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Inducing tunable switching behavior in a single memristor

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Abstract

Non-volatile resistive switching based on complex perovskite oxides have demonstrated an immense potential for future neuromorphic and compact logic applications. The adaptation of a functional oxide to exhibit different resistive switching characteristics is an important step in

harnessing the full suite of capabilities that such material system has to offer. Further, an understanding of the underlying phenomena that results in such adaptive characteristics is required. In this study, we show that multiple (threshold and bipolar) resistive switching behaviors can be achieved in a bilayer stack of titanium and selectively chromium-doped strontium titanate. High resolution transmission electron microscopic and electron energy loss spectroscopic compositional and micro/nano-structural analyses reveal that the interfacial oxidation of the titanium layer to Ti_2O_3 introduces an oxide heterostructure with chromium-doped strontium titanate. The concentration and distribution of oxygen vacancies in the heterostructure controls the switching behaviors, which can be controlled by defining the current compliance during the initial electroforming. The existence of current compliance dependent switching behaviors broadens the scope of applications of such selectively doped functional material for resistive memories by making them versatile thereby rendering the technology adaptable to different applications.

1. Introduction

Resistance change oxide memories have emerged as potential candidates for future nonvolatile memory applications owing to their distinct advantages over traditional charge-based memories. Their key features include excellent stability down to the sub-nm regime, high endurance, low power consumption and the ability to implement neuromorphic computing architectures [1-5]. To date, various resistive switching mechanisms have been proposed, which can be mainly classified as electrochemical metallization (ECM) and valence change mechanisms (VCM). The ECM represents the cation-based memory systems where electrochemical deposition and dissolution of metallic cations define the resistive switching whereas in VCM the resistive

switching is attributed to the electric field induced redox reactions and migration of point defects (such as oxygen vacancies, V_{O} s) [1]. Transition metal oxides are known to exhibit VCM based resistive switching and have demonstrated diverse switching behaviors – namely, unipolar, bipolar (BP) and complementary resistive switching (CRS) – which highlights the complex nature of VCM [6-12].

To date a variety of material systems, including metal-organic semiconductors [13, 14], binary metal oxides [5, 15-17] and transition metal oxides [18-21], have demonstrated resistive switching. Among the transition metal oxides, strontium titanate (SrTiO_3 , STO) – regarded as a model perovskite system – has shown enormous potential for VCM based resistive switching memory due to its versatile defect chemistry, mixed anionic-electronic and nonlinear switching kinetics [1, 10, 22-24]. The STO-based resistive memories are known to exhibit bipolar (BP) resistive switching behavior, but there are few reports on the transition between unipolar and BP resistive switching behaviors in a single memory cell [25, 26]. Moreover, no clear and direct evidence is available that elaborates the switching behaviors and the driving mechanisms for this versatile functionality. Therefore, to achieve and precisely control the existence of more than one switching behaviors in the perovskite STO-based systems, insights into the structural and electrochemical factors are important to understand the multifunctional switching behaviors. Herein, we report the presence of BP (clockwise and counter-clockwise) and threshold (CRS and “*peculiar*” CRS) resistive switching behaviors in single units of chromium-doped amorphous oxygen-deficient STO ($\text{Cr}:a\text{-STO}_x$) based metal–insulator–metal (MIM) devices. The distinct resistive switching behaviors are permanently induced by the current compliance limit and applied bias polarity during the initial electroforming step. The distinct presence of discrete switching behaviors in a simple two-terminal MIM device and their control by a single parameter

(*i.e.*, current compliance), offers an application based selection of the device behavior. The BP switching characteristics offer non-volatile data storage, whereas a threshold switching behavior offers selector-less bi-directional memory with multi-state data storage. Through detailed compositional and electrochemical analyses of the Cr:*a*-STO_x MIM devices, the observed multiple resistive switching behaviors are attributed to the distribution and concentration of V_{os} generated, and their drift/diffusion under the influence of set current compliance. It is also observed that the locally-created crystalline regions (formed by the Joule heating) provide a localized conductive path for the anionic-electronic transport across the asymmetric switching MIM cell. Based on the electrical and material characterizations, a physical mechanism is also proposed to interpret the switching kinematics of the presented multiple resistive switching behaviors. Considering the advantages offered by the switching behaviors (BP and threshold resistive switching) demonstrated in our devices and their on-demand selectivity, this study is an important milestone in understanding and tuning multifunctional behaviors in a single STO-based memory cell (and potentially transferrable to other oxides). This can significantly widen its applications in future high density memory and computational architectures

2. Characterization of Cr:*a*-STO_x

Fig. 1a illustrates a schematic of the Cr:*a*-STO_x based MIM device fabricated in a cross-point structure where a stack of Ti (8 nm)/ Cr:*a*-STO_x (25 nm) is sandwiched between Pt electrodes. In order to evaluate the chemical composition of sputtered Cr:*a*-STO_x thin films, comparative compositional analysis is carried out between Cr-doped and un-doped *a*-STO thin films by using high resolution X-ray photoelectron spectroscopy (XPS, see Experimental for details). The core-level XPS spectra of Ti 2*p* from Cr:*a*-STO_x (Fig. 1b) show two spin-orbit pairs (with splitting of

~5.3 eV) and reveal the presence of two oxidation states *i.e.*, Ti^{4+} and Ti^{3+} corresponding to the binding energies of 458.23 eV and 456.22 eV (both $2p_{3/2}$), respectively [27, 28]. In addition, the core-level spectra of O 1s and Sr 3d show the presence of O^{2-} and Sr^{2+} oxidation states, respectively (Supporting Information, Fig. S1).

The resolved spectra of Cr $2p_{3/2}$ (Fig. 1c) show two peaks at 576.72 eV and 579.91 eV which can be assigned to Cr^{3+} and Cr^{6+} oxidation states, respectively [29-31]. It has been reported that doping of Cr in STO can either incorporate the Cr ions at Ti or Sr sites [30, 31]. In our Cr:*a*-STO_x thin films, a shift in the Ti $2p$ peaks (Fig. 1b) towards lower binding energies (by ~0.16 eV), as compared to the un-doped oxygen deficient *a*-STO_x (Supporting Information, Fig. S2), together with the presence of Cr^{6+} species suggest that the Cr doping mainly affects the Ti sites in Cr:*a*-STO_x [30, 31]. Also, the Cr^{6+} prefers to accommodate at the Ti-site instead of Sr-site. This is because the ionic radius of Cr^{6+} (0.0440 nm) is similar to that of Ti^{4+} (0.0605 nm). In contrast, the ionic radius of Sr^{2+} (0.1180 nm) is much larger, which does not satisfy the limits of tolerance factor defined by Goldshmidt to retain the structure of an ABO_3 -type complex oxide [31]. Furthermore, the substitutional Cr doping in *a*-STO_x with a low concentration ($\text{Cr}/\text{Ti} \approx 0.025$) is not expected to distort the chemical structure of *a*-STO_x perovskite oxide [32].

The electronic structure of Cr:*a*-STO_x is assessed by obtaining the photoluminescence (PL) spectra at room temperature using a 325 nm (3.82 eV) laser excitation source. Fig. 1d shows the PL spectra obtained from bare Cr:*a*-STO_x thin films. A high intensity broad peak, centered at 535 nm (2.32 eV) was observed which could be de-convoluted into multiple emission bands. Such a broad emission at room temperature is characteristic of doped [33, 34] and un-doped *a*-STO thin films [35-37]. In un-doped *a*-STO thin films, room temperature PL emission is associated with the presence of TiO_5 defects [34, 36, 37]. On the other hand, Cr is known to

modify the electronic structure of STO by forming CrO₅ defect structures with V_{Os} and introducing in-gap electronic states above the valance band edge [31, 34, 38-40]. The emission energy of 2.32 eV in Cr:*a*-STO_x (Fig. 1d) is comparatively lower than that of our previously reported un-doped *a*-STO_x (by 0.94 eV) at the same excitation energy [33] which indicates the presence of in-gap electronic states in Cr:*a*-STO_x. The XPS and PL analyses suggest that a low concentration Cr doping (Cr/Ti $\approx$ 0.025) in *a*-STO_x, primarily influences the Ti sites, resulting in oxygen deficient [TiO₅V_o] and [CrO₅V_o] complexes that give rise to the in-gap electronic states [34]. Consequently, the introduction of these additional states can offer the possibility of manipulating the switching behaviors of our MIM devices using different applied electric fields, which is discussed later in the manuscript.

3. Resistive switching in Cr:*a*-STO_x MIM devices

In order to activate the resistive switching in the STO based MIM devices, usually an initial high voltage sweep (higher than the subsequent switching threshold voltages) is required as an electroforming step which creates extended defects (*i.e.*, nanofilament) through redox processes in the oxide [1, 10, 27, 41]. In our Cr:*a*-STO_x MIM devices, the multiple resistive switching characteristics have been achieved (regardless of the device area) by controlling the initial bias polarity and current compliance during the electroforming process (Supporting Information, Section S2).

3.1. Threshold switching

3.1.1. Complementary resistive switching

The complementary resistive switching (CRS) is considered as one of the possible solutions to eliminate the sneak currents in a passive crossbar array for high density memory integration [42]. The Cr:*a*-STO_x MIM devices electroformed at low current compliances (in the range 1-5 μ A, see Supporting Information, Fig. S3) exhibit CRS behavior, as depicted in **Fig. 2**. A commonly known CRS cell comprises of two BP switching cells connected anti-serially through an intermediate electrode (in a tri-layer structure) and each cell can be reversibly switched between low resistive state (LRS) and high resistive state (HRS) under opposite applied voltage polarities. Unlike bipolar characteristics where two resistive states (HRS and LRS) define the device state, three states HRS-1, HRS-0, and ON represent the different configurations of the resistive states in the CRS operation [11, 42]. Both HRS-1 and HRS-0 states give high resistance at low READ voltages (V_{READ}) than a certain threshold voltage (which is an intrinsic property of the CRS mechanism to suppress sneak currents in a memory array) while ON state gives low device resistance at high V_{READ} .

In our Cr:*a*-STO_x MIM devices, transition of resistive states from HRS-1 to ON and from ON to HRS-0 occurs at positive threshold voltages during cyclic voltage sweeps and are denoted by $V_{TH,1}$ and $V_{TH,2}$, respectively, as shown in **Fig 2a**. Similarly, the transition from HRS-0 to ON and from ON to HRS-1 occurs at negative threshold voltages as denoted by $V_{TH,3}$ and $V_{TH,4}$, respectively. In CRS, both HRS-1 and HRS-0 are regarded as HRS at low V_{READ} (between $V_{TH,3}$ and $V_{TH,1}$) whereas ON is a transition state (between HRS-1 and HRS-0) that separates resistive states at higher V_{READ} (such as $V_{TH,1} < V_{READ} < V_{TH,2}$ or $V_{TH,3} < V_{READ} < V_{TH,4}$) [11, 42]. Fig. 2b

shows the statistical distribution of $V_{TH,1}$ and $V_{TH,3}$ for 1000 cycles and the average values are calculated to be 1.43 V and -1.65 V, respectively.

3.1.2. Peculiar complementary resistive switching

In a conventional readout operation of CRS devices, generally a higher V_{READ} (than transitional thresholds $V_{TH,1}$ and $V_{TH,3}$) is required, as the stored states (HRS-1 and HRS-0) cannot be distinguished at lower V_{READ} . This can change the resistive state of the CRS device and re-writing of the resistive state is required as a result of the destructive readout operation [43, 44]. Interestingly, our Cr:*a*-STO_x MIM devices, electroformed at moderate current compliance limits (in range 10-15 μ A, see Supporting Information Fig. S3), show a reproducible “*peculiar*” CRS (*p*-CRS) behavior **Fig. 3a**, where the stored resistive states can be distinguished at lower read voltage (*i.e.*, $V_{READ,1}$) in a non-destructive readout. The prominent feature of *p*-CRS (as compared to the conventional CRS) is the possibility of three-level memory states where LRS, HRS and ON can be distinctively stored in a single cell and the inherent switchable diode characteristics of *p*-CRS can facilitate the implementation of complete logic operations [45]. As depicted in Fig. 3a, the devices switch the states from LRS to ON at $V_{TH,1}$ and from ON to HRS at $V_{TH,2}$. Also the transition from HRS to ON occurs at $V_{TH,3}$ and ON to LRS at $V_{TH,4}$. The average values of transition thresholds $V_{TH,1}$ and $V_{TH,3}$ are calculated to be +1.45 V and -1.35 V, respectively, from their statistical distribution (Fig. 3b) and the values of $V_{TH,2}$ and $V_{TH,4}$ are +1.8 V and -1.8 V, respectively.

Fig. 3c shows the retention of the *p*-CRS regime for 10^5 s. Constant READ voltages $V_{READ,1}$ of +0.2 V and $V_{READ,2}$ of +1.6 V are used to measure the HRS/LRS and ON state resistances, respectively. Distinguishable HRS and LRS with an average switching ratio (HRS/LRS) of ~ 9

suggests the capability and stability of bi-level storage of the p -CRS behavior in our Cr: α -STO_x MIM devices. Fig. 3d shows the endurance characteristics of the p -CRS regime for <5000 switching cycles. The loss of resistive states after 4.3×10^3 cycles can be attributed to the cycling-induced degradation due to relatively higher $V_{READ,2}$ and dual V_{SET} pulses in each cycle (as depicted inset of Fig. 3d) [46, 47]. During the endurance measurements, a train of short pulses with a duration of 50 μ s are used to WRITE/ERASE/READ the devices (inset of Fig. 3d). For each complete WRITE/ERASE/READ cycle, a positive pulse with an amplitude of +2.3 V switches the devices to HRS followed by a $V_{READ,1}$ pulse with an amplitude of +0.2 V. A negative pulse of -2.3 V amplitude switches the devices to LRS/ON followed by $V_{READ,1}$ (+0.2 V) and $V_{READ,2}$ (+1.6 V) pulses to READ the LRS and ON states, respectively. Finally, a second negative pulse of -2.3 V is required to restore the LRS/ON states, prior to the next cycle. The p -CRS characteristics are evaluated for more than 15 devices which reveal that our Cr: α -STO_x MIM devices exhibit reproducible p -CRS behavior (Section S2, Supporting Information, Fig. S5).

3.2. Bipolar resistive switching

As depicted in **Fig. 4**, two different electroforming-polarity dependent BP resistive switching behaviors (see Supporting Information, Fig. S3) are observed in our Cr: α -STO_x MIM devices. Both BP resistive switching behaviors are induced at higher current compliances than the CRS and p -CRS during the initial electroforming step. While applying positive bias on the top electrode, the electroforming processes with current compliance in 40-100 μ A range, sets the Cr: α -STO_x MIM devices into the clockwise BP (CW-BP) resistive switching regime. Fig. 4a shows repeatable and well-defined CW-BP switching cycles which are a signature of α -STO devices (RESET on positive bias and SET on negative bias) [10, 27]. Fig. 4b shows stable

retention characteristics for 10^5 s with an average switching ratio (HRS/LRS) of ~ 19 at a constant V_{READ} of +0.2 V. Fig. 4c shows the endurance of MIM devices (pre-set into CW-BP switching behavior) for 10^4 cycles. On the other hand, applying positive bias on the bottom electrode during the electroforming process (with current compliance in 40-100 μ A range) induces a counter-clockwise BP (CCW-BP) resistive switching (Fig. 4d). The retention of CCW-BP switching behavior is measured for 10^5 s (Fig. 4e) and shows no degradation with an average switching ratio of ~ 25 at a constant V_{READ} of +0.2 V. Fig. 4f shows endurance of CCW-BP switching behavior for 10^4 cycles.

The existence of multiple resistive switching behaviors (in identical MIM devices) suggests that the intrinsic Schottky contact at the bottom Cr:*a*-STO_x/Pt interface [48, 49] and an expected Ohmic contact at the top Pt/Ti/Cr:*a*-STO_x interface [50] are modified under the influence of different current compliance limits and applied polarities during the electroforming step [19]. The oxidation of the top Ti layer into a sub-stoichiometric titanium oxide (as discussed in the following sections) introduces another functional switching layer at the top interface which contributes in defining and executing the multiple resistive switching behaviors. In order to understand the role of the top Ti layer, symmetric Pt/Cr:*a*-STO_x/Pt MIM devices were fabricated (Section S2, Supporting Information, Fig. S6). Regardless of the current compliance and applied polarity during the initial electroforming, no significant and well defined resistive switching characteristics are observed. This further indicates that the presence of Ti at the top interface renders our devices with the asymmetry which is responsible for the observed multiple resistive switching behaviors.

4. Spectroscopic analyses of the Cr:*a*-STO_x MIM devices

4.1. Secondary ion mass spectroscopy (SIMS)

In the electroforming process, isolated incomplete filaments can simultaneously be formed over the electroforming cathode along with a fully extended nanofilament in a MIM device (as shown in Fig. 3 of Ref.[51]). A depth profile analysis can indicate the switching mechanism through the distribution of principle elements, without distorting their oxidation states, throughout the thickness of MIM device. The dynamic secondary ion mass spectroscopy (SIMS) depth profiles are used to assess the distribution of principal elements across the Cr:*a*-STO_x MIM devices. The raw depth profile data, shown in **Fig. 5**, depicts the distribution of O⁻, TiO⁻, SrO⁻ and CrO⁻ species across three different MIM devices in three different states, namely – pristine, LRS and HRS, as a function of sputtering time during analyses. Also, the switching MIM devices were pre-set to exhibit CW-BP resistive switching behavior and subjected to *I-V* switching cycles (at least 100 cycles). An increase in signals for the O⁻ and TiO⁻ species at the top Ti/Cr:*a*-STO_x interface of the pristine MIM device indicates the partial oxidation of the Ti layer. This is consistent with our cross-sectional compositional analyses (discussed later in the manuscript) and earlier XPS depth profile analyses of the switching MIM devices [27]. The O⁻ profile in the pristine and LRS shows a uniform distribution of oxygen across the Cr:*a*-STO_x layer. However, for the device set in the HRS, the O⁻ profile clearly shows that the oxygen content drops at the bottom Cr:*a*-STO_x/Pt interface. This indicates that in HRS relatively more V_{os} accumulate at the vicinity of the bottom electrode than the top interface. The relative differences in LRS and HRS profiles suggest that the drift of V_{os} under the reverse bias polarities and nano-redox reactions induce the change in resistive states [1, 15, 52, 53].

4.2. Cross-sectional structural and compositional analyses

In order to establish the resistive switching mechanism in the Cr:*a*-STO_x MIM devices, high resolution transmission electron microscope (HR-TEM) and electron energy loss spectroscopic (EELS) analyses are carried out. As expected, the TEM micrographs of the pristine MIM device show an amorphous microstructure of the functional oxide layer along the length of the device cross-sections, owing to the room temperature sputtering of Cr:*a*-STO_x thin film (as shown in Fig. 1 of Ref. [51]). Also, the cross-sectional EELS analysis of the pristine MIM device reveals the partial oxidation of the top Ti layer and presence of a sub-stoichiometric titanium oxide layer at the top Ti/Cr:*a*-STO_x interface (as depicted in Fig. 2 of Ref. [51]).

The HR-TEM micrographs of the MIM devices exhibiting BP resistive switching characteristics illustrate the presence of localized crystalline regions in the functional Cr:*a*-STO_x layer. To analyze the structure and composition of these localized crystalline regions and the metal/oxide interfaces, regions of interest (ROIs) were identified in the lamellae prepared from MIM devices pre-set into LRS. In the MIM devices exhibiting CCW-BP resistive switching behavior, a distinguishable high contrast ROI in the bulk amorphous functional oxide layer (highlighted in **Fig. 6a**) is selected, which contains a crystalline region emanating from the bottom Pt electrode. Similar localized crystalline regions are also observed in MIM devices pre-set to HRS of CW-BP behavior prior to TEM sample preparation (as shown in Fig. 5 of Ref. [51]). The fast Fourier transform (FFT) diffraction pattern (Fig. 6b) of the ROI shown in Fig. 6a is generated to determine the constituent phases of the crystalline structures. The high intensity diffraction spots marked as spot 1 and spot 2 in Fig. 6b can be assigned to the cubic STO phase. Spot 1 with the *d*-spacing of 1.9 Å is used to generate the inverse FFT (Fig. 6c) of the ROI which outlines the predominant existence of the [200] cubic STO phase in the Cr:*a*-STO_x layer. Spot 2 with the *d*-

spacing of 2.1 Å matches the inter-planar spacing of [111] cubic STO and has a relatively less volume ratio (as observed from the extracted inverse FFT, not shown for brevity). It should be noted that due to our instrumental limitations and experimental conditions we cannot exclude the presence of other sub-stoichiometric STO phases in the ROI [54, 55] (see Fig. 5 of Ref. [51]).

Now, we assess the top interface. The ROI shown in Fig. 6d depicts a crystalline region at the top Ti/Cr:*a*-STO_x interface of the switching MIM device pre-set in a LRS prior to sample preparation. The respective FFT diffraction patterns (Fig. 6e) are used to index the existing phase in the ROI. The highest intensity diffraction spot marked as spot 3, with the *d*-spacing of 2.1 Å, is used to outline the crystalline region in the inverse FFT micrograph (Fig. 6f) and could be indexed to a [200] rhombohedral Ti₂O₃ phase. This suggests that the top Ti layer changes its microstructure from as-deposited amorphous to crystalline after the MIM devices are subjected to the electroforming (see Fig. 4 of Ref. [51]) and subsequent switching cycles [56, 57]. Moreover, the electric field induced oxygen evolution in the Cr:*a*-STO_x layer and its diffusion into the Ti layer during continues cyclic switching and electrical stress results in a gradual increase in the thickness of the sub-stoichiometric phase (such as Ti₂O₃) at the top Ti/Cr:*a*-STO_x interface [33, 58, 59]. The formation of Ti₂O₃/Cr:*a*-STO_x oxide heterostructure explains the observed threshold resistive switching behavior in our MIM devices, as discussed in the next section.

To assess the relative differences in the electronic structure of the bulk amorphous and the locally crystalline ROIs, EELS spectra from cross-sectional line and area scans were acquired from switching devices. The fine structures of Ti-*L*_{2,3} and O-*K* edges are used to analyze the oxidation states of titanium and the distribution of oxygen content, respectively, across the MIM devices. Considering the instrument limitations, we restrict to a qualitative analysis only instead

of quantifying the relative changes in the electronic structure. **Fig. 7a** shows the EELS area map of the locally crystalline ROI (indicated in Fig. 6a) to highlight the relative distribution of oxygen content across the MIM device after the cyclic CCW-BP switching. The EELS area map is generated by considering the O- K edge intensities of the collected spectra (at each pixel) after pre-edge background subtraction. It reaffirms the observations of the FFT analysis which showed that the Ti layer at the top Ti/Cr: a -STO $_x$ interface (Fig. 6e) oxidizes to sub-stoichiometric Ti₂O₃ phase due to the electrochemical redox reactions. The relatively lower oxygen concentration in the upper region of the ROI indicates the sub-stoichiometric nature (oxygen-deficient) of the top Ti/Cr: a -STO $_x$ interface relative to the bottom Cr: a -STO $_x$ /Pt interface. Furthermore, the oxygen deficient regions (*i.e.*, V_{os}) extending from top Pt electrode (acting as cathode), through the Cr: a -STO $_x$ layer towards the bottom Pt electrode (acting as anode), indicate the filamentary path across the MIM structure in the LRS. Spatially isolated oxygen deficient hotspots in the bulk Cr: a -STO $_x$ layer, identified in the EELS map, indicate the oxygen deficient stoichiometry of the functional oxide which is explained earlier in the XPS analysis (Fig. 1). The presence of oxygen content within the top and bottom Pt electrodes can be attributed to the out-diffusion of oxygen ions along the Pt grain boundaries during the cyclic switching [60, 61]. In order to assess the distribution of V_{os} in the HRS of CW-BP behavior, the EELS area map of the ROI (indicated in Fig. 5 of Ref. [51]) shows the accumulation of V_{os} at the anode without their extension to the cathode (see Fig. 6 of Ref. [51]). Based on the observed distribution of V_{os} in LRS and HRS, it can be inferred that the bias polarity induced migration of V_{os} and the associated formation and rupture of the oxygen deficient path is responsible for the switching in our Cr: a -STO $_x$ MIM devices. In the following section, we provide further evidence that indicates that these oxygen

deficient pathways are the conductive routes for the charge transportation due to the change of Ti valance from Ti^{4+} to Ti^{3+} .

Fig. 7b depicts the relative change in the fine structures of the background-subtracted Ti- $L_{2,3}$ and O- K edges along the EELS cross-sectional line scans passing over the locally crystalline ROI highlighted in Fig. 6a. The edge profiles at the distinct points such as the top Pt/Ti interface, Ti/Cr:*a*-STO_x interface, center of the oxide layer and at the bottom Cr:*a*-STO_x/Pt interface are highlighted. The gradual evolution of the Ti oxidation states from the top Pt/Ti interface to the bottom Pt electrode are clearly observed in the Ti- $L_{2,3}$ edge profiles. On the other hand, O- K and Cr- $L_{2,3}$ edge spectra collected from the EELS line scan are weak and exhibit low signal-to-noise ratio which can be associated with the resolution limit of the instrument and low doping concentration of Cr ($\text{Cr/Ti} \approx 0.025$). So we rely on the Ti- $L_{2,3}$ edge profiles to qualitatively analyze the electronic structure of the locally crystalline ROI. Since each V_o introduces two electrons into the Ti 3*d* orbital, the resulting change in the Ti valence band can be observed from the Ti- $L_{2,3}$ edge [53, 62]. At the top Pt/Ti interface, the Ti- $L_{2,3}$ profiles with broad peaks and relatively weak intensities indicate the presence of mixed Ti^{2+} and Ti^{3+} oxidation states [58, 63, 64]. At the Ti/Cr:*a*-STO_x interfacial region, the crystal-field splitting of the Ti- L_3 and Ti- L_2 peaks into t_{2g} and e_g peaks which can be attributed to the presence of Ti^{3+} and Ti^{4+} oxidation states [58, 63, 65]. However, as we move away from the top interface and towards the bottom, more pronounced t_{2g} and e_g peaks indicate the dominant presence of the Ti^{4+} oxidation state. The change in Ti oxidation states across the MIM device suggest that the top Pt/Ti/Cr:*a*-STO_x interface is more oxygen deficient compared to the bottom Cr:*a*-STO_x/Pt interface which is consistent with the EELS O- K area map of the ROI (Fig. 7a).

5. Mechanism of resistive switching in Cr:*a*-STO_x MIM devices

Based on the extensive material and interfacial characterization as well as the electrical characteristics, we propose a mechanism for the unique behavior of our Cr:*a*-STO_x MIM devices. The inherent V_{os} in the Ti–O₆ octrahedra that are created by preferentially removing the oxygen atoms due to the heavy Ar⁺ ion bombardment during the sputtering process [27], generate conduction band electrons in the Ti 3*d* states. However, doping with Cr (*via* co-sputtering from a metallic Cr target) localizes the conduction band electrons by trapping them at Cr sites, which reduces the Cr from Cr⁴⁺ to Cr³⁺ species [66, 67]. Consequently, no conduction electrons are introduced in the Ti 3*d* states and therefore the pristine Cr:*a*-STO_x oxide exhibits an insulating nature. Prior to the electroforming, all Cr:*a*-STO_x MIM devices exhibit device resistances of >1 GΩ. It is widely accepted that the electroforming process generates V_{os} and alters their distribution in metal oxides through subsequent electrochemical redox processes [1, 2, 16, 52]. Consequently, a localized channel for current flow through the oxide system is created which is essentially an oxygen deficient filamentary pathway. Moreover, the subsequent resistive switching is attributed to the rapture and formation of the filamentary path at its weakest part, most likely close to the electroforming anode [7], through the Joule heating and drift of V_{os} under the influence of applied bias.

In our Cr:*a*-STO_x MIM devices, Cr doping further increases the concentration of V_{os} which facilitates the formation of a conductive filamentary path during the electroforming process [68]. The locally confined current flow through the filamentary pathway may induce local Joule heating causing the formation of locally extending crystalline regions in the bulk amorphous Cr:*a*-STO_x layer. Also, the top Ti layer (that develops into a sub-stoichiometric Ti₂O₃ layer) introduces an additional switching layer that is electrochemically different to the Cr:*a*-STO_x.

This causes a change in the mobility [69] and formation energies of V_{os} [70-72]. Ti_2O_3 is known to exhibit semiconductor-metal transition at an elevated temperature and is potentially responsible for the threshold resistive switching in our MIM devices. During the switching cycles, the Joule heating produced by the electrical bias switches the Ti_2O_3 to its conducting phase resulting in a minimal electric field drop on Ti_2O_3 and as such it sustains the electrical bias without further reduction. Therefore, the current compliance and bias polarity dependent generation of V_{os} and the formation of filamentary paths in the $Ti_2O_3/Cr:a-STO_x$ oxide heterostructure govern the multiple resistive switching behaviors in our $Cr:a-STO_x$ MIM devices. When the electroforming bias is applied across the MIM devices the applied electric field initializes the generation of V_{os} which is driven by the movement of oxygen ions towards the anode and several localized spots, including Cr doped sites, becoming oxygen deficient [73]. Under the influence of applied electroforming bias, the positively charged V_{os} drift towards the electroforming cathode and start to accumulate at its vicinity whereas their density extends towards the anode, forming an extended oxygen deficient filamentary pathway.

At lower current compliances (*i.e.*, 1-15 μA) during the electroforming, relatively less density of V_{os} are generated [73]. Also the insufficient driving force for their migration prohibits the complete formation of the filamentary pathway across the $Ti_2O_3/Cr:a-STO_x$ interface. This results in the formation of two distinctive filamentary paths in the Ti_2O_3 and $Cr:a-STO_x$ layers. Depending on the bias polarity, each layer switches (to LRS and HRS) individually to define the resistive state of the MIM device. Under these conditions, we explain the threshold switching behavior in our MIM devices by the repetition of processes schematically depicted in the bottom panel of **Fig. 8**. Post-electroforming electrical characteristics of the CRS and *p*-CRS behaviors

suggest that both resistive switching behaviors follow a similar switching mechanism in terms of V_o distribution and migration in Ti_2O_3 and $Cr:a-STO_x$ layers.

On the other hand, electroforming at higher current compliances (40-100 μA) generate a higher density of V_o s and sufficient driving force is available for their migration across the $Ti_2O_3/Cr:a-STO_x$ interface. The top panel in Fig. 8 schematically depicts the subsequent mechanism of the CCW-BP resistive switching behavior where the complete formation of extended oxygen-deficient filamentary path across the $Ti_2O_3/Cr:a-STO_x$ corresponds to the LRS and ruptured filamentary path (under reverse bias) set the HRS in MIM devices. Similar switching mechanism with opposite bias polarities can be applied to explain the CW-BP resistive switching behavior.

Conclusion

In conclusion, we report the presence of bipolar and threshold resistive switching behaviors in a single-layered $Pt/Ti/Cr:a-STO_x/Pt$ memory device. The multiple switching behaviors are defined by the current compliance limit during the initial electroforming step. The electroforming polarity-dependent BP and threshold resistive switching behaviors are also presented. In order to understand the existence of multiple resistive switching behaviors, rigorous compositional and micro/nano-structural analyses were carried out on the bare $Cr:a-STO_x$ oxide and cross-sectional MIM devices. It was observed that top Ti layer oxidized to a sub-stoichiometric oxide under the applied bias and introduced a $Ti_2O_3/Cr:a-STO_x$ heterostructure in the MIM devices. Joule heating created local crystalline regions, providing a route for the migration of V_o s across the oxide heterostructure. Finally, to explain the observed multiple switching behaviors, a physical mechanism is proposed where current compliance during electroforming defines the concentration and distribution of V_o s in the heterostructure and the subsequent switching

behaviors are combined effect of local redox reactions and Joule heating. The existence of multiple resistive switching behaviors in a Cr:*a*-STO_x based memory cell and their addressability through a single physical parameter, *i.e.*, the current compliance during electroforming, opens new pathways for incorporation of memristors in ultra-dense memory architectures and conventional/non-conventional computation.

Experimental

Material deposition and device fabrication: The *a*-Cr:STO_x resistive switching devices in cross-point configuration are fabricated *via* standard photolithography/lift-off and thin film deposition processes. After patterning through a photolithography (chrome) mask, the bottom Pt (7 nm)/Ti (3 nm) electrodes are evaporated onto a SiO₂ (300 nm)/Si substrate by electron beam evaporation (Kurt J. Lesker PVD75 Pro-line). A 25 nm thin film of amorphous Cr doped oxygen-deficient STO is sputtered (Kurt J. Lesker PVD75 sputtering system) in a pure argon atmosphere at room temperature from a commercial ceramic STO target (99.95%, Testbourne Ltd) by using 200 W RF (13.54 MHz) plasma and under a sputtering pressure of 3.5×10^{-3} Torr. Cr was incorporated into STO by co-sputtering of metallic Cr target (99.95%, Testbourne Ltd) by using 4 W DC power. Detailed description on sputtering *a*-STO oxides with different stoichiometries conditions can be found in our earlier report [24, 27]. Finally, following the photolithographic patterning, top Pt (35 nm)/Ti (8 nm) electrodes are evaporated by electron beam evaporation at $<5 \times 10^{-7}$ Torr base pressure. The *a*-Cr:STO_x MIM cross-point devices with active area of $2 \times 2 \mu\text{m}^2$, $4 \times 4 \mu\text{m}^2$, $10 \times 10 \mu\text{m}^2$, $20 \times 20 \mu\text{m}^2$, $40 \times 40 \mu\text{m}^2$, $80 \times 80 \mu\text{m}^2$ and $100 \times 100 \mu\text{m}^2$ are fabricated.

Electrical characterization: The electrical characterizations of Cr:*a*-STO_x MIM devices are performed using an Agilent 2912A sourcemeter for two-probe measurements.

X-ray photoelectron spectroscopy: X-ray photoelectron spectroscopy (XPS) analysis is conducted by using a Thermo Scientific K-Alpha instrument utilizing an aluminum *K* α radiation source (1486.6 eV) is used. The XPS spectra are collected from bare o (Cr-doped and un-doped) *a*-STO oxide thin films, sputtered on SiO₂/Si substrates, after *in-situ* argon ion assisted surface cleaning step. Being aware of the fact that the argon ions can reduce the Ti oxidation states, we initially characterized the argon ion damage to minimize the preferential oxygen removal. By using a stoichiometric crystalline STO substrate it was found that a short (<5 s) argon milling step with low beam energy (<200 eV) caused minimal oxygen removal. All spectra were resolved by using the standard Gaussian-Lorentzian function followed by the Shirley background correction.

Photoluminescence spectroscopy: The photoluminescence emission spectra are obtained using a Horiba Scientific FluoroMax-4 spectrofluorometer. All spectra are collected at room temperature from as-deposited bare Cr:*a*-STO_x thin films sputtered on SiO₂/Si substrates. A laser source with 325 nm of wavelength is used to excite the sputtered oxides.

Secondary ion mass spectroscopy: Dynamic secondary ion mass spectrometry (SIMS) analyses are carried out with a CAMECA NanoSIMS 50L. Elemental depth profiles are obtained using a Cs⁺ primary ion source with a beam diameter of approximately 100 nm, impact energy of 16 keV and a beam current of approximately 3 pA. The instrument is operated in multi-collector mode, allowing the simultaneous detection of O⁻, TiO⁻, SrO⁻ and CrO⁻. The raster size is 15 μm^2 , however, only secondary ions from the central 10 μm^2 are used to determine the depth profiles.

The mass spectrometer is calibrated using a commercial stoichiometric SrTiO₃ single-crystal (100) substrate and pure Ti and Cr metals, prior to the characterization of the MIM devices.

Cross-sectional analyses: The transmission electron microscopy (TEM) and electron energy loss spectroscopic (EELS) analyses are performed on pristine, electroformed and switching (at least for 100 cycles and subjected to constant bias stresses) Cr:*a*-STO_x MIM devices using a JEOL 2100F scanning transmission electron microscope (STEM) with attached Tridium Gatan image filter with an entrance aperture of 5 mm. Thin TEM lamellae are prepared by focused ion beam (FIB) cuts through the MIM structure by using a FEI Scios DualBeamTM system. Cross-sectional STEM micrographs and EELS spectra are collected using a <1.5 nm beam spot. EELS spectra are collected with a dispersion of 0.3 eV per pixel which allowed simultaneous recording of the titanium *L*_{2,3} (Ti-*L*_{2,3}) edge and oxygen *K* (O-K) edge in the regions of interest (ROIs) and across the MIM cross-sections. A power law fit is adopted for the pre-edge background correction while the influence of nearby peaks and plural scattering are reduced by narrow signal windows.

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Fig. 1 Device structure and functional oxide characterization. (a) Schematic illustration of a cross-point Cr:a-STO_x MIM device. The XPS core-level spectra of (b) Ti 2p and (c) Cr 2p_{3/2}. (d) Photoluminescence spectra of Cr:a-STO_x collected at an excitation wavelength of 325 nm.

Fig. 2 Complementary resistive switching behavior of the Cr:a-STO_x MIM devices. (a) The CRS characteristics are repeated for 1000 cycles, while 1st, 10th, 100th, and 1000th cycles (green, magenta, blue, and red lines, respectively) are highlighted. Inset shows the biasing scheme during CRS switching cycles. (b) Statistic histograms of the CRS threshold voltages, under positive ($V_{TH,1}$, orange bars) and negative ($V_{TH,3}$, cyan bars) voltages for 1000 cycles.

Fig. 3 Peculiar complementary resistive switching of the Cr:a-STO_x MIM devices. (a) Characteristic $I-V$ sweeps for 100 cycles. 1st, 10th, and 100th cycle (green, blue, and red lines, respectively) are highlighted. Inset shows $I-V$ sweeps of 100 cycles on a linear scale along with the bias scheme. (b) Statistic histograms of $V_{TH,1}$ (orange bars) and $V_{TH,3}$ (cyan bars) for 100 p -CRS switching cycles. (c) The retention performance of LRS and HRS measured at constant $V_{READ,1}$ of +0.2 V and ON resistive state measured at constant $V_{READ,2}$ of +1.6 V for 10^5 s. (d) The endurance of p -CRS threshold switching for <5000 cycles. Inset shows a train of pulses in a complete switching cycle where each pulse has duration of 50 μ s.

Fig. 4 Electroforming polarity-dependent bipolar resistive switching behavior of the Cr:a-STO_x MIM devices. (a) Characteristic I - V sweeps of CW-BP resistive switching for 100 cycles, where the representative 1st, 10th, and 100th cycle (green, blue, and red line, respectively) are highlighted. Inset shows the biasing scheme and I - V sweeps for 100 cycles on a linear scale. (b) Retention performance of CW-BP resistive switching behavior for 10^5 s under a constant V_{READ} of +0.2 V. (c) Endurance of CW-BP resistive switching for 10^4 switching cycles. Inset depicts a schematic of a switching cycle where V_{RESET} of +3 V, V_{SET} of -2.7 V and V_{READ} of +0.2 V are applied as short pulses each with the duration of 50 μ s. (d) The characteristic I - V sweeps of CCW-BP resistive switching for consecutive 100 cycles, the representative 1st, 10th and 100th

cycle (green, blue and red line, respectively) are highlighted. Inset shows the biasing scheme and I - V sweeps for 100 cycles on a linear scale. (e) Retention performance of CCW-BP resistive switching behavior for 10^5 s under a constant V_{READ} of +0.2 V and (f) endurance of CCW-BP resistive switching for 10^4 switching cycles. Inset depicts a schematic of a switching cycle where pulses of 50 μ s duration (as V_{SET} of +2.4 V, V_{RESET} of -3 V and V_{READ} of +0.2 V) are applied.

Fig. 5 Nano-SIMS depth profile of the pristine and CW-BP resistive switching Cr:a-STO_x MIM devices. The elemental profiles are obtained across the MIM devices in their pristine state (green lines), HRS (red lines), and LRS (blue lines).

Fig. 6 Morphological analyses of a representative Cr:*a*-STO_x MIM device cross-section from a device exhibiting CCW-BP resistive switching behavior and pre-set to LRS . (a) TEM micrograph of the MIM device subjected to at least 100 switching cycles and set to LRS prior to the lamella preparation. ROI is enclosed in the box. (b) The FFT diffraction patterns generated from the ROI in (a). (c) The inverse FFT obtained from spot 1 in (b) and highlighted on ROI in (a). (d) TEM micrograph of the top Pt/Ti/Cr:*a*-STO_x interface with ROI enclosed in

the box. (e) The FFT diffraction patterns generated from the ROI in (d). (f) The inverse FFT obtained from spot 3 in (e) and highlighted on ROI in (d). All scale bars correspond to 10 nm.

Fig. 7 Electronic structure and compositional analysis of the filamentary path induced by CCW-BP resistive switching. (a) The EELS O- K edge area map of the conductive filament. The area map is collected over the ROI indicated in Fig. 6a. Scale bar: 10 nm. (b) The Ti- $L_{2,3}$ and O- K edge profiles along a line scan across the MIM structure, passing over the conductive filamentary path in (a).

Counter-clockwise bipolar resistive switching

Threshold switching

Fig. 8 Schematic illustrations of the possible resistive switching mechanisms induced by variation in the current compliances during initial electroforming. The top panel depicts the changes during and after electroforming in the MIM devices exhibiting CCW-BP switching behavior. The lower panel illustrates the threshold resistive switching mechanism. The red spheres represent the V_os and dark structures in the center of schematics represent crystalline regions.