How Ligands Affect Resistive Switching in Solution-Processed HfO$_2$ Nanoparticle Assemblies

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Abstract

Rapid growth of resistive random access memory (ReRAM) requires fully understanding the various complex, defect-mediated underlying mechanisms to further improve performance. While thin film oxide materials have been extensively explored, the switching properties of nanoparticle assemblies remain underexplored, due to difficulties in
fabricating ordered structures. Here a simple flow coating method for facile deposition of highly ordered HfO₂ nanoparticle nanoribbon assemblies is employed. We observe the resistive switching character of nanoribbons comprising HfO₂ nanoparticles as a function of ligand length, using oleic, dodecanoic, and undecenoic acid capping layers. Through direct comparisons of the forming process, operating set/reset voltages, and resistance states, we demonstrate tunability in the resistive switching response as adjusted by varying the ligand types, thus providing a base correlation for solution-processed ReRAM device fabrication.

Introduction

Due to the scaling limits of flash memory, recent studies have focused on emerging non-volatile devices such as resistive random access memory (ReRAM),¹⁻³ phase change memory (PCM)⁴ and ferroelectric random access memory (FeRAM)⁵. Of these, ReRAM exhibits outstanding properties such as fast switching speed, good reliability and low power consumption, thus the promise for the next generation nonvolatile memory device.¹⁻² Resistive switching behavior describes a reversible change between a high resistance state (HRS) and low resistance state (LRS) within a metal-oxide-metal structure that depends on the history of an applied electric field.⁶ Generally, an electroforming process creates ionic defects within the oxide layer of the pristine device under a high applied bias, thus initiating the subsequent SET/RESET operations. Despite intense research focus on the fabrication and characterization of resistive switching oxide thin films,⁷⁻¹⁰ nanoparticles,¹¹ and nanowires,¹² the development of rapid and low-cost solution-processed systems as an alternative to complicated multistep lithographic approaches remains stunted. Hafnia, HfO₂, is a prototype resistive switching binary oxide that exhibits excellent scalability, reliability, and CMOS compatibility in both amorphous and crystalline structure.¹³ Here we introduce a facile, low-cost method to prepare HfO₂ nanocrystals in highly ordered nanoribbon arrays via convective self-assembly. Recent studies demonstrated the charge transport effect
within solution-processed semiconductors such as colloidal CdSe quantum dots, \(^{14}\) and PbS photovoltaic nanoparticles, \(^{15}\) but not for resistive switching nanoparticles where the capping ligand interparticle interface can profoundly affect the response. \(^{16-17}\) Correlating the changes in ligand chemistry with operating voltages, device stability, and switching mechanism are therefore critical to modulating and improving the performance of solution-processed systems.

This study systematically compares the resistive switching behavior of individual nanoribbons comprising single-crystalline HfO\(_2\) nanocrystals (NCs) capped with oleic, dodecanoic, and undecanoic acid ligands of various lengths. The convective self-assembly approach addresses typical issues facing nanocrystal assembly (i.e. scalability and periodicity) to produce ordered nanostructure arrays without the complexity of fabrication templates or lithographic patterning. \(^{18}\) We previously demonstrated memristive functionality within nanoribbons comprising perovskite strontium titanate (SrTiO\(_3\)) nanocubes that retained or changed its memristive functionality as transferred from the original substrate to a second, arbitrary substrate. \(^{19}\) In this study HfO\(_2\) nanoribbons exhibit both threshold switching (TS) and bipolar resistive switching (BRS) induced by controlling the conductive filament morphology, similar to recent studies of HfO\(_2\) thin films. \(^{20}\) We determined that both the forming voltage and SET voltage scale with ligand length, suggesting that the interparticle tunnel distance is responsible for the carrier transport within HfO\(_2\) ribbon.

**Results and discussion**

HfO\(_2\) nanocrystals are synthesized from hafnium chloride and benzyl alcohol in a solvothermal process according to De Roo et al. \(^{21-22}\) After synthesis, the nanocrystals as washed with diethyl ether and functionalized with a carboxylic acid (oleic acid, dodecanoic acid, or undecenoic acid). Deposition of the HfO\(_2\) NCs into nanoribbon assemblies required the implementation of the ‘stop-and-go’ flow coating method previously demonstrated for other colloidal systems. \(^{1-3}\) Details are introduced in the method section. Nanoribbons were fabricated
comprising HfO$_2$ NCs capped with three types of ligands; oleic acid, dodecanoic acid, and undecenoic acid, labeled hereafter as HfO$_2$-O, HfO$_2$-D and HfO$_2$-U, respectively. Figure 1 shows the nanocrystalline morphology of the HfO$_2$ nanoparticles and schematic illustration of the convective self-assembly processes. The transmission electron microscopy (TEM) image of HfO$_2$-D in Figure 1a shows the as-prepared nanocrystal morphology, while the inset shows a high-resolution TEM image that indicates NP dimensions on the order of 5 nm. The x-ray diffraction (XRD) in Figure 1b reveals the phase pure, monoclinic structure of HfO$_2$ NPs. The stop-and-go flow coating method, as illustrated in Figure 1c, deposits nanoparticles onto a hard substrate by flowing a colloidal solution under the flexible coating blade. The height and the width of the ribbon can be precisely controlled from nanoscale to bulk dimensions by varying the stop time of the state shift, thus enabling the direct fabrication of nanostructures ranging from individual nanoribbons to nanocrystal films. The optical microscopy image in Figure 1d shows highly ordered arrays of individual HfO$_2$ nanoribbons prepared by flexible blade deposition with an average width of 6 µm. Figure 1e shows the three-dimensional topographic profile of an individual HfO$_2$ nanoribbon collected via atomic force microscopy (AFM), indicating that nanoribbons possess a wedge-like cross sectional profile.

Conductive AFM (c-AFM) is a powerful tool for studying RS behavior with the ability to spatially resolve local heterogeneities within the electronic response, and probe the current distribution simultaneously.$^{11, 23-24}$ Figure 2a illustrates the general c-AFM setup, where a Pt/Ir coated silicon tip is placed in direct contact with the surface of individual HfO$_2$ nanoribbons, creating a Pt/Ir/HfO$_2$ NCs/Pt test structure. Here the bias is applied to the bottom Pt electrode, with the current flowing through the ribbon vertically, which is then read via a grounded, conductive tip rastering along the top surface of the nanoribbon.

No current is measured across the nanoribbons before a forming process is induced under a large voltage of 10 V applied to the ribbon locally. The large applied field manifests as a bright
spot corresponding to a highly conductive region, as shown in Figure 2b on the HfO$_2$-D system. Current imaging was conducted by scanning a single nanoribbon with an applied voltage of +2.5 V (Figure 2b), followed by a scan under -2 V applied bias (Figure 2c), suggesting the conducting path formed during forming/SET process.

The electroforming process induced filament formation within HfO$_2$ nanoribbons capped with the three ligand systems is shown in Figure 3a, where the HfO$_2$-U, HfO$_2$-D and HfO$_2$-O systems displayed forming voltages of 6.1 V, 8.2 V and 10 V, respectively. Note that HfO$_2$-O requires an applied voltage larger than 10 V, which is the limit of the external bias source of the instrument. Figure 3b shows the semi-log I-V response of the three ligand capped HfO$_2$ nanoribbons. They all display typical bipolar switching character, where the SET and RESET process occur under positive and negative voltage, respectively, and exhibit a clear variation in operating voltage, current level and the resistance ratio between them. Here we found the HfO$_2$-D displays a smaller set voltage of 1.2 V while HfO$_2$-O requires a larger set voltage of 2 V. A standard 1 MΩ resistor was used to transition between operative bipolar resistive switching and threshold switching modes in the nanoribbons. The current-voltage (I-V) character observed in Figure 3c represents the threshold behavior under voltage sweeping ($\pm$2 V, 1 Hz) when the resistor is connected in series with the HfO$_2$-U system. Unlike the bipolar switching the threshold switching shows a symmetric I-V curve. Moreover, it shows a high resistance ($10^9$ Ω) initially followed by an abrupt increase in current level upon reaching a threshold voltage of approximately +1 V. The ribbon maintains LRS and recovers to the HRS suddenly at a hold voltage of +0.25 V. This threshold behavior can be tuned with the external resistor for each sample, exhibiting similar operating voltage ranges and stability. Figure 3d shows 50 switching cycles within a single HfO$_2$-U nanoribbon, suggesting the TS behavior remains stable, with a selectivity of $10^3$. When the resistor is removed, the typical bipolar resistive switching hysteresis is observed.
To evaluate the effect of ligand length on memristive behavior we estimated the interparticle spacing of the three samples based on the covalent chain length: HfO$_2$-U (1.44 nm), HfO$_2$-D (1.57 nm), HfO$_2$-O (2.2 nm). Figure 4a plots the SET and RESET voltage distribution for bipolar switching as a function of the ligand length. The SET voltage clearly scales with increasing ligand length, while the RESET voltage exhibits a smaller dependence on length. An increase in the $V_{\text{SET}}$ distribution can also be observed in the statistical plot with the increased ligand length, while for $V_{\text{RESET}}$, however, no clear correlation is found. Figure 4b presents the cumulative distribution function of the LRS and HRS of the three ligand types. The results were collected using DC sweeping mode at a read voltage of 0.5 V. The resistance in LRS exhibits a much smaller variation compared to the large variations observed for HRS for all three types. The HfO$_2$-O system shows a large HRS fluctuation range of about $10^4$ while the HfO$_2$-U and HfO$_2$-D systems show improved uniformity of about $10^3$ and $10^2$, respectively. Furthermore, HfO$_2$-U possesses a higher HRS resistance that results in a smaller leakage current, which is attributed to its shorter ligand length. In general, the variation of LRS and $V_{\text{RESET}}$ come from either varying filament diameter size or the number of conducting filaments formed during the SET process, while the variation in HRS and $V_{\text{SET}}$ is highly dependent on variations in the tunneling gap.$^{13}$

Previous studies of PbSe NCs showed that the carrier mobility depends on nanoparticle size and the ligand length, the latter of which determines the interparticle tunnel distance.$^{16}$ Using the same nanoparticle size for all samples, we posit the variation in the ligand length causes the observed difference in RS behavior. The charge transport mechanism involves sequential electron hopping through nanoparticles, as described by an Arrhenius-type activated tunneling model.$^{17}$

$$\sigma(\delta, T) = \sigma_0(e^{-\beta\delta})e^{-E_A/k_BT}, \quad (1)$$
where $\beta$ is the electron-tunneling coefficient that is determined by the chemical nature of the ligand, $\delta$ is the average interparticle spacing depends on the length of the ligand and $E_A$ is the activation energy. Here $E_A$ is determined by the equation:

$$E_A = \frac{e^2}{8\pi \varepsilon \varepsilon_0} \left( \frac{1}{r} - \frac{1}{r+\delta} \right), \quad (2)$$

where $r$ is the average radius of the particles, $\delta$ is the interparticle distance, and $\varepsilon$ is the dielectric constant of the matrix by the ligand. Here both the forming (Figure 3a) and the subsequent SET process (Figure 4a) display a ligand length dependence, as both $V_F$ and $V_{SET}$ increase with increasing ligand length.

During the charge transfer process the ligand facilitates electron tunneling by effectively serving as an insulating spacer.\textsuperscript{25} Using the c-AFM tip as the top electrode forms a Pt/Ir tip-HfO$_2$ NCs-bridge-metal structure, where the term bridge indicates the capping ligand separating neighboring NCs and the metal bottom electrode with the bulk HfO$_2$ NCs. When a positive voltage is applied to the bottom electrode during the electroforming process, the high electric field enables the creation of oxygen vacancies within the NCs and induces migration toward the tip along the grain boundary to form a low resistance conductive path.\textsuperscript{26} The electrons injected from the tip under the negative voltage thus pass through the conductive channel and tunnel between NPs, inducing a transition from HRS to LRS. When a negative voltage is applied to the bottom electrode, the oxygen vacancies migrate towards the counter electrode as driven by the electric field of opposite sign, thus severing the conductive channel. The observed TS and BRS characteristics are explained by variations in the morphology of the conducting filament. Limiting the current flow with an external resistor induces an instability within the filament, ultimately resulting in filament rupture after the applied voltage is removed. Once the conducting filament formed, any subsequent growth is suppressed due to the small amount of current passing through, resulting
in a fragile filament. Conversely, the current increases when the resistor is removed such that a stronger, more continuous filament is formed, manifesting as bipolar resistive switching.

To demonstrate a solution-processed memristive platform, we fabricated a crossbar device with a flow-coated HfO$_2$-U thin film sandwiched between Ti top and Pt bottom electrode. The schematic of the cross-point HfO$_2$-U test structure is shown in Figure 5a. Using the same solution concentration, the width of the ribbon is simply extended by varying the stopping distance and substrate velocity. Using the longer stopping distance, we fabricated a 5x5 µm$^2$ crossbar type device comprising a 40 nm thick HfO2-U thin film sandwiched between 30 nm thick Pt electrodes. The bipolar resistive switching I-V response was measured by sweeping a DC voltage from -0.5 V to +1.5 V after a forming process using a compliance current of 100 µA (Figure 5b). An ALD-deposited 10 nm HfO$_2$ ReRAM device with the same area was fabricated for comparison. Here the solution-processed HfO$_2$-U device clearly exhibits smaller operating voltages, narrow distribution/increased uniformity, and larger ON/OFF ratio as shown in Figure 5c, d. The average SET and RESET voltages were 0.97 V and -0.36 V, respectively for HfO$_2$-U; the ALD-deposited HfO$_2$ displayed values of 3.2 V and -2.5 V, respectively. The ON/OFF ratio improved from 10 for ALD HfO$_2$ to $10^5$ for the HfO$_2$-U at the expense of a small decrease in the uniformity of the resistance. Thus, the solution-processed device exhibits both stable switching behavior and small operating voltages that are competitive with more commonly employed ALD-deposited HfO$_2$ ReRAM devices.

**Conclusion**

In summary, we introduced a facile, inexpensive and versatile fabrication method to produces memristive nanoribbon structures comprising solution-processed, binary hafnium oxide nanoparticles. We demonstrated that ligand length direct affects the resistive switching behavior by comparing three commonly employed ligand chemistries. Our c-AFM results showed that individual HfO$_2$ nanoribbons demonstrated both threshold switching and bipolar resistive...
switching modes, dependent upon an external resistance applied to the system, which attributed to changes in the filament morphology. The forming and SET voltage scale strongly with increasing ligand length, while the reset voltage displays only a slight dependence. Moreover, different ligands affect the stability of the resistance in HRS due to the variation in the tunneling distances. We conclude that intrinsic oxygen vacancies formed during hydrothermal process are responsible for the switching behavior, and the operating parameters correlate directly with ligand length. Finally, our solution-based device demonstrated promising advantages, including low cost and time saving process, lower operating voltages, increased uniformity, and larger ON/OFF ratio compares to the typical ALD thin film HfO₂ memory device. The chosen ligands for this study are frequently used for nanoparticle stabilization, and thus should immediately apply to optimizing resistive switching behavior in other complex oxide nanoparticle systems.

**Methods.** HfO₂ nanocrystals (0.4 mmol HfO₂) were synthesized from HfCl₄ and benzyl alcohol according to De Roo et al.[cite] After solvothermal synthesis and washing with diethyl ether, the nanocrystals are redispersed in chloroform (4mL). 0.2 mmol of fatty acid (oleic acid, dodecanoic acid, or 10-undecenoic acid) was added to the milky suspension. In case of 10-undecenoic acid, 5 % of dodecanoic was also added to ensure colloidal stability. Under stirring or ultrasonication, oleylamine (0.15 mmol or 50 µL) was added until a transparent and colorless suspension was obtained. Finally, the particles are purified three times by adding acetone to induced precipitation, followed by centrifugation and resuspension in chloroform. After the last purification, the nanocrystals were dispersed in toluene.

**HfO₂ Nanoribbon Convective Self-Assembly:** The custom-built flow coating instrument uses a silicon wafer (University Wafer Inc.) cut to an edge length of 15 mm as a fixed blade. This blade is attached to a tilt-translation stage with pitch, roll and height control capability. With visual guidance, the blade edge is aligned parallel to the substrate at the approximate height 150-300 µm for all coating procedure. The substrate is attached to a programmable nanopositioner.
(Burleigh Inchworm controller 8200), which performs a series of stop-and-go steps. Here the primary variables that control the nanoribbon geometry (height, width) are solution concentration, stop time ($t_d$), spacing ($d$) and velocity ($v$). The HfO$_2$ nanoribbons in this study were prepared using the following parameters: $v = 1500$ µm/s, solution concentration = 1 mg/ml, $d = 200$ µm, and a $t_d$ between 1000 to 6000 ms. Different stop times were used to vary the nanoribbon height ($h$) and width ($w$), $t_d = 1000$ ms ($h = 80$ nm, $w = 8$ µm), $t_d = 3000$ ms ($h = 160$ nm, $w = 13$ µm), and $t_d = 6000$ ms ($h = 230$ nm, $w = 17$ µm). A fixed volume of HfO$_2$ NC solution (10 µl) is injected between the fixed blade and the substrate, where capillary forces confine the solution to the blade edge. The HfO$_2$ NC nanoribbons were deposited directly on silicon wafer substrates (undoped <100>, University Wafer Inc.). Before deposition all substrates and blades were rinsed with isopropyl alcohol and toluene then dried after each step with a filtered stream of N$_2$ gas.

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Figures and Figure Captions

Figure 1 a, TEM image shows the crystalline structure of HfO$_2$ nanoparticles with the scale bar denotes 50 nm. Inset: HRTEM image of NCs indicates the lattice fringe and size of 5 nm. b, X-ray diffraction patterns of monoclinic HfO$_2$. c, An illustration of the “stop-and-go” flow coating process. The shape and profile of the ribbon are confirmed by d, three-dimensional AFM image. e, An optical micrograph (scale bar 200 µm) showing highly ordered ribbons comprising HfO$_2$ nanoparticles.
Figure 2a, An illustration of the c-AFM measurement setup across an individual HfO$_2$ nanoribbon. 

b, Current mapping of individual HfO$_2$-D ribbon with an applied voltage of +2.5 V, displaying a yellow conducting spot formed after a forming voltage of +6 V. c, Corresponding current mapping of the area with an applied voltage of -2 V. No observed conducting spot indicates the locally reset process occurred.
Figure 3  

(a) I-V curves for the forming process of HfO$_2$-U, HfO$_2$-D and HfO$_2$-O, respectively. 

(b) Representative I-V response of BRS for three samples. 

(c) I-V curve of the TS behavior of HfO$_2$-U sample. 

(d) 50 cycles endurance of TS by sweeping at a read voltage of 0.5 V, showing a selectivity of $10^3$. 

Selectivity $\sim 10^3$
Figure 4 a, The statistical distribution plot of switching voltages as a function of ligand length. Both $V_{SET}$ and its distribution scale with increasing ligand length. b, The cumulative probability for the LRS and HRS of HfO$_2$-U (purple; square), HfO$_2$-D (green; circle), and HfO$_2$-O (orange; triangle), respectively.
Figure 5 a. Schematic of a single Pt/HfO2-U/Pt ReRAM device. b, The representative I-V characteristics of Pt/HfO2-U/Pt ReRAM device. c, Comparative statistic cumulative probability of the operating voltage for HfO2-U and ALD-prepared HfO2. d, The cumulative probability of the resistances in each state of HfO2-U and ALD-prepared HfO2.

References

