale characterization of anodic titanium oxides was performed by means of conductive atomic force microscopy (C-AFM), which allowed to assess the electrical properties of nanometer-size spots on the oxide surface: results indicated that oxide properties are far from being homogeneous, with resistive switching spots embedded in a nonconductive matrix and located mostly at grain boundaries [49]. More recently, efforts were made in the direction of producing real devices and testing the material at the microscale. Anodizing was performed on tantalum [81] and on titanium [84] metallic films deposited on glass, in borate buffer solution or in diluted phosphoric acid, respectively, at cell voltages of 5–20 V. Micrometer-size conductive metal pads (either Pt or Cu) were then deposited by lithography, allowing better characterization of the devices, which also included endurance evaluation.

In all abovementioned cases, the anodic oxides showed parameters compatible with requirements identified for resistive switching materials: high $R_{off}/R_{on}$ ratio (> 10, with best values in the order of 80), set/reset values lower than 1 V and possibility to obtain multilevel switching [81]. Moreover, in several works, the oxides produced were electroforming-free: this can be ascribed to the anodic oxidation process itself, which is known to generate non-stoichiometric oxides, therefore the content of oxygen vacancies natively present in the oxide is already sufficient to produce the switching [49, 83, 84].

In this respect, metal electrode ions injection has also been proposed as a possible mechanism for the onset of switching, which would indicate the establishing of a CB mechanism [81]. Nevertheless, proofs of the actual onset of a VCM are provided through the observation of switching with C-AFM measurements, where no top electrode is present: analyses have been conducted both on the top surface of the anodic oxide [49], and on a lateral device, where no electrode metals are available [85].

Memristive nanotubes were also produced on titanium [86–88]. In these cases, either longer anodizing times (hours) and/or higher voltages (up to 120 V) are required, and thicker oxides, some hundreds of nanometers thick, are achieved. Yet, the limited adherence and mechanical stability of these oxides compared with compact ones, and the higher thickness introduced, make them less appealing for real applications.

## 4. Applications in neuromorphic computing

Recent implementations of emerging computing capabilities leverage on the capability offered by non-volatile memory (NVM) storage and information processing. Two main approaches have been proposed:

- Hybrid logic/memory integration: the logic and the memory layers are implemented in two different substrates or levels, typically an Application Specific Integrated Circuit (ASIC) is developed to emulate artificial neuron functionality while memory layers are integrated either on a separate chip or occupy a separated area. The main advantage lies in the improved communication bandwidth between the different logic and memory layers.
- Logic-in-memory: memory elements are distributed in a circuit to play a role in the realization of the logic operations, aiming both at ultra-low power and highly expressive logic circuits. Thus, general-purpose computation functions can be implemented by configuring non-volatile switches. NVMs are naturally suited for performing implication logic instead than standard logic. Recently, stateful logic operations, for which memristor devices work as gates and latches that use resistance as a physical state variable, have been demonstrated [89].

Energy efficiency benefits of array computing have also been demonstrated with various technologies (including spin-torque oscillators) in relatively small-scale circuits. For example, in [89], a data clustering algorithm mapped to a memristive array was demonstrated. In [90], the FPAA architecture was used to implement neuronal array-based sparse coding, applicable in the early stages of visual processing. Furthermore, integration of memristors and an FPAA circuit was demonstrated in small scale in [91]. Cognitive computing algorithms, which can be mapped to array processing/associative memory architectures, have also been described [92–94]. However, hardware architectures and design tools to realize these algorithms energy-efficiently on a relevant scale do not currently exist.

The challenge in the application of memristor technology for large-scale memory-based computing architectures is the development of new physical device models for memristor devices

and analyzes the adaptation of algorithms with respect to device variation and scalability. Since the discovery of memristive behavior at the nanoscale at Hewlett Packard laboratories in 2008, the scientific community has devoted a large deal of efforts to derive suitable models that capture the nonlinear dynamics of memristors. Pickett's model is a reference model that is well suited for describing the physical mechanisms at the origin of memristor dynamics. Simplified versions aiming at fitting the behavior of Pickett's model are the TEAM and V-TEAM models, Biolek's model and the boundary condition model for a comprehensive review [95]. It is worth noting that such models are not oriented toward nonlinear circuit synthesis. In order to effectively analyze the dynamic behavior of memristors, and also in view of their simulation and emulation, it is fundamental to develop circuit memristor models, that is, models obtained by interconnecting basic nonlinear blocks. This will be pursue along the lines of the general method for device modeling in [96] and exploiting recent techniques for the identification of switching and PWA (piece-wise-affine) systems.

There is an increasing interest in the implementation of oscillators using nanoscale devices as memristors. As remarked in [97], a source of controllable chaotic behavior that can be implemented by a single scalable electronic device and incorporated into a neural-inspired circuit may be an essential component of future computational systems. In this framework, the memristor is required to display a quasi-static voltage-current characteristic with a negative differential resistance (NDR). Various classes of relaxation oscillators displaying a tunable range of periodic and chaotic self-oscillations have been implemented during recent years and their importance in neuromorphic applications, such as pattern recognition and signal processing tasks in real time, have been demonstrated. They can also be used as core devices with a rich variety of nonlinear dynamics within the framework of reservoir computing architectures. Work so far has been mainly based on experimental and phenomenological observations of oscillations and complex phenomena, while a circuit model and a clear analytic understanding of the underlying nonlinear dynamics and bifurcations is basically missing. Recently, a new method, named Flux-Charge Analysis Method (FCAM), has been developed to effectively analyze a wide class of nonlinear circuits containing ideal memristors in the flux-charge domain [98]. FCAM permits to bring back the dynamic analysis to that of a lower-order circuit, with respect to that in the standard voltage-current domain, using flux and charge as state variables. This enables to obtain a clear picture of the dynamical behavior displayed by memristor circuits. In particular, some peculiar aspects, such as the presence of invariant manifolds and the coexistence of different dynamics for the same set of (fixed) circuit parameters, are singled out. Also, it is possible to assess the presence of a new interesting phenomenon of bifurcations which emerge without changing the system parameters, namely, bifurcations due to changing the initial conditions for the state variables for a fixed set of circuit parameters (BWP) [99]. Using FCAM, the dynamics of classes of oscillators and chaotic circuits with ideal memristors have been deeply analyzed assessing the occurrence of Hopf and period-doubling BWPs and quite rich complex dynamics. In addition, it has been shown that FCAM can be combined with techniques, such as the harmonic balance method citare, to effectively analyze and control such BWPs. Moreover, by suitably exploiting BWPs, it turned out that different chaotic dynamics in a class of Chua's oscillators can be programmed by means of suitable current or voltage pulses [100]. Synchronization aspects in arrays of coupled oscillators have been analyzed as well [101].

## 5. Conclusions

We here provided an overview of the typical oxide materials used to produce memristive devices and of their switching behavior. With specific reference to anodic oxides, their potential as switching components has been demonstrated, and the possibility to have an easy control over their thickness and composition with excellent repeatability is particularly appealing for the specific application envisioned. Yet, some open issues can be identified in this frame, namely, the downscaling of oxide area, and related problems of technological transfer at the sub-micrometric scale, and the verification of compatibility of such electrochemical wet process with CMOS fabrication.

## Acknowledgements

The authors would like to acknowledge the financial support of Fondazione Cariplo and Regione Lombardia, project ProACTIV-MOX—PROmoting research on AnodiC memrisTIVe Metal OXide films for nanoelectronics.

## Conflict of interest

The authors declare no conflict of interest.

## Author details

Andrea Brenna[1], Fernando Corinto[2], Seyedreza Noori[1], Marco Ormellese[1], MariaPia Pedeferri[1] and Maria Vittoria Diamanti[1]*

*Address all correspondence to: mariavittoria.diamanti@polimi.it

1 Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, "Giulio Natta", Milan, Italy

2 Department of Electronics and Telecommunications, Politecnico di Milano, Torino, Italy

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