

Chapter 2

Synthesis and Characterization of Micro-Thick TiO_2 and HfO_2 Memristors

2.1 Introduction

Even though memristors with nanoscale thickness geometry have been extensively investigated as potential replacements for flash memory technology in simple analog- and digital-computing applications [1–6], on the horizon, a growing number of fundamental studies on nanosized memristors are emerging in sensing applications [7–12]. Although this field is yet to be developed, biological implementation holds the biggest share where implant- or portable-based memristor sensors are nowadays considered highly attractive for reducing the overall operational costs of vital prognostic tools [13, 14]. In bio-sensing, geometry and chemical adaptations of the nanoinsulator component have both been reported essential to establish both the fluidic operation and the label-free recognition (specific or non-specific) of target species with the use of the memristive electrical fingerprint for sensing [10, 15]. Typically, the alteration of the I – V characteristics (e.g., voltage gap or $R_{\text{OFF}}/R_{\text{ON}}$ ratio [11, 12, 16]) in response to an external actuation (i.e., a change in physical or chemical environment) is considered to be the lead approach to exploiting the underlying operational features of memristor devices in sensing applications.

Micro-thick metal-oxide memristive devices are seldom reported in literature. In 2014, Gale et al. [17] presented a 37- μm -thick amorphous TiO_2 memristor while investigating the solgel drop-coating as simple route for general device fabrication. In their study, micro-thick TiO_2 memristors made with aluminum (Al) electrodes exhibited a memristive I – V behavior, while others constructed with both gold (Au) or mixed Al/Au contacts completely failed to electrically switch under external bias. Consequently, the role of the chemically active aluminum electrode material in accomplishing the memristive switching was particularly emphasized. Working devices were shown to be fairly functional within ± 6 V sweep window, giving a maximum $R_{\text{OFF}}/R_{\text{ON}} \ll 10$, without electroforming.

In this chapter, the solgel drop-coating approach reported by Gale et al. [17] is advanced to understand the switching mechanism upon tuning the electrode material, and hence allow the development of micro-thick memristors with suitable I - V properties for potential use in sensing applications. Moreover, micro-thick memristors are fabricated and presented using alternatively the hafnium-oxide (HfO_2) chemistry for the active material. Hafnium-oxide-based nano-thick memristors are getting recently significant attention due to their enhanced electrical properties especially for memory and computing applications [18]. The main focus of the micro-thick HfO_2 devices presented in this chapter is to investigate the switchability of the novel system and to study the effect of changing key parameters such as (i) the electrode material and (ii) the drying temperature during solgel processing on the resistive switching behavior. The results presented in this chapter highlight important structure to performance findings that provide guidance and insights on optimizing the solgel drop-coating of micro-thick memristor devices.

2.2 TiO_2 Micro-Thick Devices

2.2.1 *Materials and Methods*¹

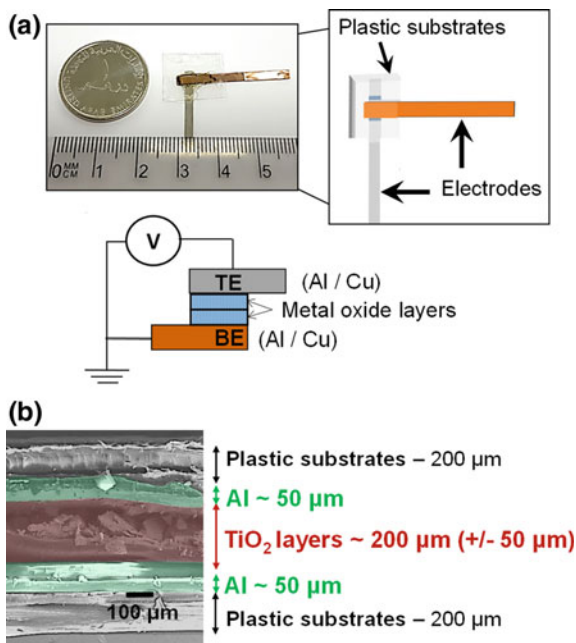
2.2.1.1 Device Synthesis

Drop-coated TiO_2 memristors were advanced based on Gale et al. protocol [19]. All chemical reagents were used as sourced (Sigma Aldrich, St. Louis, USA). Typically, 10 ml 2-methoxyethanol (99.9%) as solvent, 2.5 ml titanium (IV) isopropoxide (99.999%) as titania precursor, and 1.0 ml ethanolamine (>99%) as gelation agent and amine additive were introduced into a predried three-necked flask, under atmospheric room temperature conditions. The mixture was subjected to constant stirring under dried nitrogen flow and was progressively heated to reflux at 80 °C for 1 h, followed by 120 °C for 30 min. The reaction container was subsequently allowed to cool to room temperature before adding 10 ml dried methanol (HPLC-grade, >99.9%) and turning off the nitrogen flow. The obtained solution was stored in a tight polypropylene bottle to slow down side polycondensation reactions induced by atmospheric humidity (average relative value ~ 50%) and to further minimize the adsorption of metal-oxide precursors onto the inner walls of the container. Differently, the final sol mixture (containing approximately 0.4 mmol-Ti/g solution) was applied for coating without further purification or dilution. Drop-coated memristor prototypes were fabricated with low-cost materials purchased from local bookstore and electronic shops. Typically, two layers of flexible polyethylene sheets (individual film thickness = 100 μm) were utilized as plastic substrate for each electrode. Al and Cu foil tapes (metal

¹Device synthesis and characterization were performed at Khalifa University.

Fig. 2.1 Physical characteristics of a micro-thick TiO₂ memristor device fabricated in this work.

a Photograph of the device next to 1 UAE Dirham coin, and a schematic illustration showing the orthogonally stacked electrodes, supported onto plastic substrates. **b** SEM photograph of a physical Al/Al memristor device, imaged in a cross-sectional view under secondary electron mode (accelerating voltage, 5 kV; magnification, $\times 60$; working distance, 12 mm); *color code* is added for visual aids



thickness $\leq 50 \mu\text{m}$; Kunshan Meile Aluminum foil printing Co., Ltd., China) were applied as electrode materials. Typically, two narrow strips of Al or Cu foil tape were separately mounted on precut plastic substrates. Then, $4.0 \mu\text{l}$ of metal-oxide precursor solution was dropped onto each metal electrode. The drop-coating procedure was repeated five times with an interval evaporation-drying time of 10 min between applications (The overall amount of precursor dropped was roughly equivalent to $7.2 \mu\text{mol}$ of Ti.). The coating was left to dry overnight for 15 h under atmospheric room temperature conditions, giving an amorphous TiO₂ phase ($\alpha\text{-TiO}_2$) [17, 20]. To construct a device, a strong fast-acting ethyl cyanoacrylate adhesive (Alteco super glue, Japan) was used to stack the drop-coated electrodes orthogonally in a crossbar MIM geometry (Fig. 2.1a), making an active area of about $2 \text{ mm} \times 2 \text{ mm}$.

2.2.1.2 Device Characterization

Scanning electron microscopy (SEM) imaging of fabricated devices (Fig. 2.1b) was carried out with JSM-7610F Schottky field-emission microscope (JEOL LTD., Japan). Standardless quantitative X-ray microanalysis was performed via energy dispersive spectroscopy using an X-ray detector (Oxford Instruments, United Kingdom) that was attached to SEM equipment. The semi-quantitative energy dispersive X-ray (EDX) measurements were estimated from five iterations using the ZAF matrix correction approach (i.e., considering atomic number, X-ray absorption

and X-ray fluorescence corrections). Cross sections were cut with a sharp chisel blade. Prior to analysis, all specimens were sputtered-coated under air–vacuum conditions with approximately 6 nm of platinum (autofine coater, JEOL LTD., Japan). As shown in Fig. 2.1b, drop-coated devices possess an average metal-oxide thickness of about 200 μm ($\pm 50 \mu\text{m}$; $n = 5$ devices), which is approximately 6 times greater than that reported by Gale et al. [17].

A Keithley 4200-SCS Parameter Analyzer (Tektronix) was used in the electrical measurement of the I – V characteristics of the fabricated devices, using a voltage sweep mode. A voltage pulse mode was also adopted for (i) electroforming (when required), (ii) endurance testing, and for (iii) holding the desired bias during irradiation studies. Memristors made with Al/Al electrodes were tested without prior electroforming, while hybrid Al/Cu systems were subjected to -5 V bias, applied onto the Al electrode for approximately 30 s. The compliance current was generally SET to its highest instrumental level (100 mA) to examine the maximum $R_{\text{OFF}}/R_{\text{ON}}$ ratio obtained by a device. In all characterization results, the voltage step and pulse duration are fixed to 0.05 V and 0.1 s, respectively. Thus, the switching speeds of the devices can be directly indicated from the switching voltage. Devices that exhibit less switching voltage indicate faster switching speed.

2.2.2 Results and Discussions

To understand and optimize the resistive switching properties of micro-thick TiO_2 memristors presented here, several devices were investigated based on different combinations of Al and Cu electrodes.

2.2.2.1 Micro-Thick TiO_2 Memristors with Al/Al Electrodes

A batch of drop-coated Al/a- TiO_2 /Al memristors (devices D1, $n > 10$) was assessed in terms of I – V curve characteristics. As depicted in Fig. 2.2a example, a microscale Al/a- TiO_2 /Al memristors generally exhibit a pinched hysteresis I – V curve with clockwise loop regardless of the voltage polarity. The bidirectional turn-on behavior is observed below 1 V threshold magnitude. The current measured on a pristine device originally subjected to an initial positive voltage sweep reaches about 30 μA at +2.5 V. In contrast to a classic unipolar switching mode, the device does not retain an ON state, and it returns to higher resistance state than that initially observed. On flipping the sweep polarity, the device is gradually turned on but eventually retains again a higher resistance state under the application of the voltage sweep.

To understand the switching characteristics of such structure, a pristine device D1 was tested under repeated voltage sweeps from 0 to +2.5 V, as illustrated in Fig. 2.2b. Following to the first sweep (#1'), the clockwise I – V loop recorded with the device gradually declines toward lower current values and becomes further

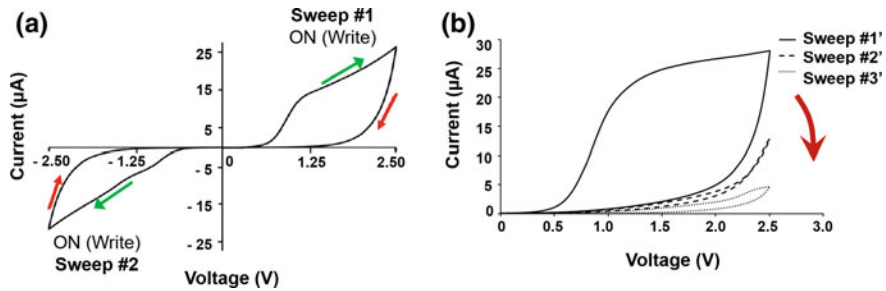


Fig. 2.2 A typical I - V curve of a device D1 (i.e., Al/a-TiO₂/Al) in response to **a** initial positive sweep from 0 $\rightarrow$ +2.5 V followed by a negative sweep from 0 $\rightarrow$ -2.5 V, and to **b** successively repeated sweeps #1' $\rightarrow$ #2' $\rightarrow$ #3' in the forward bias, from 0 $\rightarrow$ +2.5 V. Devices were tested without prior electroforming

pinched (sweeps #2' and #3'), which indicates a progressive buildup of internal resistance. The I - V results presented in Fig. 2.3, which were obtained for eight consecutively increasing voltage sweep magnitudes, additionally support this theory. On every new sweep, a higher threshold voltage was always found required to achieve an equal or higher flux to that recorded in the preceding run. The cumulative internal resistance and increasing turn-on threshold voltage observed both suggest that a long-term interfacial chemical change is induced within the device upon electrical operation. For typical microscale memristors, Gale et al. [17] previously demonstrated the presence of Al₂O₃ species on the surface of aluminum electrodes, using X-ray photoelectron spectroscopy, suggesting as well a critical role of these species in the switching mechanism of Al/a-TiO₂/Al memristors. The experimentally recorded device limitations in both Figs. 2.2b and 2.3 results could

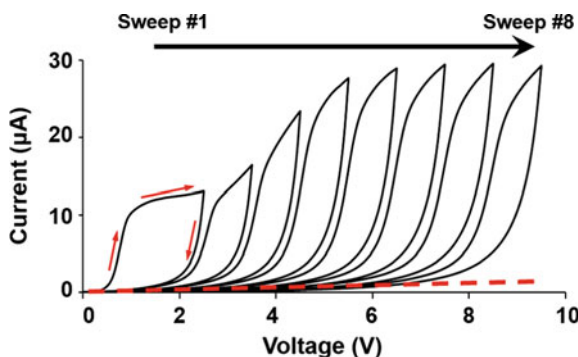


Fig. 2.3 Typical I - V curves measured for a D1 device (i.e., Al/a-TiO₂/Al) in response to successively increasing voltage sweep windows ranging from 0 to a maximum bias defined between +2.5 V and +9.5 V. Compliance current = 100 mA. The device was tested without prior electroforming. Beyond 5 V, the maximum flowing current reaches saturation around 30 μ A, a value which is about three orders of magnitude below the specified compliance range (100 mA)

hence be explained by a dynamic formation of a passivation layer of aluminum oxide species, increasing the Schottky barrier energy at both a- TiO_2/Al junctions as the metal/insulator interface is chemically altered after successive voltage sweeps.

To elucidate how the passivation layer is electrically generated in microscale $\text{Al/a-TiO}_2/\text{Al}$ memristors (devices D1), a valence-change switching mechanism involving the migration of oxygen-ions and subsequent creation of conductive nanofilamentary vacancy channels is assumed [21, 22–24]. The intrinsic electrical conductivity of the solgel-derived a- TiO_2 is correlated with the presence of ionic point defects (e.g., interstitial Ti^{3+} and oxygen vacancies), which occur due to high carbon contamination under atmospheric room temperature processing conditions usually leaving behind unreacted alkoxide moieties [25, 23, 24, 26]. In this work, semi-quantitative X-ray microanalysis (EDX) of the inner surface of pristine drop-coated Al electrodes (at $\sim 1\text{--}2\ \mu\text{m}$ penetration depth) reveals the presence of non-stoichiometric AlO_x phase, where $x \sim 0.26 (\pm 0.03)$. The substoichiometric AlO_x layer ($0 < x \ll 1.5$) depicted in Fig. 2.4 (stage 1) would occur beyond atmospheric corrosion of aluminum surface due to further oxidation induced by the alkaline solgel ethanolamine additive. Consequently, an oxygen-rich and oxygen-deficient region exists at the Al/a-TiO_2 interface and in the bulk a- TiO_2 layer, respectively. Considering the strong oxygen affinity of aluminum (as inferred from the high heat of formation of Al_2O_3 compared to that of TiO_2 [27]), progressive diffusion of interfacial oxide ions can occur onto Al surface, increasing the population of oxidized species until thermodynamic equilibrium is achieved.

Considering a chemically closed memristor system, when a relatively small negative bias is applied onto one of the Al contacts (Fig. 2.4-stage 2), lattice oxygen atoms existing within the a- $\text{TiO}_2/\text{AlO}_x$ interface drift away from the negatively charge electrode via Joule heating and field transport, leaving behind oxygen vacancies. When enough extended vacancy defects form initial conductive filaments, a switch-on current may be generated (see Fig. 2.3 sweep#1). At the

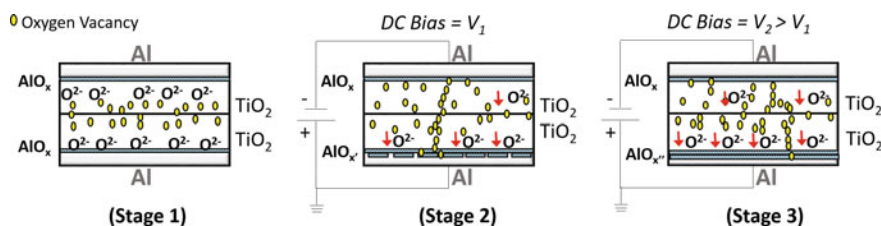


Fig. 2.4 A schematic representation of the electrical shielding phenomenon occurring in microscale $\text{Al/a-TiO}_2/\text{Al}$ memristors, under applied bias field, assuming a valence-change switching mechanism (VCM) involving the formation of conducting filaments via oxygen vacancies. A single device is sketched as a cross section of stacked TiO_2 drop-coated Al electrodes: (stage 1) pristine stage (no electroforming required); (stage 2) after applying initial voltage sweep of small magnitude; (stage 3) after applying consecutive voltage sweeps of similar or increasing magnitude. Dimensions are for illustration purposes. Red arrows indicate the movement of oxygen species by field-induced defect formation. AlO_x refers to aluminum oxide species, where $0 < x$ (stage 1) $< x'$ (stage 2) $< x''$ (stage 3) ≤ 1.5 (stoichiometric Al_2O_3)

same time, other oxide anions accumulate near the positively charged aluminum electrode, increasing gradually the population of AlO_x species owing to enhanced diffusion equilibrium. Jeong et al. [25, [28] previously evidenced similar interfacial microscopic changes by investigating the SET and RESET processes in nanoscale Al/a-TiO₂/Al memristors, using high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) techniques. In microscale devices, the passivation layer progressively developing under the applied bias (Fig. 2.4 stage 2) creates a screening effect for weaker conductive filaments, which causes the overall device resistance to raise as seen from the reduced passing currents in Fig. 2.2b (sweeps #2' and 3'). To maintain the level of flowing current (Fig. 2.3, sweeps# 2–8), the bias magnitude needs to be increased (Fig. 2.4 stage 3), to strengthen and force a number of the existing filaments through the passivation layer. Reversing the bias polarity from stage 2 or 3 would produce similar cascade diffusion phenomena onto the opposite electrode, without promoting electrical breakdown of the earlier-formed passivation. Indeed, the comparative literature data in Table 2.1 show that the unipolar and increasingly resistive switch-on property of Al/a-TiO₂/Al memristors is only seen with micro-sized TiO₂ thicknesses, as opposed to nanoscale geometries giving the bipolar turn-on/turn-off behavior.

Table 2.1 Switching behavior of Al/a-TiO₂/Al memristors studied in this work versus literature data

Device reference	Electrodes (deposition method)	Active material (TiO ₂)		Switching behavior
		Deposition method	Thickness	
D1 (This work)	Al/Al (tape)	Solgel drop-coating	~ 200 μm	Unusual unipolar (switch-on under voltage bias followed by intrinsic switch-off after a period of operation)
[17]	Al/Al (tape)	Solgel drop-coating	~ 37 μm	Unusual unipolar (mechanism not reported but results are comparable with that of devices D1 developed in this work)
	Al/Al (RF-sputtering)			
[43]	Al/Al (thermal evaporation)	Solgel spin-coating	~ 60 nm	Bipolar
[19, 44, 45]	Al/Al (RF-sputtering)	Solgel spin-coating	~ 44 nm	Bipolar
[46]	Al/Al (RF-sputtering)	Plasma-enhanced atomic layer deposition	~ 14 nm	Bipolar
[25, 28, 29]	A/Al (thermal evaporation)	Plasma-enhanced atomic layer deposition	~ 13 nm	Bipolar

Using isothermal I - V mapping studies, Jeon et al. [29] found that the bipolar resistance switching behavior in nano-Al/a- TiO_2 /Al memristors is governed by an interplay between a bulk trap-controlled space-charge-limited current (SCLC) and an Al/ TiO_2 interface-controlled Schottky emission, involving oxygen-ion diffusion. According to our study, back and forth drifting or diffusion of oxygen and vacancy species from Al/a- TiO_2 /Al junctions could be more facilitated through nano- TiO_2 thicknesses acting as smaller oxygen source as opposed to micro-metal-oxide layers. In conclusion, the resistive switching mechanism in micro-thick Al/a- TiO_2 /Al devices can be considered highly dominated, and rather quenched by the dynamic interfacial passivation of the aluminum electrodes. Failure to reconstitute the memristive functionality of these devices, in addition to their very limited $R_{\text{OFF}}/R_{\text{ON}}$ performance (~ 2.5), was both regarded as major disadvantages for implementing micro-thick oxide-based Al/Al memristors in sensing applications.

2.2.2.2 Micro-Thick TiO_2 Memristors with Al and Cu Electrodes

To improve the electrical performance of micro-thick a- TiO_2 memristors, substitution of aluminum with a higher work-function electrode, such as copper, was explored ($\phi_{\text{Cu}} \sim 5.1$ eV; $\phi_{\text{Al}} \sim 4.26$ eV [30]), as an approach to address the irreversible passivation problems mentioned. Copper is a relatively cheap noble metal with low affinity for oxygen chemisorption as inferred from the positive standard heat of formation of copper oxide species [27]. Compared with the yellow aluminum coating (Fig. 2.5a), the TiO_2 layer deposited onto copper surface had a blue/black appearance (Fig. 2.5b), inferring that a side-corrosion reaction had taken place during the gelation step. Supporting EDX elemental analysis of the coatings, shown in Fig. 2.5c, confirms the presence of copper element in the bulk blue/black TiO_2 phase generated on copper, with a loading estimated about 1:0.27 as Ti/Cu mol ratio. The corrosion was ascribed to the reaction between the alkaline ethanolamine agent from the coating solution with copper, causing substantial release of Cu(I/II) cations. The blue/black color resulting from room temperature drying indicates that these ions occurred in the bulk TiO_2 phase as in the form of copper (II)-ethanolamine complexes [31] and copper oxide species ($\text{Cu}_2\text{O}/\text{CuO}$) [32]. In this study, the electrical properties of a series of micro-thick memristors configured with either Al/Cu (D2, D2', and D2'' series) or Cu/Cu stacks (D3) were explored and compared to the original Al/Al structure (devices D1), as summarized in Table 2.2.

Al/Cu stacks containing a Cu(I/II)-doped TiO_2 layer (D2 memristors) were originally found in OFF resistance state (>10 M Ω) after fabrication, which could have been due to enhanced absorption of atmospheric oxygen upon corrosion of the copper surface. To initiate switching events in these devices, a -5 V bias was applied onto the aluminum electrode for approximately 30 s. After electroforming, bipolar switching characteristics with “RESET” and “SET” operations could be observed within ± 1 V window (Fig. 2.6a). The $R_{\text{OFF}}/R_{\text{ON}}$ value recorded at the

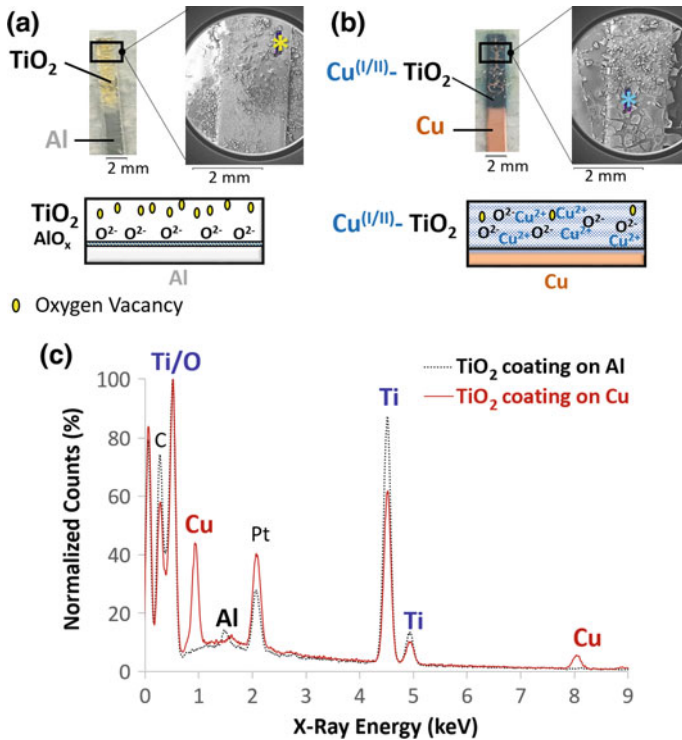


Fig. 2.5 Optical and SEM photographs of the titanium dioxide coating on **a** aluminum and **b** copper surface with suggested schematic representation. **c** Comparative EDX analysis results of the two TiO₂ coatings (probed areas are marked with *asterisks* on the SEM photographs of figures (a, b). SEM-EDX conditions: accelerating voltage, 16 kV; magnification, $\times 25$; EDX dwell time, 120 s

maximum instrumental compliance (100 mA) is relatively very high, about 10^6 , which is similar in magnitude to that often reported for nanoscale memristive devices [2]. The high flowing current (limited by the instrumental compliance) indicates the creation of highly branched conductive pathways during electroforming. The basic endurance results showing the ON/OFF current levels maintained for about 15 consecutive switching cycles, in Fig. 2.6b, demonstrate some level of electrical robustness, inferring particularly a good viability of the conductive pathways created by the forming step.

To explain the improved performance of these memristors and gain insight into the working mechanism of these memristors, cross-sectional EDX elemental analysis of a pristine versus a used stack was compared (see Fig. 2.7a, b). The elemental line-scan map of the electrically cycled device revealed a higher population of oxygen species toward the aluminum side, substantiating a history of oxygen-ion diffusion that could have occurred during electroforming and the subsequent ON/OFF switching tests. The evidenced oxygen-ion migration in D2

Table 2.2 Summary of the electrical properties of devices studied in this work (minimum tested = 3)

Device	Electrodes	Coating source (resulting switching layers) ^a	Resistance behavior ^b
D1	Al/Al	Precursor solution (TiO ₂ /TiO ₂)	Unipolar switching with dynamically increasing intrinsic resistance ($R_{\text{OFF}}/R_{\text{ON}} < 10$ and depends on voltage)
D2	Al/Cu	Precursor solution (TiO ₂ /Cu ^(I/II) -TiO ₂)	Bipolar switching at low voltage ($R_{\text{OFF}}/R_{\text{ON}} \sim 10^6$, at -1 V and 100 mA cc)
D2'	Al/Cu	Precursor solution w/o ethanolamine additive (TiO ₂ /TiO ₂)	No switching event (highly resistive stack)
D2''	Al/Cu	Pure ethanolamine on Cu (CuO _x)	Ohmic current regime (constant resistance at room temperature)
D3	Cu/Cu	Precursor solution (Cu ^(I/II) -TiO ₂ /Cu ^(I/II) -TiO ₂)	Single switching event ($R_{\text{OFF}}/R_{\text{ON}} \sim 10^3$, at -1 V and 100 mA cc)

^aAll switching layers are carbon-contaminated (see the characteristic EDX-peak of carbon in Fig. 2.5c)

^bDevices D1 were not electroformed due to dynamically increasing R_{ON} resistance. All other device series were first tested against a ± 1 V sweep, before -5 V electroforming was applied. D2'' displayed the ohmic contact character without pre-electroforming

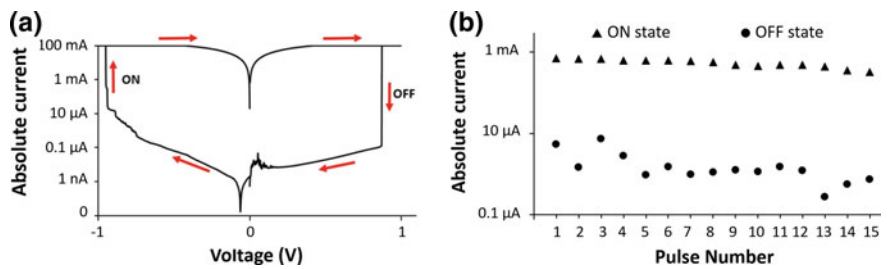


Fig. 2.6 Electrical characteristics of fabricated Al/TiO₂/Cu devices (D2). **a** I - V curve characteristic recorded in response to ± 1 V sweeps. For the “SET” operation, a negative voltage sweep is applied onto aluminum electrode, while the copper electrode is grounded; and for the “RESET” process, aluminum is subjected to reverse polarity sweep. The compliance current is fixed at maximum value of 100 mA to identify the maximum OFF/ON resistance ratio of the memristor. **b** ON/OFF endurance test of D2 device for fifteen consecutive pulses of ± 1 V (pulse width = 30 s), at low compliance current of 1 mA

junctions can be explained by a classic valence-change resistive switching mechanism (VCM) [1], similar to described for the Al/Al memristor (D1). However, the resettable I - V characteristics of the D2 stack, which are clearly different from the write-once behavior demonstrated for Al/Al memristors, suggest a substantial facilitating role of the mixed (Cu (I/II)-TiO₂)/copper interface. To elucidate such implication, few variations in the fabrication were explored, as summarized in

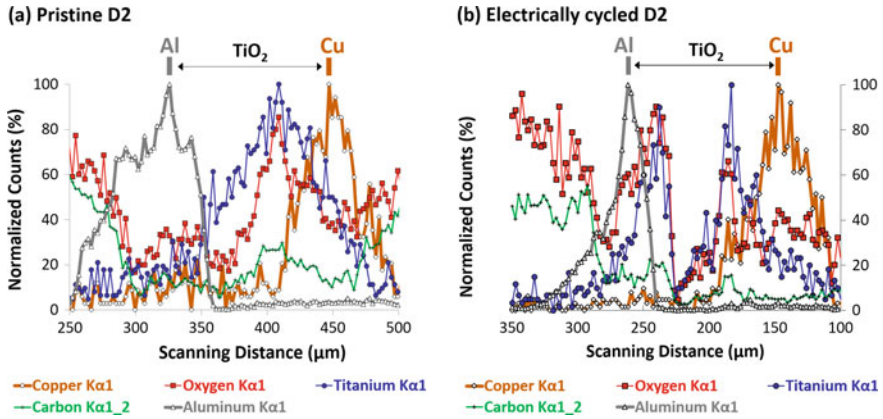


Fig. 2.7 Comparative EDX elemental line-scan mapping of a cross-sectional cut of micro-thick Al/Cu–TiO₂ memristors (D2 series) **a** pristine device, **b** working device with a history of electroforming (-5 V for 30 s applied on Al electrode) and multiple ± 1 V ON/OFF switching cycles. Experimental conditions are similar to Fig. 2.5c (accelerating voltage, 16 kV; magnification, $\times 25$; EDX dwell time, 120 s). Each EDX curve is normalized to the maximum response of the corresponding element. The x-scale in **(b)** is flipped for visual aids

Table 2.2. Al/Cu–D2’ series, prepared in absence of the corrosive ethanolamine agent in the coating solution, were found highly resistive and incapable to switch-on even when longer pre-electroforming durations were applied at -5 V (e.g., 7 min compared with 30 s used for D2). In absence of ethanolamine, the chemistry of both TiO₂ junctions in Al/Cu–D2’ devices can be considered as close to that of Al/Al memristors (D1). Although Al/Al stacks were found to possess some switching characteristics due to the implication of the aluminum electrode, the inability of Al/Cu–D2’ devices to pass the current suggests an impeding Schottky barrier formed at the TiO₂–Cu interface due to lower oxygen affinity of copper electrode. Consequently, having an inert electrode in conjunction with Al does not improve the memristive switching properties of micro-thick TiO₂ memristors, in agreement with previous Gale et al. [17] observations with Au contacts.

Oppositely, Al/Cu–D2’’ memristors, made with pure ethanolamine as sole coating source (i.e., without the rectifying TiO₂ phase), displayed an ohmic conductor character, which can be ascribed to faster electronic transport properties of copper oxides compared with titania (e.g., the bandgap energy ranges between 1.6 and 2.3 eV in Cu₂O and CuO, respectively [33], while it is reported above 3.4 eV in amorphous TiO₂ [34]).

Furthermore, when both TiO₂ junctions were doped with copper ions, as in Cu/Cu–D3 series, a single and irreversible switch-on event was observed at -1 V, after which the “ON” state was found to be maintained as if short circuit was in situ created. The corroded copper surface along with the copper doping found in TiO₂ can create a favorable heterojunction, facilitating charge transfer at the interface

between the copper metal and the semiconductor coating [35]. In addition to that, under a voltage sweep of -1 V, copper (I/II) ions existing at the vicinity of the negatively charged Cu electrode can be reduced into Cu^0 metallic species due to lower characteristic standard reduction potential (i.e., <1 V [36]). These copper atoms act in turn as localized negatively charged metallic contacts, promoting thus a cascade of reduction reactions of copper ions until growing metallic filaments form a closed contact with the grounded electrode. As sketched in Fig. 2.8a, the formation of shorted paths in Cu/Cu stacks can be explained via the electrochemical metallization (ECM) process, in agreement with observations made by Guan et al. [37] for copper-doped ZrO_2 nanomemristors with Cu/Pt electrodes. Based on the analysis of the various configurations of micro-thick TiO_2 memristors reported in Table 2.2, an associative ECM switching mechanism occurring within the copper-doped TiO_2 junction layer is proposed to justify the reversible turn-on/turn-off behavior of the optimal Al/Cu–D2 memristors. The SET operation of D2 devices illustrated in Fig. 2.8b can be concluded as follows: When the Al electrode is subjected to a negative bias during a switch-on operation, oxygen-ions drift away into the bulk amorphous TiO_2 junction, leaving behind conductive vacancy channels, which act as carriers according to the VCM mechanism. While a same continuing mechanism can take place within the copper-doped TiO_2 layer, branched conductive copper filaments (possibly initiated through the electroforming step) can additionally grow inward toward the grounded copper electrode via a synergistic ECM process. These strong metallic filaments may explain the large amplitude of sustainable turn-on current through the device, as reported in Fig. 2.6a results. Observation of conducting filament growth in resistive memories is reported in [38] using transmission electron microscopy (TEM) image, which exhibits physical changes in the active layer occur during the forming, the SET and RESET operations. For the RESET process (upon reversing the voltage polarity), conductive channels have been extensively suggested to be broken by electric field effects and localized Joule heating, with the former route being more prominent in

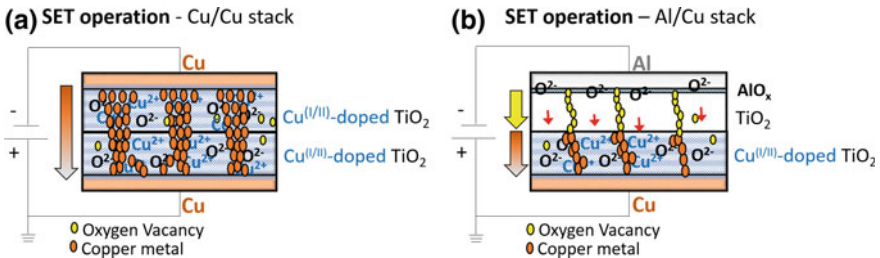


Fig. 2.8 A sketch of a switch-on operation in micro-thick TiO_2 memristors based on **a** drop-coated Cu/Cu (or D3) and **b** drop-coated Al/Cu (or D2). The *orange arrow* indicates the speculated direction of metallic filament growth from the negative cathode to the grounded anode. The *yellow arrow* illustrates the suggested direction for oxygen-vacancy migration within the un-doped TiO_2 phase, when the negative switch-on bias is applied onto Al electrode

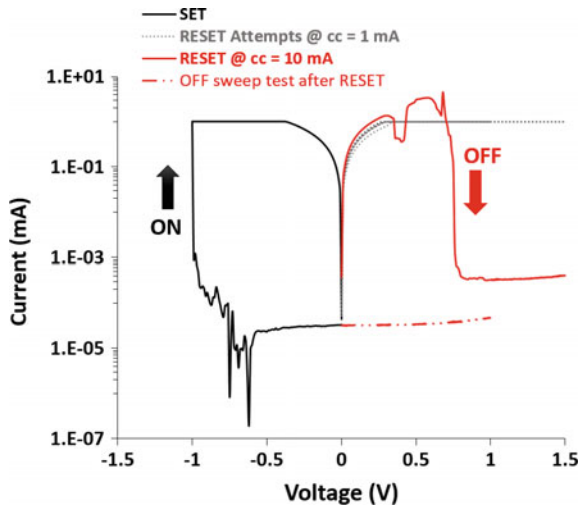


Fig. 2.9 Bipolar RESET switching in Al/Cu–D2 memristors within ± 1 V window (bias was applied onto Al electrode while Cu was kept grounded). Following to initial SET operation in the negative polarity mode (*plain black hysteresis on left*), four consecutive RESET attempts were applied in the positive mode at $cc = 1$ mA (*dotted gray lines near compliance on right*). After these unsuccessful RESET attempts, the positive sweep was repeated at higher compliance value of 10 mA (*plain red curve on the right*). Finally, the turn-off current level was checked with an additional OFF sweep test after successful RESET (*dashed red baseline on the left*)

bipolar switches [1]. Given the microscopic scale Al/Cu–D2 memristors investigated in this work, Joule heating could additionally play a substantial role in the RESET behavior beyond the electric field effect that ascertains the bipolar nature. To identify the role of internal Joule heating in controlling the rupture of conductive channels in the devices, a deeper exploration of the current effect (Fig. 2.9) was conducted at 100 times lower compliance than that reported in Fig. 2.6. According to Fig. 2.9 results, the bipolar SET and RESET cycle could not be well fully achieved at 1 mA of compliance. Following to the initial negative turn-on process, multiple backward sweeps to +1 V failed to switch-off the device, as observed through the gray dotted lines at 1 mA compliance level. When the compliance level was increased 10-fold, under same voltage sweep conditions (i.e., equal electric field magnitude), a small current jump was recorded above 1 mA, at about +0.6 V, after which a sharp drop in current was observed. A repeated sweep in the same mode confirmed that switch-off occurred to an off resistance state equivalent to that observed before initial turn-on. The apex observed gives evidence of internal Joule heating, while the following sudden current downturn can be associated with thermal fusion or breakdown of conductive filaments [39] [40]. The Al/TiO₂/Cu–D1 devices developed in this section are explored and assessed for radiation sensing, and the results are presented in Chap. 5.

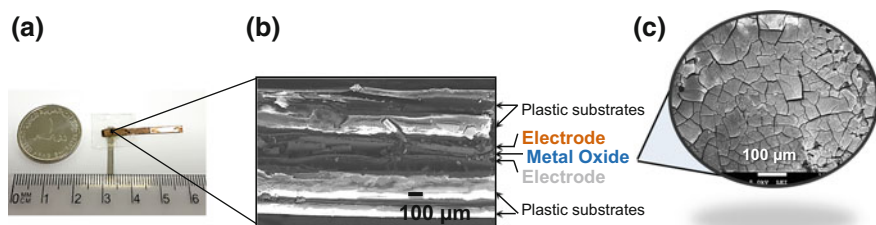


Fig.2.10 Physical characteristics of a micro-thick HfO_2 devices fabricated in this work. **a** Photograph of the device next to 1 UAE Dirham coin, and a schematic illustration showing the orthogonally stacked electrodes, supported onto plastic substrates. **b** SEM photographs of an example $\text{Cu}/\text{HfO}_{2-x}/\text{Al}$ stack in cross-sectional view and **c** SEM photograph of dried oxide layer on Cu electrode. SEM conditions: secondary electron imaging mode at 5 kV, magnification $\times 70$, working distance WD = 10 mm

2.3 HfO_2 Micro-Thick Devices

2.3.1 Materials and Methods (See Footnote 1)

2.3.1.1 Device Synthesis

Microscale HfO_{2-x} memristors were prepared through solgel methodology. Typically 15 ml dry isopropanol (99.9%), 0.8 g hafnium (IV) isopropoxide (99.9%), and 1.0 ml ethanolamine ($>99\%$) were introduced at room temperature into a predried three-necked flask. The mixture was constantly stirred under dried nitrogen flow and was gradually heated to reflux at 110°C for 2 h. The container was allowed to cool to room temperature upon which the nitrogen flow was stopped. The final solution containing about 0.14 mmol of Hf (IV)/1 g solution was applied without further purification. Drop-coated memristor prototypes were constructed with polyethylene sheets (thickness = $100\ \mu\text{m}$) as plastic substrates and various metal foil tapes comprising of aluminum, copper, titanium, or palladium as electrode materials (metal thickness ranging from 50 to $125\ \mu\text{m}$). Typically, two narrow strips of metal foil ($\sim 2\ \text{mm}$ in width) were separately glued on precut plastic substrates. Then, $4.0\ \mu\text{l}$ of hafnium-oxide precursor solution was dropped on each metal electrode, five times. An evaporation-drying time of 15 min was applied between the coatings. The coating was left to dry for 3 h at 60 or 80°C in oven, at atmospheric pressure. Finally, the two coated electrodes were orthogonally taped in $2\ \text{mm} \times 2\ \text{mm}$ active metal-insulator-metal configuration (see Fig. 2.10)

2.3.1.2 Electrical Characterization

A Keithley 4200-SCS Parameter Analyzer was used for I - V measurements. No prior electroforming was necessary to activate the resistive switching in the devices.

Five as-fabricated devices from each system were electrically tested in voltage sweep mode with the following cycling applied subsequently: ± 5 ; ± 7 , and ± 10 V. In all experiments, the bias step was fixed at 0.05 V, and the hold-up time was equal to 0.1 s. Depending on the arrangement of metals used for the electrodes, the voltage was supplied to one of the contacts while the other was kept grounded. Furthermore, the compliance current was fixed at 1 mA.

2.3.2 Results and Discussions

As the Al/Cu electrodes combination presented in Sect. 2.2 showed promising electrical characteristics especially for sensing applications, it was of first priority to investigate the switchability of the HfO₂ system starting from the same electrodes combination. Following the same procedure explained in Sect. 2.3.1, which is aligned with the steps followed for preparing the TiO₂ devices, the synthesized Al/HfO₂/Cu memristors exhibited low resistivity and showed ohmic I - V characteristics. One way to increase the resistivity of the active layer and consequently improve its switchability is to increase its thickness, which requires an increased number of the drops used to coat the metal electrodes. Thus, further device optimization is required to improve the switching characteristics of the Al/HfO₂/Cu system.

As mentioned earlier, the focus of this section is mainly placed on assessing the switching behavior of the memristor devices prepared via the drop-coating technique as a function of key parameters such as (i) electrode material (including titanium, aluminum, copper, and palladium) and (ii) the post-coating drying temperature (60 and 80 °C). This can give insights to important factors to be considered during device fabrication.

2.3.2.1 Effect of Electrode Material

The I - V curves of memristors made with symmetric HfO₂/metal stacks, dried at 60 °C, are shown in Fig. 2.11. It can be seen that devices based on either Cu or Ti electrodes (Fig. 2.11a, b) showed classic ohmic characteristics, giving a linear relationship between current and voltage ($V = IR$) regardless of the bias window tested. However, Al- and Pd-based systems (Fig. 2.11c, d) demonstrated memristive behavior by showing a “hysteresis” with different OFF and ON resistance states, for every read voltage in a loop. The orientation of the hysteresis loop as illustrated from the red arrows in both positive and negative half-cycles (i.e., $0 \rightarrow +V \rightarrow 0$ or $0 \rightarrow -V \rightarrow 0$) shows a clockwise direction, which means that these systems can be equally switched off to lower current in both polarities and hence possess a unipolar switching behavior regardless of the bias polarity applied. Figure 2.11c, d results particularly show that the shape of hysteresis is dependent on the electrode material. For example, Al/Al system displays a pinched hysteresis

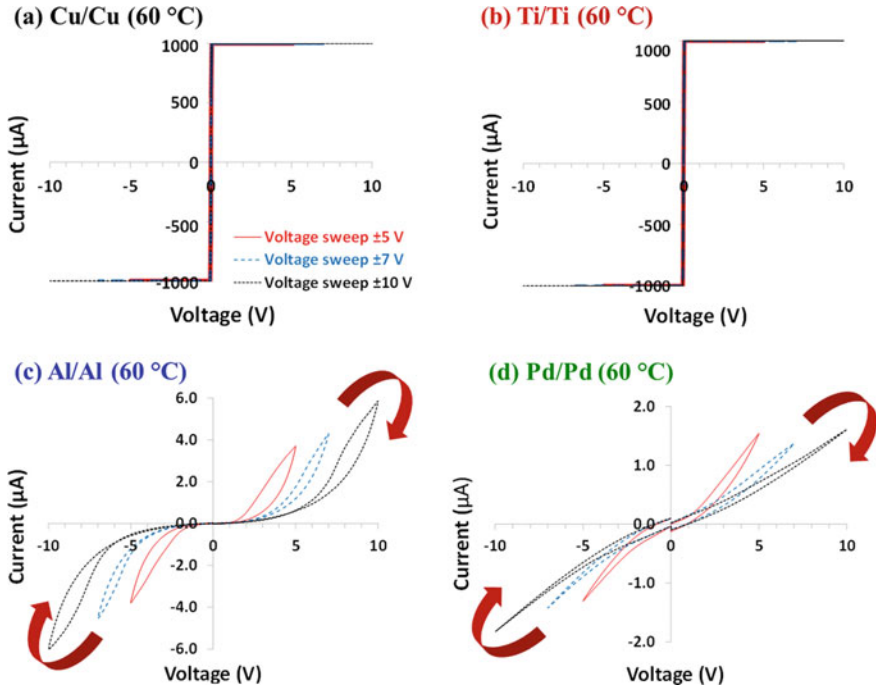


Fig. 2.11 The effect of electrode material on I - V characteristic of devices constructed with symmetric HfO_{2-x} /metal stacks dried at 60 °C. Memristors with **a** Cu/Cu and **b** Ti/Ti electrodes exhibited ohmic contacts while that made with **c** Al/Al and **d** Pd/Pd electrodes showed hysteresis. Voltage sweeps of ± 5 V, ± 7 V, and ± 10 V were, respectively, applied in that order

behavior, as depicted by the zero current at zero applied voltage. The turn-off voltage in this system is found to dynamically increase with the sweep magnitude, reflecting progressive interfacial modification and increase in the resistance of Al-oxide Schottky contacts, similar to what is exhibited by Al/ TiO_2 /Al devices presented in Sect. 2.2.

For Pd/Pd system, a non-pinned hysteresis with nonzero crossing current is recorded in both modes at 0 V bias. This nonzero current indicates an inherent battery storage capacity as a typical fingerprint of residual mem-capacitive behavior. The hysteresis of the Pd/Pd memristor is seen to drop to lower current values in both polarity modes, when the sweep magnitude is gradually increased from ± 5 to ± 7 and then ± 10 V (Fig. 2.11d) curves: plain red, dashed blue, and dotted black, respectively. The increase in the turn-off voltage indicates an increase in the resistance of Pd-oxide Schottky contacts. The maximum flowing current range in Pd/Pd memristors is almost half than that achieved with Al/Al system. However, the maximum $R_{\text{OFF}}/R_{\text{ON}}$ ratio achieved with both systems is found to be in the same order of magnitude, with a value of 2.6 for Pd/Pd system and 1.6 for

Al/Al-based memristor, as estimated from hysteresis curves recorded with ± 10 V sweeps.

It is worthy to mention that the compliance current, which has been established as key parameter in promoting the RESET operation of nanoscale unipolar devices through Joules heating, shows no effects on the micro-thick Al/Al and Pd/Pd systems. This observation suggests an interfacial-based resistive switching mechanism [41] as opposed to the widely described filamentary conduction behavior.

Comparing all symmetric systems together, the electrode material seems to completely modify the behavior of the micro-thick HfO_{2-x} device from resistive to memristive characteristics, suggesting different degrees of surface interaction with the solgel coating, leading to different Schottky contacts with distinctive behaviors under applied electric field.

2.3.2.2 Effect of Drying Temperature

The I - V plots of devices made from symmetric metal oxide/metal stacks, dried at 80 °C, are shown in Fig. 2.12. Compared with Fig. 2.11 results, Fig. 2.12a shows that memristors made with Cu/Cu contacts remain ohmic regardless of the change in drying temperature made. However, devices based on symmetric Ti/Ti contacts, as in Fig. 2.12b results, exhibit a resistive switching behavior where both the positive and negative sweep half-cycles display a clockwise hysteresis loop orientation.

There is clear indication of the effect of the drying temperature on the resistive behavior of the HfO₂ layer sandwiched between Ti metal electrodes. The pinched I - V profile and dynamic increase in the turn-off voltage with increasing bias sweeps resembled that obtained with Al/Al system fabricated at 60 °C (Fig. 2.11c). This indicates that the Ti/Ti system is becoming more resistive and requires a higher threshold voltage to switch it back on.

For Al/Al system, the general memristive switching properties were equally seen at the higher drying temperature of 80 °C (Fig. 2.12c) compared to observations made with devices synthesized at 60 °C (Fig. 2.11c). The maximum flowing current across the device nearly doubled with the higher drying temperature. The initial clockwise hysteresis orientation (Fig. 2.12c) was also obtained; however, it is flipped near the end of sweeps exceeding 5 V magnitudes (see dashed blue and dotted black hysteresis corresponding to 7 V and 10 V windows, respectively). The onset voltage marking the flip in the loop orientation was particularly found to increase along the sweep magnitude (e.g., the flip is observed at ± 5 V for 7 V windows, whereas it occurs at ± 8 V for 10 V windows). The anticlockwise loop directionality (i.e., orientation toward higher current levels) equally seen in both polarity modes suggests the creation of more conductive pathways through the Al/HfO₂ Schottky contact under high electrical fields. Typical flip could infer a role of the drying temperature in controlling the oxygen vacancy concentration within the active HfO₂ layer.

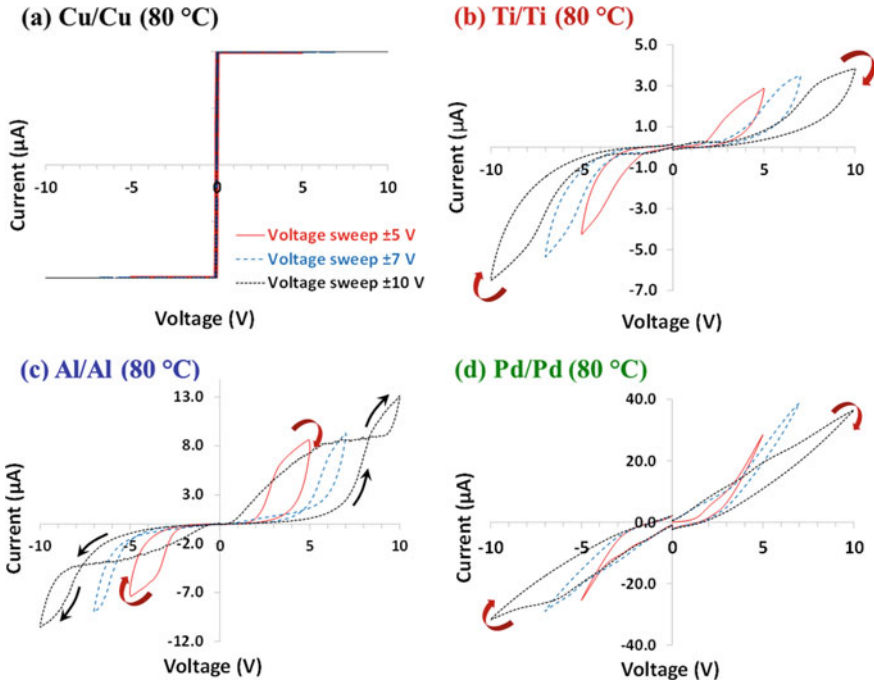


Fig. 2.12 I - V curve characteristics of microscale HfO_{2-x} memristors processed at 80 °C, with symmetric *bottom/top* electrodes: **a** Cu/Cu, **b** Ti/Ti, **c** Al/Al, and **d** Pd/Pd. Voltage sweeps of ± 5 , ± 7 , and ± 10 V were, respectively, applied in that order

For Pd/Pd system, the effect of drying temperature is also highly noticeable from the recorded I - V curves, as shown in Figs. 2.11 and 2.12d plots. Although the Pd/Pd system retains its electrical switching behavior when the drying temperature was increased from 60 to 80 °C, its mem-capacitive property became more pronounced, and the maximum flowing current across the device was multiplied by a factor of 20. Typical increase in the overall flowing current confirms the temperature effect on the intrinsic oxygen vacancy population within the active oxide layer.

Besides affecting the hysteresis direction or the maximum current level, the drying temperature seems to control the $R_{\text{OFF}}/R_{\text{ON}}$ ratio to an extent that generally depends on the stack configuration. The maximum $R_{\text{OFF}}/R_{\text{ON}}$ ratio of Al/Al and Pd/Pd systems made at 80 °C is found to have increased within the same order of magnitude when compared to 60 °C synthesis conditions. The maximum $R_{\text{OFF}}/R_{\text{ON}}$ ratio estimated from hysteresis curves recorded with ± 10 V sweeps nearly doubled (from 2.6 to 4.8); for the Pd/Pd system, it increased approximately nine times (from 1.6 to 9.8) for the Al/Al system [42].

It is clear that the memristive behavior is significantly affected by some key parameters including the active material, the type of electrode, and the drying

temperature. Analyzing and understanding the effect of these parameters on the switching behavior of the device can potentially be utilized to optimize the synthesized memristors according to the desired applications.

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