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Electronegative metal dopants improve switching variability in Al₂O₃ resistive switching devices

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Abstract

Resistive random access memories are promising for non-volatile memory and brain-inspired computing applications. High variability and low yield of these devices are key drawbacks hindering reliable training of physical neural networks. This study shows that doping an oxide electrolyte, Al₂O₃, with electronegative metals makes resistive switching significantly more reproducible, surpassing the reproducibility requirements for obtaining reliable hardware neuromorphic circuits. Based on density functional theory calculations, the underlying mechanism is hypothesized to be the ease of creating oxygen vacancies in the vicinity of electronegative dopants, due to the capture of the associated electrons by dopant mid-gap states, and the weakening of Al-O bonds. These oxygen vacancies and vacancy clusters also bind significantly to the dopant, thereby serving as preferential sites and building blocks in the formation of conducting paths. We validate this theory experimentally by implanting different dopants over a range of electronegativities in devices made of multiple alternating layers of Al₂O₃ and WN, and find superior repeatability and yield with highly electronegative metals, Au, Pt and Pd. These devices

also exhibit a gradual SET transition, enabling multibit switching that is desirable for analog computing.

I. INTRODUCTION

Compact and energy efficient solid-state resistive switching devices are actively being investigated as fundamental units for use as high-density non-volatile memories, and for enabling energy-efficient analog computing via physical neural networks[1-4]. These devices are capable of both data storage and computation, while being scalable to the nanometer regime[5,6]. Such collocation of computing and memory functions in the same unit gives them great promise to circumvent the latency and energy challenge of data movement[1] that plague current computing systems based on von-Neumann architecture with separate memory and computing units. One class of such devices is the resistive switching random access memory (RRAM)[7,8], which consists of a metal-insulator-metal (MIM) stack. The insulating solid electrolyte layer primarily made of chalcogenides or metal oxides becomes the switching medium. The reversible migration and redistribution of metals such as Ag or Cu[9,10], or of defects such as oxygen vacancies (V_o) through the electrolyte under the application of a voltage forms localized, tunable conductive regions that are responsible for switching[2,4,11,12]. The electrical modulation of the electronic conductance in an analog way in such resistive switching units is fundamental to brain-inspired analog computing[13,14].

Two key barriers preventing the widespread use of RRAMs are their high switching variability[5,6,15-19] and poor device yield[11,18,20,21]. These arise due to the inherent stochastic nature of the individual switching events. Variation in the location and the local chemistry and structure of such filaments leads to cycle-to-cycle and device-to-device variations in switching voltages and resistances, causing inconsistent switching[15,16,19,22,23]. In addition, pristine devices typically require an initial electroforming step, in which a voltage much higher than the set voltage is applied to form the first conductive path in the insulating electrolyte[24]. Such large forming biases can sometimes deform and destroy the devices[11,21], resulting in poor device yield. Poor switching repeatability and poor device yield adversely affect device stability,

increase peripheral circuit complexity, and importantly, reduce computational accuracy of hardware-implemented neural networks, as highlighted by Gokmen et al.[25] and Li et al.[26]

Correspondingly, multiple strategies have been attempted to improve the switching variability and yield of RRAM devices. For example, multilayer structures (such as $\text{AlO}_x/\text{HfO}_x$ [27,28], $\text{TiO}_x/\text{Al}_2\text{O}_3$ [29-31] and $\text{HfO}_x/\text{TiO}_x/\text{HfO}_x/\text{TiO}_x$ [32]) are thought to enhance switching variability by confining the filament formation and rupture pathways within very thin oxide layers[27-29,32]. Interdiffusion among the oxide layers and potential short-circuits across thin films of 1 to 2 nm thickness are limiting factors[29,33] to this approach. Alternatively, nanocrystals[34,35] and nanodots[36] in the electrolyte (such as Ru[34] and Ag[35] nanocrystals in Al_2O_3) enhance the local electric field, and preferentially accelerate V_O migration and cation dissolution, thereby reducing the randomness in filament formation, but to fabricate such embedded nanostructures is not trivial or inexpensive. Other experiments suggest that introduction of metal dopants[20,37-43] (such as Ge[39]- and Al[38,44]-doped HfO_2) into oxide electrolytes improves switching variability. Doping through co-sputtering is common, but recent efforts using energetic doping, such as by ion implantation[45], appears to more significantly improve the characters of resistive switching. This is likely due to the modification of the intrinsic defects in the oxide[46] and the different distribution of dopants since co-sputtering deposition is frequently affected by island growth. First principles calculations have suggested that reduced V_O formation energies near the dopant[39,40,42,43,47-49] should increase switching uniformity by localizing the current path. Many of these devices still needed high electroforming voltages[27,29,35,36,40]. Significant variability is still observed[27-29,32,34,38-40] and current compliances[29,34,36,38,40,41,50] are still used. Oxygen vacancy enrichment in an oxide can be achieved by different mechanisms; i.e. aliovalent doping which is charge compensated by oxygen vacancies, or dopants that are easier to reduce than the host oxide under an electrochemical potential. It is important to understand and establish the dopant properties as descriptors for the V_O formation ease and uniformity in the performance of oxide RRAM devices.

In this study, we hypothesize that dopant electronegativity can be used as a descriptor for predicting the ease of V_O formation in an insulating oxide, with implications for RRAM switching uniformity. Highly electronegative dopants such as Au, Pt, Pd, Rh on oxides are known to catalyze several important reactions, such as CO oxidation, water-gas shift, and NO reduction[51]. These

dopants weaken metal-oxygen bonds in the host oxide lattice[51] while assisting these surface reactions. Following this, we hypothesize that dopants with high electronegativity can give rise to lower switching variability in Al_2O_3 by acting as preferential sites for V_O formation. Highly electronegative dopants reduce the formation energy of oxygen vacancies, because they weaken the metal-oxygen bonds, and create in-gap states and capture the electrons resulting from neutral oxygen removal (a process that is energetically impossible in undoped Al_2O_3).

In this study, we combine the above advantages of multilayer thin films and metal dopants to develop a device with superior switching variability and high yield, that requires no external control circuitry, and is electroforming-free. Our original device consists of alternating layers of Al_2O_3 and WN deposited on Si, with the highly electronegative Au as the top electrode material. WN acts as a barrier layer of Al_2O_3 with its lower interdiffusion tendency[52], which is an improvement from previous device configurations[29]. Au atoms were implanted into the Al_2O_3 electrolyte as dopants alongside focused ion beam (FIB) milling while defining the device area. Density functional theory (DFT) calculations revealed a significant lowering of V_O formation energy in the vicinity of Au, due to the changes in the electronic structure brought about by Au's high electronegativity. Thus, cohesive clusters of oxygen vacancies anchored around the electronegative dopants act as the fundamental units that form an extended switchable network. Multilayer devices doped in this way with Au had superior cycle-to-cycle and device-to-device switching variability than the undoped devices, consistent with the prediction of stable conducting paths obtained by the DFT model. Using this as the control device, we focused our study on predicting and experimentally validating that other highly electronegative dopants such as Pt and Pd similarly increase the uniformity of resistive switching among multiple devices and cycles, in contrast to active metals such as Cu, Ti and Al. Furthermore, our device exhibits a gradual SET transition, which, coupled with its high uniformity, makes it a favorable candidate for use in multibit switching applications.

II. METHODS

A. Computational

Density functional theory calculations: The energetics of the $2 \times 2 \times 1$ perfect supercell ($a=9.62 \text{ \AA}$, $c=13.13 \text{ \AA}$) and of all the defects were calculated using density functional theory (DFT) using a plane-wave basis set, projector-augmented wave pseudopotentials[53] and the Perdew-Burke-

Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA)[54] as the exchange-correlation functional, as implemented in the Vienna ab initio Simulation Package (VASP)[55] v.5.4.1. A kinetic energy cutoff of 520 eV and a gamma-centered 2x2x2 k-point mesh was used, resulting in a convergence accuracy of $< 1\text{meV/atom}$. All calculations were performed with a Gaussian smearing width of 0.05 eV and spin-polarized setting. Atomic positions were relaxed until the force on each atom was below $0.02\text{ eV/\AA}$.

The formation energy of a neutral oxygen vacancy (V_O) in bulk Al_2O_3 was calculated as

$$E_f = E_{DFT}^{V_O} - E_{DFT}^{perf} + \mu_O \quad (1)$$

where E_f is the formation energy of V_O in bulk Al_2O_3 ; $E_{DFT}^{V_O}$ is the DFT energy of the supercell with a V_O ; E_{DFT}^{perf} is the DFT energy of the perfect supercell with no defects, and μ_O is the chemical potential of oxygen in the system, calculated in the oxygen-rich limit as given in Equation 3.

The formation energy of V_O nearest neighbor (NN) to a dopant, with the dopant occupying the octahedral interstitial site of Al_2O_3) was calculated as

$$E_f = E_{DFT}^{V_O-D} - E_{DFT}^D + \mu_O \quad (2)$$

where E_f is the formation energy of V_O at the NN site to the dopant; $E_{DFT}^{V_O-D}$ is the DFT energy of the supercell with the dopant and V_O at its NN site; E_{DFT}^D is the DFT energy of the supercell with the dopant at the interstitial site, and μ_O is the chemical potential of oxygen in the system, calculated in the oxygen-rich limit at 300 K, i.e.,

$$\mu_O(T, P_{O_2}) = \frac{1}{2} \left[E_{O_2}^{DFT} + E_{over} + \mu_{O_2}^0(T, P^0) + kT \ln \left(\frac{P_{O_2}}{P^0} \right) \right] \quad (3)$$

where $E_{O_2}^{DFT}$ is the DFT energy of the O_2 molecule, E_{over} is the correction for the O_2 overbinding error caused by GGA, taken as 1.36 eV as identified by Wang et al.[56] $\mu_{O_2}^0(T, P^0)$ is the difference in chemical potential of O_2 gas between $T = 0\text{ K}$ and the temperature of interest (300 K), at a reference pressure of $P^0 = 1\text{ atm}$, as obtained from thermo-chemical tables; P_{O_2} is the partial pressure of oxygen gas (1 atm in the O-rich limit).

The cluster formation energy (per V_O) in undoped Al_2O_3 was calculated as

$$E_f = (E_{DFT}^{nV_O} - E_{DFT}^{perf} + n\mu_O)/n \quad (4)$$

and in doped Al_2O_3 , it was calculated as

$$E_f = (E_{DFT}^{nV_O-D} - E_{DFT}^D + n\mu_O)/n \quad (5)$$

where E_f is the formation energy of V_O cluster in the undoped and doped case respectively, $E_{DFT}^{nV_O}$ is the DFT energy of the supercell with only the n V_O ($n = 4$) cluster, $E_{DFT}^{nV_O-D}$ is the DFT energy of the supercell with the dopant and n V_O ($n = 4$) cluster, E_{DFT}^D is the DFT energy of the supercell with only the dopant at the interstitial site, E_{DFT}^{perf} is the DFT energy of the perfect supercell with no defects, and μ_O is the chemical potential of oxygen in the system, calculated in the oxygen-rich limit as in Equation 3.

The cluster binding energy (per V_O) in the undoped case was calculated as

$$E_b(nV_O) = (nE_f^{V_O} - E_f^{nV_O})/n \quad (6)$$

and in the doped case, it was calculated as

$$E_b(nV_O - D) = (nE_f^{V_O} + E_f^D - E_f^{nV_O-D})/n \quad (7)$$

where $E_f^{V_O}$, E_f^D have been defined before, and $E_f^{nV_O}$, $E_f^{nV_O-D}$ are the formation energies of the V_O cluster in the undoped and doped cases respectively.

B. Experimental

ALD deposition of WN/ Al_2O_3 stack: N-type degenerate Si wafers were purchased from University Wafer. Wafers were dipped in 1:50 HF:H₂O for 60s to remove native oxide and spin rinsed dried. Next, a wafer was loaded into an Oxford FlexAL ALD machine for plasma-enhanced deposition of alternate layers of WN and Al_2O_3 to give the stack Si/7.5nm WN/2.0nm Al_2O_3 /3.0nm WN/2.0nm Al_2O_3 /3.0nm WN/2.0nm Al_2O_3 . The bottom electrode of the resistive switching device is the 7.5nm WN. The purpose of this WN is to build the stack starting from a well-defined layer to avoid wafer to wafer variations from an uncertified supply of Si wafers. WN is used instead of

other commonly used metals due to CMOS requirements imposed on this shared ALD machine. For a 2-layer or 1-layer Al_2O_3 device, the thickness of each oxide layer will be increased to 3.0nm and 6.0nm respectively so that the combined oxide layer thickness remains constant. Deposition was done at 300°C. The deposition of WN is a N_2/H_2 plasma-enhanced reaction with bis(tert-butylimino)bis(dimethylamino)tungsten(VI) (BTBMW) precursor. The deposition of Al_2O_3 is an O_2 plasma-enhanced reaction with trimethylaluminum (TMA) precursor. Both recipes were supplied by the manufacturer. The thin film thicknesses were determined via X-ray reflectivity using a Rigaku SmartLab X-ray diffractometer, with both single films on wafers or composite films on wafers measured. The growth rate of WN and Al_2O_3 was deduced to be 0.5Å/cy and 1.0Å/cy respectively on the Oxford FlexAL ALD machine.

Au deposition and FIB ion milling: Au deposition is typically performed on a Balzers tabletop sputterer at 130V and 40mA for 150s to give a film thickness of 30nm. There is no difference in device performance when Au is instead being deposited with a AJA International magnetron sputterer or an e-beam deposition machine. No additional metal adhesion layer is used for Au deposition. A 30keV Ga ion beam on a FEI Helios NanoLab 600i DualBeam FIB/SEM was used to mill away material to produce a square mesa where each side of this square is 50µm and the width of the milled border is 1µm. The SEM mode was used to image the chip to set-up for the FIB so there is no unintended FIB damage except as intended around the perimeter of the mesa. The milling was performed to a depth that exposes the Si substrate. This corresponds to an areal Ga ion dose of 80 to 120pC/µm². Resistive switching devices start in the LRS after ion beam milling without a need for electroforming.

Electrical measurements: Probing of the mesa was done with a 25µm diameter gold wire tip to contact the topmost Au film of a typical device on a custom-built probe station. The gold wire is soft and is great for avoiding scratches to the top film. Electrical contact to the bottom WN electrode was made through the degenerately doped Si substrate. A standard tungsten probe from Signatone (probe tip no. SE-T) can also be used. No difference in device performance was observed regardless whether the probe is an Au wire or a tungsten probe. The stiffer tungsten probe was necessary if the top film was Cu, Al, Ti and not Pt, Pd or Au because the Au wire is unable to punch through the native oxide of these metals. A Keithley 2450 sourcemeter was used to source voltage and measure current.

III. RESULTS AND DISCUSSION

A. Effect of Au doping on device switching variability

We tested our hypothesis about the effect of dopant electronegativity on switching variability first on Au-doped Al_2O_3 . Au is one of the most electronegative metals in the periodic table[57]. More than 100 samples of multilayer RRAM devices were fabricated and tested. These RRAM devices were made of alternating layers of Al_2O_3 separated by conductive WN layers, with Au as the top electrode and WN as the bottom electrode. The cross-section of the fabricated device, imaged using a transmission electron microscope (TEM), is shown in Figure 1a. The device schematic, and the effect of Au doping on switching variability is shown in Figure 1b-f. In Figure 1c, when FIB milling is used to define the device area after depositing the Au top electrode, the switching variability reduces dramatically. Estimations from Stopping and Range of Ions in Matter (SRIM) simulations indicate that the high-energy FIB milling process results in the implantation of Au atoms from the top electrode into the Al_2O_3 electrolyte (Supplemental Material Figure S1-S3[58]). This is a critical requirement for achieving superior switching characteristics, because depositing the Au top electrode after FIB milling results in poor switching, as shown in Figure 1b. This rules out other hypotheses, such as implanted Ga and FIB milling damage, for the observed superior switching. Figure 1d and 1e show the cumulative distribution function (CDF) plots of the obtained high- and low-resistance states (HRS and LRS) at the device-level and at the cycle-level, respectively. To evaluate the variability in LRS and HRS, we use a new and more reliable measure of switching variability, the logarithmic coefficient of variation (C_{lv})[59], defined as the difference between the 10th and 90th percentile of the logarithm of resistance values. Compared to $C_{lv} \sim 1.5$ for other Al_2O_3 -based RRAMs reported in literature[60,61], our devices have significantly lower C_{lv} of 0.1 and 0.34 for the LRS and HRS respectively, as plotted in Figure 1d. This slight switching variability arises mainly from fabrication-related variation, which may be further reduced by enforcing stringent manufacturing procedures. From Figure 1e, it is clear that cycle-to-cycle variation has an even smaller spread of about 0.04 and 0.05 for the LRS and HRS states, respectively. Thus, the intrinsic switching variability of each device is very low, indicating substantial reduction in the stochasticity of formation and rupture of conduction channels. Such

low variability is valuable for facilitating multibit switching schemes[18], and meets and surpasses the reproducibility requirement (with a C_{IV} of about 0.32) needed to implement accurate hardware neural networks[25]. Additionally, these multilayer, Au-implanted devices exhibit a perfect yield. All the 100 devices under test are in LRS upon fabrication without the need for electroforming (shown in Supplemental Material Figure S5[58]). The complexity of peripheral circuitry in RRAM arrays is reduced without the functional need for electroforming, and the resulting higher yield from electroforming-free devices would lead to improved accuracy of neural networks[26]. Moreover, the devices exhibit resistive switching with a gradual SET transition. This gradual SET transition is key to multibit switching and analog processing, as explained in forthcoming sections.

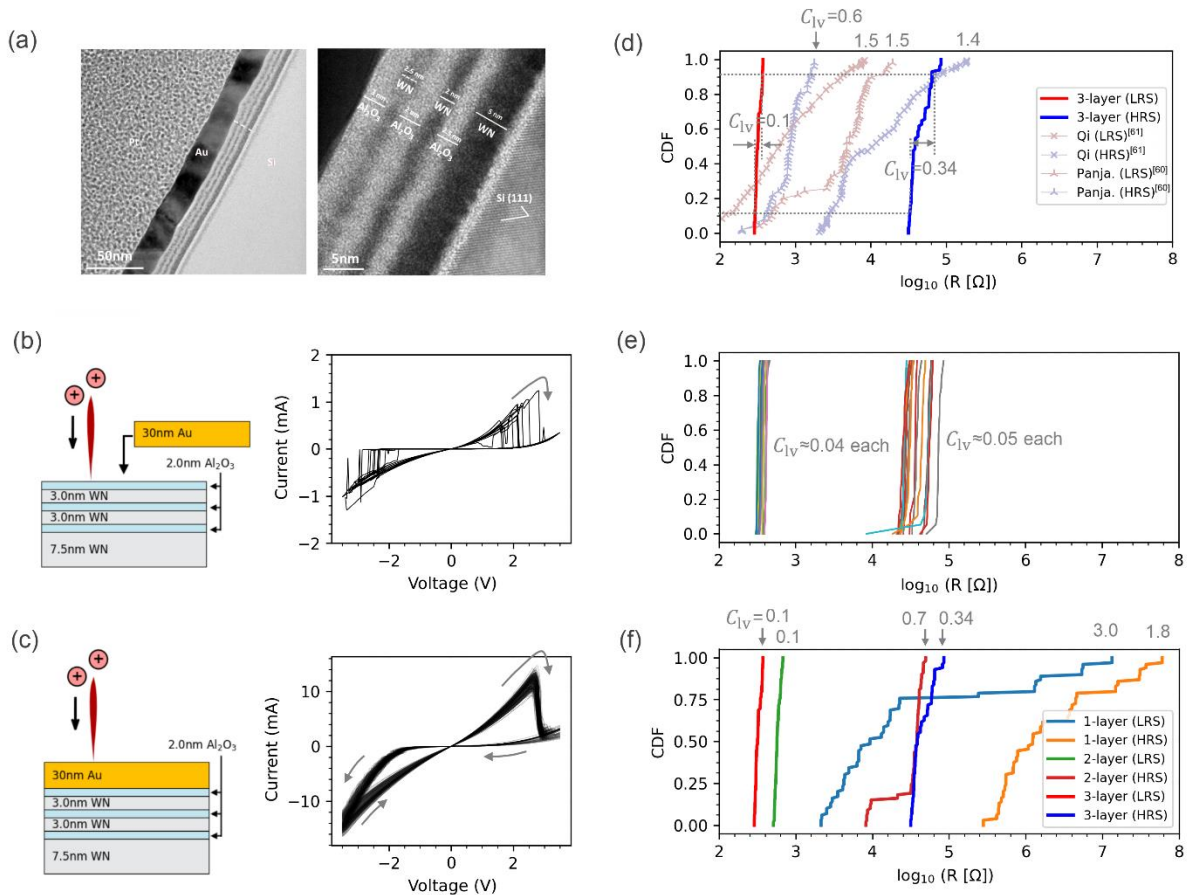


Figure 1. Electronegative Au dopants and multilayering of the oxide films are two key factors to enable low variability switching. (a) Device cross-section imaged using transmission electron microscopy (TEM). For further elaboration on device design and TEM imaging, see Figure 2 and Supplemental Material Figure S7[58]. Panels (b) and (c) compare the device performance without and with Au dopant implanted into the multilayered switching devices. (b) Multilayer Al_2O_3 cannot switch consistently when FIB milling is performed to define the device area before Au deposition. (c) Multilayer Al_2O_3 switches consistently when FIB milling is performed to define the device area after Au deposition. These devices did not require electroforming. The I-V plot shows 300 superimposed switching cycles (15 devices x 20 consecutive cycles in each device). (d) The variability improvement using the Au doping strategy can be seen from the short span of resistances in the cumulative distribution functions (CDFs), observed over the 300 switching cycles, covering only 0.10 and 0.34 decades for the LRS and HRS, respectively. Typical spans of other Al_2O_3 [60,61] devices from literature are shown for comparison. (e) The device-to-device CDF in (d) can be displayed separately for the 15 devices to show cycle-to-cycle variations smaller than 0.05, indicating that most of the variation seen in (d) comes from device-to-device differences. (f) CDF plots show the narrowing of the spread in the LRS and HRS resistances from a few orders of magnitude down to 0.10 and 0.34, respectively, with increasing the number of oxide layers from one to three.

Switching from high resistance to low resistance state in our device is likely due to the formation of a network of cohesive clusters made of oxygen vacancies (V_O). The dependence of switching current on the FIB-processed device perimeter indicates areal switching, as shown in Figure 2. In particular, Figure 2a shows the device schematic and denotes the dimensions of the device ($50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$) and the FIB milling region ($1\text{ }\mu\text{m}$ to $4\text{ }\mu\text{m}$ width around device). Figure 2b shows the scanning electron microscopy (SEM) image of the device edge near the FIB-milled region. Figures 2c and 2d respectively show the schematics of the multilayer device and the network of oxygen vacancies that likely form near the edges of the device (where Au is believed to be implanted). Figure 2e & 2f shows the variation in device conductance with FIB milling length, where it is seen that increasing the length of the line increases the device conductance. Notably, there is no dependence of conductance on contact pad area. Thus, areal switching from Figure 2f indicates

the presence of a network of conducting zones near the periphery of the device. This conducting zone is potentially in the form of a network of conducting filaments; or in the limit of a dense network, it is made of a host chemistry with higher conductance. It is unlikely that conducting zone is made of Au filaments via dissolution of the Au top electrode. Au is resistant to oxidation and is in fact commonly used as the inert electrode in RRAM devices, as opposed to metals like Ag and Cu, which are typical active electrode candidates[62,63]. Additionally, the TEM image shown in Figure 1a was taken at the edge of the device, where Au atoms are expected to be implanted (as per our SRIM calculations in Supplemental Material Figure S3[58]). If there indeed were metallic filaments of Au, they would have shown up as a contrast in the TEM image. Thus, we believe that the role of Au dopant is through its catalytic effect on V_O formation in Al_2O_3 rather than through Au metal filament formation. Future work can incorporate techniques like atom probe tomography to directly image the Au atoms, which is not possible to achieve with the detection limits of TEM and other spectroscopy techniques like electron energy loss spectroscopy and energy dispersive X-ray spectroscopy. Note also that while Figure 2f shows a linear scaling of the device conductance down to a FIB-milled length of $0.5\mu m$, switching of devices with nanometer dimensions might have more device-to-device variation due to the discrete atomistic nature of doping.

Low switching variability is observed in only multilayer devices doped with Au. The CDF plot for one-, two- and three-layer devices in Figure 1f shows that the switching variability improves as the number of layers is increased from one to three, while keeping the total thickness of Al_2O_3 constant. This is likely because thinner oxide layers require shorter conducting paths, thereby lowering stochasticity in the formation and disruption of conductive channels of oxygen vacancies bridged by Au dopants, giving rise to high uniformity as observed in previous studies on multilayer oxides[27-29,32]. Thus, having a multilayer and Au-doped electrolyte together form a necessary and sufficient condition to achieve low switching variability in our system.

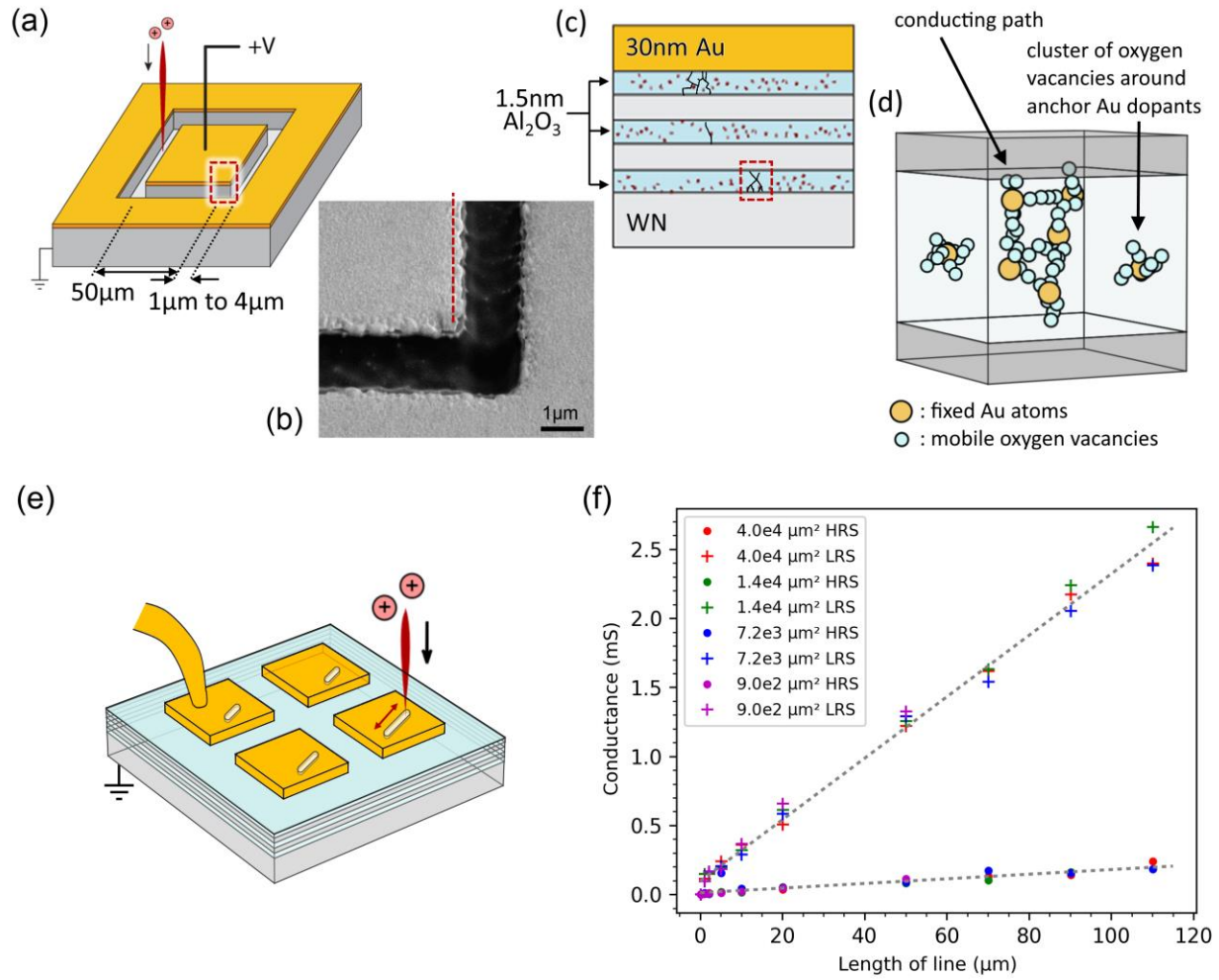


Figure 2. Experimental investigation on the effect of FIB-processed device perimeter to measure conductance of individual devices at high resistance (HRS) and low resistance (LRS). (a) 3D perspective view of the FIB milling carried out to define the area of a single resistive switching device. (b) SEM image of region outlined with red dashed lines in (a). The darker region shows the exposed Si substrate while the lighter regions are the top Au film. The red dash line (cross-section shown in (c)) will be affected by Au implantation due to the proximity to the FIB milling. (c) Stack schematic showing the layers deposited above a Si substrate. The FIB milling implants Au atoms sideways into the edge of Al_2O_3 layers. An atomistic schematic of the regions outlined in red dashed lines is shown in (d). (e) An alternative fabrication scheme where a 30nm thick Au contact pad of variable size was deposited with e-beam deposition through a shadowmask onto the usual triply repeated WN/ Al_2O_3 stack. A line with variable length was then FIB milled into this

Au contact pad. (f) Measured device conductance data indicates a linear relation with increasing FIB milled lengths but no dependence on the contact pad area.

B. Effect of Au doping on switching variability: model based on first principles calculations

We have carried out density functional theory (DFT) calculations to identify the effect of Au doping on neutral oxygen vacancy (V_O) formation. Irradiation processes such as FIB milling result in the creation and distribution of defects such as vacancies and interstitials. Here, we focus on the effect of Au at the interstitial site in Al_2O_3 . ~~The effect of Au at the substitutional site on Al is considered in Supplemental Material Table S1[58] and follows similar trends.~~ The concentration of dopants in our simulations is $\sim 4\%$. This is consistent with the range of implanted dopant concentration as estimated by SRIM simulations (shown in Supplemental Material Figure S3[58]). Table I shows the formation energy of V_O in undoped Al_2O_3 and at the nearest neighbor site of the interstitial Au dopant in Al_2O_3 . The formation energy of V_O next to the Au dopant is drastically lowered, by over 6 eV. This indicates that V_O preferentially forms at the vicinity of the Au interstitial dopant. Since the Au atoms are pinned and stationary, the locations at which V_O is formed are also fixed. This minimizes the randomness in V_O formation, thus creating defined local regions that are easily reduced, which then connect to form conducting paths.

Table I. (left) Oxygen vacancy (V_O) formation energies in undoped Al_2O_3 and at the nearest neighbor (NN) site of the interstitial dopants (Au, Pt, Pd, Cu, Ti, and excess Al) in doped Al_2O_3 ; (right) Oxygen vacancy (V_O) cluster formation energies and binding energies (per V_O) in undoped and doped Al_2O_3 .

Defect	Formation energy [eV]	Defect cluster type	Formation energy [eV]	Binding energy [eV]
V_O	7.19	V_O cluster	7.01	0.18
V_O NN to Au	0.64	V_O cluster with Au	4.32	2.87
V_O NN to Pt	0.47	V_O cluster with Pt	4.73	2.48
V_O NN to Pd	1.91	V_O cluster with Pd	4.73	2.48
V_O NN to Cu	3.61	V_O cluster with Cu	5.29	1.90
V_O NN to Ti	4.38	V_O cluster with Ti	5.36	1.83
V_O NN to Al	3.63	V_O cluster with Al	5.40	1.79

In addition to the ease of formation of V_O point defects, it is important to investigate the effect of the Au dopant on V_O cluster formation. V_O clusters act as building blocks for the formation of conducting paths or networks of conducting channels via which resistive switching occurs. Table I shows the calculated V_O cluster formation energies in undoped and Au-doped Al_2O_3 . Cluster formation energy (per V_O) represents the tendency of forming a V_O cluster in the presence of Au. It is clear that introduction of Au dopant into the cluster markedly lowers cluster formation energy.

The reduction in the formation energy of V_O next to the Au dopant can be rationalized by investigating the density of states (DOS) and electron redistribution of the doped Al_2O_3 system. Oxygen vacancy formation in undoped Al_2O_3 is an energetically costly process because the electrons that are left behind upon removing an oxygen atom cannot occupy the high energy, empty cation states and consequently, localize at the oxygen vacancy site. In contrast, in the DOS plots of the Au-doped Al_2O_3 shown in Figure 3a i and ii, it is clear that the Au interstitial introduces additional states at the valence band maximum (VBM) of Al_2O_3 , along with mid-gap states. Upon the removal of an oxygen atom, the low-lying mid-gap states trap the electrons left behind, completing the Au 6s orbital electron configuration ($[Xe]4f^{14}5d^{10}6s^1 \rightarrow [Xe]4f^{14}5d^{10}6s^2$). The ability to uptake these electrons to the low-energy states decreases the V_O formation energy. This capture mechanism of electrons from V_O by the Au atom can be seen in the DOS plot in Figure 3a ii, where the Au mid-gap states shift lower in energy. The corresponding partial charge density plot of the mid-gap states is shown in Figure 3b, where an electron cloud around Au is clearly seen.

Additionally, Au is a noble metal with a high electronegativity of 2.3[57], close to that of oxygen. This leads to electron redistribution from Al to Au in Al_2O_3 , facilitated by Au electronic states near the VBM of Al_2O_3 as noted above and shown in Figure 3a i and ii. The calculated Bader charge[64,65] (relative to the respective neutral atom) on Au, nearest-neighbor Al and nearest-neighbor O in Au-doped Al_2O_3 is -0.4 e, +2.41 e, and -1.55 e, respectively. The magnitude of charge on nearest-neighbor O is lower than in the undoped case, where O has a charge of -1.65 e. The presence of Au dopant thus leads to electron transfer from Al to the Au atom instead of to O. Charge transfer from Al to Au weakens the nearest-neighbor Al-O bonds in the Al_2O_3 lattice, resulting in the lowering of the V_O formation energy. Electron transfer from Al_2O_3 to Au dopant

has been observed experimentally in prior work[66,67], for example in Au-Al₂O₃ nanocomposites[67] as well as upon adsorption of Au monomers on Al₂O₃/NiAl[66].

The initial structure of the Au-doped V_O cluster with Au at the interstitial site in Al₂O₃ is shown in Figure 3d, with the positions of V_O marked with black circles. The oxygen vacancy cluster introduces multiple discrete mid-gap states, shown in Figure 3b i and ii. Introducing Au gives rise to additional mid-gap states, particularly near the top of the valence band and the bottom of the conduction band. As seen in Figure 3b, the dominant mid-gap states are from V_O, and these states can provide a path for electrons to tunnel through the oxide barrier from the cathode to the anode[16]. It is expected that, as the concentration of oxygen vacancies increases under applied field, the number of localized states from V_O in the band gap will increase, ultimately closing the band gap, giving rise to metallic conduction. In fact, this is seen in the density of states plots of the Au-doped vacancy filament path model in Supplemental Material Figure S9 and S10 (additional details regarding the filament model can be found in Supplemental Material Table S1-S3[58]). The partial charge density of all the defect states within the band gap of the relaxed, Au-doped system with V_O cluster is shown in Figure 3e, revealing a localized, conductive cluster arising from the states introduced by oxygen vacancies.

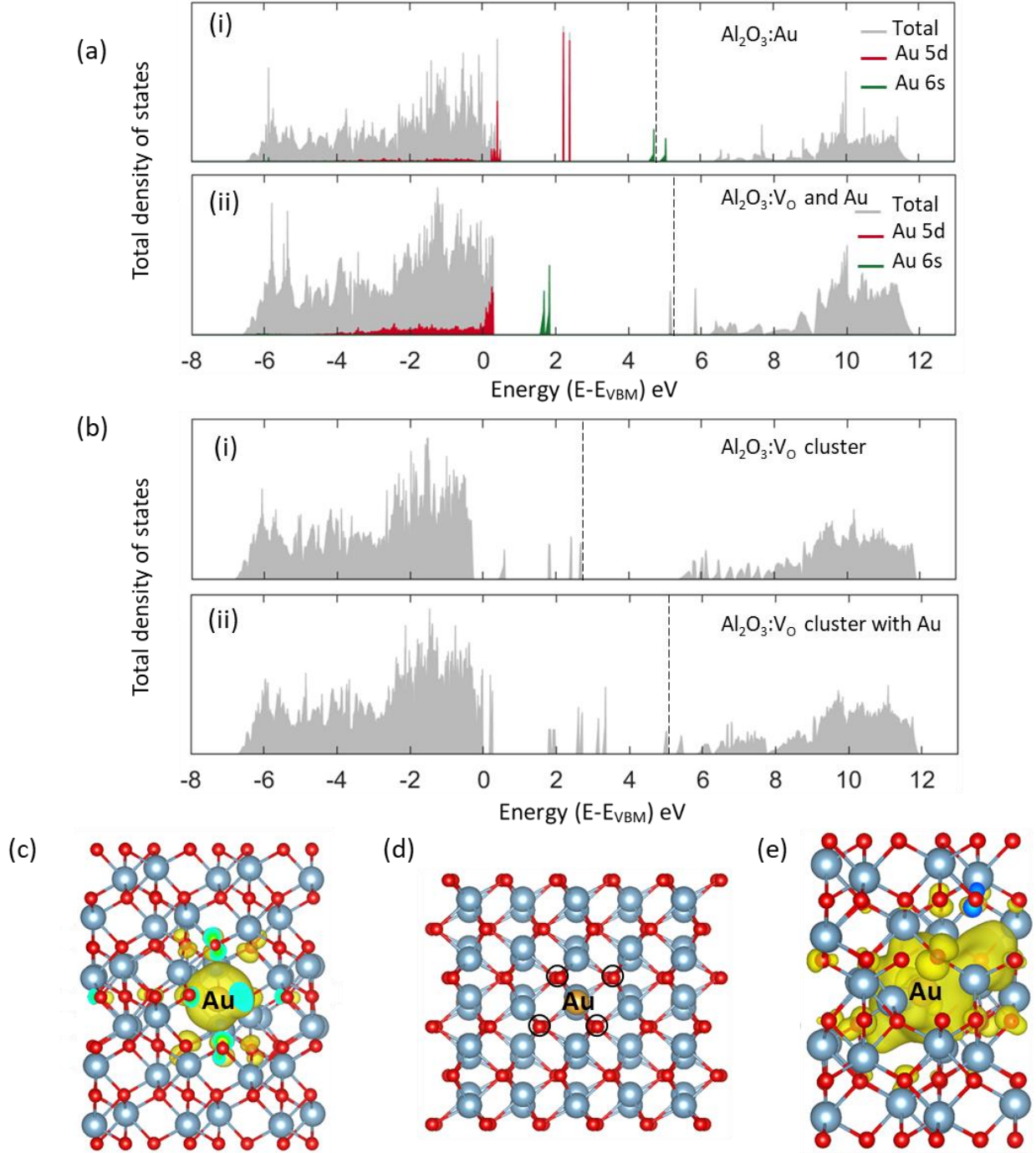


Figure 3. (a) Total density of states (DOS) of Au-doped Al₂O₃ (i) and of Au-doped Al₂O₃ with one V_O at nearest neighbor site to Au (ii). (b) Total DOS of undoped Al₂O₃ with a 4-V_O cluster (i) and Au-doped Al₂O₃ with a 4-V_O cluster (ii). In all DOS plots, valence band maximum is at 0 eV, and both spin up and spin down states are plotted. The dotted line marks the position of the Fermi level. (c) Band decomposed charge density profile of Au s-orbital in relaxed Au-doped Al₂O₃ with

a single V_O (Isosurface: 0.003 eV/Å³), showing charge transfer to Au. (d) Initial structure of the V_O cluster in Au-doped Al₂O₃ (positions of the nearest neighbor V_O 's are marked by black circles). (e) Band decomposed charge density profile of electronic states within the bandgap for the relaxed Au-doped Al₂O₃ with a 4- V_O cluster around Au (Isosurface: 0.01 eV/Å³).

Next we assess the V_O cluster binding energies which are reflective of the preferential position of vacancy or vacancy cluster formation. Table I tabulates the V_O cluster binding energies in undoped and Au-doped Al₂O₃. Cluster binding energy (per V_O), calculated as $E_b(nV_O - D) = (nE_f^{V_O} + E_f^D - E_f^{nV_O-D})/n$, represents the energy required to dissociate the cluster into isolated V_O and Au. The binding energy of the V_O cluster in the undoped case as calculated in this study matches well with previous theoretical studies on V_O chains[68] and V_O pairs[69]. It is clear that the presence of the Au dopant increases cluster binding energy (per V_O). The positive binding energy indicates that the cluster is cohesive. Thus, introduction of Au not only makes V_O cluster formation more energetically favorable, but also enhances cluster cohesion. Such short-range cohesive clusters can then act as building blocks for the formation of conducting paths across the entire oxide layer. When Au is present, formation of vacancies and vacancy clusters preferentially occur near the Au atoms, thereby, reducing stochasticity in the formation of conducting paths and increasing the cohesion and stability of these paths.

Given the favorable formation and binding energies of V_O and V_O clusters near the Au dopant, a reasonable question arises about whether this binding leads to a reduction in mobility of V_O . As shown in Supplemental Material Figure S11-S13 and Supplemental Material Table S4 and S5[58], we have calculated V_O migration barriers in the Au-doped system. In all the paths studied, we find that the migration barriers are lower by ~0.5 eV compared to that in undoped Al₂O₃. Thus, V_O is more mobile in the Au-doped system as compared to the undoped system. This is due to charge transfer from V_O to Au, reducing the trapped electron density in V_O , and thereby making the migration of V_O easier than in the undoped Al₂O₃. These results reveal favorable implications for switching speed and energetics via V_O formation and migration in Au doped Al₂O₃.

It is worthwhile to add here that in this study, we focus only on neutral defects, such as neutral oxygen vacancies. This is because the conductive networks in Al₂O₃ arise from cohesion between

these neutral defects, making them the most important defect to consider[68]. However, it is important to note that high-energy irradiation processes such as FIB milling can create a wide range of defects with non-equilibrium concentrations and different charge states. A thorough investigation of these defects would require other methods such as Monte Carlo or molecular dynamics approaches, which is out of scope for this work but is of key interest for future studies. Finally, we also clarify here that the trends in binding energy given in Table I will hold irrespective of the Fermi level or the chemical potential of the species, since complex formation does not change the number and nature of participating species.

C. Prediction of other dopants and their device tests

Given the above proposed connection between dopant electronegativity and switching variability as explained in the previous section, we have assessed the effect of more and less electronegative dopants on the V_O point defect and V_O cluster formation energies, and on device switching repeatability. A range of dopants across the electronegativity scale[57] was studied, namely, Pt (2.1), Pd (2.0), Cu (1.8), Ti (1.6) and Al (1.5) interstitials. This expands the device design space as well as further strengthens the link between dopant electronegativity and device variability.

As seen in Table I, while the formation energy of nearest-neighbor V_O is generally lowered regardless of the interstitial dopant, for the highly electronegative Pt and Pd dopants, the formation energy is very significantly lowered. Thus, similar to Au, electronegative dopants like Pt and Pd also reduce the V_O point defect and cluster formation energy considerably, and have higher cluster binding energy. The relaxed structures of V_O at the nearest neighbor site of these interstitial dopants can be found in Supplemental Material Figure S14, and the total DOS of the doped V_O clusters can be seen in Supplemental Material Figure S15[58]. ~~It is worthwhile to mention here that we have also studied the resulting change in the V_O formation energy when these dopants were placed as substitutional at the Al site, and we have found similar trends as the interstitial dopants (Supplemental Material Table S1[58]).~~

Bader charge analysis[64,65] revealed that, similar to the case with Au, charge transfer takes place from Al to Pt and Pd, but not to Cu, Ti or Al interstitial (Supplemental Material Table S6). Investigating the electronic DOS, low-lying states near the VBM and mid-gap states are observed

in the Pt- and Pd-doped cases as well, but not in the Al-, Cu- and Ti-doped cases (see Supplemental Material Figure S16 for local DOS plots for all cases[58]). The states near the VBM facilitate electron redistribution around the electronegative Pt and Pd dopants, easing Al-O bond breakage. The mid-gap states trap the electrons left behind upon removal of an oxygen atom, thus, lowering V_O formation energy significantly.

It is noteworthy to point out here that while the difference between the electronegative and non-electronegative elements is clear, the relative trend between the electronegative dopants can also be explained. It is seen that V_O defect formation energy next to Au and Pt is lower than Pd, by over ~ 1 eV. This can be attributed to the relativistic contraction of the s- and p-orbitals of Au and Pt, due to their significantly higher mass compared to Pd. As explained by Pyykko and Desclaux[70], this contraction leads to the 6s state of Pt and Au lying deeper in the atom (as compared to that in Pd[71]), resulting in significant energy gains upon filling it.

We have validated these predictions on the role of electronegativity of the dopant on creating preferential zones of higher conductivity, by performing switching experiments on these compositions. Multilayer devices with the same geometry as shown in Figure 1c were fabricated with Pt, Pd, Cu, Ti and Al top electrode layers, and FIB milled after top electrode deposition to define the device area. The I-V curves and corresponding CDF plots are shown in Figure 4. In line with our computational predictions, devices doped with noble metals with high electronegativities such as Pt and Pd exhibit markedly consistent switching behaviors, whereas the more reactive metals with lower electronegativities are seen to have erratic switching cycles. It is highly encouraging that the consistent switching of the Au/Pt/Pd-doped devices is seen across multiple devices. We recognize that our top electrode/ Al_2O_3 interface changes along with the implanted dopant, which could be an additional cause behind the different switching properties. However, previous studies have found that the top metal electrode has a limited effect on the switching properties[72]. Additionally, if our devices were dependent entirely only on the Schottky barrier changes at different metal/ Al_2O_3 interfaces, we should have observed a dependence on the metal contact **before** the FIB milling was done. However, we see a dependence on the metal only **after** FIB milling. This indicates that the implanted dopants play the main role in ensuring low switching variability. However, to unequivocally rule out the effect of the top electrode/ Al_2O_3 interface, future studies could **use commercial ion implanters to directly implant** the different metal dopants

while keeping the top electrode material the same across devices. We also recognize that there is room for improvement for increasing the resistances of the HRS of these devices. Since our devices switch via an areal mechanism, this can be achieved by scaling the device down laterally to limit the size of the conductive network that participate in the switching. Dopants with lower electronegativities (Cu, Ti, Al) exhibit erratic switching, and with poor ON-OFF ratios. C_{IV} of the devices doped with the more electronegative metals is almost two orders of magnitude lower than those doped with Cu, Ti and Al. Finally, we also recognize that the dopants employed also differ based on their n-type vs. p-type nature. Further investigation of the observed trends based on n-type and p-type nature of the dopants would be interesting. However, this would require evaluating the equilibrium Fermi level established upon doping Al_2O_3 , and the resulting defect compensation mechanisms, which was not the focus of this work. Additionally, given the high-energy irradiation process of FIB milling, it is unlikely that such equilibrium trends will be established in the material. Therefore, we focused on linking the dopant electronegativity on the V_O formation energies in this work. However, we plan to account for the p-type vs. n-type nature of dopants in our future work.

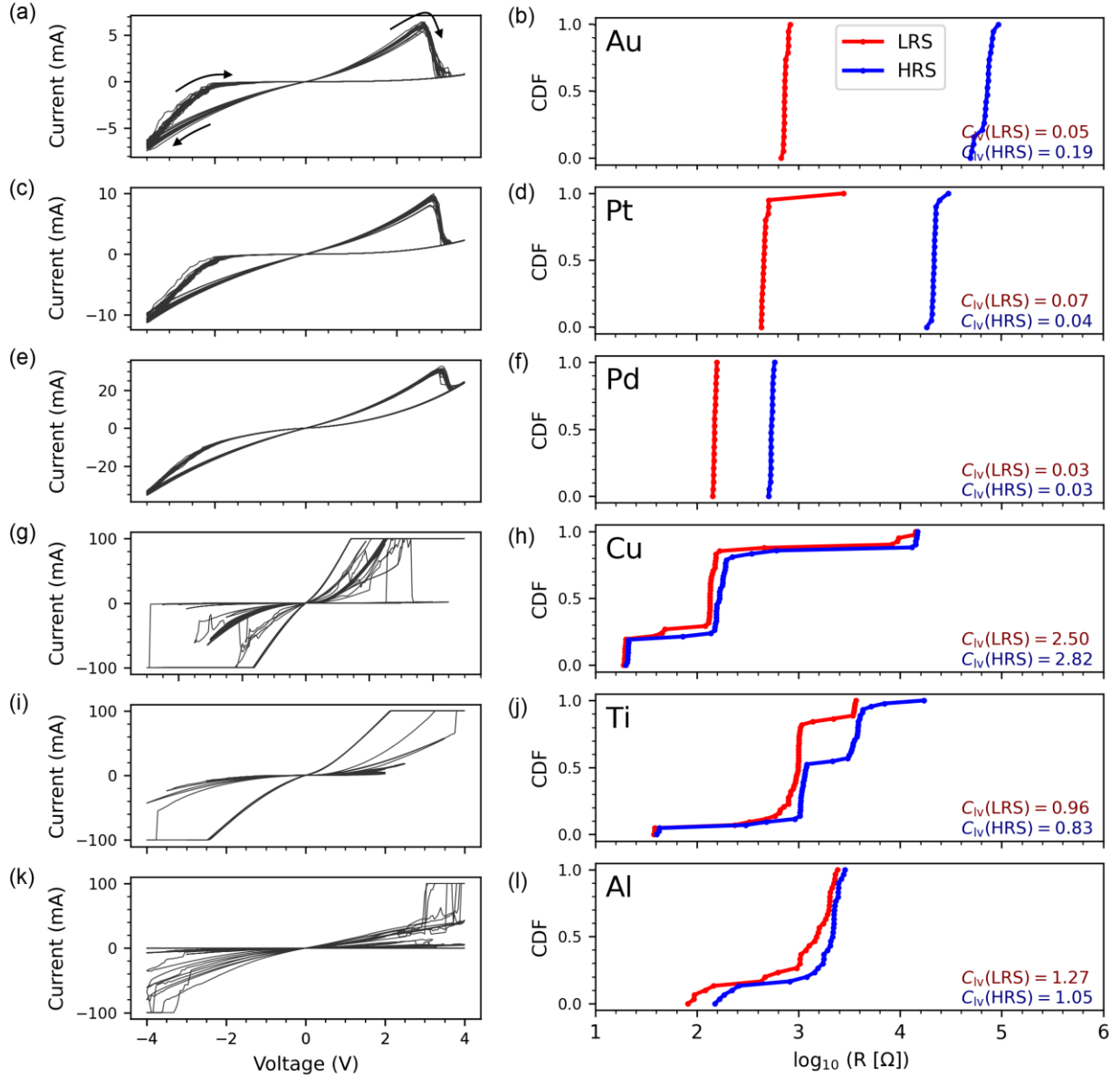


Figure 4. Dopant metals from a range of electronegativities- Au, Pt, Pd, Cu, Ti, Al (corresponding to (a), (c), (e), (g), (i), (k))- were tested to observe their effects on switching variability of Al_2O_3 . The cumulative distribution function for the LRS and HRS resistances are plotted in (b), (d), (f), (h), (j), (l). Dopants with higher electronegativities (Au, Pt, Pd) have CDF plots with narrower widths, indicating that Al_2O_3 layers doped with these metals have low variability switching, consistent with predictions of easier Vo and Vo cluster formation shown in Table I and Figure 3.

D. Multibit switching

This high switching consistency demonstrated by Au, Pt and Pd dopants in Al_2O_3 is beneficial for achieving multibit switching. From the I-V plots in Figure 5 (and also in Figure 4a,c,e), it can be observed that these doped devices exhibit a gradual SET transition. The gradual SET transition allows the modulation of resistance states in a continuous manner, a key requirement for analog computing. The choice of a different terminating cycle voltage in the voltage-sweep measurements leads to different final resistance states with distinct I-V traces, as seen in Figure 5a. A more negative terminating voltage puts the device in a more conductive LRS state (plotted in Figure 5b and 5c), and subsequently also has a RESET transition that occurs at a larger voltage. The gradual increase in conductivity during SET is likely via the increase in the volume and/or number of conductive pathways[16]. One possible mechanism for the controllable multi-bit switching is the lowered formation energy of oxygen vacancies, along with their distribution next to the electronegative dopants, that aid in the formation of multiple short conductive clusters with gradual increases in the magnitude of applied bias. The larger the change in the resistance state upon set, the larger the positive reset voltage that is needed, as also seen in Figure 5a. It is worthwhile to point out here that this multibit switching is demonstrated using a blind strategy, i.e., without any feedback control to read the resistance state and make adjustments. Additionally, no external control circuitry was used to enforce a SET current compliance. This simplifies the circuit design significantly, which will be useful in reducing the effective footprint of each cell for future multibit RRAM arrays. This feature of multilevel resistance states, along with the superior switching variability, makes these devices favorable candidates for multibit resistive switching. The multibit switching exhibited here could also extend the range of programming options for neuromorphic computing applications[73-75] which currently relies on voltage or current pulses to update each device.

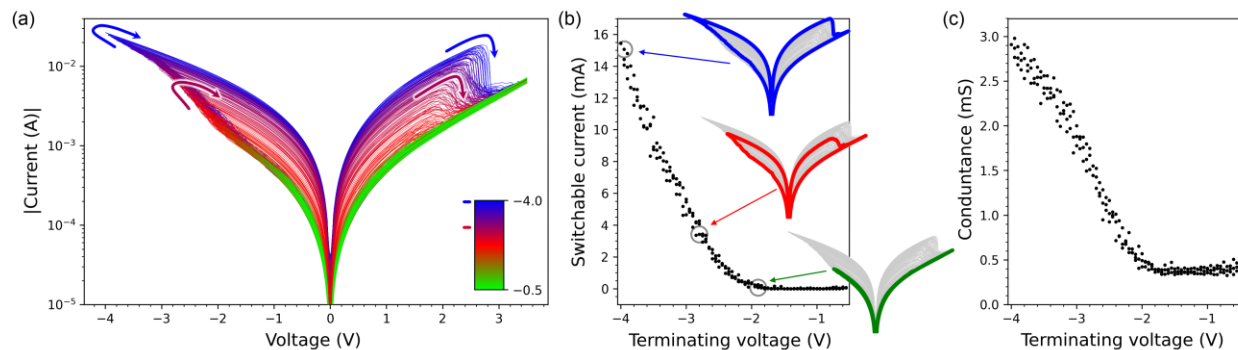


Figure. 5. The gradual SET process is convenient for demonstrating multibit switching in Al_2O_3 . In (a), multiple switching cycles were performed with variable terminating voltages between -0.5 to -4V, and a fixed maximum voltage at 3.5V. Each switching cycle is color-coded according to the most negative terminating voltage used. For example, a voltage sweep from -4V to 3.5V is shown in blue, has the largest hysteresis that indicates the largest extent of switching, and the sharpest RESET onset at about 2.8V. On the other hand, a voltage sweep from -1V to 3.5V is shown in green and has barely any hysteresis or switching. Subplot (b) and (c) shows that the simple use of a chosen terminating voltage is able to put the device into a predictable state as characterized by the switchable current in (b) and the device conductance in (c). The switchable current is defined as the difference in the device current as set and the lowest current measured in the OFF (highest resistance) state. The green, red and blue overlays in (b) show the nature of one I-V sweep when the device is set by -2V, -2.8V and -3.9V as terminating voltages, respectively. No current compliance was needed to be programmed in the sourcemeter used for these measurements.

IV. CONCLUSION

In conclusion, this study has identified that doping the insulating oxide electrolyte in the RRAM device with electronegative metal dopants can potentially improve the device switching variability. Our computational analysis reveals that electronegative dopants act as preferential sites for the formation of V_O point defects and clusters, and also increase the binding energy of the V_O clusters in Al_2O_3 . This is because the midgap states introduced by the electronegative metal dopants capture the electrons left behind upon removal of oxygen, and also weaken Al-O bonds, facilitating V_O formation. These clusters then act as building blocks for the formation of conductive and cohesive V_O networks. Thus, electronegative dopants reduce the number of possible conductive pathways and thereby increase the uniformity of each device. Additionally, the mid-gap states that are introduced dominantly by the V_O clusters provide a path for easy electron conduction. The devices doped with electronegative dopants, Au, Pt, Pd, have a cycle-to-cycle variation of just ~ 0.05 in log-scale for the HRS and LRS, and have a logarithmic coefficient of variation almost two orders of magnitude lower than those doped with active elements, Cu, Ti, Al. This high uniformity, coupled with the gradual SET transition of the device, was used to demonstrate multibit switching

capability without any external circuitry. Thus, this work can enable the development of a high yield, electroforming-free RRAM device, superior switching variability and multibit capability. While there may be Schottky barrier changes at the top electrode/ Al_2O_3 interface due to the different metal contacts, our findings indicate that the doping arising from FIB milling is likely the main effect behind low switching variability. To unequivocally resolve the two effects, future studies could use direct ion implantation techniques to implant the dopant atoms into the electrolyte, while keeping the top electrode/electrolyte interface fixed. Future experiments could also incorporate atom probe tomography to image the implanted dopant atoms. This will benefit efforts in RRAM device design and integration into crossbar arrays for use in neuromorphic computing applications.

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