

# A 1D Vanadium Dioxide Nanochannel Constructed via Electric-Field-Induced Ion Transport and its Superior Metal–Insulator Transition

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Nanoscale manipulation of materials' physicochemical properties offers distinguished possibility to the development of novel electronic devices with ultrasmall dimension, fast operation speed, and low energy consumption characteristics. This is especially important as the present semiconductor manufacturing technique is approaching the end of miniaturization campaign in the near future. Here, a superior metal–insulator transition (MIT) of a 1D VO<sub>2</sub> nanochannel constructed through an electric-field-induced oxygen ion migration process in V<sub>2</sub>O<sub>5</sub> thin film is reported for the first time. A sharp and reliable MIT transition with a steep turn-on voltage slope of <0.5 mV dec<sup>−1</sup>, fast switching speed of 17 ns, low energy consumption of 8 pJ, and low variability of <4.3% is demonstrated in the VO<sub>2</sub> nanochannel device. High-resolution transmission electron microscopy observation and theoretical computation verify that the superior electrical properties of the present device can be ascribed to the electroformation of nanoscale VO<sub>2</sub> nanochannel in V<sub>2</sub>O<sub>5</sub> thin films. More importantly, the incorporation of the present device into a Pt/HfO<sub>2</sub>/Pt/VO<sub>2</sub>/Pt 1S1R unit can ensure the correct reading of the HfO<sub>2</sub> memory continuously for 10<sup>7</sup> cycles, therefore demonstrating its great possibility as a reliable selector in high-density crossbar memory arrays.

especially important as the state-of-the-art semiconductor manufacturing technique is approaching the end of miniaturization campaign in the near future.<sup>[1]</sup> In view of this, the electric field-driven ion transport phenomena and related solid-state redox reaction provide a powerful platform.<sup>[2–6]</sup> The formation of nanoconductive filaments in insulating media not only leads to reversible resistive switching behavior for high-density information storage devices,<sup>[7–11]</sup> but also capable of producing functional nanostructures that demonstrate obvious response to the magnetic, optical, thermal, and other stimuli for novel electronic device applications.<sup>[12–17]</sup>

On the other hand, owing to its intriguing electrical, optical, and magnetic characteristics, vanadium dioxide (VO<sub>2</sub>) distinguishes itself as a model strongly correlated electron material for immense electronic applications.<sup>[18]</sup> In particular, the reversible transition between the metallic and insulating states and the concomitant threshold switching behavior makes it promising candidate for selector in high-density crossbar memory array and biomimetic neurons.<sup>[19]</sup> To date, the switching physics has been mainly categorized into pure electron–electron correlation,<sup>[20]</sup>

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electron–phonon interaction,<sup>[21]</sup> or a combined effect,<sup>[22]</sup> while there still lacks an effective approach to regulate the metal–insulator transition (MIT) reproducibility and reliability during successive cycling.

Phenomenologically, heat- or electric-field-induced VO<sub>2</sub> MIT appears mostly as an in-plane random 2D percolative behavior over the entire sample.<sup>[23]</sup> Due to the inhomogeneous coexistence and cascading evolution of multiple transitioning nano-domains, namely, tetragonal (R) metallic and monoclinic (M1) insulating phases,<sup>[24]</sup> avalanche multistep jumps in the transition behavior with much reduced sharpness and uniformity are usually observed.<sup>[25]</sup> The fluctuation in the MIT transition of VO<sub>2</sub> hinders itself from direct application at the moment. Great efforts have been devoted to improving the performance of VO<sub>2</sub> MIT, by deliberately optimizing its structure, microstructure, dimension, etc. For instance, single-crystal or epitaxial VO<sub>2</sub> films are fabricated at elevated temperature to receive sharp MIT transition with large change in the device resistance.<sup>[23,25,26]</sup> Fluctuation in the transition parameters can be greatly suppressed by reducing the total amount of transitioning domains in high-quality VO<sub>2</sub> samples with larger crystal grains and fewer grain boundaries.<sup>[27]</sup> The transition temperature can be further lowered when freestanding VO<sub>2</sub> nanowire, nanobeam, or nanobelt is used to release the residual strains.<sup>[28]</sup> Spatial confinement in VO<sub>2</sub> nanostructure may also lead to exotic physiochemical properties by surface atoms, reconstruction, and/or lattice distortion.<sup>[29]</sup> However, the high-temperature fabrication of single-crystal/epitaxial samples,<sup>[27]</sup> or the use of freestanding nanomaterials,<sup>[30]</sup> is not directly applicable to the state-of-the-art complementary metal-oxide semiconductor (CMOS) technology. It is thus highly desired to develop VO<sub>2</sub> thin film device in metal/oxide/metal (MOM) sandwich structure at low temperature, as well as to explore and control its MIT and transport behavior on nanometer scale toward CMOS-compatible device applications.

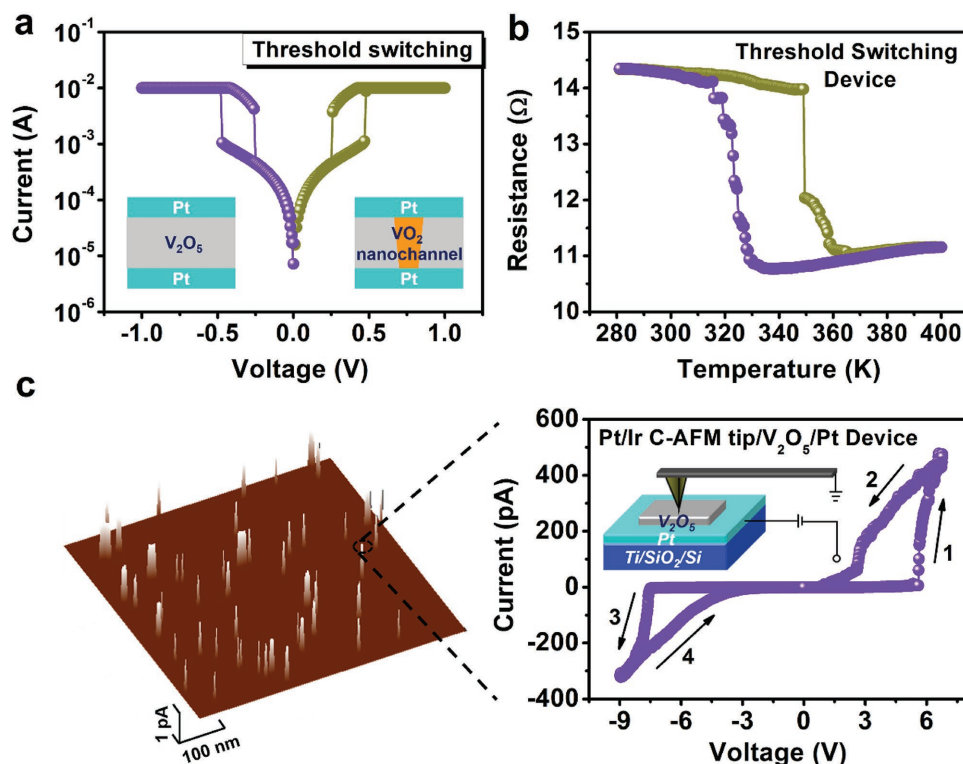
With this concern, herein we report the room-temperature construction of 1D VO<sub>2</sub> nanochannel via electrically induced oxygen ion migration in V<sub>2</sub>O<sub>5</sub> thin film device. Sharp and reliable MIT transition behaviors with a steep turn-on voltage slope of <0.5 mV dec<sup>-1</sup>, fast switching speed of 17 ns, low energy consumption of ≈8 pJ, and low variability of less than 4.3% for both the switching voltages and device resistances in hundreds of voltage sweeping cycles are demonstrated. The as-fabricated VO<sub>2</sub> nanochannel devices with superior threshold switching behavior could be used as reliable selectors in large-scale crossbar memory arrays. We demonstrate that Pt/HfO<sub>2</sub>/Pt/VO<sub>2</sub>/Pt 1S1R memory devices can be correctly written and read for over 10<sup>7</sup> cycles in a 20 × 20 array, confirming the effectiveness of optimizing VO<sub>2</sub> MIT through constructing CMOS-compatible nanostructures via electric-field-induced ion transport procedures.

The key issue of using vanadium dioxide for practical application is to improving its MIT performance, viz., transition sharpness, switching speed, energy consumption, and reproducibility, in thin film devices. Fortunately, the nanoconductive filament formed via electric-field-induced ion migration in resistive switching devices provides a powerful platform in this direction,<sup>[2–6]</sup> adopting which perpendicularly aligned 1D VO<sub>2</sub> nanochannel may be constructed in V<sub>2</sub>O<sub>5</sub> thin films

(inset of Figure 1a). According to this idea, we fabricated V<sub>2</sub>O<sub>5</sub> thin film on commercially available Pt/Ti/SiO<sub>2</sub>/Si substrate by radio-frequency (RF) magnetron sputtering (see the Experimental Section for sample preparation details).<sup>[31]</sup> The thickness and surface roughness of the as-prepared sample are ≈80 and 2.58 nm (Figure S1a, Supporting Information), respectively. X-ray diffractive pattern and Raman spectrum indicate that the V<sub>2</sub>O<sub>5</sub> thin film is (001)-textured with orthorhombic structure and *c*-axis residing in the out-of-plane direction (Figure S1b,c, Supporting Information). Then the transport properties are characterized in the Pt/V<sub>2</sub>O<sub>5</sub>/Pt sandwich structure by capping the V<sub>2</sub>O<sub>5</sub> thin film with Pt top electrode (TE) (Figure S2 and S1a, Supporting Information). Consistent with the insulating nature of orthorhombic V<sub>2</sub>O<sub>5</sub>, the pristine device shows small current in the range of 10<sup>-7</sup> A when scanned from 0 to 9 V. An abrupt jump in the *I*–*V* characteristic is observed when the applied voltage reaches 9.8 V, leading to a significant increase in the device current to the compliance preset of 0.01 A (upper panel of Figure S2, Supporting Information). This positively biased scanning process is equivalent to the forming procedure in ionic-based resistive switching devices.<sup>[7–11]</sup> The device remains in high conductive state after removing the applied electric field, indicating the observed resistive switching is nonvolatile in nature. Then a cc-free negative dual scan between 0 and –1 V can serve as the reset operation to transform the device back to low conductive state (lower panel of Figure S2, Supporting Information). Afterward, threshold switching behaviors in both polarities are received (Figure 1a), which may be attributed to the MIT transition between VO<sub>2</sub> (M1) and VO<sub>2</sub> (R) polymorphs.<sup>[32]</sup>

In accordance with the threshold switching phenomenon, the VO<sub>2</sub> device also demonstrates phase transition behavior in resistance–temperature (*R*–*T*) characteristics (Figure 1b). Initially, the as-fabricated V<sub>2</sub>O<sub>5</sub> thin film shows insulating nature with its resistance decreasing monotonically as the sample temperature increases (Figure S3a, Supporting Information). When electroformed, the device behaves as metallic conductor showing monotonically increasing *R*–*T* responses (Figure S3b, Supporting Information). Upon annealing in the cc-free negative reset process, the obtained threshold switching device shows an obvious decrease in the device resistance when being heated over 349 K (insulator-to-metal transition, IMT). On the contrary, the device transits from low to high resistance state (MIT) upon cooling below 323 K. The transition temperatures (*T*<sub>IMT</sub> ≈ 349 K, *T*<sub>MIT</sub> ≈ 323 K) are well consistent with those of VO<sub>2</sub> documented in the literatures,<sup>[33]</sup> while the minor discrepancy may be arising from the different correlation effects in the bulk and nanoscale VO<sub>2</sub> samples. In both the heating and cooling procedures, the high-temperature device behaves as a metallic conductor with positive *R*–*T* coefficients of ≈6 × 10<sup>-4</sup> K<sup>-1</sup>. Considering the fact that the electroformed device is nonvolatile and highly conductive while a cc-free annealing process can turn it into a threshold switching device, a direct hypothesis may be raised that the electroforming process can convert the orthorhombic insulating V<sub>2</sub>O<sub>5</sub> locally into metallic VO<sub>2</sub> (B) phase, whereas the following high-current annealing process further transforms the VO<sub>2</sub> (B) into VO<sub>2</sub> (R) and VO<sub>2</sub> (M1) phases sequentially.

Moreover, conductive atomic force microscopy (C-AFM) analysis reveals that the threshold switching is highly localized



**Figure 1.** a) Current–voltage characteristics of the Pt/VO<sub>2</sub>/Pt device showing threshold switching processes. Inset shows the schematic illustration of the VO<sub>2</sub> nanochannel electroformed in the V<sub>2</sub>O<sub>5</sub> matrix. b) Resistance–temperature properties of the threshold switching devices. c) Nanoscale current mapping image and localized threshold resistive switching behavior of the device. Experimental setup for conductive-atomic force microscopy (C-AFM) analysis is shown in the inset of (c). The numberings and arrows in (c) indicate the scanning sequence.

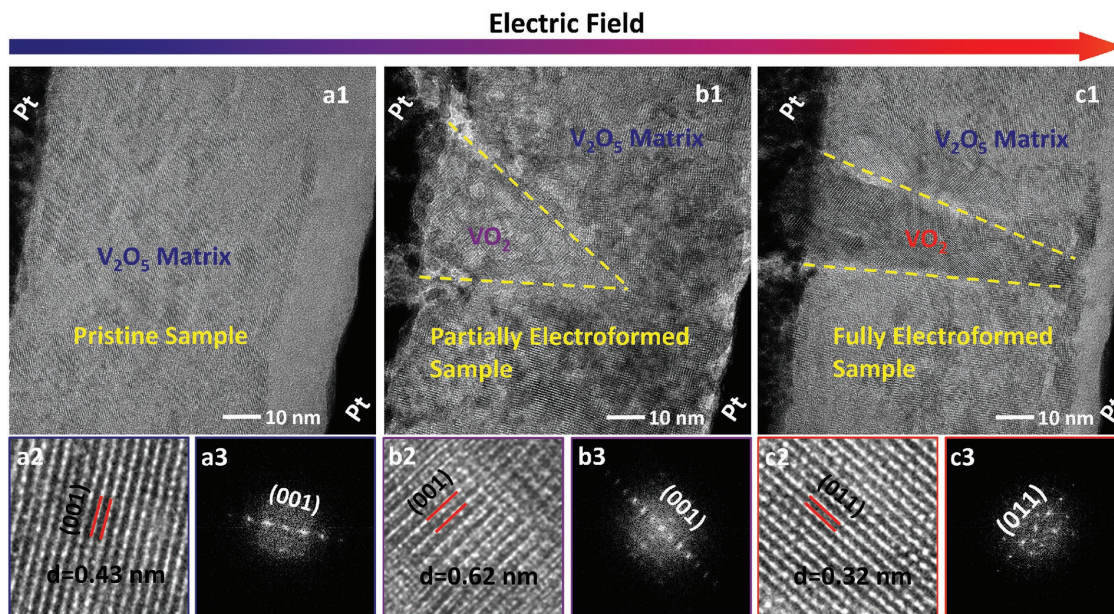
in nanoscale regions. For instance, the C-AFM current map of the V<sub>2</sub>O<sub>5</sub> film does not exhibit significant difference under a low biased voltage of 0.5 V, suggesting that pristine device has a poor conductivity. After applying a biased voltage of 1 V, several bright spots with the diameter of about ≈10 nm, associated with the localized conductive regions, appear (left panel of Figure 1c). The *I*–*V* characteristic of each conductive spot demonstrates threshold switching behavior similar to that of the macroscopic devices (right panel of Figure 1c). Moreover, the forming high-current annealing–threshold switching cycles of macroscopic devices can be repeated locally via C-AFM technique. By placing the C-AFM probe at an arbitrary position on the surface of the V<sub>2</sub>O<sub>5</sub>/Pt sample, the current–voltage response of the C-AFM probe/V<sub>2</sub>O<sub>5</sub>/Pt structure well resembles the forming and switching behavior of the macroscopic sample (Figure S4, Supporting Information). As such, it can be preliminarily supposed that VO<sub>2</sub> nanochannels are constructed in V<sub>2</sub>O<sub>5</sub> matrix via the proposed electric-field-induced ion migration approach.

In order to clarify the physics underlying the observed interesting MIT behavior, extensive and careful high-resolution transmission electron microscopy (HRTEM) analysis was performed to visualize the structure modification of the samples (Figure 2). As shown, the pristine vanadium oxide thin film shows uniform lattice fringe of (001) crystal planes with a *d*-spacing of 0.43 nm (Figure 2a), indicating that the as-fabricated sample has a majority phase of orthorhombic V<sub>2</sub>O<sub>5</sub> structure. The corresponding fast Fourier transformed image also

verifies this claim. Minor amorphous component can be found near the platinum electrode, which may be ascribed to the non-thermodynamic equilibrium growth of interfacial species due to lattice mismatch between the orthorhombic V<sub>2</sub>O<sub>5</sub> and Pt electrode. When the device is electroformed, crystallographic features clearly different from that of the V<sub>2</sub>O<sub>5</sub> background can be distinguished, corresponding to partially and fully developed new phases. Other than the orthorhombic V<sub>2</sub>O<sub>5</sub> matrix, the partially formed nanoprotusion has a sharp conical shape indexed with (001) crystal plane of B-phase VO<sub>2</sub> showing *d*-spacing of 0.62 nm (Figure 2b). When fully developed (Figure 2c), the nanochannel becomes cylinder in shape and shows monoclinic VO<sub>2</sub> (M1) polymorph with *d*-spacing of 0.32 nm for (011) crystal plane. Therefore, the construction of VO<sub>2</sub> nanochannel in V<sub>2</sub>O<sub>5</sub> matrix is confirmed directly through HRTEM observation, which is in good agreement with our proposed strategy. This work also reports for the first time that MIT transition still persists in ultrasmall dimension VO<sub>2</sub> nanochannel. Although electric-field-induced oxygen ion migration process may also generate other VO<sub>x</sub> species (e.g., conductive hexagonal V<sub>2</sub>O<sub>3</sub> with *d*-spacing of 0.36 nm), their presence is considered minor if not eliminable, as the conductive characteristics of these sub-oxides are contrary to the room-temperature insulating nature of the threshold switching device.

The key information about the geometry, dimension, structure, composition, and density of the electric-induced VO<sub>2</sub> nanoprotusion and nanochannel is further examined. The wider and narrower diameters of the nanochannel are 24 and 12 nm



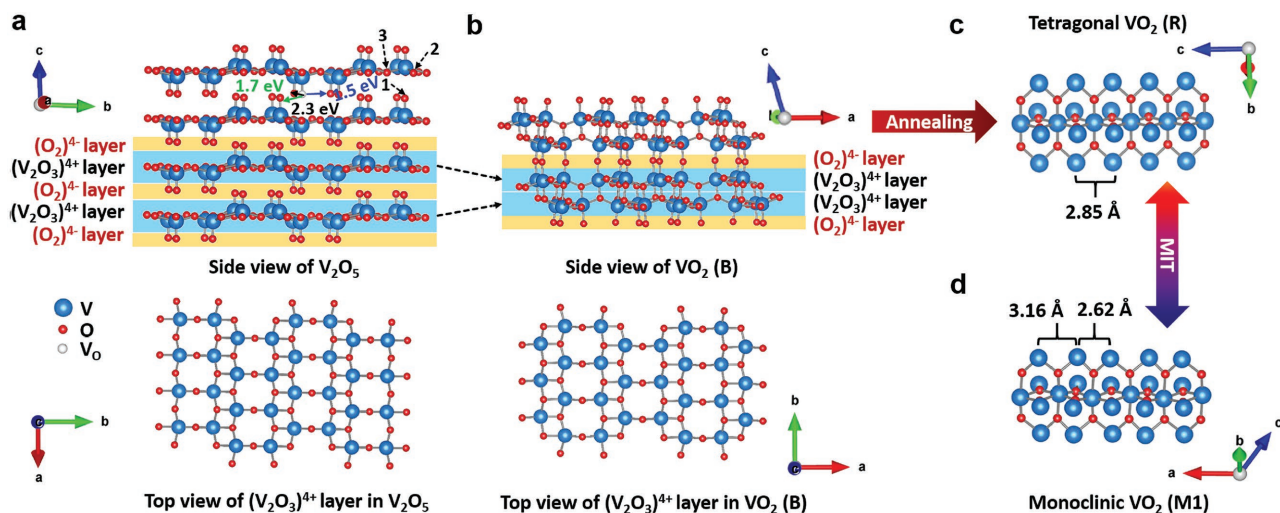


**Figure 2.** Cross-sectional HRTEM images, zoom-in view of lattice fringes and fast Fourier transformed images of a1–a3) the pristine  $\text{V}_2\text{O}_5$  thin film sandwiched between two Pt electrodes, the electroformed device with b1–b3) partially and c1–c3) almost fully developed  $\text{VO}_2$  nanochannels, respectively.

at the anode and cathode, respectively, which are close to that of the conductive spots shown in the C-AFM current map of Figure 1c. Both the conical protrusion and cylindrical nanochannel grow straightly from the anode toward the cathode, as verified by the presence of  $\text{VO}_2$  protrusion near the anode and the direction of protrusion front pointing toward the cathode. This is in good agreement with the fact that oxygen ions migrate more readily along the direction of the applied electric field.<sup>[2–6]</sup> Close examination of Figure 2 also reveals that the formation of  $\text{VO}_2$  nanochannel occurs preferentially at the position where the electrode/vanadium oxide interface is imperfect, as the concentrated electric field will facilitate the migration of charged species in solid thin films. Interestingly, although several partially formed  $\text{VO}_2$  (B) protrusion exist in the  $3\ \mu\text{m}$  wide TEM specimen, only one almost fully connected nanochannel is observed. Considering the small dimension of the TEM specimen, this does not necessarily mean that only one fully developed  $\text{VO}_2$  nanochannel is formed in the macroscopic device. Instead, multiple  $\text{VO}_2$  nanochannels may be present throughout the entire  $\text{V}_2\text{O}_5$  film, as documented in the literature.<sup>[7]</sup> This is consistent with the ion migration model of valence change resistive switching memories (VCM), wherein the migration of oxygen ions can initialize the nucleation and growth of multiple conductive filaments. Considering the  $\approx 2000$  time difference in the conductivity of the as-formed  $\text{VO}_2$  nanochannel and the insulating  $\text{V}_2\text{O}_5$  matrix (as estimated from the Figure 1a and upper panel of Figure S2, Supporting Information), it is reasonable that once one of these nanofilaments is fully developed and connects the cathode, large current will flow preferentially and mostly through this metallic pathway.<sup>[2–7]</sup> Other parts of the device with insulating  $\text{V}_2\text{O}_5$  matrix and even partially developed  $\text{VO}_2$  protrusion will be short-circuited due to the significant difference in their conductivity as compared to that of the fully developed  $\text{VO}_2$  conductive nanochannel. The voltage drop

across the device will also decrease significantly when the current level reaches the compliance preset, therefore preventing other filaments in adjacent region from further growth. The failure of being further subjected to external electric stressing (especially the high-current annealing in the cc-free negatively biased process) also accounts for the observation of solo  $\text{VO}_2$  (B) component in the partially developed protrusion. As such, improved transition performance is observed in the  $\text{VO}_2$  nanochannel device. This essential information about the location, morphology, dimension, and density of  $\text{VO}_2$  nanochannels also helps to guide the fabrication of high-performance  $\text{VO}_2$  devices.

First-principle density functional theory (DFT) calculations were also performed to better understand the formation process of nanoscale  $\text{VO}_2$  in  $\text{V}_2\text{O}_5$  matrix under external electric field. Generally,  $\text{V}_2\text{O}_5$  crystallizes in orthorhombic structure consisting of layers of  $\text{VO}_5$  square pyramids in edge- and corner-sharing configuration (Figure S5, Supporting Information).<sup>[34]</sup> Due to the loose bounding of the  $\text{VO}_5$  square pyramids, intercalation of molecular species is enabled within the interlayer sites.<sup>[35]</sup> The interlayer spaces also facilitate the transport of ionic species.<sup>[36]</sup> Deep examination of the  $\text{V}_2\text{O}_5$  atomic structure reveals that three types of oxygen atoms exist in the square pyramids, among which species 1 is pointing toward the interlayer space while species 2 and 3 are residing in the same plane of the vanadium atoms (side view, upper panel of Figure 3a). As such,  $\text{V}_2\text{O}_5$  can also be visualized as consisting of alternating layers of  $(\text{V}_2\text{O}_3)^{4+}$  (top view, lower panel of Figure 3a) and  $(\text{O}_2)^{4-}$  in  $-\text{O}_2-\text{V}_2\text{O}_3-\text{O}_2-\text{V}_2\text{O}_3-\text{O}_2-$  sequence, as labeled by light blue and yellow shadows. Considering the fact that oxygen vacancies usually exist in physically fabricated oxide thin films, herein we first check the formation energy of oxygen vacancies at atomic sites 1, 2, and 3, respectively. We find that it is energetically favorable to form oxygen vacancy in the  $(\text{O}_2)^{4-}$  layer, as the formation energy of site 1 (in  $\text{O}_2$  layer) vacancy is



**Figure 3.** a) Side view of the alternating  $(V_2O_3)^{4+}$  and  $(O_2)^{4-}$  layers (upper panel) and top view of the  $(V_2O_3)^{4+}$  layer (lower panel) in  $V_2O_5$ , b) side view of the alternating  $[(V_2O_3)^{4+}]_2$  and  $(O_2)^{4-}$  layers (upper panel) and top view of the  $(V_2O_3)^{4+}$  layer in  $VO_2$  (B), and crystal structures of the c)  $VO_2$  (R) and d)  $VO_2$  (M1) polymorphs, respectively. The Arabic numbers and dashed arrows in a label indicate the three types of oxygen species existing in the orthorhombic  $V_2O_5$ , respectively. The solid arrows indicate the energy barrier of oxygen vacancy diffusion to its neighboring atomic sites, respectively.

0.196 and 0.229 eV per formula unit cell lower than that of site 2 and 3 oxygen vacancies. The diffusion energy barriers of the site 1 oxygen vacancies are relatively small, for example, 1.5, 1.7, and 2.3 eV to its neighboring positions, respectively, therefore allowing the oxygen ions to migrate in the  $(O_2)^{4-}$  layer and be extracted through crystalline boundaries by external electric field.

With the presence of these oxygen vacancies, the valence states of the vanadium species will be lowered, which corresponds to their transformation from  $V_2O_5$  to  $VO_x$ . Several structural polymorphs of  $VO_x$  exist in reality, among which  $VO_2$  (B),  $VO_2$  (M1), and  $VO_2$  (R) receive most of the research interest due to their wide spectrum of interesting electrical and optical properties for information and energy technologies.<sup>[20,29a]</sup> Interestingly, B-phase  $VO_2$  carries similar open framework of orthorhombic  $V_2O_5$  among all the vanadium suboxides,<sup>[37]</sup> wherein the identical  $(V_2O_3)^{4+}$  layers are merged in pairs and are stacked alternatively with  $(O_2)^{4-}$  layer along the  $c$ -axis in  $-O_2-V_2O_3-V_2O_3-O_2-V_2O_3-V_2O_3-O_2-$  sequence (Figure 3b). It is reported that the extraction of oxygen from  $V_2O_5$  through annealing  $V_2O_5$ /metal/ $V_2O_5$  sandwich structure at high temperature can produce B-phase  $VO_2$ .<sup>[38]</sup> Therefore, the formation of  $VO_2$  (B) polymorph may also be possible upon removing oxygen species from  $V_2O_5$  via electric-field-induced vacancy formation and migration. Nevertheless, the metallic  $VO_2$  (B) polymorph is metastable and undergoes irreversible phase change into tetragonal  $VO_2$  (R) upon thermal annealing,<sup>[39]</sup> while further cooling of  $VO_2$  (R) to room temperature produces monoclinic  $VO_2$  (M1) phase. The  $VO_2$  (R) polymorph has a uniform V–V separation of 2.85 Å, allowing the  $d^1$  electrons to itinerate over the entire phase and leading to an intrinsic metallic ground state (Figure 3c). In the  $VO_2$  (M1) phase, the neighboring V atoms dimerize along the  $c$ -axis, resulting in periodic lattice distortion with alternating V–V separations of 2.62 and 3.16 Å (Figure 3d). Due to the charge ordering on V–V dimers,

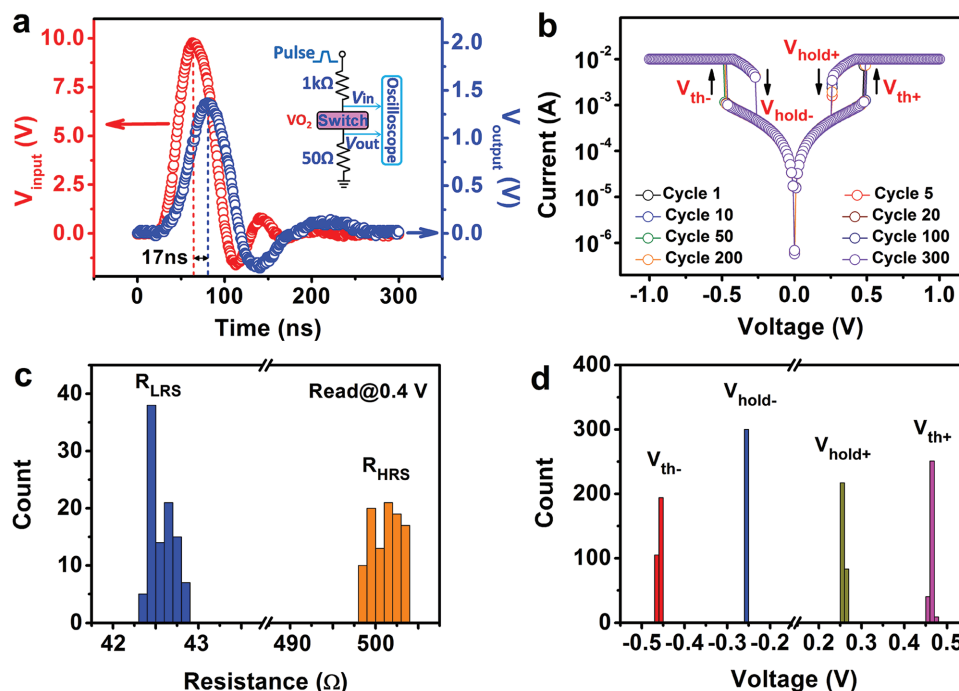
$VO_2$  (M1) phase is intrinsically insulating. Thereafter, both electric and thermal stimuli can trigger reversible transition between the  $VO_2$  (M1) and  $VO_2$  (R) phases with obvious contrast in device resistances. Noting that electric-field-induced ion migration process usually occurs in a filamentary manner,<sup>[2–6]</sup> pseudo 1D  $VO_2$  nanochannel can be constructed at room temperature in  $V_2O_5$  thin film with the present strategy.

Associated with the nanoconfinement of  $VO_2$  MIT in localized regions,<sup>[40]</sup> the transition behavior is well enhanced as compared to the macroscopic polycrystalline counterparts. The turn-on voltage slope of the device is estimated to be  $<0.5$  mV  $dec^{-1}$ , which is the sharpest reported so far (Figure S6, Supporting Information).<sup>[41]</sup> Theoretically, the transition speed of  $VO_2$  MIT can be derived with the following equation

$$V = \lambda v_D \exp(-\Phi/kT) \quad (1)$$

where  $\lambda$  and  $v_D$  are estimated to be 1 Å and  $10^{12}$  s $^{-1}$ , respectively, while  $\Phi \approx kT_{MIT}$  is the activation barrier,  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J K $^{-1}$ ), and  $T$  is the temperature.<sup>[42]</sup> Taking the  $T_{MIT}$  of 349 K, the transition speed is derived to be  $\approx 40$  m s $^{-1}$  and the transition time of our 80 nm  $VO_2$  nanochannel device is  $\approx 2$  ns. This is in good agreement with that measured by time-resolved near-edge X-ray absorption spectroscopy.<sup>[43]</sup> We have also monitored the latency between the input and output voltage pulses of the  $VO_2$  nanochannel device in the electrical circuit shown in Figure 4a to experimentally confirm its MIT transition speed. As shown, the transition time of the  $VO_2$  switching device is measured to be  $\approx 17$  ns, which is fast enough for practical applications. The energy consumption for threshold switching is  $\approx 8$  pJ.

Electrical measurement also provides a fast characterization of the device stability, as compared to the thermal cycling operation which involves time-consuming heating and cooling procedures. When scanned between  $\pm 1$  V in the



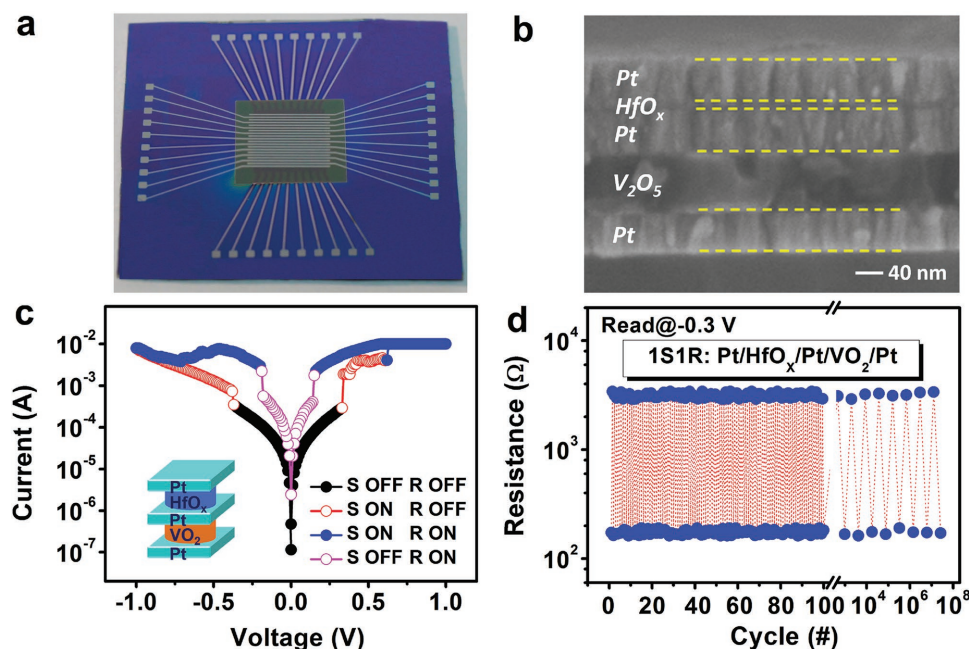
**Figure 4.** a) Circuit design and input/output signal evolution for switching speed measurement of VO<sub>2</sub> MIT. b) Threshold switching characteristics of the VO<sub>2</sub> device for over 300 consecutive cycles. Histograms of the device c) resistances recorded at a read voltage 0.4 V and d) switching voltages for 300 cycles.

out-of-plane direction for 300 consecutive cycles, the VO<sub>2</sub> threshold switching device demonstrates great reproducibility, with the switching parameters showing only negligible variations (Figure 4b). For instance, the device resistances ( $R_{HRS}$  ( $501.25 \pm 2.23 \Omega$ ),  $R_{LRS}$  ( $42.58 \pm 0.14 \Omega$ )), threshold switching voltages ( $V_{th+}$  ( $0.46 \pm 0.0039$  V),  $V_{th-}$  ( $-0.46 \pm 0.0048$  V)), and holding voltages ( $V_{hold+}$  ( $0.26 \pm 0.0045$  V),  $V_{hold-}$  ( $-0.26 \pm 0$  V)) are all distributed in a very narrow range (Figure 4c,d). The dispersion coefficients for both the device resistances and programming voltages are less than 4.3%. The transition amplitude ( $R/R_0$ ) is kept at  $\approx 11.8$  over the continuous electric cycling. We have also used Weibull analysis to further quantify the uniformity of the switching parameters. The Weibull exponents ( $k$ ) are 282.52 for  $R_{HRS}$ , 653.154 for  $R_{LRS}$ , 431.57 for  $V_{th+}$ , 681.44 for  $V_{hold+}$ , 176.67 for  $|V_{th-}|$ , and  $\sim \infty$  for  $|V_{hold-}|$ , while the standard deviation ( $\Delta$ ) to mean ( $\mu$ ) ratios ( $\Delta/\mu$ ) are 0.0044 for  $R_{HRS}$ , 0.0033 for  $R_{LRS}$ , 0.0084 for  $V_{th+}$ , 0.0174 for  $V_{hold+}$ , 0.01 for  $V_{th-}$ , and  $\approx 0$  for  $V_{hold-}$ , respectively (Figure S7, Supporting Information). The large  $k$  and small  $\Delta/\mu$  values of the present device again suggest that the proposed approach of inducing metal-insulator transition in VO<sub>2</sub> nanochannel can lead to superior uniformity and reliability in the MIT transition behaviors.

In practice, the present Pt/VO<sub>2</sub>/Pt sandwich structure with superior MIT transition and threshold switching characteristics can be used as selector device to suppress the sneaking path and misreading problem of high-density crossbar memory arrays. To verify the effectiveness of this approach, we have integrated the VO<sub>2</sub> device (S) with HfO<sub>2</sub> resistive switching memory cells (R) into 1S1R architecture of a  $20 \times 20$  crossbar array (Figure 5a,b) and tested their electrical properties. Before evaluating their performance in the crossbar array,

the current-voltage characteristics of individual memory, selector, and separate 1S1R structure were first studied with Pt/Ti/SiO<sub>2</sub>/Si substrate as the universal bottom electrode (BE) and round-shape Pt pad with the diameter of 100  $\mu$ m as the separate top electrode (TE). As shown in Figure S8 (Supporting Information), the HfO<sub>2</sub> memory element itself exhibits a nonvolatile bipolar resistive switching from HRS to LRS at a set voltage ( $V_{set}$ ) of  $\approx 0.6$  V and from LRS to HRS at a reset voltage ( $V_{reset}$ ) of  $\approx -0.9$  V. The HRS/LRS currents are  $\approx 7.9 \times 10^{-4}$  A/0.01 A (read at 0.35 V). Coincidentally, the threshold switching process of the VO<sub>2</sub> selector demonstrates  $I-V$  curves in the same operation ranges. The switching voltages are  $\approx \pm 0.46$  V and the HRS/LRS currents are  $\approx 6.6 \times 10^{-4}$  A/0.01 A (read at 0.35 V), respectively. As such, the serially connected selector and memory elements can be turned on and off effectively (Figure 5c). Moreover, the 1S1R unit can be switched continuously for  $10^7$  switching cycles under pulse operation with the set/reset voltage pair of 1 V/−1 V and triggering period of 20 ns (Figure 5d). Both the HRS and LRS are retractable with an ON/OFF resistance ratio of more than 10. Then the selecting performance of VO<sub>2</sub> nanochannel device is evaluated in the  $20 \times 20$  crossbar array (Figure S9a, Supporting Information), wherein switching and proper reading of the 1S1R structure is observed (Figure S9b,c, Supporting Information). It is noteworthy that the configuration and geometry of the device in the crossbar array is significantly different from that of a separate 1S1R structure, which may account for the difference in the  $I-V$  characteristics of Figure 5c and Figure S9b (Supporting Information).<sup>[44]</sup> Herein, Cell #1 is a designated HRS cell surrounded by three undesigned LRS cells (#2–4). Due to the presence of VO<sub>2</sub> selector in the 1S1R structure, the high





**Figure 5.** a) Top-view digital image of a  $20 \times 20$  crossbar array consisting of 400 Pt/HfO<sub>2</sub>/Pt/VO<sub>2</sub>/Pt 1S1R units. b) Cross-sectional scanning electron microscopy image of a 1S1R unit with the device structure of Pt/HfO<sub>2</sub>/Pt/V<sub>2</sub>O<sub>5</sub>-VO<sub>2</sub>/Pt. c)  $I$ - $V$  characteristics of the Pt/HfO<sub>2</sub>/Pt/VO<sub>2</sub>/Pt 1S1R structure in the S-OFF R-OFF, S-ON R-OFF, S-ON R-ON, and S-OFF R-ON stages, respectively. d) Endurance performance of the 1S1R structure with the writing/erasing pulse pair of ( $\pm 1$  V, 20 ns) and read voltage of  $-0.3$  V, respectively.

resistance state of the HRS cell #1 can be read out correctly with the device current in the range of  $1 \times 10^{-9}$  to  $5 \times 10^{-8}$  A. In direct contrast, the device currents of the other three LRS cells are in the higher range of  $3 \times 10^{-9}$  to  $4 \times 10^{-6}$  A, respectively. Therefore, it is confirmed that the present VO<sub>2</sub> nanochannel device can be used as reliable selector for correct reading of the crossbar resistive switching memory arrays.

To summarize, we have demonstrated a simple yet effective approach for the control of VO<sub>2</sub> metal-insulator transition behavior on nanoscale. By employing electric-field-induced oxygen ion migration process to construct VO<sub>2</sub> nanochannels in V<sub>2</sub>O<sub>5</sub> matrix, superior VO<sub>2</sub> MIT behavior is observed with a sharp response of  $<0.5$  mV dec<sup>-1</sup>, fast switching speed of 17 ns, low energy consumption of  $\approx 8$  pJ, and much reduced switching randomness with variability of  $<4.3\%$  for both the switching voltages and device currents. As such, VO<sub>2</sub>-based CMOS-compatible and highly reliable threshold switching device is made possible as selector elements for high-density information storage applications.

## Experimental Section

**Sample Preparation:** 80 nm thick V<sub>2</sub>O<sub>5</sub> film was deposited on commercial Pt/Ti/SiO<sub>2</sub>/Si substrates by RF magnetron sputtering a V<sub>2</sub>O<sub>5</sub> target at room temperature. Ar and O<sub>2</sub> with the O<sub>2</sub>/Ar ratio of 1:4 were introduced into the chamber during deposition. Then, Pt TE was deposited by RF magnetron sputtering at room temperature with a diameter of 100  $\mu$ m through a metal shadow mask onto the V<sub>2</sub>O<sub>5</sub> film. For the Pt/HfO<sub>2</sub>/Pt/VO<sub>2</sub>/Pt 1S1R structure, HfO<sub>2</sub> film was prepared according to the method reported in the literature.<sup>[10]</sup> The bit/word line width and length of the crossbar array are  $\approx 150$   $\mu$ m and  $\approx 10$  mm, respectively.

**Characterization:** The cross-sectional scanning electron microscopy image of the device was visualized using a Hitachi S-4800 field-emission scanning electron microscope. Cross-sectional HRTEM and scanning transmission electron microscopy (STEM) images of the as-fabricated and electroformed samples were recorded on a FEI Titan Themis 200 transmission electron microscope by SAE Magnetics (H.K.) Ltd. Spatial resolutions of the TEM and STEM observations are 0.1 and 0.08 nm, respectively. The TEM specimens were prepared on a FEI Helios 450S dual beam focus ion beam (FIB) workstation with the dimension of 500 nm height  $\times$  3  $\mu$ m width  $\times$  40 nm thickness. Two types of TEM specimens, namely, pristine and electroformed devices, were examined. The pristine specimen was cut randomly from a fresh-made Pt/V<sub>2</sub>O<sub>5</sub>/Pt device, while the electroformed specimen was obtained in the area close to the blow-off region of the top platinum electrode. Blow-off of the top electrode is probably arising from the exhaust of oxygen gas during forming process, and may correspond to a location where the strongest nanochannel is developed.<sup>[7]</sup> The surface morphology of the as-fabricated V<sub>2</sub>O<sub>5</sub> thin film was monitored on a Dimension Icon scanning probe microscope, which is equipped with a Pt/Ir-coated conducting cantilever for conductive atomic force microscopy measurements. The crystalline structure of the as-deposited V<sub>2</sub>O<sub>5</sub> film was investigated by grazing-incidence X-ray diffraction (XRD) technique (Bruker AXS, D8 Discover) using Cu-K $\alpha$  radiation and Raman spectra (Renishaw Via-reflex). Room-temperature current-voltage ( $I$ - $V$ ) characteristics of the devices were recorded on a Lakeshore probe station with a Keithley 4200 semiconductor parameter analyzer in direct current (dc) voltage-sweeping mode. The biased voltage was applied onto the Pt TE while the Pt BE was grounded. Current compliance (0.01 or 0.1 A) was applied to protect the devices. The resistance-temperature ( $R$ - $T$ ) relationship of the devices was examined on a physical property measurement system (PPMS, Quantum Design) with conventional two-probe method. Top electrodes were interconnected with thin platinum wires using highly conductive silver glue, followed by welding of the Pt wires to PPMS sample stage. During  $R$ - $T$  measurements, a constant-current mode with a small excitation current of 1  $\mu$ A (to prevent large current from having influence on the device) was used.

**First-Principles Calculation:** To model oxygen vacancies, a  $2 \times 2 \times 2$  supercell of  $V_2O_5$  with 56 atoms was employed. Because of structural symmetry there are three types of oxygen vacancy positions as indicated in Figure 3a. The lattice constant and internal atomic positions were fully relaxed. Density functional theory calculations were performed with the VASP (Vienna ab initio simulation package) code using the generalized gradient approximation (GGA-PBE) functional for electronic exchange and correlation and a  $6 \times 6 \times 6$   $k$ -point grid including the Gamma point.<sup>[45]</sup> The oxygen vacancy diffusion energy barriers were calculated using nudged elastic band method implemented in VASP.<sup>[46]</sup>

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

metal–insulator transitions, nanoconfinement, oxygen ion migration, resistive switching, nanochannels

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