Self-assembly of an NbO₂ interlayer and configurable resistive switching in Pt/Nb/HfO₂/Pt structures

Sanjoy Kumar Nandi, Xinjun Liu, Dinesh Kumar Venkatachalam, and Robert Glen Elliman

Citation: [Applied Physics Letters](#) **107**, 132901 (2015); doi: 10.1063/1.4932096

View online: <http://dx.doi.org/10.1063/1.4932096>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/107/13?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Interface engineering for improving reliability of resistance switching in Cu/HfO₂/TiO₂/Pt structure](#)

Appl. Phys. Lett. **107**, 072901 (2015); 10.1063/1.4928710

[Study of resistive switching and magnetism modulation in the Pt/CoFe₂O₄/Nb:SrTiO₃ heterostructures](#)

Appl. Phys. Lett. **107**, 063502 (2015); 10.1063/1.4928337

[Role of metal-oxide interfaces in the multiple resistance switching regimes of Pt/HfO₂/TiN devices](#)

Appl. Phys. Lett. **107**, 023504 (2015); 10.1063/1.4926340

[Anomalous effect due to oxygen vacancy accumulation below the electrode in bipolar resistance switching Pt/Nb:SrTiO₃ cells](#)

APL Mater. **2**, 066103 (2014); 10.1063/1.4884215

[Well controlled multiple resistive switching states in the Al local doped HfO₂ resistive random access memory device](#)

J. Appl. Phys. **113**, 164507 (2013); 10.1063/1.4803076

A promotional banner for Applied Physics Reviews. On the left is a small image of the journal cover, which shows a 3D diagram of a device structure. The main part of the banner has a blue background with a glowing light effect. The text 'NEW Special Topic Sections' is written in large, white, sans-serif font. Below this, in a smaller white font, is 'NOW ONLINE' followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends'. On the right side, the 'AIP Applied Physics Reviews' logo is displayed in white.

Self-assembly of an NbO₂ interlayer and configurable resistive switching in Pt/Nb/HfO₂/Pt structures

Sanjoy Kumar Nandi,^{1,2,a)} Xinjun Liu,^{1,b)} Dinesh Kumar Venkatachalam,¹ and Robert Glen Elliman¹

¹*Department of Electronic Material Engineering, Research School of Physics and Engineering, The Australian National University, Canberra ACT 2601, Australia*

²*Department of Physics, University of Chittagong, Chittagong-4331, Bangladesh*

(Received 12 August 2015; accepted 20 September 2015; published online 30 September 2015)

A configurable resistive switching response is reported for Pt/Nb/HfO₂/Pt devices subjected to different set compliance currents. When operated at a low compliance-current ($\sim 100 \mu\text{A}$), devices show uniform bipolar resistive switching behavior. As the compliance current is increased ($\sim 500 \mu\text{A}$), the switching mode changes to integrated threshold-resistive (1S1M) switching, and at still higher currents ($\sim 1 \text{ mA}$), it changes to symmetric threshold switching (1S) characteristic of threshold switching in NbO_{2- δ} . These switching transitions are shown to be consistent with the development of an NbO_{2- δ} interlayer at the Nb/HfO₂ interface that is limited by the set compliance current due to its effect on oxygen transport and local Joule heating. The proposed mechanism is supported by finite element modeling of the 1S1M response assuming the presence of such an interlayer. These findings help to understand role of interface reactions in controlling device performance and provide a means for the self-assembly of integrated 1S1M resistive random access memory structures. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4932096>]

Resistive random access memory (ReRAM) based on transition metal-oxides (TMO) is of interest as a potential replacement for flash memory due to its simple metal-insulator-metal structure and impressive resistive switching characteristics.^{1–3} This application relies on the creation of a filamentary conduction path in the oxide and the ability to open and close a gap in the filament under the action of an electric field or current.⁴ In this case, the filament is non-volatile and only changes state when an appropriate voltage is applied. Many TMOs also exhibit volatile threshold switching in which the oxide transforms from an insulating to conducting state when subjected to an appropriate stimulus (e.g., voltage, temperature) but reverts to its original insulating state when the stimulus is removed.⁵ For example, both VO₂ and NbO₂ are known to undergo a thermally induced insulator-metal transition (IMT) when heated above a critical temperature.^{6,7} In thin-film form, these materials have been shown to act as nonpolar (or bidirectional) switches, becoming conductive above a threshold voltage and insulating below the threshold, possibly due to local Joule heating.^{6,8}

The threshold switching response is of particular interest as a potential selector element (1S) in ReRAM arrays where it can be used to reduce current sneak paths.^{9,10} Sneak paths arise from the fact that resistive memory devices pass current in either direction when in the “on” (low resistance) state and can thereby give rise to unintended addressing of memory elements via indirect addressing routes.¹¹ The integration of a threshold switch in series with the ReRAM memory element acts to limit the current at voltages below the threshold value and can enable unambiguous memory addressing in high-density memory arrays.^{10,12} In its simplest form an integrated selector-memory (1S1M) element can be fabricated as a TMO

bilayer comprised of resistive switching and threshold switching oxide layers.^{8,13} Recent studies have demonstrated the efficacy of such 1S1M structures in which the selector element was based on threshold switching in NbO_{2- δ} .¹⁴

One of the problems with this approach is that the selector element typically requires a high forming current ($\sim 5 \text{ mA}$) to initiate the threshold switching response, and because the memory element is necessarily subjected to the same current, it is typically formed in a very low resistance state. As a consequence, the memory element requires a large initial reset current and often exhibits unipolar operation (thermally driven) with a large on/off resistance ratio. This does not preclude subsequent bipolar operation, but it can directly affect device uniformity and reliability. Clearly alternative approaches are required to achieve reliable low-power, bipolar memory operation in integrated 1S1M structures.

In this study, we report configurable switching modes in a Pt/Nb/HfO₂/Pt device structure as a function of the set compliance current and show that these changes (bipolar 1M to 1S1M and 1S) are consistent with the formation of an NbO_{2- δ} interlayer at the Nb/HfO₂ interface, the extent of which is controlled by the compliance current. The role of an active NbO_{2- δ} interlayer is supported by a physics based model, which reproduces the experimental reset response of the proposed 1S1M structure.

The test structures employed in this study consisted of simple metal-insulator-metal structures of the form: Pt/Nb/HfO₂/Pt as shown in Fig. 1(a). Ti (10 nm) and Pt (25 nm) bottom contact layers were deposited onto an oxidized Si wafer (150 nm SiO₂/Si) by electron-beam evaporation. A 20 nm HfO₂ layer was subsequently deposited on the electrode by atomic layer deposition. This involved heating the substrates to 200 °C and exposing them to alternating pulses of pure tetrakis-(dimethylamido)-hafnium (Hf(NMe₂)₄) and H₂O vapor, with N₂ purge of the reaction chamber between pulses. The

^{a)}Electronic address: sanjoy.nandi@anu.edu.au

^{b)}Electronic address: xinjun.liu@anu.edu.au

FIG. 1. (a) Schematic and (b) XTEM image of the fabricated Pt/Nb/HfO₂/Pt structure ReRAM.

top electrode, consisting of 70 nm Nb and 10 nm Pt layers, was then deposited by dc magnetron sputtering. The top contact layers were deposited through a shadow mask to define 100 μ m diameter contact pads. The final layer structure is shown in Fig. 1(b), which depicts a cross-sectional transmission electron microscopy (XTEM) image of the fabricated sample. Current-voltage (I-V) characteristics of these devices were measured at room temperature using a semiconductor parametric analyzer (Agilent B1500A).

As-fabricated devices were highly insulating and required an electroforming process with a current compliance of $\sim 10 \mu$ A prior to switching. Three distinct current-voltage (I-V) responses were observed after initial forming depending on the set compliance current employed, as illustrated in Fig. 2.

For a set compliance of $\sim 100 \mu$ A devices exhibited bipolar resistive switching (Fig. 2(a)) with excellent switching characteristics, including uniform high (HRS) and low (LRS) resistance states and good cycling endurance. The bipolar switching behavior can be understood in terms of established models of resistive switching;¹⁵ During electroforming a filamentary HfO_{2-x} conduction path is created in the stoichiometric HfO₂ layer and oxygen ions are transported to the Nb-HfO₂ interface. Switching is then controlled by the opening and closing of a tunnelling gap in the filament due to field-induced transport of oxygen ions at the interface and devices exhibit bipolar resistive switching as shown in Fig. 2(a). While the low compliance current was maintained ($\leq 100 \mu$ A in the present case), these devices continued to exhibit stable bipolar operation suggesting that oxygen transport is conservative (i.e., there is no net loss or gain).

When the compliance current was subsequently increased to $\sim 500 \mu$ A (with a -2 V, 2 V voltage sweep) the device transitioned to a new mode of operation and after repeated sweeps (3–5 cycles) exhibited characteristic 1S1M behavior, as shown in Fig. 2(b). Comparison with the response of related NbO₂-based 1S and 1S1M structures (see References 14 and 16) suggests that the 1S response results from threshold switching in an NbO_{2- δ} interlayer. The formation of such a layer is not unreasonable as similar intermediate oxides have been reported during resistive switching of Ta₂O₅ for a wide range of metal contacts (e.g., Ni, Co, Al, Ti, Zr, and Hf).¹⁷ On this basis, the 1S1M switching characteristics would result from a combination of threshold switching in the NbO_{2- δ} layer and bipolar resistive switching in the HfO_{2-x} layer, as observed in Fig. 2(b). During the positive cycle, as the voltage increases to the threshold value V_1 , the filament in the memory layer reforms (set) and simultaneously induces the IMT in

FIG. 2. (a) Typical bipolar current-voltage (I-V) curves during the set/reset process with the arrows showing switching direction. (b) Transition from bipolar to 1S1M switching mode in the same device at 500 μ A. Negative cycle contains components of threshold and memory switching. (c) Nonpolar/unipolar switching transitions in the same device at higher compliance (1 mA).

the NbO₂ due to local Joule heating. As the applied voltage is reduced the NbO₂ volume cools and reverts to its insulating state. This results in a reduction in current at V_2 as the selector turns “off” but the memory remains in a “LRS” as shown in Fig. 2(b). During a subsequent reset operation (i.e., negative bias) the temperature of NbO_{2- δ} volume rises again due to Joule heating and this induced the IMT at V_3 . At the end of the sweep, at bias V_4 , the selector remains “on” and the memory layer is in a “HRS.” (This mechanism is discussed later.)

When the compliance current is further increased to 1 mA, the device transitions to a threshold switching mode, and after five cycles (red curve in Fig. 2(c)) exhibits symmetric threshold switching behavior characteristic of the IMT in NbO₂, as discussed above. It is noteworthy that during the first few cycles at this higher compliance the device exhibits transitional nonpolar/unipolar resistive switching, consistent with the development of a lower resistance filament in the HfO₂ layer. This is expected as a consequence of additional O-ion transport from the filament to the NbO_{2- δ} layer, and as the number of switching cycles increases the conducting filament in the HfO_{2-x} layer becomes more stable and finally acts as a permanent filament and virtual electrode.¹⁸ The resulting active device structure has the form Nb/NbO_{2- δ} /metallic-HfO_{2-x} and exhibits symmetric threshold

switching. The response of the device is then controlled by the $\text{NbO}_{2-\delta}$ layer and exhibits volatile switching as this layer switches between insulating and conductive states. The $\text{NbO}_{2-\delta}$ exhibits IMT at threshold voltage ($V = V_{\text{th}+}$) and reverts to an insulating state at hold voltage ($V = V_{\text{th}-}$) when bias direction is reversed.

A finite element model was constructed to represent the 1S1M behaviour based on the above understanding. Specifically, the model considers the evolution of a “memory” filament in a HfO_2 layer and the threshold switching response in a NbO_2 layer, as shown in Fig. 3(a). The threshold switching response of NbO_2 is assumed to result from a thermally-induced IMT as proposed by Pickett and Williams.⁷ A 10 nm NbO_2 interfacial oxide is considered for the threshold switching layer. This is similar to that reported for related material systems¹⁷ but the simulation results are not strongly influenced by this value. The temperature distribution in the device is determined by solving the Fourier heat equation, taking account of Joule heating, and the IMT is modeled by assigning temperature dependent electrical and thermal conductivities for the NbO_2 layer.¹⁴ Switching in the memory layer is based on the drift and diffusion of charged oxygen vacancies with temperature-dependent mobility and diffusivity and requires the solution of a suitable transport equation subject to local temperature and electric field.¹⁹ The sample structure is defined in a 2-D axisymmetric geometry (Fig. 3(a)) and solved self-consistently in time-dependent solver. Results from the simulation are depicted in Fig. 3(b) which compares the experimentally measured 1S1M and the simulated reset responses. The simulation is seen to accurately reproduce the experimental data, with the reset transition starting at ~ 0.8 V and the resistance gradually increasing with increasing voltage up to a voltage of -2 V.

The physical basis of 1S1M switching is further clarified in Fig. 3(c), which shows 2D plots of the temperature (upper row) in the selector and memory layers and the defect density (lower row) in the memory layer during a reset sweep.

The plots correspond to the five different points A, B, C, D, and E indicated in Fig. 3(b). The panel A in Fig. 3(c) reflects the pre-reset situation corresponding to point A at -0.5 V. As the voltage increases during the negative sweep, the temperature increases as a result of Joule heating and initiates an IMT in the NbO_2 layer at the threshold voltage (point B and panel B). As soon as the temperature of the NbO_2 filament reaches the IMT temperature the current increases abruptly and reaches its maximum value, at which point the IMT region acts as a virtual cathode. A gap then opens in the memory filament due to defect drift and diffusion, and this increases with the increasing applied voltage (panel C-E), as shown in Fig. 3(c)). The migration of ions is localized close to the $\text{NbO}_2/\text{HfO}_2$ interface due to the strong temperature dependence of the ion mobility, but the gap is self-limiting due to the reduction in electric field and temperature as the gap increases, dependencies that gives rise to the gradual reset response. At the end of the reset cycle, the NbO_2 volume reverts to its insulating state leaving the broken filament in the memory layer. In one reset cycle, the hybrid device therefore undergoes the following sequence: S-off/M-LRS $\rightarrow$ S-on/M-LRS $\rightarrow$ S-on/M-HRS $\rightarrow$ S-off/M-HRS, where the S-on/M-HRS and S-on/M-LRS can be recognized as logic “0” and “1” states, respectively. The read voltage V_{read} is usually chosen to lie between V_3 and V_4 , where logic “0” and “1” states can be detected and the $R_{\text{OFF}}/R_{\text{ON}}$ resistance ratio calculated.

In summary, it has been shown that the switching mode of Pt/Nb/HfO₂/Pt ReRAM devices depends on the compliance current employed for the set operation. When operated at low compliance current (~ 100 μA) the devices exhibited uniform bipolar resistive switching, as expected for filamentary switching in the HfO_2 layer. At intermediate currents (~ 500 μA), the response transitioned to integrated 1S1M behavior and this was shown to be consistent with the development of an $\text{NbO}_{2-\delta}$ interlayer at the Nb/HfO₂ interface, with the switching characteristics reflecting the combined

FIG. 3. (a) Geometry of the simulated device structure assuming formation of NbO_2 interlayer. (b) The comparison of simulated and experimental 1S1M reset I-V characteristics of Pt/Nb/HfO₂/Pt. (c) 2D plots of temperature (upper row) for NbO_2 and HfO_2 layers, and defects (lower row) only for HfO_2 layer at five distinct points ((A)–(E)) as shown in the I-V curve of the simulation results.

filamentary resistive-switching in the HfO_2 layer and threshold switching in the $\text{NbO}_{2-\delta}$ interlayer. At high currents (~ 1 mA), the devices exhibited 1S threshold switching which was attributed to the development of a permanent filament in the HfO_2 layer and threshold switching in the $\text{NbO}_{2-\delta}$ interlayer. These changes were explained by an increase in oxygen ion transport from the conductive filament to the Nb/ HfO_2 interface with increasing compliance current, and its reaction with the Nb electrode to form an $\text{NbO}_{2-\delta}$ interlayer. This was supported by an observed reduction in filament resistance with increasing set compliance current and by comparing measured characteristics with those predicted by finite element modeling. These results demonstrate the important role of interface reactions in controlling device performance and provide a basis for the self-assembly of integrated 1S1M ReRAM structures.

This work was made possible by funding from the Australian Research Council. The authors also acknowledge the NCRIS-Australian Nanotechnology Fabrication Facility (ANFF) ACT node for research support.

¹R. Waser and M. Aono, *Nat. Mater.* **6**(11), 833–840 (2007).

²M.-J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, and S. Seo, *Nat. Mater.* **10**(8), 625–630 (2011).

³A. Sawa, *Mater. Today* **11**(6), 28–36 (2008).

⁴G. H. Kim, J. H. Lee, J. Y. Seok, S. J. Song, J. H. Yoon, K. J. Yoon, M. H. Lee, K. M. Kim, H. D. Lee, and S. W. Ryu, *Appl. Phys. Lett.* **98**(26), 262901 (2011).

⁵F. Chudnovskii, L. Odyets, A. Pergament, and G. Stefanovich, *J. Solid State Chem.* **122**(1), 95–99 (1996).

⁶S. Kumar, M. D. Pickett, J. P. Strachan, G. Gibson, Y. Nishi, and R. S. Williams, *Adv. Mater.* **25**(42), 6128–6132 (2013).

⁷M. D. Pickett and R. S. Williams, *Nanotechnology* **23**(21), 215202 (2012).

⁸X. Liu, S. M. Sadaf, M. Son, J. Shin, J. Park, J. Lee, S. Park, and H. Hwang, *Nanotechnology* **22**(47), 475702 (2011).

⁹M. Son, J. Lee, J. Park, J. Shin, G. Choi, S. Jung, W. Lee, S. Kim, S. Park, and H. Hwang, *IEEE Electron Device Lett.* **32**(11), 1579–1581 (2011).

¹⁰S. Kim, X. Liu, J. Park, S. Jung, W. Lee, J. Woo, J. Shin, G. Choi, C. Cho, and S. Park, paper presented at the 2012 Symposium on VLSI Technology (VLSIT), 2012.

¹¹E. Linn, R. Rosezin, C. Kögeler, and R. Waser, *Nat. Mater.* **9**(5), 403–406 (2010).

¹²E. Cha, J. Woo, D. Lee, S. Lee, J. Song, Y. Koo, J. Lee, C. Park, M. Yang, and K. Kamiya, paper presented at the Proceedings of IEEE International Electron Device Meeting (IEDM), 2013.

¹³H. Mahne, H. Wylezich, S. Slesazek, T. Mikolajick, J. Vesely, V. Klemm, and D. Rafaja, paper presented at the 5th IEEE International Memory Workshop (IMW), 2013.

¹⁴S. K. Nandi, X. Liu, D. K. Venkatachalam, and R. G. Elliman, *J. Phys. D: Appl. Phys.* **48**(19), 195105 (2015).

¹⁵S. K. Nandi, X. Liu, S. Li, D. K. Venkatachalam, and R. G. Elliman, “Resistive switching behavior in HfO_2 with Nb as an oxygen exchange layer,” in *Conference on Optoelectronic and Microelectronic Materials & Devices (COMMAD)* (IEEE, 2014), pp. 290–293.

¹⁶L. Xinjun, S. K. Nandi, D. K. Venkatachalam, K. Belay, S. Song, and R. G. Elliman, *IEEE Electron Device Lett.* **35**(10), 1055–1057 (2014).

¹⁷C. Chen, S. Gao, F. Zeng, G. Tang, S. Li, C. Song, H. Fu, and F. Pan, *J. Appl. Phys.* **114**(1), 014502 (2013).

¹⁸F. Nardi, S. Balatti, S. Larentis, and D. Ielmini, paper presented at the 2011 IEEE International Electron Devices Meeting (IEDM), 2011.

¹⁹S. Larentis, F. Nardi, S. Balatti, D. C. Gilmer, and D. Ielmini, *IEEE Trans. Electron Devices* **59**(9), 2468–2475 (2012).