Oxygen vacancy engineering of TaO\textsubscript{x}-based resistive memories by Zr doping for improved variability and synaptic behavior

João H Quintino Palhares\textsuperscript{1,2,*}, Yann Beilliard\textsuperscript{2,3,4,*}, Fabien Alibart\textsuperscript{2,3,5,*}, Everton Bonturim\textsuperscript{6,*}, Daniel Z de Florio\textsuperscript{1,*}, Fabio C Fonseca\textsuperscript{7,*}, Dominique Drouin\textsuperscript{2,3,4,*} and Andre S Ferlauto\textsuperscript{1,2,*}

\textsuperscript{1} CECS, Federal University of ABC, Santo André 09210-580, SP, Brazil
\textsuperscript{2} Institut Interdisciplinaire d'Innovation Technologique (3IT), Université de Sherbrooke, Sherbrooke J1K 0A5, Canada
\textsuperscript{3} Laboratoire Nanotechnologies Nanosystèmes (LN2)—CNRS UMI-3463—3IT, CNRS, Sherbrooke J1K 0A5, Canada
\textsuperscript{4} Institut Quantique (IQ), Université de Sherbrooke, Sherbrooke J1K 2R1, Canada
\textsuperscript{5} Institute of Electronics, Microelectronics and Nanotechnology (IEMN), Université de Lille, F-59650, Villeneuve d’Ascq, France
\textsuperscript{6} Department of Chemistry, School of Engineering, Mackenzie Presbyterian University, 01302907, São Paulo, SP, Brazil
\textsuperscript{7} Nuclear and Energy Research Institute, IPEN-CNEN, São Paulo, 05508-000, Brazil

E-mail: quij2205@usherbrooke.ca, andre.ferlauto@ufabc.edu.br and dominique.drouin@usherbrooke.ca

Received 21 April 2021
Accepted for publication 23 June 2021
Published 12 July 2021

Abstract

Resistive switching (RS) devices are promising forms of non-volatile memory. However, one of the biggest challenges for RS memory applications is the device-to-device (D2D) variability, which is related to the intrinsic stochastic formation and configuration of oxygen vacancy (VO) conductive filaments (CFs). In order to reduce the D2D variability, control over the formation and configuration of oxygen vacancies is paramount. In this study, we report on the Zr doping of TaO\textsubscript{x}-based RS devices prepared by pulsed-laser deposition as an efficient means of reducing the VO formation energy and increasing the confinement of CFs, thus reducing D2D variability. Our findings were supported by XPS, spectroscopic ellipsometry and electronic transport analysis. Zr-doped films showed increased VO concentration and more localized VO clusters due to the interaction with Zr. DC and pulse mode electrical characterization showed that the D2D variability was decreased by a factor of seven, the resistance window was doubled, and a more gradual and monotonic long-term potentiation/depression in pulse switching was achieved in forming-free Zr:TaO\textsubscript{x} devices, thus displaying promising performance for artificial synapse applications.

Supplementary material for this article is available online

Keywords: TaO\textsubscript{x}, oxygen vacancy engineering, memristor, variability, doping, resistive switching, synaptic behavior

(Some figures may appear in colour only in the online journal)
1. Introduction

Resistive switching (RS) memories based on oxide thin films are a promising technology for next-generation high-density non-volatile memory applications and the hardware implementa-
tion of artificial neural networks [1–4], due to their impressive switching operation performance in terms of speed, endurance, scaling and multistate resistance modulation [5–8]. However, both cycle-to-cycle (C2C) and device-
to-device (D2D) variability in the switching characteristics still hinders the widespread use of this technology, as these reduce the average performance and generate cost increases due to the need for complex overhead circuits [5, 9, 10]. RS is generated by the creation and dissolution of conductive channels within an oxide layer in a capacitor-like structure, as a result of the nanoionic movement of oxygen vacancies \( \text{VOs} \) under the application of high electric fields [11, 12]. An initial operation step called a forming process is typically required in order to generate sufficient \( \text{VOs} \) to allow for the formation of conductive filaments (CFs). The stochastic nature of the forming and switching steps leads to slightly different CF configurations for each device, resulting in D2D and C2C variability [5, 10, 12–16]. Understanding and control of the formation, movement and arrangement of \( \text{VOs} \) in RS devices is therefore paramount [13, 17, 18].

Various strategies have been explored for the creation of excess oxygen vacancies in a controlled manner, in order to mitigate forming-induced variability [19–21]. The most common and direct method of \( \text{VO} \) generation is intrinsic doping, i.e., the use of low oxygen partial pressure during fabrication of the oxide layer, using methods such as reactive sputtering or pulsed-laser deposition (PLD). This approach has been particularly successful for tantalum oxide films [20–22]. Intrinsic doping has certain limitations, however, as it is difficult to control, relies on external parameters and is subject to instabilities in the processing conditions [17, 23–25]. A more reliable alternative is extrinsic doping, which consists of adding dopant atoms with a valence that is lower than the host metal cation; this leads to the formation of \( \text{VOs} \) in order to maintain electroneutrality [12, 17, 26, 27]. Extrinsic doping also helps to reduce the randomness of \( \text{VO} \) generation. Theoretical studies of \( \text{Ta}_2\text{O}_5 \) doped with Ti, Zr and Al have indeed shown that the formation of \( \text{VOs} \) is favored near the dopant species [26]. In these cases, charged \( \text{VOs} \) are compensated and attracted by p-type dopants, forming dopant-\( \text{VO} \) complexes. These complexes trap \( \text{VOs} \), and can interconnect to form CFs. A reduction in variability has been experimentally observed for extrinsically doped \( \text{TaO}_x \) [28] and \( \text{HfO}_x \) based [29, 30] devices. It has been claimed that implanted or embedded dopant elements (e.g., Gd, Al) in \( \text{HfO}_2 \) help to localize \( \text{VO} \) formation and lead to more confined CFs, resulting in significantly lower device variability. This interaction between the dopant species and \( \text{VOs} \) can change the switching dynamics and switching voltage operation [18], meaning that extrinsic doping can be leveraged to further optimize switching performance for specific applications, such as artificial synapses.

In this work, we report the fabrication of TaO\(_x\)-based memristors with reduced D2D variability and controllable pulse switching dynamics, thanks to doping of the active layer with Zr. For comparison purposes, Zr-doped (Zr:TaO\(_x\)) and pure TaO\(_x\)-based devices were prepared in an oxygen-poor atmosphere using PLD. Oxygen-poor conditions are used to suppress electroforming step and its effect on the active layer properties. The chemical compositions of both types of devices were investigated using x-ray photoelectron spectroscopy (XPS) analysis and spectroscopic ellipsometry (SE). RS investigations in DC and pulsed mode revealed that D2D variability was decreased by a factor of seven, the resistance window was doubled and more gradual and monotonic long-term potentiation and depression (LTP/LTD) in pulse switching was achieved in Zr:TaO\(_x\) devices. By analyzing the device current density-electric field (\( J-E \)) curves using a hopping transport model, we demonstrate that Zr:TaO\(_x\) devices have a higher \( \text{V}_0 \) concentration and a lower variability of this concentration between different devices.

2. Methods

Devices were fabricated on silicon substrates covered with 200 nm of SiO\(_2\) (figure 1(a)). Sputtering was used to deposit tungsten (W) on the bottom (BE) and top electrodes. The latter were patterned to give 80 \( \mu \)m round pads, using UV photolithography and lift-off. TaO\(_x\) and Zr:TaO\(_x\) layers were deposited at room temperature via PLD (with a TSST system) using a Ta\(_2\)O\(_5\) target and a Ta\(_2\)O\(_5\):20 mol\% ZrO\(_2\) target, respectively, at a target-substrate distance of 45 mm, with a laser fluence of 3 J cm\(^{-2}\) and a repetition rate of 10 Hz under an oxygen flow of 2 scm. Layer thickness was estimated to be 10 nm by using the growth rate as determined by SE measurements. Based on previous studies [22], we used an O\(_2\) partial pressure of \( 2 \times 10^{-2} \) mbar to induce the formation of slightly sub-stoichiometric active layers. The generation of \( \text{VOs} \) by extrinsic and intrinsic doping was investigated using XPS (KRATOS Axis UltraDLD), SE (JA Woollam, model M-2000) and \( J-E \) conduction transport analysis of the devices. The electrical properties of the RS devices under DC and pulsed conditions were carried out with a Keithley S4200 semiconductor parameter analyzer and a Keithley 4225-PMU module. For all measurements, the BE was grounded and the signals were applied to the top electrodes.

3. Results and discussions

The thin films were analyzed using XPS and SE. The ratios (O/M) between oxygen and the sum of the metal atoms (M = [Ta] for TaO\(_x\) and M = [Ta] + [Zr] for Zr:TaO\(_x\)) was determined by quantification of the Ta 4f, Zr 3d and O 1s peaks shown in figures 1(b)–(d). Due to the low pO\(_2\) during deposition, TaO\(_x\) and Zr:TaO\(_x\) films had O/M ratios of 2.45 and 2.25, respectively. This is lower than the value of O/M = 2.5 corresponding to the oxygen concentration of the stoichiometric tantalum pentoxide (Ta\(_2\)O\(_5\)), thus indicating the presence of \( \text{V}_0 \) [20, 21]. This effect was also confirmed
The presence of Ta in a lower oxidation state is expected to result from the partial reduction of tantalum oxide via SE.

As expected, the Zr-doped films are more sub-stoichiometric, since the presence of Zr$^{4+}$ cations induces VO formation according to the reaction

$$2\text{ZrO}_2 + \text{Ta}_4\text{O}_9 \rightarrow 2\text{Zr}_2\text{Ta}_2 + \text{V}_0 + 4\text{O}_2.$$  

Furthermore, as shown in figure 1(c), the O 1s peaks have an asymmetric line shape that can be deconvoluted into two components centered at 531.3 and 530.0 eV; these can be assigned to non-lattice (O$_0$) and lattice oxygen, respectively. The non-lattice oxygen peak can be associated with the presence of VO$_3$ [33, 34]. The fact that Zr:TaO$_x$ films contain a larger percentage of non-lattice oxygen (26%) compared to TaO$_x$ films (20%) suggests that Zr$^{4+}$ substitution indeed promotes VO$_3$ formation. This is in agreement with results reported by Park et al [35] for KNBO films doped with Cu$^{2+}$, and by Kim et al [36] for Si-doped tantalum oxide-based memristors. The XPS spectrum for the Zr 3d peak was deconvoluted into Zr 3d$_{5/2}$ and Zr 3d$_{3/2}$, centered at 182.4 and 184.7 eV respectively [37–39], corresponding to Zr$^{4+}$ states (figure 1(d)). The nominal relative concentration of Zr with respect to the concentration of Ta atoms [Zr]/[Ta] was determined as 8%.

Figure 1(e) shows the optical absorption spectra obtained by fitting the ellipsometry data using a Tauc-Lorentz analytical function, which is widely used to describe the optical properties of amorphous and polycrystalline semiconductors and dielectric films [40, 41]. In this function, the imaginary part of the dielectric function is described by a Tauc expression for photon energies above the gap, and is forced to zero below the band gap. The overall interband transition in the higher range of photon energies analyzed here is described by a Lorentz oscillator. Although this function can be used to describe pure stoichiometric dielectric Ta$_2$O$_5$ films, absorption in the sub-gap region is observed for sub-stoichiometric films. This feature can be modeled using a broad Lorentz function. Sub-gap absorption has been observed previously in sub-stoichiometric Ta$_2$O$_5$ films [42], and was associated with the presence of VO$_3$ [43–45]. From figure 1(e), it can be seen that the optical responses of both TaO$_x$ and Zr:TaO$_x$ exhibit considerable sub-gap absorption, thus confirming the XPS results. It is interesting to note that the optical absorption intensity is similar for both samples, even though the Zr-doped films have a higher VO$_3$ concentration. One possible explanation for this is that the dopant-VO$_3$ interaction may suppress the optical activity of the VO$_3$ due to changes in the charge [18, 44].

To gain insight into the effects of Zr doping on the characteristics and variability of RS, current- and DC voltage-controlled sweeps were used for SET and RESET operations, respectively. For each device, in the SET and RESET operation, the current compliance and the maximum operation voltage values, respectively, were defined to maximize the device resistance window while avoiding irreversible damage. These values slightly vary among devices due to an intrinsic variation in the threshold voltage and maximum resistance window of each device. Figure 2 shows RS characterizations of W/TaO$_x$/W (figure 2(a)) and W/Zr:TaO$_x$/W (figure 2(b)) devices. Up to five full RS cycles were performed on each device, and the resistance state was measured at 0.2 V. For
more RS cycles and performance information see supplementary material (available online at stacks.iop.org/NANO/32/405202/mmedia). In each RS plot, ten switching curves (the last RS cycle of each device) are given, corresponding to ten different devices with the same stack structure. The coefficient of variation (CV), defined as the standard deviation (σ) divided by the average value (μ) of a given device parameter, is used to account for the variability and dispersion. Table 1 summarizes the statistical data for main RS parameters. In the pristine state, most devices had resistance values ranging between the subsequent high resistance states (HRSs) and low resistance states (LRSs), and hence a forming process was not required. Few devices had initial resistance values higher than the HRS values, and these were switched with a voltage that was lower than in the subsequent SET and RESET operations. For both the Zr:TaO and TaO devices, the forming-free behavior was due to the high vacancy concentrations resulting from both intrinsic and extrinsic Zr\(^{4+}\) doping [20, 21]. The devices showed bipolar switching, with the SET operation occurring with a positive bias (V\(_{\text{SET}}\)) and the RESET operation with a negative bias (V\(_{\text{RESET}}\)) for all devices. The average values of V\(_{\text{RESET}}\), V\(_{\text{SET}}\) were slightly increased for Zr:TaO devices (up to ~2.3 V as compared with ~2 V for TaO\(_x\)), an effect that can be ascribed to the dopant-V\(_{\text{O}}\) interaction that may lead to defect clustering and consequent change in defect mobility. In addition, the current density values (@0.2 V) were slightly higher for the Zr:TaO\(_x\) devices, which can be explained by the increased V\(_{\text{O}}\) concentration. C2C variability in LRS and HRS resistance was similar for both the Zr:TaO\(_x\) and TaO\(_x\) devices, with average values for the CV of around 18% and 14%, respectively (see the curves in the supporting information). On the other hand,

![Image](80x530 to 518x773)

**Figure 2.** Current–voltage (I–V) characteristics for the 10 devices tested, with a statistical analysis of the resistance states per device: (a) W/TaO\(_x\)/W RS devices and (b) W/Zr:TaO\(_x\)/W RS devices. To improve visibility, the switching curve for one random device is shown in color. The resistance was measured at 0.2 V. The resistance values for the Zr:TaO\(_x\) devices exhibit improved D2D variability.

**Table 1.** Comparison of key parameters of Zr:TaO\(_x\) and TaO\(_x\)-based memristors

|               | Zr-TaO\(_x\) (μ ± σ) | TaO\(_x\) (μ ± σ) | CV (%) |
|---------------|----------------------|------------------|--------|
| LRS/HRS       | 21.8 ± 3.3           | 12.5 ± 7.6       | 60.8   |
| R\(_{\text{LRS}}\) (kΩ) @0.2 V | 0.70 ± 0.07          | 3.7 ± 2.7        | 73.0   |
| R\(_{\text{HRS}}\) (kΩ) @0.2 V | 14.5 ± 2.2           | 46.5 ± 49.6      | 106.7  |
| J (A cm\(^{-2}\)) @0.2 V – LRS | 6.0 ± 0.7            | 1.4 ± 0.7        | 50.0   |
| J (A cm\(^{-2}\)) @0.2 V – HRS | 0.30 ± 0.05          | 0.20 ± 0.10      | 50.0   |
| V\(_{\text{SET}}\) (V)    | 2.3 ± 0.4            | 1.7 ± 0.5        | 29.4   |
| V\(_{\text{RESET}}\) (V) | 2.3 ± 0.5            | 2.0 ± 0.6        | 30.0   |
| a (nm) – HRS   | 0.6 ± 0.1            | 0.7 ± 0.2        | 29.0   |
| a (nm) – Pristine | 1.0 ± 0.2           | 1.6 ± 0.7        | 43.8   |
| \([n_v_o]\) \((10^{21}/cm^3) – HRS\) | 6.6 ± 3.4           | 5.5 ± 4.4        | 80.0   |
| \([n_v_o]\) \((10^{21}/cm^3) – Pristine\) | 1.5 ± 1.4           | 1.1 ± 1.8        | 163.6  |
significant contrast was observed in the D2D variability, and especially in the resistance values in both the LRS and HRS states, in which the CV for the Zr:TaO\textsubscript{x} device in the LRS was reduced from 68\% to 9\% and in the HRS from 110\% to 15\% compared to TaO\textsubscript{x} (see table 1). Another important feature observed for the Zr:TaO\textsubscript{x} devices was an increase in the average resistance window, from 12.5 for the TaO\textsubscript{x}-based devices to 21.8 for the Zr-doped ones. A similar contrast was previously noted in a comparison of sub-stoichiometric to purely stoichiometric TaO\textsubscript{x} devices [20], and was attributed to CF confinement and an increase in carrier concentration, which results in higher current densities. This localized Joule effect gives rise to greater filament dissolution and thus a larger resistance window [20]. These results indicate that Zr doping helps to improve RS performance by lowering D2D variability.

To further evaluate the effects of doping on the transport mechanisms, we conducted a carrier transport analysis by applying a hopping model that has been used previously in studies of tantalum oxide-based devices [46–48]. The J–E curves for the devices in both the pristine state and the HRS were fitted using the following expression [47, 49, 50]

\[
J = qavn \exp\left(\frac{qaE}{k_BT} - \frac{\phi_i}{k_BT}\right),
\]

where \(a\) denotes the average distance between trap sites, \(\phi_i\) is the trap energy, \(k_B\) is the Boltzmann constant, \(q\) is the electronic charge, \(n\) is the carrier concentration and \(\nu\) is the attempt-to-escape frequency. As can be seen from figures 3(a)–(d), the I–V characteristics are well described by the hopping model (the fitted curves and parameters extracted for all devices are provided in the supplementary material). The values obtained for the average distance between traps for pristine Zr:TaO\textsubscript{x}- and TaO\textsubscript{x}-based devices were 1.0 ± 0.2 and 1.6 ± 0.7 nm, respectively (see table 1). The HRS trap distances were 0.6 ± 0.1 and 0.7 ± 0.2 nm for Zr:TaO\textsubscript{x} and TaO\textsubscript{x} devices, respectively. The trap concentration for each type of device can be estimated by calculating [51, 52]

\[
[N_{\text{traps}}] = a^{-3}.
\]

Pristine Zr:TaO\textsubscript{x} devices had a higher concentration of traps, with a value of \((1.5 \pm 1.4) \times 10^{21} \text{ cm}^{-3}\) compared with \((1.1 \pm 1.8) \times 10^{21} \text{ cm}^{-3}\) for TaO\textsubscript{x} devices. The same trend was observed for the HRS states: the Zr:TaO\textsubscript{x}-based device has a trap concentration of \((6.6 \pm 3.4) \times 10^{21} \text{ cm}^{-3}\) as compared to \((3.6 \pm 1.1) \times 10^{21} \text{ cm}^{-3}\) for TaO\textsubscript{x}.

The transport mechanism in TaO\textsubscript{x} films depends critically on the V\textsubscript{O} concentration. TaO\textsubscript{x} exhibits Fermi glass behavior, in which V\textsubscript{O} complexes are trap sites and transport occurs via electron hopping [53, 54]. An increase in V\textsubscript{O} concentration gives rise to a percolation process, and once the fraction of hopping sites exceeds a certain threshold, they form a continuous conductive path. The results in figure 3 indicate that the distances between traps for both Zr:TaO\textsubscript{x} and TaO\textsubscript{x} devices are in good agreement with reference values [44, 48, 54, 55]. The shorter distance in the Zr:TaO\textsubscript{x}-based devices explains the increased current density (@0.2 V). It is also important to emphasize that the variability of the devices is directly correlated with the variability in the distance between V\textsubscript{O} or V\textsubscript{O}\textsubscript{S} concentration, indicating that extrinsic doping is a more controllable way of changing the V\textsubscript{O} configuration.

In order to assess the synaptic-like behavior of the devices, the switching dynamics were evaluated using pulsed measurements. We investigated comparative potentiation and depression characteristics using same time interval for LTD and LTD. As shown in figure 4(a), a sequence of 200 pulses for each LTD and LTP process was performed using time intervals of 200 µs and 600 ns, respectively. The LTD voltage amplitudes used were 2.4 V and 3.2 V, and LTP voltages were 2.1 V and 3.0 V for the TaO\textsubscript{x} and Zr:TaO\textsubscript{x} devices, respectively. The values of the applied voltage for the TaO\textsubscript{x} and Zr:TaO\textsubscript{x} devices were different because the voltage for RS operation is higher for the latter, as previously discussed. However, even at a higher voltage amplitude, it was observed that Zr:TaO\textsubscript{x} had more gradual potentiation and depression dynamics in its operation at a similar LRS/HRS ratio, as shown in the normalized pulse switching curves in figures 4(b), (c). CV for both maximum and minimum conductance states are given for nine full LTD/LTP cycles. A non-monotonically increase in conductance can be seen in the first few potentiation pulses in the TaO\textsubscript{x}-based device, and it has been claimed that this is related to a competition between thermal- and field-driven effects on the movement of V\textsubscript{O}\textsubscript{S} and the consequent CF stability [56]. This feature is detrimental for synaptic applications where weight update dynamics should be monotonic. The LTP curve for Zr:TaO\textsubscript{x} devices does not exhibit this problem however. This improvement can be attributed to the additional energy needed to overcome the attractive interaction between V\textsubscript{O}\textsubscript{S} and Zr cations. Although extrinsic doping generates a higher vacancy concentration, the trapping of V\textsubscript{O}\textsubscript{S} by dopant-Vo complexes also leads to a reduction in the overall V\textsubscript{O} kinetics. This tunability of the
switching dynamics through extrinsic doping can be generalized to other p-type dopants, as previously mentioned by Lübben et al [18].

Low C2C and D2D variability has been associated with a more reproducible formation and homogenous distribution of CFs [14, 57]. In this work, the decrease in D2D variability cannot be attributed solely to the higher concentration of VO, but is also related to the interaction between VO$_x$S and dopant species, which promotes VO localization around the dopant cations. This interaction has been well described for several doped oxides, in both experimental and theoretical simulation studies [26–28]. This localization may provide a guiding path for the formation of CFs, resulting in a less random distribution of CFs along the active layer. Moreover, simulation has shown that the presence of dopants reduces the VO formation energy [26, 27]. It is interesting to note that Ambrogio et al [58] have demonstrated that device variability is associated with fluctuations in VO energy barrier for hopping conduction. It can be argued that the presence of the dopant reduces this fluctuation, thus pinning the VO energy to a fixed value and reducing the variability. The VO-dopant interaction is also reflected in the slower VO kinetics and the consequent change in the pulsed switching dynamics.

In this study, we have demonstrated that doping can be used to tune the VO content and consequently the defect trap density and CF configuration in tantalum oxide-based memristor devices. It was shown that Zr doping (extrinsic doping) and control over the partial pressure of oxygen during PLD (intrinsic doping) can promote VO$_x$ formation and lead to forming-free devices. In addition, extrinsic doping proved to be better in terms of controlling the VO$_x$ configuration and content. The unique effect of Zr doping is that it localizes VO$_x$S and consequently reduces the D2D variability. It was also used to tune the pulse switching dynamics for the devices. This enhancement in device parameters in terms of switching variability and dynamics reinforces the importance of exploring vacancy engineering for the tuning of memristor behavior for high-density memory applications and memristor-based artificial synapses.

See the supplementary material for additional information on target preparation, C2C variability, device performance (endurance), hopping model fitted curves, retention measurements and thin film topography using an atomic force microscope.

Acknowledgments

This work was supported by Natural Sciences and Engineering Research Council of Canada (NSERC). Financial support of CNPq (INCT Carbon Nanomaterials), CNEN, Center for Innovation on New Energies-CINE SHELL (ANP) / FAPESP 2017/11937-4, FAPESP (14/50279-4) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil (CAPES)-Finance Code 001, is acknowledged. This research was undertaken thanks in part to funding from the Canada First Research Excellence Fund. We would like to acknowledge Abdelouadoud El Mesoudy and Wellington de Oliveira Avelino from 3IT for their help and insightful discussions regarding device electrical characterizations, and Sonia Blais from Plateforme de Recherche et d’Analyse des Matériaux (PRAM) at the Université de Sherbrooke for her support with XPS measurements. We also acknowledge LCPNano at the Federal University of Minas Gerais (UFMG) for providing access to the clean room facility and for ellipsometry measurements.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

João H Quintino Palhares https://orcid.org/0000-0002-2820-1627
Yann Beilliard https://orcid.org/0000-0003-0311-8840
References

[1] Waser R, Dittmann R, Staikov M, and Szot K 2009 Redox-based resistive switching memories nanoionic mechanisms, prospects, and challenges Adv. Mater. 21 263–62

[2] Strakov D B, Snider G S, Stewart D R, and Williams R S 2008 The missing memristor found Nature 453 80–3

[3] Wang J and Zhuge F 2019 Memristive synapses for brain-inspired computing Adv. Mater. Technol. 4 1–20

[4] Amirsoleimani A, Alibart F, Yon V, Xu J, Pazhouhandeh M R, Eoffley S, Beillard Y, Genov R, and Drouin K 2020 In-memory vector-matrix multiplication in monolithic complementary metal-oxide-semiconductor-memristor integrated circuits: design choices, challenges, and perspectives Adv. Intell. Syst. 2 2000115

[5] Yang J J, Strukov D B, and Stewart D R 2013 Memristive devices for computing Nat. Nanotechnol. 8 13–24

[6] Lee M et al 2011 A fast, high-endurance and scalable nonvolatile memory device made from asymmetric Ta2Ox/…/Ta2O5 bilayer structures Nat. Mater. 10 625–30

[7] Yang J J, Zhang M X, Strachan J P, Miao F, Pickett M D, Kelley R D, Medeiros-Ribeiro G, and Williams R S 2010 High switching endurance in Ta2O5 memristive devices Appl. Phys. Lett. 97 6–9

[8] Torrezan A C, Strachan J P, Medeiros-Ribeiro G, and Williams R S 2011 Sub-nanosecond switching of a tantalum oxide memristor Nanotechnology. 22 485203

[9] Kim K M, Yang J J, Strachan J P, Grafula E M, Ge N, Melendez N D, Li Z, and Williams R S 2016 Voltage divider effect for the improvement of variability and endurance of Ta2O5 memristor Sci Rep. 6 1–6

[10] Guan X, Yu S, and Wong H S P 2012 On the switching parameter variation of metal-oxide RRAM: I. Physical modeling and simulation methodology IEEE Trans. Electron Devices 59 1172–82

[11] Celano U, Goux L, Degraeve R, Fantini A, Richard O, Bender H, Jurczak M, and Vandervorst W 2015 Imaging the three-dimensional conductive channel in filamentary-based oxide resistive switching memory Nano Lett. 15 7970–5

[12] Lee J and Lu W D 2018 On-demand reconfiguration of nanomaterials: when electronics meets ionics Adv. Mater. 30 1–33

[13] Baumeier C et al 2017 Subfilamentary networks cause cycle-to-cycle variability in memristive devices ACS Nano 11 6921–9

[14] Fantini A, Goux L, Degraeve R, Wouters D J, Raghavan N, Kar G, Belmonte A, Chen Y Y, Govoreanu B, and Jurczak M 2013 Intrinsic switching variability in HfO2 RRAM 2013 5th IEEE Int. Mem. Work. IMW 30–3

[15] Joshua Yang J, Miao F, Pickett M D, Ohlberg D A A, Stewart D R, Lau C N, and Williams R S 2009 The mechanism of electroforming of metal oxide memristive switches Nanotechnology 20 215201

[16] Sharma A A, Noman M, Abdelmoula M, Skowronski M, and Bain J A 2014 Electronic instabilities leading to electroformation of binary metal oxide-based resistive switches Adv. Funct. Mater. 24 5522–9

[17] Schmitt R, Spring J, Korobko R, and Rupp J L M 2017 Design of oxygen vacancy configuration for memristive systems ACS Nano 11 8881–91

[18] Lübben M, Cluppers F, Mohr J, von Witzleben M, Breuer U, Waser R, Neumann C, and Valov I 2020 Design of defect-chemical properties and device performance in memristive systems Sci. Adv. eaaz9079

[19] Wu X et al 2011 Chemical insight into origin of forming-free resistive random-access memory devices Appl. Phys. Lett. 99 133504

[20] Skaja K, Andrá M, Rana V, Waser R, Dittmann R, and Baeumer C 2018 Reduction of the forming voltage through tailored oxygen non-stoichiometry in tantalum oxide ReRAM devices Sci. Rep. 8 1–7

[21] Sharath S U, Joseph M J, Vogel S, Hildebrandt E, Schmitt R, Spring J, Korobko R, and Rupp J L M 2017 Design optimization of TaOx memory vector configuration for memristive systems Adv. Intell. Syst. 9 16296–304

[22] Stevens J E, Lohn A J, Decker S A, Doyle B L, Mickel P R, and Marinella M J 2014 Tuning tantalum oxide stoichiometry and oxidation states for optimal memristor performance J. Vac. Sci. Technol. A 32 051403

[23] Stevens J E, Lohn A J, Decker S A, Doyle B L, Mickel P R, and Marinella M J 2014 Reactive sputtering of substoichiometric TaOx for resistive memory applications J. Vac. Sci. Technol. A 32 021501

[24] Lohn A J, Stevens J E, Mickel P R, and Marinella M J 2013 Optimizing TaOx memristor performance and consistency within the reactive sputtering ‘forbidden region’ Appl. Phys. Lett. 103 063502

[25] Jiang H and Stewart D A 2017 Using dopants to tune oxygen vacancy formation in transition metal oxide resistive memory ACS Appl. Mater. Interfaces 9 16296–304

[26] Yildirim H and Puchter R 2019 Extrinsic dopant effects on oxygen vacancy formation energies in ZrO2 with implication for memristive device performance ACS Appl. Electron. Mater. 1 467–77

[27] Misha S H, Tamanna N, Woo J, Lee S, Song J, Park J, Lim S, Park J, and Hwang H 2015 Effect of nitrogen doping on variability of TaOx-RRAM for low-power 3-bit MLC applications ECS Solid State Lett. 4 P25–8

[28] Zhang H, Liu L, Gao B, Qiu Y, Liu X, Lu J, Han R, Kang J, and Yu B 2011 Gd-doping effect on performance of HfO2 based resistive switching memory devices using implantation approach Appl. Phys. Lett. 98 1–4

[29] Yu S, Gao B, Dai H, Sun B, Liu L, Liu X, Han R, Kang J, and Yu B 2010 Improved uniformity of resistive switching behaviors in HfO2 thin films with embedded Al layers Electrochem. Solid-State Lett. 13 36–9

[30] Kasatikov S, Filipova E, Sakhonenkov S, Konashuk A, and Makarova A 2019 Relationship between Ta oxidation state and its local atomic coordination symmetry in a wide range of oxygen nonstoichiometry extent of TaOx J. Phys. Chem. C 123 6849–60

[31] Kröger F and Vink H J 1956 Relations between the chemical properties and device performance in memristive systems Nature 178 609–11

[32] Tuyliev G and Angelov S 1988 The nature of excess oxygen in Co3O4 Appl. Surf. Sci. 32 381–91
Nanotechnology 32 (2021) 405202
J H Quintino Palhares et al

[34] Naem M, Hasanain S K, Kobayashi M, Ishida Y, Fujimori A, Buzby S and Shah S I 2006 Effect of reducing atmosphere on the magnetism of Zn1-xCoxO (0 ≤ x ≤ 0.10) nanoparticles Nanotechnology 17 2675–80

[35] Park S M, Hwang H G, Woo J U, Lee W H, Chae S J and Nahm S 2020 Improvement of conductance modulation linearity in a Cu35+-doped KnBO3 memristor through the increase of the number of oxygen vacancies ACS Appl. Mater. Interfaces 12 1069–77

[36] Kim S, Choi S, Lee J and Lu W D 2014 Tuning resistive switching characteristics of tantalum oxide memristors through Si doping ACS Nano 8 10262–9

[37] Ismail M, Hashmi A, Rana A M and Kim S 2020 Eradicating negative-Set behavior of TiO2-based devices by inserting an oxygen vacancy rich zirconium oxide layer for data storage applications Nanotechnology 31 325201

[38] Sarma D D and Rao C N R 1980 XPES studies of oxides of second- and third-row transition metals including rare earths J. Electron Spectrosc. Relat. Phenom. 20 25–45

[39] Liu J, Liao M, Imura M, Tanaka A, Iwai H and Koide Y 2014 Low on-resistance diamond field effect transistor with high-k ZrO2 as dielectric Sci Rep. 4 6395

[40] Jellison G E and Modine F A 1996 Parameterization of the optical functions of amorphous materials in the interband region Appl. Phys. Lett. 69 371–3

[41] Ferlauto A S, Ferreira G M, Pearce J M, Wronski C R, Jellison G E and Modine F A 1996 Parameterization of the optical functions of amorphous semiconductors from thin film photovoltaics J. Appl. Phys. 92 2424–36

[42] Demiryont H, Sites J R and Geib K 1985 Effects of oxygen content on the optical properties of tantalum oxide films deposited by ion-beam sputtering Appl. Opt. 24 490

[43] Lee J, Lu W D and Kioupakis E 2017 Electronic and optical properties of oxygen vacancies in amorphous Ta2O5 from first principles Nanoscale 9 1120–7

[44] Lee J, Schell W, Zhu X, Kioupakis E and Lu W D 2019 Charge transition of oxygen vacancies during resistive switching in oxide-based RRAM ACS Appl. Mater. Interfaces 11 11579–86

[45] Gritsenko V A, Volodin V A, Perevalov T V, Kruchinin V N, Gerasimova A K, Aliev V S and Prosvirin I P 2018 Nanoscale potential fluctuations in nonstoichiometrics tantalum oxide Nanotechnology 29 425202

[46] Graves C E, Dávila N, Merced-Grafals E J, Lam S T, Strachan J P and Williams R S 2017 Temperature and field-dependent transport measurements in continuously tunable tantalum oxide memristors expose the dominant state variable Appl. Phys. Lett. 110 123501

[47] Zaima S 1990 Conduction mechanism of leakage current in Ta2O5 films on Si prepared by LPCVD J. Electrochem. Soc. 137 2876

[48] Zhang Y, Deng N, Wu H, Yu Z, Zhang J and Qian H 2014 Metallic to hopping conduction transition in Ta2O5-x/TaO2 resistive switching device Appl. Phys. Lett. 105 1–5

[49] Chiu F C 2014 A review on conduction mechanisms in dielectric films Adv. Mater. Sci. Eng. 2014 578168

[50] Fang R, Chen W, Gao L, Yu W and Yu S 2015 Low-temperature characteristics of HfO2 based resistive random access memory IEEE Electron Device Lett. 36 567–9

[51] Perevalov T V, Gritsenko V A, Gerasimova A K, Aliev V S and Prosvirin I A 2018 Electronic structure and charge transport in nonstoichiometric tantalum oxide Nanotechnology 29 264001

[52] Gritsenko V A, Perevalov T V, Voronkovskii V A, Gismatulin A A, Kruchinin V N, Aliev V S, Pastovarov V A, Prosvirin I P and Roizin Y 2018 Charge transport and the nature of traps in oxygen deficient tantalum oxide ACS Appl. Mater. Interfaces 10 3769–75

[53] Gollfarb I and Williams R S 2014 Conduction centers in a Ta2O5–δ Fermi glass Appl. Phys. A 114 287–9

[54] Gollfarb I, Miao F, Yang J J, Yi W, Strachan J P, Zhang M X, Pickett M D, Medeiros-Ribeiro G and Williams R S 2012 Electronic structure and transport measurements of amorphous transition-metal oxides: observation of fermi glass behavior Appl. Phys. A 107 1–11

[55] Wei Z et al 2011 Demonstration of high-density ReRAM ensuring 10-year retention at 85 °C based on a newly developed reliability model 2011 International Electron Devices Meeting pp 31.4.1–4

[56] Wang C, He W, Tong Y and Zhao R 2016 Investigation and manipulation of different analog behaviors of memristor as electronic synapse for neuromorphic applications Sci. Rep. 6 1–9

[57] Prakash A, Deleruyelle D, Song J, Bocquet M and Hwang H 2015 Resistance controllability and variability improvement in a TaO2-based resistive memory for multilevel storage application Appl. Phys. Lett. 106 233104

[58] Ambrogio S, Member S, Balatti S, Member S, Cubeta A, Calderoni A, Ramaswamy N, Member S, Ielmini D and Member S 2014 Statistical fluctuations in HfO2, resistive-switching memory: I. Set/reset variability IEEE Trans. Electron Devices 61 2912–9