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UNIVERSITY OF CALIFORNIA SAN DIEGO

New Materials and Techniques for Resistive Switching Devices and Neuromorphic Computing

A dissertation submitted in partial satisfaction of the
requirements for the degree
Doctor of Philosophy

in

Materials Science and Engineering

by

Min-Han Lee

Committee in charge:

Professor Ivan K. Schuller, Chair
Professor Prabhakar R. Bandaru
Professor Eric E. Fullerton
Professor Ying Shirley Meng
Professor Oleg G. Shpyrko

2021

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The Dissertation of Min-Han Lee is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2021

DEDICATION

To my wife *Shin-Pei Wang* and my family

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VITA

Education

2021	Ph.D., Materials Science and Engineering	University of California San Diego (UCSD), La Jolla, CA
2016	M.S., Materials Science and Engineering	University of California San Diego (UCSD), La Jolla, CA
2013	B.S., Nano Science and Engineering	National Chiao-Tung University (NCTU), Hsinchu, Taiwan

Publications

1. **M.-H. Lee**, Y. Kalcheim, J. del Valle, and I. K. Schuller. “Controlling metal- insulator transitions in vanadium oxide thin films by modifying oxygen stoichiometry.” ACS Appl. Mater. Interfaces, 13, 887 (2021).
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ABSTRACT OF THE DISSERTATION

New Materials and Techniques for Resistive Switching Devices and Neuromorphic Computing

by

Min-Han Lee

Doctor of Philosophy in Materials Science and Engineering

University of California San Diego, 2021

Professor Ivan K. Schuller, Chair

The development of new materials and electronic devices which exhibit unique physical properties will allow for the next technological leap toward brain-inspired computing. Among all functional materials, vanadium oxides such as VO_2 and V_2O_3 are at the forefront of condensed matter physics/materials science research and are considered promising candidates for memory and computing applications. These oxides are well-known Mott insulators that feature metal-

insulator transitions (MITs) and resistive switching (RS). In response to temperature, electric field or other external stimuli, a significant change in electrical resistivity can be observed during the phase transition. Neuronal or synaptic functionalities could be thus implemented using these properties, which serve as the fundamental building blocks for neuromorphic technologies. Despite this interest, the underlying physical mechanisms responsible for these phenomena are still not clear. The aim of this dissertation is to investigate and understand the MITs and RS behavior in different vanadium oxides using novel synthesis/characterization methods. To begin with, this dissertation discusses a high-vacuum gas evolution technique, in which the oxygen partial pressure and temperature can be precisely adjusted to strategically control the oxygen stoichiometry in vanadium oxide thin films. Using this technique, we successfully stabilized the V_3O_5 exotic phase despite its extremely narrow phase stability range. In addition, we were able to control the phase transformation between VO_2 , V_3O_5 , and V_2O_3 , and ultimately manipulate the MITs between different phases. Furthermore, the electrically induced resistive switching effects of these strongly correlated oxides and the applications of neuromorphic computing devices will be discussed. A joint study of ex-situ electrical transport measurements and in-situ characterization techniques was carried out to investigate the volatile and non-volatile resistive switching mechanisms. We demonstrated that vanadium oxide based switching devices can exhibit both neuron-like or synapse-like functionalities under electric stimuli. Our work presents a comprehensive investigation of new material/technique development, fundamental physical mechanisms, and electronic device applications. We believe our findings can help pave the way for the development of next generation computing technologies.

Chapter I – Introduction: novel materials lead the way to next-generation computing

1.1 Motivation

For over 50 years, semiconductor technologies have relied on “Moore’s law,” which predicts the number of tiny transistors on an integrated circuit chip doubles approximately every 2 years. [1] However, one of the great challenges of future nanoscale transistor development is the physical scaling limits. It is believed that the end of Moore’s law is quickly approaching. In addition, computation operating under the existing Von Neumann architecture will inevitably reach a speed limit because of the fundamental serial nature of communication. [2] Due to these limitations, scientists are searching for the next technological revolution with increasing urgency. We have entered an era of massive information and the development of brain-inspired, highly parallel computing could lead to breakthrough innovations. New materials which exhibit unique physical properties are able to replace a great number of transistors for computing tasks and therefore improve the performance, power dissipation and scalability. The main motivation of this dissertation is to explore, investigate and understand new functional oxides which will enable novel electronic properties with neuromorphic computing functionalities. Recently, Mott insulators have been proposed as new candidates for memory and computing applications. For instance, vanadium oxides are well-known Mott insulators that displays metal-insulator transitions (MITs) and resistive switching (RS) under external stimuli. [3-4] Neuronal or synaptic functionalities could be implemented using these properties. [2] However, one of the main scientific challenges with these materials is the limited understanding of the phase transition triggered by an electric field. For technological applications, it is desired to fabricate high quality vanadium oxide thin films with reliable electronic performance. However, the existence of multiple V-O phases leads to a very complicated V-O phase diagram. [5-6] It is very

difficult to control the oxygen stoichiometry in these complex oxides and stabilize specific V-O phases. (Figure 1.1) A comprehensive understanding of the complex vanadium-oxygen phase stability diagram is still lacking. In the dissertation, Chapter 2 will discuss a novel gas evolution technique which allows for the effective control of oxygen stoichiometry in vanadium oxide thin films. This technique in thin-film growth has allowed for the exploration of new, exotic phases for resistive switching devices. In Chapter 3 & 4, a joint study of ex-situ electrical transport measurements and in-situ transmission electron microscopy was carried out to investigate the volatile and non-volatile resistive switching in these materials. Chapter 5 will discuss a new vanadium oxide phase synthesized using the gas evolution technique for neuromorphic applications. In addition, an in-situ optical imaging technique was used to capture the filament formation process during volatile resistive switching. In Chapter 6, the key findings of this dissertation will be summarized and the prospective studies of related research fields will be discussed.

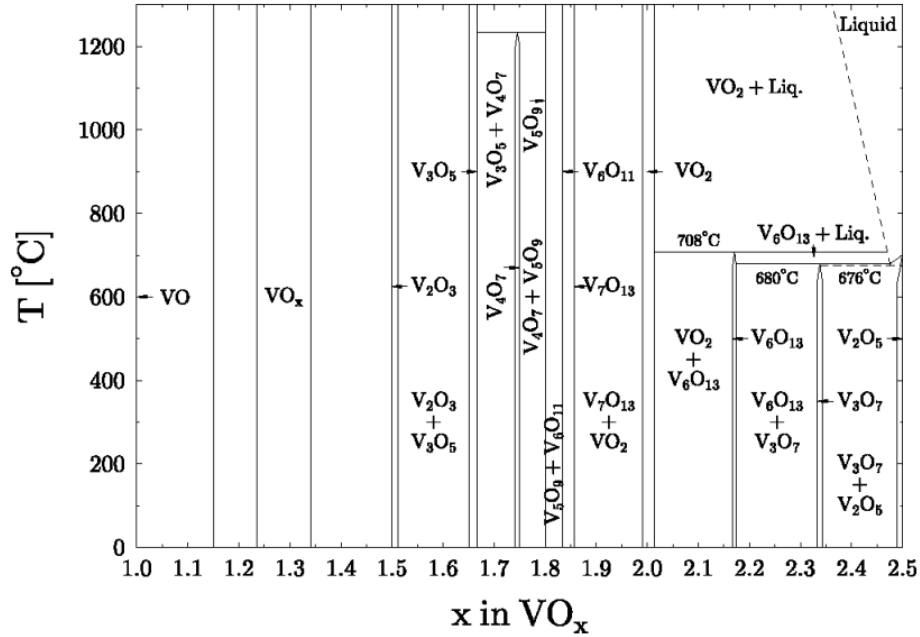


Figure 1.1: V-O Phase diagram. The existence of multiple VO_x phases leads to a complicated V-O phase diagram. Adapted with permission from [5].

1.2 Metal-insulator transition and structural phase transition in vanadium oxides

Metal-insulator transitions (MITs) in oxides have been of special interest in condensed matter physics [1-6] and technology [7] in past decades. Specifically, Mott insulators such as vanadium oxides are considered very promising materials for next-generation oxide electronics. For instance, VO_2 has attracted much attention due to its MIT near room temperature ($T_{\text{MIT}} \sim 340$ K) (Figure 1.2), in which a large change in electric resistivity is accompanied by a structural phase transition (SPT). [8-9] Figure 1.3 shows the temperature dependent X-ray diffraction spectra for VO_2 thin film. The VO_2 exhibits a clear structural phase transition from a high temperature rutile phase to a low temperature monoclinic insulating phase. Additional interest in VO_2 concerns the possibility of modulating this transition by external stimuli. [10-12] The significant change in electrical resistivity offers a platform for resistive switching [13] and neuromorphic computation [14-15] related applications. In pure and Cr-doped V_2O_3 , the concurrence of metal-insulator, structural and magnetic phase transitions has been the subject of much fundamental research. [16-19] When cooled down to around 160 K, it exhibits a corundum-to-monoclinic structural transition. (Figure 1.3) The V_3O_5 phase, as one of the only two VO_x members with a MIT above room temperature ($T_{\text{MIT}} \sim 430$ K) (Figure 1.2c), is an excellent candidate for use in silicon-based technologies [20] and switching device applications. [21-23] During this MIT transition, the lattice structure remains monoclinic with a change in space group symmetry from $I2/c$ to $P2/c$. The possibility to trigger the MIT without a significant structural change is a great advantage of V_3O_5 -based switching devices. Overall, the complexity and variety of physical properties in these materials offer a great platform for resistive-switching based neuromorphic computing.

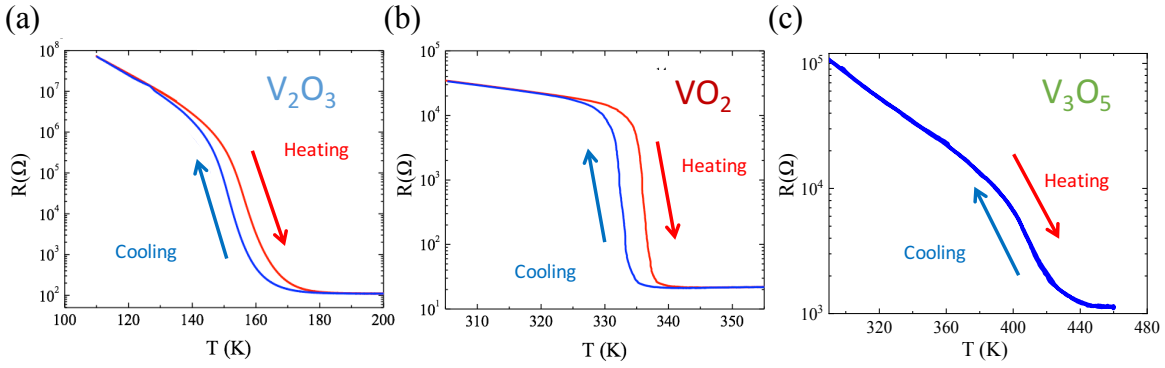


Figure 1.2: Metal-insulator transition in vanadium oxides: Resistance vs temperature of (a) V_2O_3 , (b) VO_2 and (c) V_3O_5 thin films. The red/blue curves represent the different heating/cooling branches during the R-T measurements.

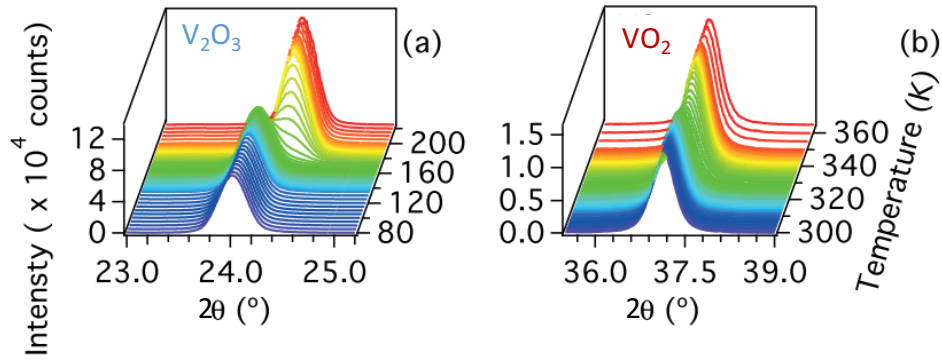


Figure 1.3: Structural phase transition in vanadium oxides. Temperature-dependent XRD scans for (a) V_2O_3 , (b) VO_2 thin films. Adapted with permission from [18].

1.3 Electrically Driven Metal-Insulator Transition

MITs in vanadium oxides usually involve drastic changes in structural, optical, and magnetic properties. [3-5] These phase transitions can be induced by different control sources such as temperature, electric field, magnetic field or optical stimuli. [7, 14] Figure 1.4 demonstrates the typical features of MIT. The electrically triggered MIT can be observed using a two-terminal metal-insulator-metal device setup. A significant change in resistivity can be

induced using different external stimuli. Figure 1.4c shows the strong nonlinear current-voltage (I-V) curves of the MIT in Mott insulators. This behavior could be observed in different material systems such as VO_2 [25], V_2O_3 [26] and NbO_2 [27]. The blue/red curve represents the voltage controlled and current controlled resistive switching, respectively. As the voltage or current ramps up, there will be a sudden drop in resistivity from the insulating state to the metallic state above a threshold value. After the removal of the electric stimulus, the resistivity will return to the original insulating state. A hysteresis in the I-V curve can be often observed. Furthermore, this MIT can also be induced using current source. Generally, the volatile switching is due to the resistive change of the MIT, rather than defect migration driven filament formation. [2] On the other hand, for non-volatile resistive switching, the resistivity change persists beyond the removal of an external stimulus. The original insulating state can only be recovered by applying new stimuli. The non-volatile behaviors are often observed in defect migration based resistive switching.

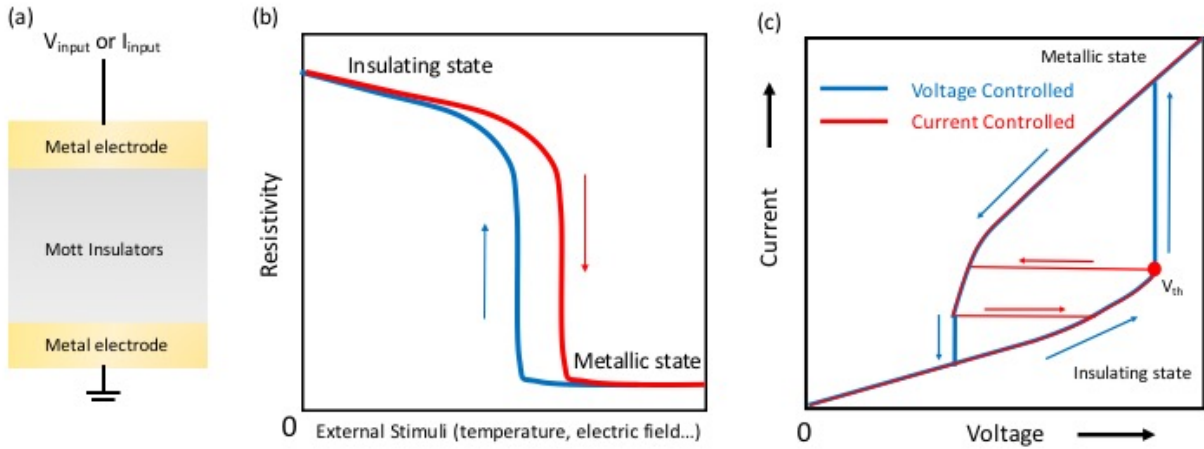


Figure 1.4: Typical features of metal-insulator transitions in Mott insulators: (a) a two-terminal metal-oxide-metal device; (b) Resistivity can be tuned by different external stimuli like temperature or electric field. (c) I-V curves of electrically induced transitions. The blue curve is the voltage driven resistive switching and the red curve is the current driven resistive switching. V_{th} denotes the threshold voltage. Above this threshold value, the resistivity changes significantly.

The generation of MIT-induced oscillation using two-terminal VO₂ devices has been reported a decade ago. Such oscillation is based on the electrically induced MIT and charging process. [28] In addition, the oscillation frequency could be modified based on the input voltage and the load resistor. In biological system, the neurons can receive/generate a series of electrical pulses, called spikes. Figure 1.5 demonstrates an example of the spiking behaviors (MIT oscillation) using VO₂ devices at room temperature. The constant voltage pulse input could lead to periodic spiking voltage/current output. It is crucial for upcoming computing technologies such as artificial neuron applications. Figure 1.6 demonstrates another example of more complex VO₂ neuron spiking behaviors. [29] By using proper circuits and several VO₂ two-terminal devices, a variety of biological neuron spiking modes can be achieved using electrically induced MIT.

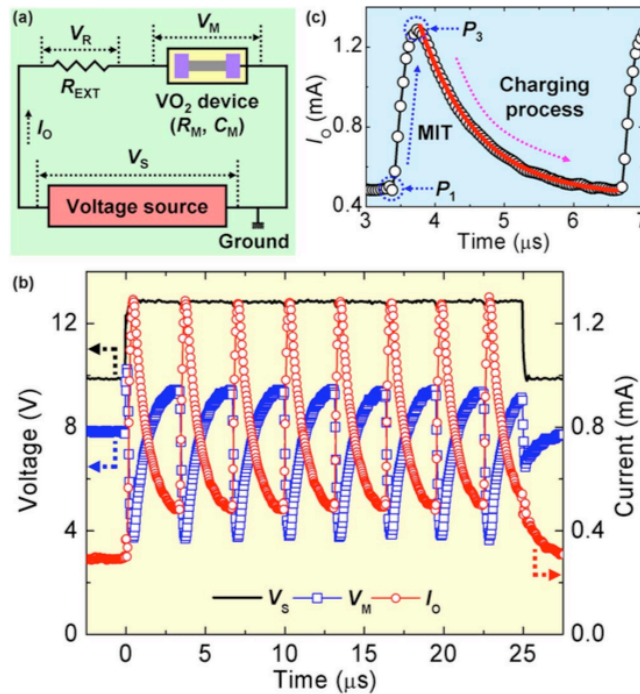


Figure 1.5: Neuron spiking behaviors (MIT oscillation) in VO₂ two-terminal device: (a) Schematic setup of the oscillation measurement; (b) Voltage and current responses during oscillations (c) Single oscillation spike of the current. Adapted with permission from [28]

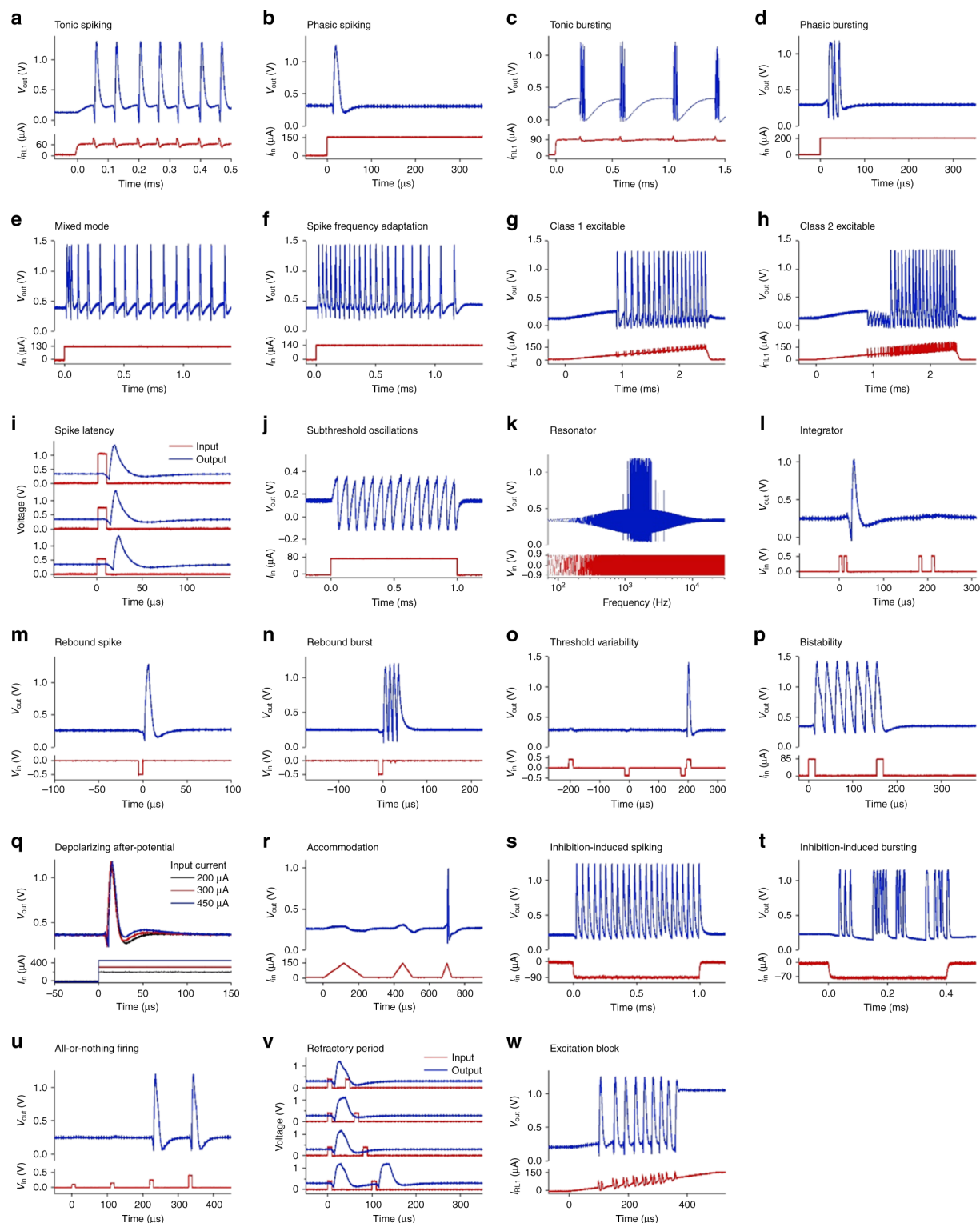


Figure 1.6: The demonstration of biomimetic neuron spiking behaviors using VO_2 two-terminal devices. Adapted with the permission from [29]. Copyright 2018 Springer Nature.

1.4 Resistive Switching and Neuromorphic Computing

As discussed in the previous section, in the resistive switching phenomenon, application of electrical stimuli to a certain material could lead to a significant change in the resistive state. The controllable volatile and non-volatile resistive switching are ideal building blocks to emulate biological functions such as artificial neurons and synapses. [2, 29-31] The development of smaller, faster and more energy-efficient resistive switching devices is crucial for realizing hardware-based neuromorphic computing. Figure 1.7 summarizes the published papers on resistive switching and neuromorphic computing over the past 25 years. An emerging research area of these two exciting topics is of significant interest recently.

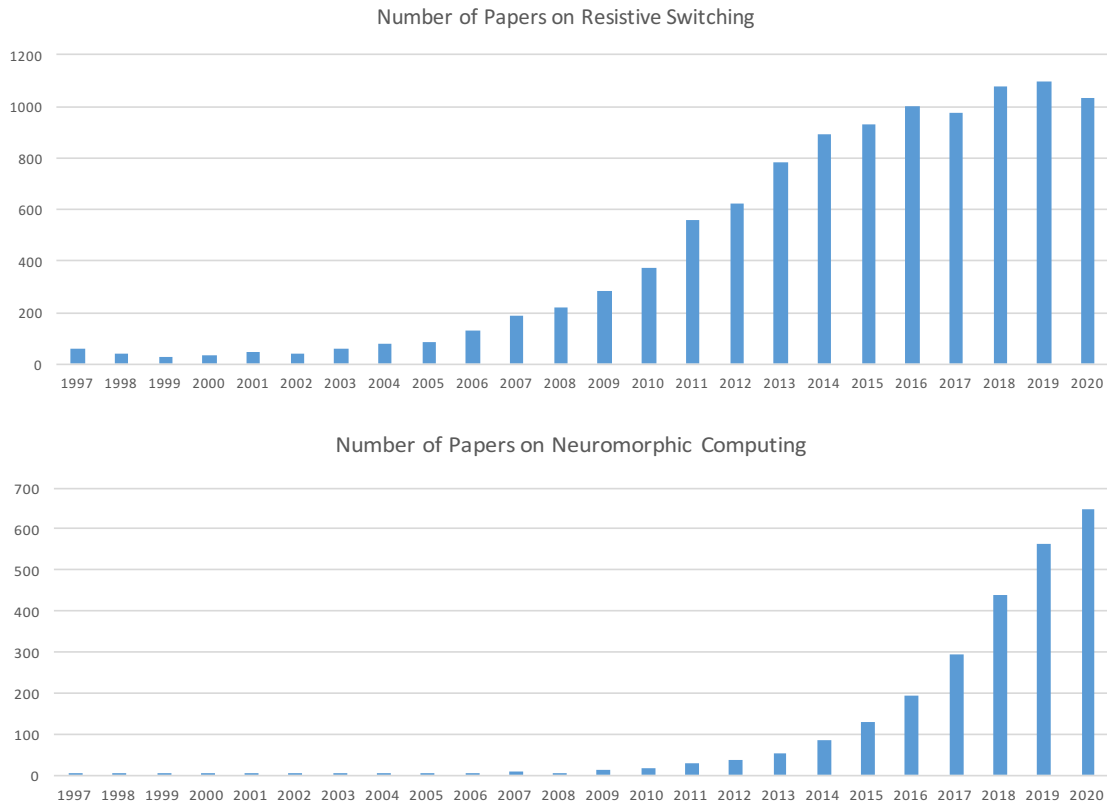


Figure 1.7: The number of papers on resistive switching and neuromorphic computing published each year, clearly showing the increasing interest in these two active research fields. Statistics from Web of Science by searching “Resistive Switching” and “Neuromorphic Computing”.

1.5 Neural Network Architecture

In this section, we will discuss how a basic neural network is constructed. In the neural network, neurons are active units which produce non-linear electric signals such as spikes under external excitations [29], while the synapses control the interconnection weight between each neuron. [2,30, 31] The input layer receives the data directly and propagates it to the hidden layers, with the final computational data passing through the output layer. (See Figure 1.8)

For each neuron, multiple input signals ($S_1 \sim S_n$) will be combined and summed with the simple formula: $Y = f(\sum_{i=1}^n S_i W_i)$; Y is the output for single neuron; S is the input signal; W is the weights between each neuron. The main function of a single neuron is to output electric signals like electrical spikes in response to input stimuli. It is crucial that the output of each neuron from the integration of the input is non-linear and time dependent. Such building blocks could provide a threshold spiking firing, rate coding and leaky integrate-and-fire (LIF) dynamics. Novel materials with volatile RS are ideal candidates to implement neuron functionalities. On the other hand, materials with non-volatile RS can have memory effect and act as synapses, tuning the weight between each neuron.

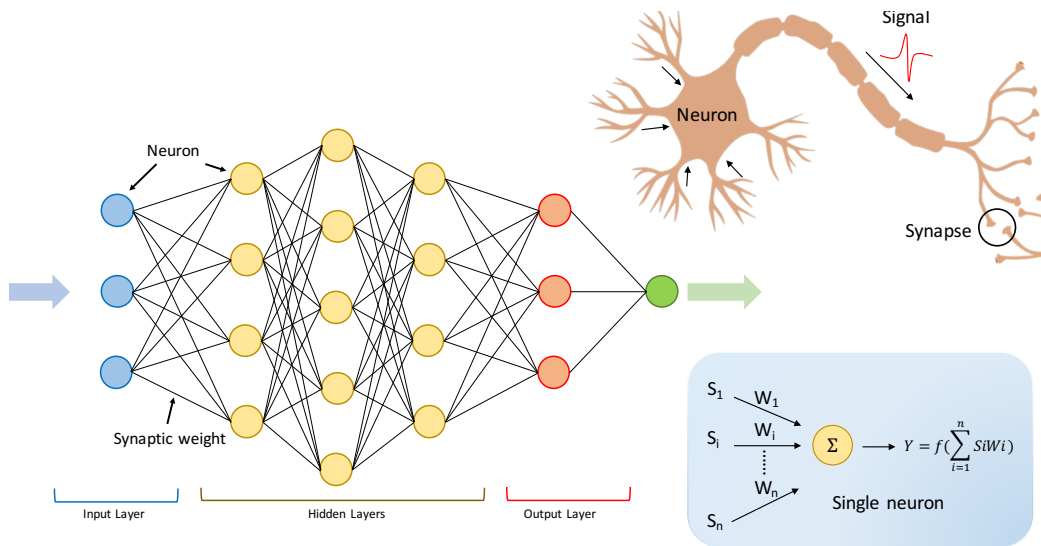


Figure 1.8: Architecture of the neural network and the functionality of the single neuron.

1.6 Potential Memory/Computing Candidates and Characterizations Techniques

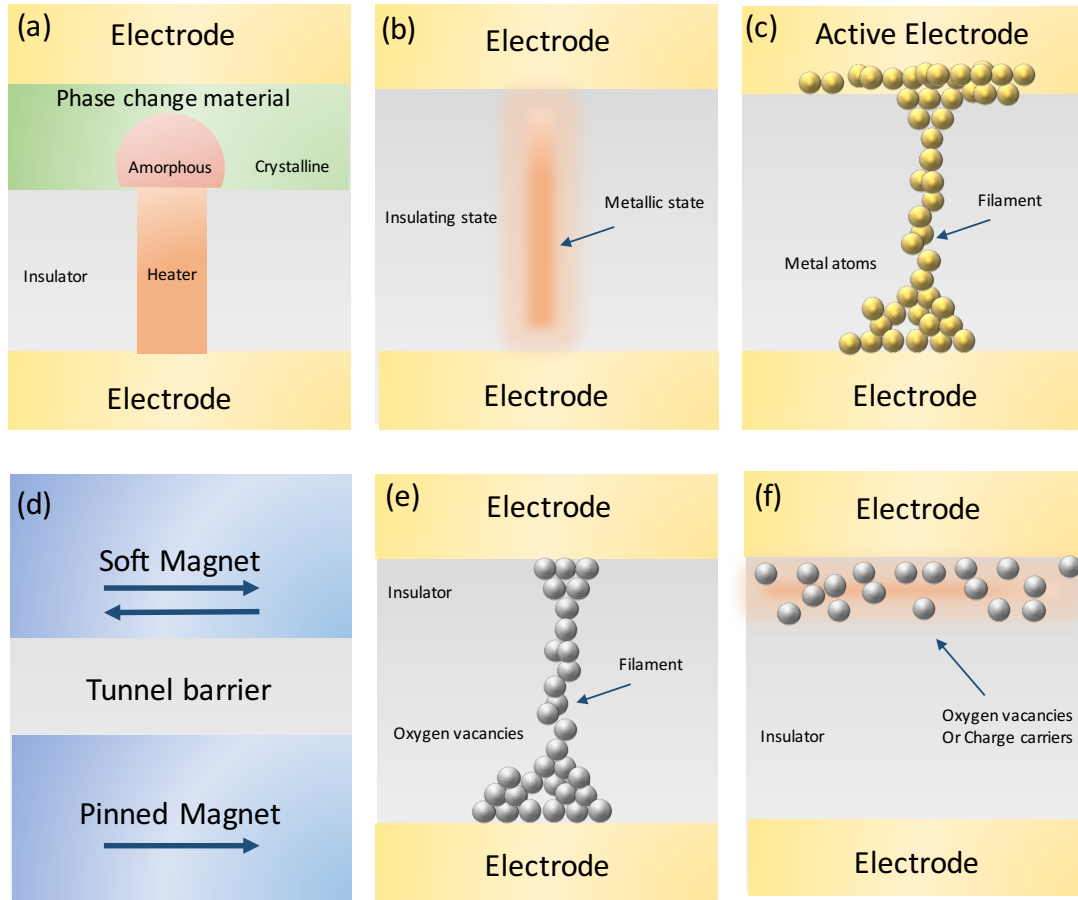


Figure 1.9: Different memory/switching devices and mechanisms. (a) phase change materials (PCM); (b) metal-insulator transition (Mott insulators); (c) conductive bridge random access memory (CBRAM); (d) Spin-transfer Torque MRAM (STT-MRAM); Resistive random access memory (ReRAM): (e) filament-type (f) interface-type.

In this section, we will discuss some potential candidates for neuron/synapse functionality implementation and several useful imaging techniques to characterize them. Figure 1.9 summarizes different electronic switching devices used in current memory/computing technologies. In phase change materials (PCM), the amorphous-crystalline phase transition can be triggered by heating up the materials using a current flow. [31, 32] The resistivity change is due to the different state between crystalline or amorphous structures. In Mott insulators, volatile

resistive switching and metallic phase filament formation is generally observed due to the MIT behavior. [14, 15] In conductive bridge random access memory (CBRAM), the metal atoms will migrate from one active electrode (ion-donor electrode) to another inert electrode, forming metal-ion based conductive filaments. [33] In spin-transfer-torque magnetic random access memory (STT-MRAM), the tunnel barrier is sandwiched by one soft magnet and one pinned magnet. The tunneling magnetoresistance (TMR) effect and spin-transfer torque will enable reading/writing of these devices. [34] In resistive random access memory (ReRAM) [35], the oxygen vacancy migration in the oxide layer will be induced under electric field, leading to the formation of oxygen vacancy-based conductive filaments. For interface-type devices, the resistance state can be changed by electric field due to the drift of oxygen vacancies or charge carriers at the interface between metal electrode and the oxides. [36] Due to the nanoscale nature of the ion migration and filament formation, understanding the switching process in these electronic devices still remains to be a challenging task. The in-situ characterization techniques with high spatial resolution are urgently needed. Figure 1.10 summarizes the spatial resolution of different in-situ/ex-situ imaging techniques. [33, 37] Later in this dissertation, we will describe how we applied various in-situ imaging techniques to study different resistive switching phenomena and filament formation mechanisms.

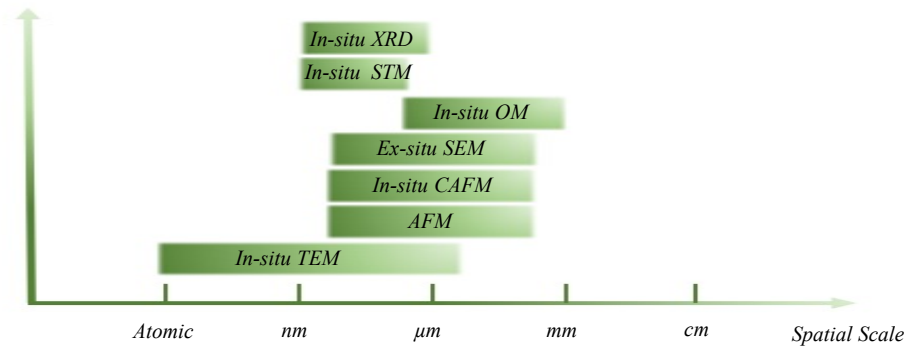


Figure 1.10: Spatial resolution of various characterization techniques to study conductive filaments.

1.7 Acknowledgements

Chapter 1 reproduces in part the following publication: Min-Han Lee*, Yoav Kalcheim, Javier del Valle, and Ivan K. Schuller “Controlling Metal-Insulator Transitions in Vanadium Oxide Thin Films by Modifying Oxygen Stoichiometry” *ACS Applied Materials & Interfaces*, **13**, 887 (2021). The dissertation author was the principal investigator/author on this paper.

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Chapter II - Controlling metal-insulator transitions in vanadium oxide thin films by modifying oxygen stoichiometry

2.1 Overview:

In the chapter 2, we begin the presentation of experimental results. In previous chapter, we have discussed the motivation and the background knowledge in the work. Here, we demonstrate the novel gas evolution technique to strategically tune the oxygen stoichiometry in complex oxides. This chapter focuses on developing new materials, exploring new synthesis techniques, and modifying transport properties across metal-insulator transitions for oxide-based resistive switching technologies. Among all electronic materials, vanadium oxides are strongly correlated insulators which display metal-insulator transitions (MITs) as well as various structural and magnetic properties that depend heavily on oxygen stoichiometry. Therefore, it is crucial to precisely control oxygen stoichiometry in these materials, especially in thin films. This work demonstrates a high-vacuum gas evolution technique which allows for the modification of oxygen concentration in VO_x thin films by carefully tuning thermodynamic conditions. We were able to control the evolution between VO_2 , V_3O_5 , and V_2O_3 phases on sapphire substrates, overcoming the narrow phase stability of adjacent Magnéli phases. A variety of annealing routes were found to achieve the desired phases and eventually control the MIT. The pronounced MIT of the transformed films along with the detailed structural investigations based on X-ray diffraction measurements and X-ray photoelectron spectroscopy show that optimal stoichiometry is obtained and stabilized. Using this technique, we find that the thin film V-O phase diagram differs from that of the bulk material due to strain and finite size effects. Our study demonstrates new pathways to strategically tune the oxygen stoichiometry in complex oxides and provides a road map for understanding the phase stability of VO_x thin films.

2.2 Introduction:

Vanadium oxides are very sensitive to changes in oxygen stoichiometry. Vanadium is a multivalent element displaying oxidation states between V^{2+} and V^{5+} , which gives rise to a series of compounds known as Magnéli (V_nO_{2n-1}) and Wadsley phases (V_nO_{2n+1}). [1-3] The existence of multiple phases leads to a complicated V-O phase diagram. [4-6] Furthermore, shrinking them into thin films or other nanoscale structures is needed to increase their functionality. [7] Typically, the V-O phase diagram is constructed with the thermodynamic data of bulk samples. However, as the size is reduced, the increase in the surface-to-volume ratio introduces an additional surface energy term in Gibbs-free energy that might affect the thermodynamically stable phase region. [8-9] Despite decades of research, a comprehensive understanding of thin-film thermodynamics in the VO_x system is still lacking. Most studies have only focused on the growth of VO_2 thin films and the improvement of their MIT properties by thermal annealing. [10-12] Other oxides such as V_3O_5 , which is the closest Magnéli phase to V_2O_3 , is particularly difficult to deposit directly because of the narrow range of allowable oxygen stoichiometry (with an O/V ratio between 1.666 and 1.668 ± 0.002). [13-14] The fabrication of V_3O_5 film in a recent work still contains small amount of V_2O_3 impurities. [15] In general, obtaining high quality thin films of a specific VO_x and understanding the thin film phase diagram remain a challenging task.

In this study, we achieved control over oxygen stoichiometry in vanadium oxide thin films using a high-vacuum gas evolution system. The experimental setup is shown in Figure 2.1a. (see the experimental section in Chapter 2 and appendix for more details) We first sputtered VO_2 or V_2O_3 thin films on sapphire ($\alpha\text{-Al}_2\text{O}_3$) substrates and then placed the samples in the center of a high vacuum tube furnace for heat treatment using high purity oxygen. A similar technique has been used to control oxygen deficiency in high-temperature superconducting $YBa_2Cu_3O_{7-x}$

samples. [16-17] Starting from single-phase VO_2 or V_2O_3 films, we are able to transform the initial material into a different VO_x film by carefully following a controlled route in the partial oxygen pressure (PO_2)-temperature (T) diagram. (Figure 2.1b) Various routes were tested to optimize the purity and enhance the MIT properties of the resulting compound. After treatment, the resulting phases were investigated using X-ray diffraction (XRD), reciprocal space mapping (RSM), X-ray photoelectron spectroscopy (XPS) and transport measurements. We show that our technique can provide excellent control over a wide-range of temperatures and oxygen partial pressures down to high vacuum conditions, allowing us to minimize the effect of other gases or contaminations and increase the reproducibility of desired phases. This offers significant advantages over normal thermal oxidation/reduction methods using a gas mixture with a limited vacuum range (≥ 0.01 torr). [18] The precision of our method is shown by obtaining single-phase V_3O_5 thin films with the pronounced MIT despite their extremely narrow phase stability range. We are thus able to modulate the MITs between different phases and construct a detailed vanadium-oxygen phase diagram for thin VO_x films.

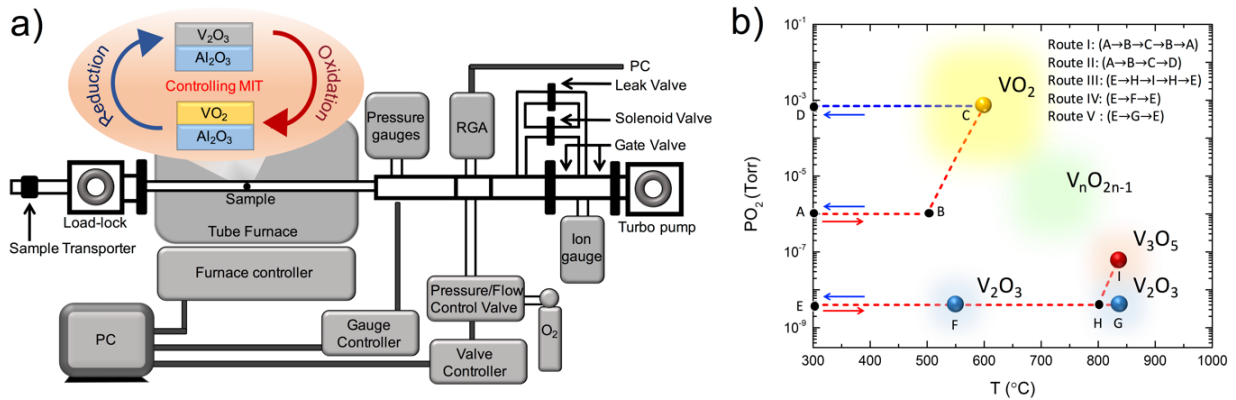


Figure 2.1: (a) Schematic illustration of the gas evolution setup used to control the oxygen stoichiometry in VO_x . (b) Synthesis pathways in the thermodynamic phase diagram of VO_x thin films. The dashed lines represent the different heating/cooling routes for preparing various phases of vanadium oxide.

2.3 Results and discussion

2.3.1 V_2O_3 to VO_2

Figure 2.2a shows the electrical transport of V_2O_3/Al_2O_3 (r-cut) thin films before and after different gas evolution treatments. The R-T curve of as-deposited V_2O_3 shows a sharp MIT at $T_{MIT} \sim 160$ K, with at least 6 orders of magnitude change in the electrical resistance and a 10 K thermal hysteresis between the heating and cooling branches. The single-phase growth of the V_2O_3 thin film on r-cut sapphire is confirmed by the XRD scan shown in Figure 2.2b. The scattering intensity of the V_2O_3 is much stronger than sapphire when the X-ray was aligned with the V_2O_3 peak. There are three out-of-plane diffraction peaks corresponding to (012), (024) and (036) corundum V_2O_3 phase. X-ray measurements on similar films [21] suggest that the V_2O_3 grows epitaxially along the crystallographic orientation of the (012) sapphire substrate. By following the annealing process (route I) in the PO_2 -T phase diagram (Figure 2.1b), this film was transformed into VO_2 , with 3 orders of magnitude MIT at $T_{MIT} \sim 340$ K (Figure 2.2a). Interestingly, this MIT was significantly improved and enhanced by following route II. The resulting VO_2 phase was confirmed by RSM (see Figure 2.2f and 2.2g). The absence of diffraction peaks from other Magnéli phases indicates the formation of single-phase VO_2 films.

Figure 2.2b shows the XRD spectra for (route I)-annealed and (route II)-annealed samples. XRD patterns for samples subjected to both routes, clearly show the diffraction peak at 37.1° , corresponding to the (200) plane of the VO_2 monoclinic structure. The resulting VO_2 films still exhibit the preferred orientation with the (200) plane pointing at $\sim 40^\circ$ to the surface normal ($\chi \sim 40^\circ$), while for the directly sputtered VO_2 films on r-cut sapphire, the (200) plane is parallel to the substrate surface ($\chi \sim 0^\circ$) (Figure 2.5b). The formation of a tilted (200) plane indicates the lack of well-aligned epitaxial layers and the appearance of disorder at the VO_2/Al_2O_3 interface, as present in many oxide heterostructures. [22] It should be noted that there are structural

similarities between rutile VO_2 and corundum V_2O_3 . Previous studies have shown that through a common parent structure with a hexagonal-close-packing arrangement, VO_2 and V_2O_3 may be derived from each other through a well-defined symmetry-breaking mechanism along the $[001]$ direction of corundum V_2O_3 and the $[100]$ of rutile VO_2 . [23] It is thus unlikely that the formation of VO_2 from V_2O_3 would be randomly oriented.

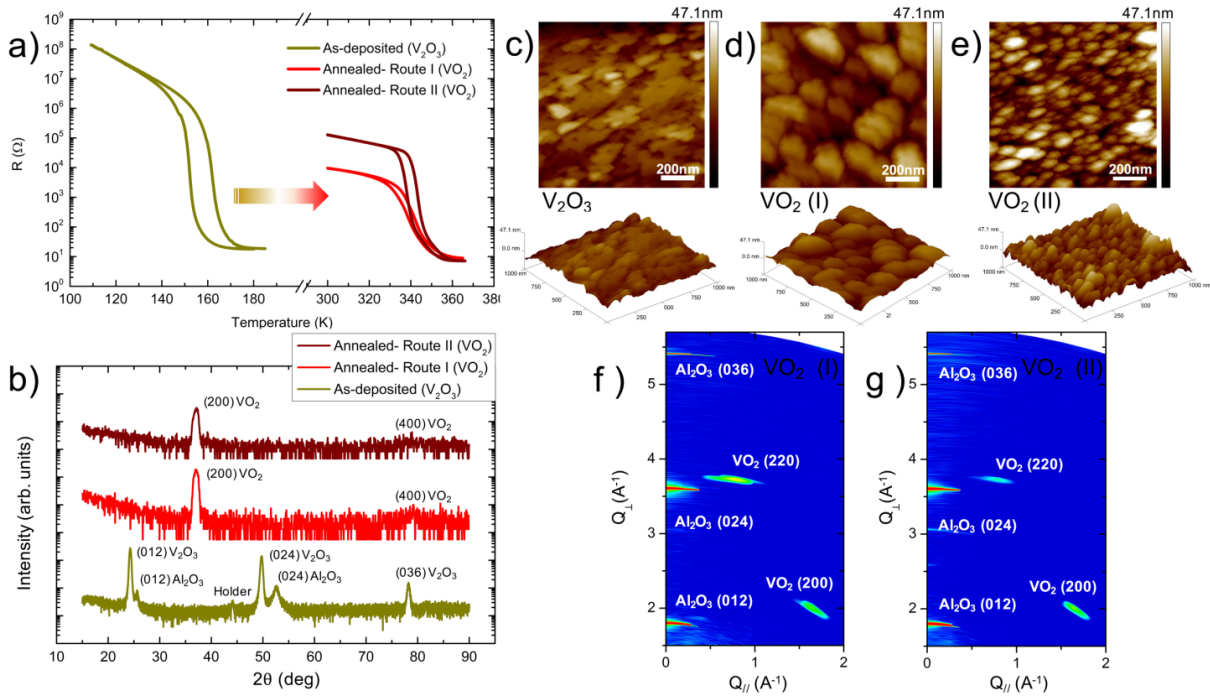


Figure 2.2: Formation of VO_2 phase from a V_2O_3 thin film on a (012) r-cut sapphire substrate. (a) Resistance vs temperature of vanadium oxide thin films under various oxidation conditions. After annealing, the thin films showed a sharp VO_2 metal-insulator transition at ~ 340 K. (b) Room-temperature XRD scans for vanadium oxide films. The different diffraction spectra correspond to the V_2O_3 phase (as-deposited) and the VO_2 phase (annealed following route I or route II). The crystallographic orientation of the VO_2 film was (200), which points along $\sim 40^\circ$ to the surface normal ($\chi \sim 40^\circ$). Angle (χ) denotes the degree between the surface normal and the diffraction plane. AFM images ($1 \times 1 \mu\text{m}^2$) showing the surface morphology of (c) as-deposited film, (d) (route I)-annealed film and (e) (route II)-annealed film. The scale bar is 200 nm for all images. Reciprocal space mapping (RSM) of (f) (route I)-annealed and (g) (route II)-annealed VO_2 films. $Q_{\perp}$ denotes the out-of-plane orientation (012) of Al_2O_3 .

The AFM images demonstrate the differences in surface morphology and roughness between the as-deposited V_2O_3 (Figure 2.2c), (route I)-annealed film (Figure 2.2d) and (route II)-

annealed film (Figure 2.2e). The root-mean-square (RMS) roughness extracted from the Figure 2.2c, 2.2d and 2.2e was 5.62 nm, 6.22 nm and 8.29 nm, respectively. The original V_2O_3 film prepared by sputtering reveals a relatively smooth surface. The quenching process along route I results in a bigger grain size (~ 190 nm assuming spherical shape) of the VO_2 film. It is this (route I)-annealed VO_2 film that exhibits a smaller width in the hysteresis loop appearing in the R-T curve at the MIT (Figure 2.2a). Consequently, our results suggest that the hysteresis loop at the MIT broadens with decreasing the grain size.[24-25] Earlier reports show that smaller grains lead to a high density of grain boundaries, resulting in a decrease in the magnitude of the resistivity change across the MIT.[26] Alternatively, the larger resistance switching ratios and smaller grains (~ 75 nm) observed in the (route II)-annealed VO_2 film suggest that the change in electrical resistance cannot be solely due to a grain size effect. Oxygen stoichiometry must also play a role in the MIT behavior of VO_2 . The activation energy (E_a) of the VO_2 insulating state ($T \leq 310$ K) can be estimated from the linear fitting of the ratio $\ln R(T)/(1/k_b T)$, as $R(T) = R_0 \exp(E_a/k_b T)$. The results obtained from (route I)-annealed and (route II)-annealed VO_2 are ~ 191 and ~ 259 meV, respectively. Quenching the (route I)-annealed VO_2 film under relatively low PO_2 is likely to increase the density of defects and promote oxygen loss. These vacancies may dope the VO_2 , thus increasing the free carriers and leading to the MIT degradation. [27,28] A detailed phase stability diagram (Figure 2.8.) also shows that annealing the sample at 600°C with a low oxygen pressure will result in oxygen-deficient VO_2 phases.

2.3.2 V_2O_3 to V_3O_5

Because of the numerous possible oxidation states, vanadium oxides are very sensitive to changes in the oxygen content. Here, we show that oxidation of V_2O_3 to form the V_3O_5 can be

achieved on c-cut and r-cut sapphire by slightly increasing the PO_2 at $\sim 840^\circ\text{C}$. Figure 2.3a displays the temperature-dependent electrical transport of a V_2O_3 film grown on c-cut sapphire before and after the gas evolution treatment. The R-T curve of the as-deposited V_2O_3 film shows a suppressed metal-insulator transition with only a slight resistance variation. We note that this V_2O_3 sample was grown under the same conditions as the one shown in Figure 2.2a, which shows a much more pronounced MIT. This suppression of the MIT in V_2O_3 grown on c-cut sapphire had been previously attributed to strain and microstructural effects between the thin film and substrate. [29,30] The lattice parameters and the c/a ratio of our epitaxial c-cut V_2O_3 thin film are ~ 2.81 ($a=b= 4.98 \text{ \AA}$; $c=14.01 \text{ \AA}$). This ratio is consistent with the reported value of c-cut V_2O_3 with unusual metal-insulator-metal behavior. [29] In previous work, we have shown that the structural phase transition and metal-insulator transition were robustly coupled to each other. Therefore, it is likely that the structural phase transition in our V_2O_3 sample is highly dependent on the a-and c-axis deformation as well. And this leads to the suppression of the MIT. The XRD pattern in Figure 2.3b shows that the corundum V_2O_3 film is highly oriented with the (001) c-cut sapphire substrate. By annealing this film along route III (Figure 2.1b), we were able to transform it into a single-phase V_3O_5 film with an MIT of more than 1 order of magnitude at $T_{\text{MIT}} \sim 417 \text{ K}$. The smooth MIT behavior above room temperature together with the absence of thermal hysteresis in $R(T)$ are signs of a second-order phase transition, as reported before. [31]

The presence of a single-phase polycrystalline structure is confirmed by RSM as shown in Figure 2.3e. The axis $Q_\perp$ points along the out-of-plane orientation (001) for the Al_2O_3 substrate. Figure 2.3b shows six diffraction peaks at $2\theta = 36.0, 38.5, 38.9, 76.2, 82.3$ and 83.4° corresponding to the (020), (202), (400), (040), (404), and (800) planes in V_3O_5 , respectively. [32] All the observed peaks shifted slightly to higher values of 2θ (i.e., the d-spacing for each

plane is contracted) with respect to the bulk values. This implies that residual strains were induced in the film after recrystallization. If annealing was interrupted before complete transformation, crystalline V_2O_3 and V_3O_5 phase coexistence was observed. The AFM image of the as-deposited V_2O_3 film (Figure 2.3c) indicates a relatively smooth film surface with 0.72 nm RMS roughness. The resulting V_3O_5 film shown in Figure 2.3d has a much rougher surface with 13.1 nm RMS roughness. Furthermore, the grain structure is highly irregular after the treatment, as suggested by the XRD and RSM data.

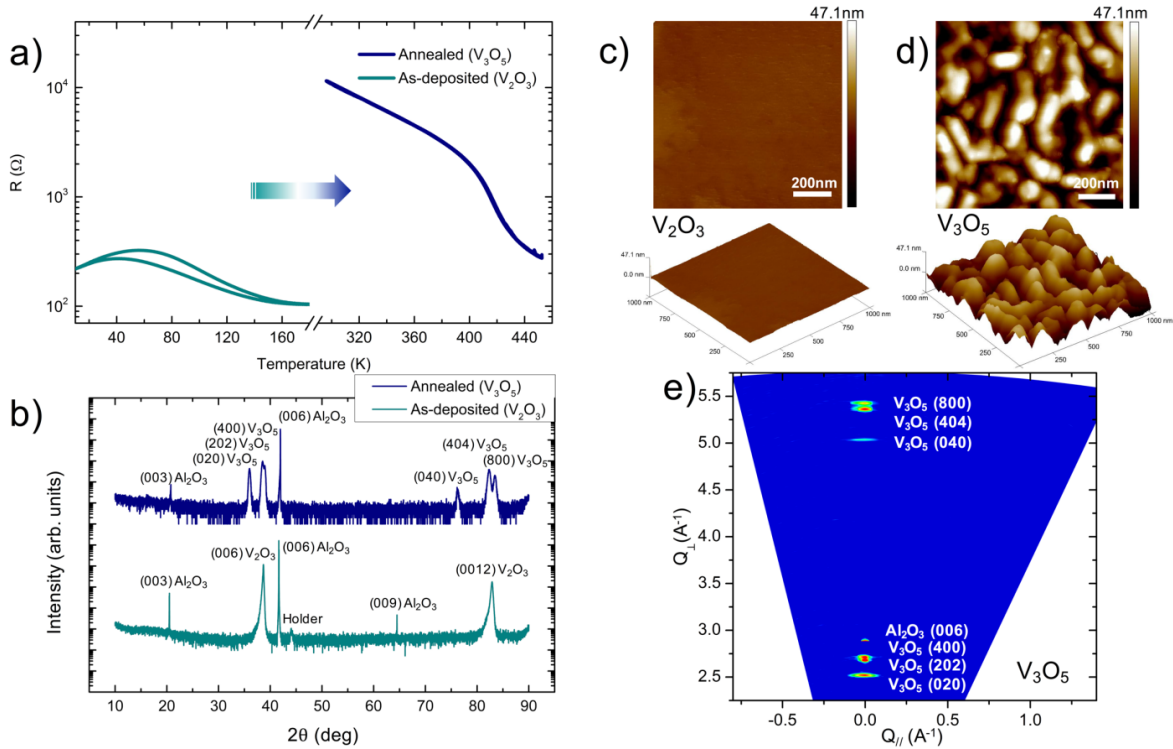


Figure 2.3: Formation of the V_3O_5 phase from a V_2O_3 thin film on a (001) c-cut sapphire substrate. (a) Resistance as a function of temperature of V_2O_3 film and resulting V_3O_5 film. The MIT temperature (T_{MIT}) of the V_3O_5 is ~ 417 K. (b) Room-temperature XRD scans. Evolution of different peaks corresponding to V_2O_3 phase (as-deposited) and V_3O_5 phase (annealed following route III). Preferred crystallographic orientations of V_3O_5 film were (020), (202) and (400). AFM images revealed the surface morphology of (c) as-deposited film and (d) (route III)-annealed film. (e) X-ray RSM of the resulting V_3O_5 film. $Q_{\perp}$ denotes the out-of-plane orientation (001) of Al_2O_3 (perpendicular to the film surface).

Figure 2.4a demonstrates the electrical transport of a V_2O_3 film on r-cut sapphire before and after gas evolution treatments along route III. After annealing at point I for 3 hours we observe an increase in the resistance in the metallic states and a reduction of the magnitude of the hysteresis. However, the large MIT at $T_{MIT} \sim 150$ K indicates that the major phase of the film is still V_2O_3 . The formation of a pure V_3O_5 phase is achieved by a second annealing process for additional 6 h along route III. The $R(T)$ starts showing a smooth MIT above room temperature ($T_{MIT} \sim 404$ K) without thermal hysteresis. A comparison of R - T curves of V_3O_5 films grown on c-cut (001) and r-cut (012) Al_2O_3 substrates is shown in Figure 2.4b. Both samples reveal an MIT of more than 1 order of magnitude. For ease of comparison, the results were normalized by the metallic state resistance (R_{450K}). As the transformed V_3O_5 films were polycrystalline, it is likely that the strain in the different grains is highly inhomogeneous. Different sapphire substrates will generate different dislocations and strain. Because of the numerous grain orientations, it is quite challenging to precisely quantify the strain in the polycrystalline thin film. By comparing the lattice spacings in V_3O_5 grown on r-cut and c-cut oriented sapphire, the structural distortion can still be estimated. Compared with the c-cut V_3O_5 thin film, the relative strains for the (100), (010), (001) planes of V_3O_5 /r-cut sapphire are considerably more compressed ($\Delta d_{100} \sim -0.71$ %; $\Delta d_{010} \sim -0.03$ %; $\Delta d_{001} \sim -2.1$ %). It is likely that a larger compressive strain leads to a lower T_{MIT} as found in a previous study, which has shown that T_{MIT} in V_3O_5 decreases with pressure. [33] The strain generated from the sapphire substrates and the difference in microstructure and grains might lead to the 14 K variation in T_{MIT} . Figure 2.4c shows the evolution of the crystalline structure for the V_2O_3 film. After 3 h of annealing, the intensity of the diffraction peaks decreased, but the thin film still remained corundum V_2O_3 . On the other hand, the second, lengthier annealing time (6 h) allowed for a complete transformation into V_3O_5 .

Besides the out-of-plane sapphire peaks, several in-plane V_3O_5 peaks can be found using RSM. For instance, one diffraction peak from the V_3O_5 (310) plane was found at $\chi \sim 17^\circ$ (Figure 2.4c and 2.4e). The RMS roughness of the transformed V_3O_5 film is 4.21 nm (Figure 2.4d).

Interestingly, a large difference in the annealing times required to form V_3O_5 is observed for the two different substrates (012) and (001) Al_2O_3 . This indicates the crystallographic orientation of the film significantly affects thermodynamic kinetics and oxygen diffusion processes. As we observe from our x-ray diffraction measurements (Figure 2.3b and 2.4c), for both substrates, in the final stage, the samples only showed diffraction peaks associated with V_3O_5 (aside from the sapphire peaks) indicating high phase purity.

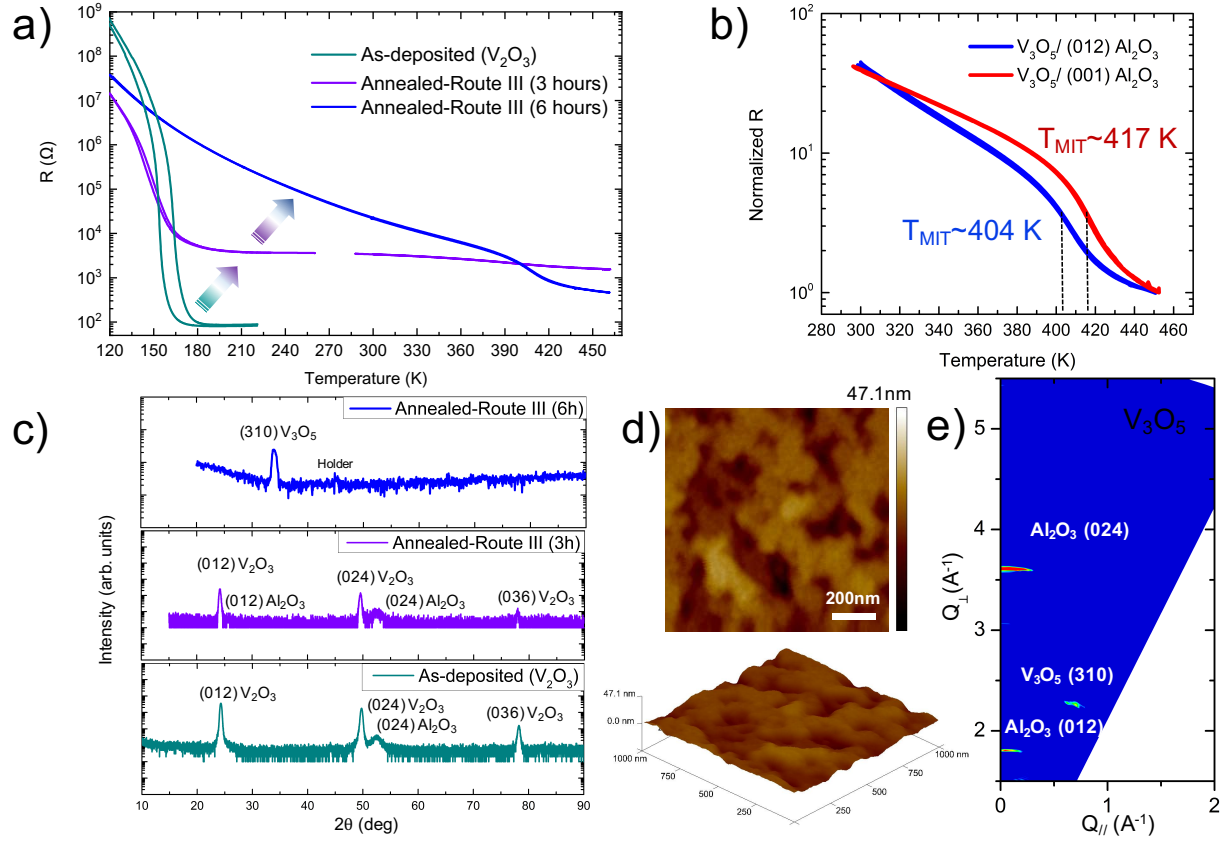


Figure 2.4: Formation of the V_3O_5 Phase from a V_2O_3 thin film on a (012) r-cut sapphire substrate. (a) Resistance as a function of temperature for a V_2O_3 film: as deposited film (cyan); after annealing for 3 h at point I (purple); after annealing for additional 6 h at point I (blue). (b) Comparison of the normalized $R(T)$ for V_3O_5 films on r-cut sapphire (blue) and c-cut sapphire (red). The black dashed lines mark the T_{MIT} for the two different samples. (c) XRD measurements of samples after time-annealed V_2O_3 thin film following route III. The preferred crystallographic orientation of the resulting V_3O_5 film was (310), which point along $\sim 17^\circ$ to the surface normal ($\chi \sim 17^\circ$). (d) AFM images revealed the surface morphology and (e) X-ray RSM of the resulting V_3O_5 film. $Q_{\perp}$ denotes the out-of-plane orientation (012) of Al_2O_3 (perpendicular to the film surface).

2.3.3 VO₂ to V₂O₃

In addition to the controlled oxidation of as-grown V₂O₃ thin films using the gas evolution technique described above, we have also demonstrated and studied the controlled reduction of as-grown VO₂ thin films on r-cut sapphire to study the thin-film phase stability. Figure 2.5a shows the electrical transport of a VO₂ film on an r-cut sapphire both before and after the gas evolution treatments along route IV. The R-T curve of as-deposited VO₂ shows a sharp MIT at $T_{MIT} \sim 340$ K, with more than 3 orders of magnitude resistance change. The single-phase growth of VO₂ is confirmed by the XRD scan shown in Figure 2.5b. Two reflection peaks corresponding to the (200) and (400) planes for monoclinic VO₂ are observed at $2\theta = 37.1^\circ$ and 79.0° , respectively. By following the annealing process (route IV) shown in Figure 2.1b, the highly textured VO₂ film was transformed into single-phase V₂O₃, now with 5 orders of magnitude MIT with $T_{MIT} \sim 145$ K. (see Figure 2.5a) This value of transition temperature $T_{MIT} \sim 145$ K, is slightly lower than the value of the transition temperature $T_{MIT} \sim 160$ K, for the directly sputtered V₂O₃ film, indicating that there might be a comparatively higher oxygen concentration in the transformed V₂O₃ film. [34] Moreover, we find no significant differences ($\Delta 2\theta \leq 0.035^\circ$) in the out-of-plane (012) and in-plane (104) XRD peaks between directly sputtered V₂O₃ and transformed V₂O₃ films, ruling out strain effects as a major cause for the decrease in T_{MIT} . Previous studies on V₂O₃ have shown that a 15K variation in T_{MIT} is caused by an excess of oxygen concentration [35,36] The presence of an epitaxial V₂O₃ film was confirmed by XRD (Figure 2.5b) and RSM scans (Figure 2.5e). Both in-plane and out-of-plane crystallographic orientations in V₂O₃ follow the substrate orientations. This indicates that the structural similarity between corundum V₂O₃ and Al₂O₃ promotes epitaxial growth during the atomic rearrangement. Therefore, it is reasonable to conclude that the coupling to the Al₂O₃ substrate plays an important

role in determining the crystallographic orientations of the transformed film. We note that this is in contrast to the case of VO_2 derived from a V_2O_3 film, which develops a different orientation after gas evolution compared to the as-grown VO_2 film. This may be due to the higher degree of compatibility between the Al_2O_3 substrate and the isostructural V_2O_3 compared to the rutile VO_2 .

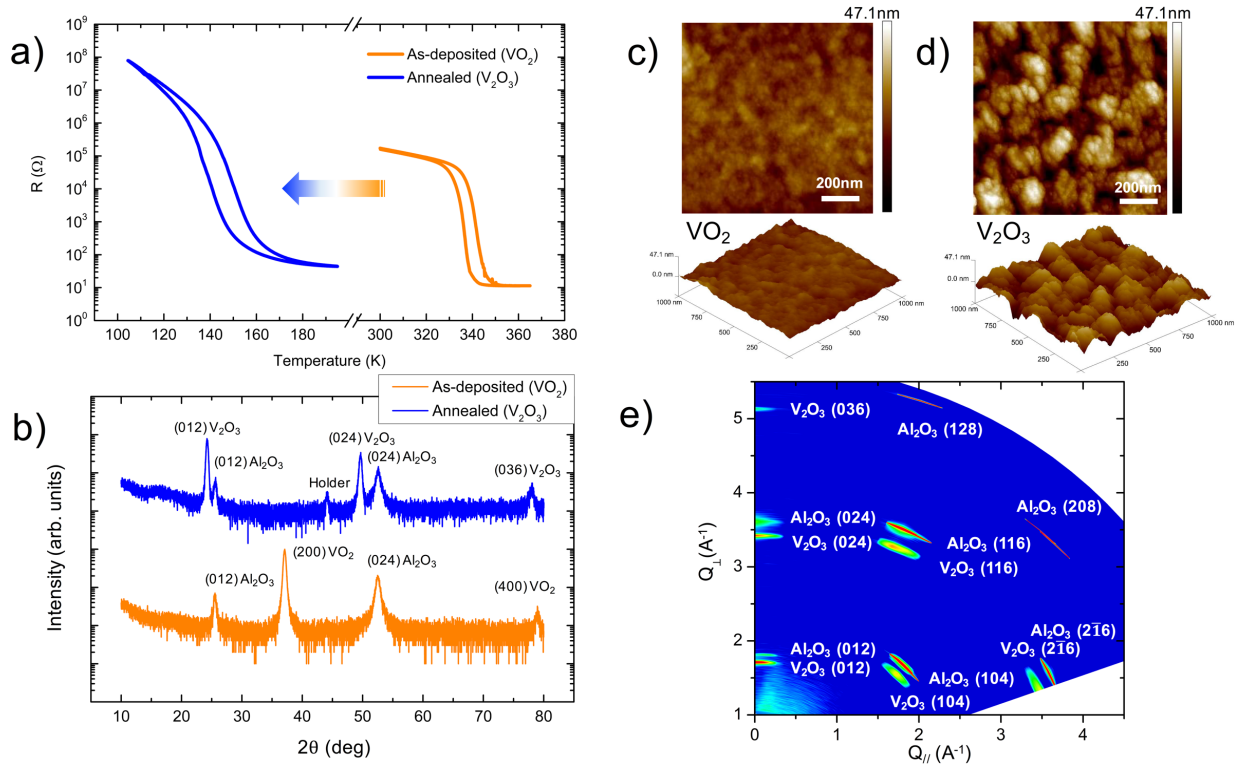


Figure 2.5: Formation of the V_2O_3 Phase from the VO_2 thin film on a (012) r-cut sapphire substrate. (a) Resistance as a function of temperature of the VO_2 film and the resulting V_2O_3 film. (b) Room-temperature XRD scans. The XRD peaks corresponding to the VO_2 phase (as-deposited) and the V_2O_3 phase (following annealing route IV). AFM images revealed the surface morphology of (c) as-deposited film and (d) annealed film. (e) Wide-range RSM of the transformed V_2O_3 film. Both in-plane and out-of-plane crystallographic orientations of the V_2O_3 film strongly followed the r-cut sapphire substrate orientations, suggesting the formation of epitaxial structures after gas evolution. $Q_{\perp}$ denotes the out-of-plane orientation (012) of Al_2O_3 .

For the transformation of as-grown VO_2 films into single-phase V_2O_3 , it takes 12 h (point F in the PO_2 -T diagram shown in Figure 2.1b) to reach an equilibrium state. We found that the as-grown VO_2 films that were subjected to a shortened annealing process of only 3 or 6 h along route IV did not exhibit any clear MIT behavior, and no XRD peaks can be found. This suggests that thermodynamic equilibrium may not have been reached in this shorter period of time. However, the reverse transformation of as-grown V_2O_3 films into single-phase VO_2 films requires a shorter annealing time of 3 h. The discrepancy between these two cases suggests that the phase evolution mechanisms are also associated with the kinetics and diffusion processes, which are beyond the scope of this work. Furthermore, the monoclinic VO_2 film could also be transformed into corundum V_2O_3 phase by following an alternate annealing treatment along route V. This indicates that point G in Figure 2.1b is still in the V_2O_3 stable region. Figures 2.5c and 2.5d show the surface morphology of the as-deposited film and (route IV)-annealed film, respectively. The VO_2 film prepared by sputtering shows a textured surface with the RMS roughness equal to 3.15 nm. The resulting V_2O_3 after the loss of oxygen shows a relatively rougher surface with roughness up to 8.35 nm.

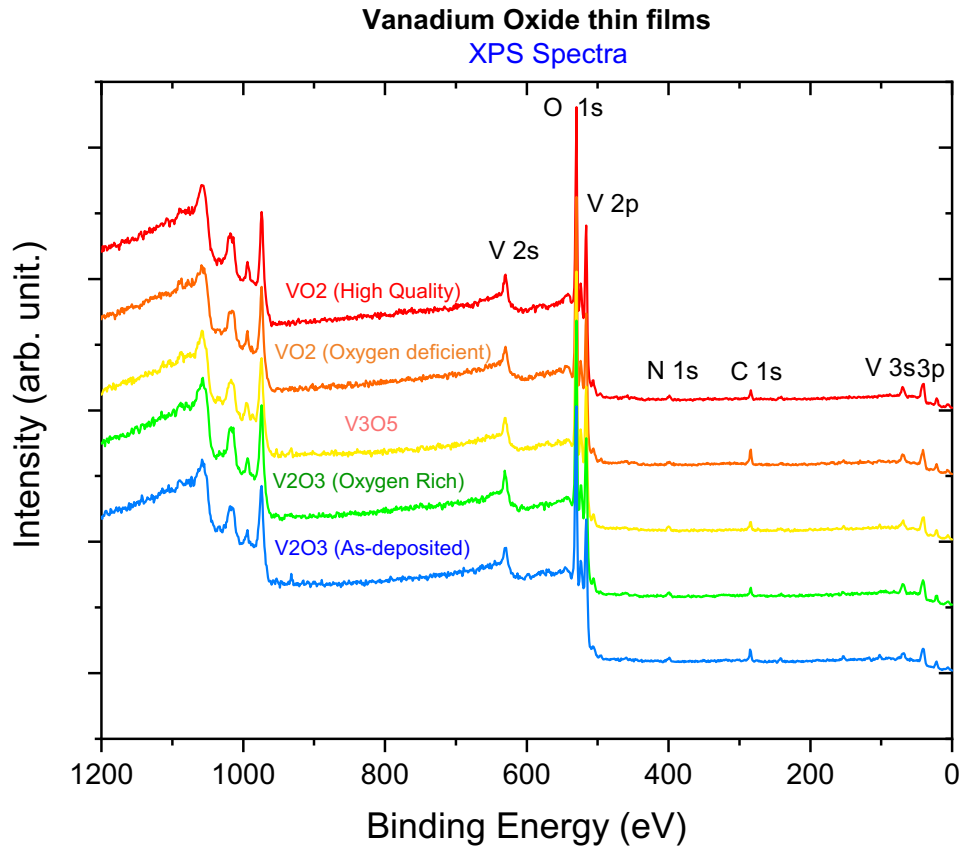


Figure 2.6: Wide-range XPS spectra of different vanadium oxide thin films. (Blue curve) as-deposited V_2O_3 film; (Green curve) (route IV)-annealed film, oxygen-rich V_2O_3 phase; (Yellow curve) (route III)-annealed film, V_3O_5 phase; (Orange curve) (route I)-annealed film, oxygen-deficient VO_2 phase; (Red curve) (route II)-annealed film, higher quality VO_2 phase.

X-ray photoelectron spectroscopy (XPS) was used to track the valence state of the as-deposited and annealed thin films on (012) sapphire substrate described above. (Figure 2.6) The binding energy (BE) calibration was done to O1s peak at 530 eV. [20,37] Shirley background was used for the peak fitting. The V2p spectra in the range of 510-526 eV show the spin-orbit splitting peak of $V2p_{3/2}$ and $V2p_{1/2}$. (Figure 2.7a) Only one component V(III) centered at 515.6 eV was used for the as-deposited V_2O_3 spectrum (Figure 2.7b), as the peak shape is symmetric. ($V2p_{3/2}$ at 515.6 eV for +3 valence state) [38] The energy difference between O1s and $V2p_{3/2}$ is 14.4 eV, well in the range of the reported value for single crystal. [38]

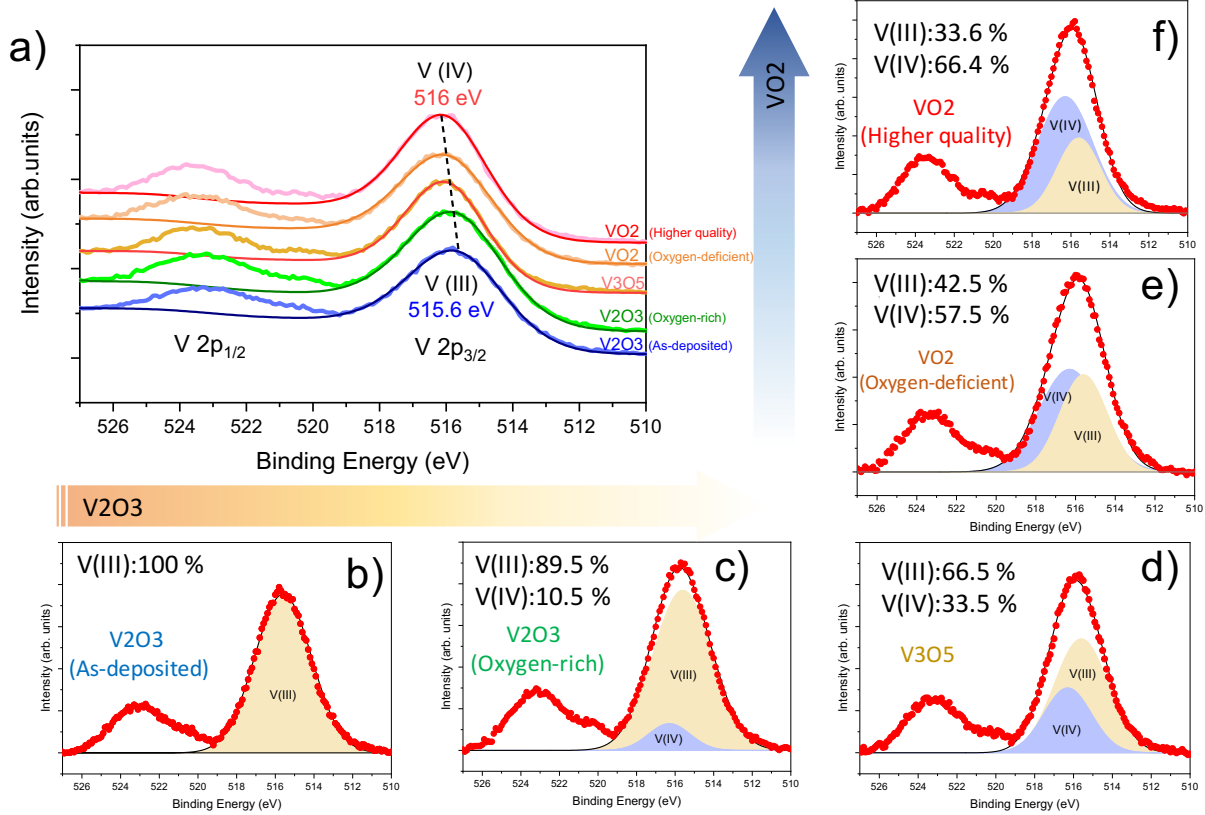


Figure 2.7: XPS spectra of vanadium oxide thin films. (a) V 2p spectra in the range of 510 eV - 526 eV. (b) as-deposited V_2O_3 film; (c) (route IV)-annealed film, oxygen-rich V_2O_3 phase; (d) (route III)-annealed film, V_3O_5 phase; (e) (route I)-annealed film, oxygen-deficient VO_2 phase; (f) (route II)-annealed film, higher quality VO_2 phase.

With increasing oxygen content in thin films, the position of $V2p_{3/2}$ peak shifts from V(III) at 515.6 eV to 516.0 eV. Similar behavior was reported previously for single crystals. [38,39] We find an increase in the V2p BE from V_2O_3 (as-deposited film) to V_2O_3 (route IV-annealed film), V_3O_5 (route III-annealed film), VO_2 (route I-annealed film), and VO_2 (route II-annealed film). Each $V2p_{3/2}$ peak can be deconvoluted into V(III) and V(IV) states centered at 515.6 eV and 516.3 eV, respectively. ($V2p_{3/2}$ at 516.3 eV for +4 valence; BE difference between O1s and $V2p_{3/2} \sim 13.7$ eV) [38] The fitting area of $V2p_{3/2}$ could be used to track the oxidation states of vanadium ions. The estimated V(III)/ V(IV) ratio in V_3O_5 thin film is 66.5%: 33.5%. (Figure 2.7c) And the valence state of vanadium is around +3.34, which is close to the theoretical value

of +3.3. On the other hand, the (route I)-annealed film (VO_2 phase) contains higher oxygen vacancies and shows higher V(III) component in figure 2.7e. This confirms that quenching the VO_2 under relatively low PO_2 will lead to oxygen loss. It should be noted that the (route II)-annealed VO_2 film still shows a small portion of V(III) charge, indicating that there are still some oxygen vacancies in this transformed VO_2 film near the surface. It is possible to achieve higher quality VO_2 thin film under higher PO_2 annealing condition.

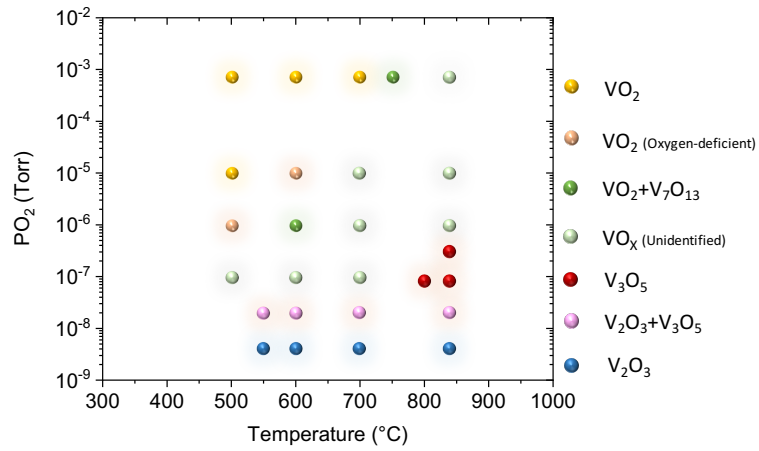


Figure 2.8: V-O phase diagram for thin film. Circles represent the tested annealing condition.

Our technique can provide excellent control over a wide-range of temperatures and oxygen partial pressures, allowing us to explore a more complete picture of thin-film phase diagram. It is worth noting that the V-O phase diagram (Figure 2.8) we obtain starting from 100 nm V_2O_3 is substantially different from the bulk V-O phase diagram. [4-6] At the present stage, among all the Magnéli phases, the only thin film we could obtain in pure form was V_3O_5 . It is possible to fabricate other Magnéli phases thin-film using our technique despite their extremely narrow phase stability range. Moreover, starting from 10 nm ultrathin films, despite tens of trials, we could not obtain the V_3O_5 phase under the same annealing conditions. These differences in conditions as compared to those of the bulk phase diagram may be due to

variations in nanoscale surface energy and the lattice interaction with the substrate. This may also explain the differences in the required annealing time found for sapphire substrates of different orientations (c-cut and r-cut), as described above.

In summary, we have developed a high-vacuum gas evolution technique that allows for the precise modification of oxygen stoichiometry in VO_x thin films. Using temperature-dependent electrical transport measurements, XRD, RSM, and XPS, we show that optimal oxygen stoichiometry is obtained in each of the transformed films. Based on our technique, the thermodynamic phase diagram can be well-defined and elucidated for the V-O system when scaling down the VO_x from bulk into thin film form. Our results may play an important role in improving and controlling transport properties across the MIT in oxide-based devices. It may open a new way to synthesize exotic or Magnéli phase oxide films, which cannot be directly grown by standard deposition techniques. We hope our work will encourage the use of gas evolution methods in other complex oxide systems.

2.4 Supplementary Information – Methods

2.4.1 Thin-film growth

Single-phase VO₂ and V₂O₃ thin films were deposited on 7×12 mm² (012) r-cut or (001) c-cut sapphire (α -Al₂O₃) substrates using RF magnetron sputtering from a V₂O₃ target. As described in previous studies [19], the growth of VO₂ was done at a substrate temperature of 520 °C in an environment of Ar/O₂ mixture (8% O₂) at 3.7 mTorr. The V₂O₃ thin films were prepared at a 700 °C substrate temperature in an environment of ultrahigh purity Ar (>99.999%) at 8 mTorr.

2.4.2 Evolution of V₂O₃ phase into VO₂

Oxidation of as-deposited V₂O₃/Al₂O₃ (r-cut) thin films with 75 nm thickness was performed in the gas evolution system by continuously controlling PO₂ and T. The annealing conditions were chosen according to the known bulk vanadium-oxygen phase diagram. [4-6] By carefully following thermodynamically stable paths, different oxidation states of vanadium could be obtained from V₂O₃. At the start of route I (A→B→C→B→A) (see Figure 2.1b), PO₂ was fixed to 1×10^{-6} Torr and the temperature was ramped up to 500 °C at a heating rate of 10 °C/min. After reaching 500 °C, the PO₂ was continuously increased along (B→C) in order to keep the sample in the potentially stable region of the VO₂ phase in PO₂-T diagram. The sample was then annealed at 600 °C for 3 h with PO₂ $\sim 7 \times 10^{-4}$ Torr (at point C in Figure 2.1b). After reaching thermodynamic equilibrium, both PO₂ and T were reduced at a cooling rate of 6 °C/min along the return path (C→B). After reaching 500 °C, the sample was then quenched to room temperature by transferring it to the load lock.

Similarly, by following route II (A→B→C→D), the oxygen stoichiometry in as-deposited V₂O₃ can be modified, leading to a transformation into a higher oxidation state. After a

3 h reaction at 600 °C (point C), the sample was cooled down to room temperature under continuous oxygen flow at $PO_2 \sim 7 \times 10^{-4}$ Torr. This method produces high-quality VO_2 thin films with sharp metal-insulator transitions. The ability to continuously and gradually control both PO_2 and T is important for maintaining thermodynamic equilibrium in the thin film sample at all times so as to prevent the formation of possible secondary phases during the process.

2.4.3 Evolution of V_2O_3 phase into V_3O_5

For the oxidation reaction of V_2O_3 into V_3O_5 , we used a similar procedure. At the start of route III (E→H→I), an as-deposited V_2O_3/Al_2O_3 (c-cut) film with thickness of approximately 100 nm was mounted in the tube furnace and the PO_2 was fixed to $\sim 4 \times 10^{-9}$ Torr. The temperature was then increased from RT to 800 °C at a rate of 10 °C/min (E→H). From point H, both the PO_2 and temperature (T) were continuously increased along the possible stable region for V_3O_5 . The thin film was then annealed for 3 h at 838 °C with $PO_2 \sim 8 \times 10^{-8}$ Torr (at point I). After reaching phase equilibrium, both PO_2 and T were continuously reduced along the return route (I→H) at a cooling rate of 6 °C/min and the sample was quenched from 800 °C to room temperature along the return path (H→E). In the case of V_2O_3/Al_2O_3 (r-cut) film, we performed the same experiment: the 100 nm film was annealed following route III. The annealing time was 3 h at point I in the first round and increased to 6 h for the second round.

2.4.4 Evolution of VO_2 phase into V_2O_3

In order to understand the phase stability of VO_2 , the as-deposited VO_2/Al_2O_3 (r-cut) films with a thickness of 75 nm were heat-treated under two different thermodynamic paths: route IV (E→F→E) and route V (E→G→E). At the start of route IV, the temperature was increased at a rate of 10 °C/min to 550 °C under $PO_2 \sim 4 \times 10^{-9}$ torr. The annealing time was optimized to 12 h. After the reduction reaction, the sample was rapidly quenched in order to

prevent the formation of other Magnéli phases that might occur during a slow cooling process. Similarly, along thermodynamic route V, the sample was stabilized at 838 °C for 12 h (point G) and also rapidly quenched to room temperature.

2.4.5 Characterizations

Room-temperature θ -2 θ x-ray diffraction (XRD) and reciprocal space mapping (RSM) were used to characterize the lattice structure and its relation to the substrate structure using a Rigaku SmartLab X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Atomic force microscopy (AFM) for room-temperature surface characterization was performed using a Veeco Scanning Probe Microscope (SPM). The scan area of each of the films was fixed to $1 \times 1 \text{ }\mu\text{m}^2$. X-ray photoelectron spectroscopy (XPS) Spectra was carried out using a Kratos AXIS Ultra DLD XPS instrument equipped with an Al X-ray source and a 165 mm electron energy hemispherical analyzer. All the spectra were calibrated to the strongest O1s component at 530.0 eV. [19,20] Samples were cleaned by Ar ion beam (4 keV) sputtering for 12 seconds prior to the measurements to remove the surface layer contamination. The N-1s, C-1s, and O 1s peaks and the V2p peak were constantly monitored to prevent the peak distortion and the change in the oxidation state of vanadium ions. [19,20] Shirley background was used for the peak fitting. Temperature-dependent electrical transport measurements using a standard four-point probe configuration were performed in a Lakeshore TTPX probe station with a Keithley 6221 current source and a Keithley 2182A nanovoltmeter.

2.5 Acknowledgements

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Chapter III – Volatile resistive switching and inherent stochasticity in VO₂

3.1 Overview

In previous Chapter, we investigated the thermally induced metal-insulator transition (MIT) in different vanadium oxide thin films and the effects of oxygen stoichiometry using gas evolution technique. So far this dissertation has focused on the development of new materials and synthesis technique to modify transport properties. The following chapters (Chapter 3-5) will focus on the resistive switching properties of these strongly correlated oxides and the applications of neuromorphic computing devices. VO₂, known as Mott insulator with a near room temperature MIT, is one of the most promising correlated oxides in the applications of neuromorphic computing and resistive switching. The electrically induced volatile resistive switching can be observed when the device temperature is close to T_{MIT}. Though its volatile switching property, which could emulate neuron spiking, has been studied widely, there are still lacking of nanoscale studies about the phase transition triggered by the electric field. In this study, using in-situ transmission electron microscopy and ex-situ resistive switching measurement, we successfully captured the structural phase transition between monoclinic and rutile VO₂ at local areas in planar VO₂/TiO₂ device configuration under external biasing. After each resistive switching, different VO₂ monoclinic crystal orientations are observed, forming different equilibrium states. We have evaluated a statistical cycle-to-cycle variation, demonstrated a stochastic nature of the volatile resistive switching, and presented an approach to study in-plane structural anisotropy. Our microscopic studies set a big step forward towards understanding the volatile switching mechanisms and the related applications of VO₂ as the key material of neuromorphic computing.

3.2 Introduction

Resistive switching (RS) in vanadium oxides has attracted much attention because of the potential applications in bio-inspired neuromorphic computing and non-volatile memories. [1-4] To emulate the neuro-biological functions, people use two kinds of switching. Spiking neurons and synapses can be mimicked with volatile RS (threshold switching), and non-volatile RS, respectively. Although these two types of switching are usually found on two different types of material, it has been recently demonstrated that some materials like VO₂, as the Mott insulators, can exhibit both functionalities when submitted to an electric field. [5] VO₂, whose MIT is above room-temperature ($T_{\text{MIT}} \sim 340$ K) [6], has been widely studied as a neuristor. [7] It is considered as a promising candidate for energy-efficient neurons due to its threshold spiking phenomenon. In pristine VO₂, it is believed that the resistive switching can be triggered by local Joule heating across the IMT. [8] In previous work [9], in-situ X-ray nano-mapping was used to track the out-of-plane monoclinic and rutile Bragg peaks during the RS. However, up to now, the nanoscale in-plane structural anisotropy and its intrinsic stochasticity between each RS are rarely explored: how the system returns from metallic state to the insulating state and how the structural phase transition influences the switching process.

In addition, the control of the switching usually appears to be imprecise, *i.e.* the voltage necessary to initiate the phase transition is not a constant value between each switch cycles (even within a single grain). [10] Therefore, it is of critical importance to understand the stochastic behavior within the neuron device and the phase transition mechanism at nanoscale under external stimuli, since the switching has to be done a large number of times during neuron firing process. In addition, the IMT of VO₂ nano-devices can show multiple jumps, which implies that the domain structures in VO₂ may influence the transition behavior [11]. Also, many physical

properties, such as electrical, magnetic, optical properties, could be significant changes during IMT process [12,13]. Here, we use *in-situ* biasing transmission electron microscopy (TEM) with *ex-situ* electrical transport measurement to capture the structural phase transition (SPT) across the volatile switching in VO₂. In-plane resistive-switching was studied in epitaxial nano-devices VO₂/TiO₂ (001). The original in-plane structural isotropy in VO₂ rutile structure (R phase) will change to anisotropy in monoclinic phase (M1 phase) after resistive switching. Multiple monoclinic domains will form when the system return to the insulating state. The IMT phase transition and the simultaneous electrical properties change have been systematically studied. Our results demonstrate that the structural anisotropy between different M1 VO₂ domains plays an important role in the insulating state. In addition, this study provides a thorough understanding of the volatile resistive switching process and show that the intrinsic variability is a key issue in developing neuromorphic networks.

3.3 Results and Discussions

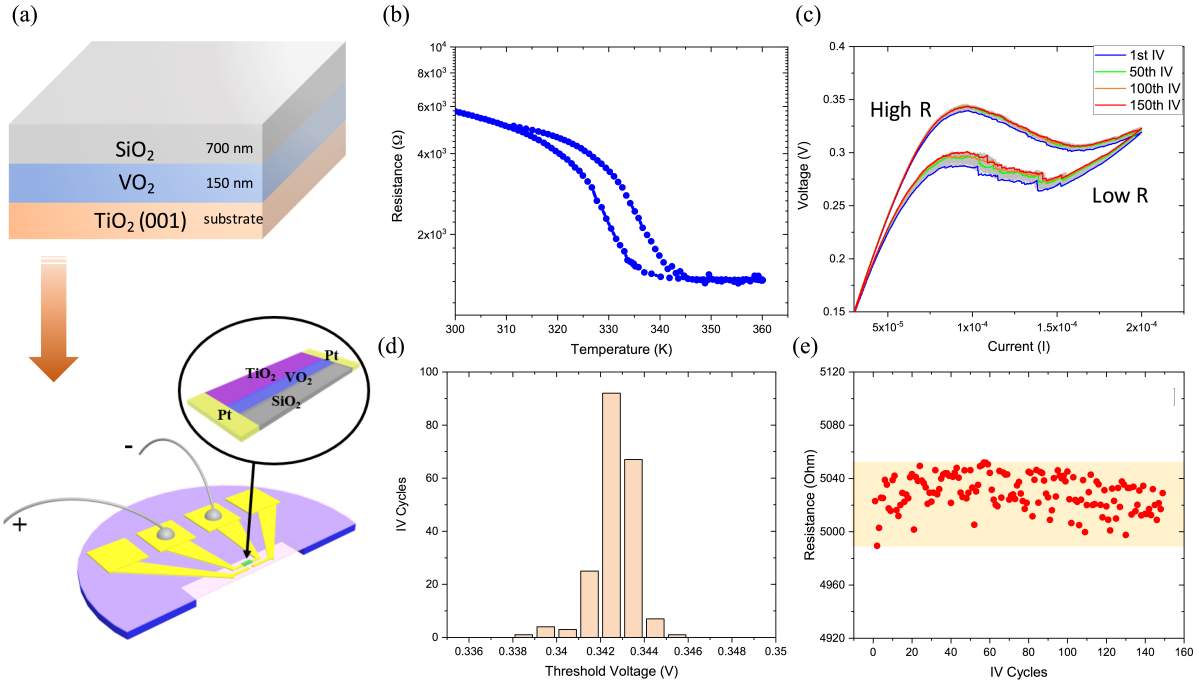


Figure 3.1 *Ex-situ* electrical transport measurement of volatile resistive switching in VO_2/TiO_2 TEM device. (a) Schematic of the $\text{SiO}_2/\text{VO}_2/\text{TiO}_2$ thin film system. The TEM device schematic is shown at the bottom. The TEM sample fabricated by FIB is enlarged for clarity. The two-terminal was applied between two Pt electrodes, forming a planar device. (b) Resistance vs temperature curve measured from the VO_2 TEM device. (c) 150 voltage-current loops measured from the same device. (d) Statistical distribution of the threshold voltage (V_{th}). (e) The initial resistance values (at $T = 300$ K) for the M1 phase VO_2 for 150 times measurement on the same device at room temperature. The current was fixed to 2.6×10^{-5} A. (Current density $\sim 1 \times 10^{-14}$ A/m²)

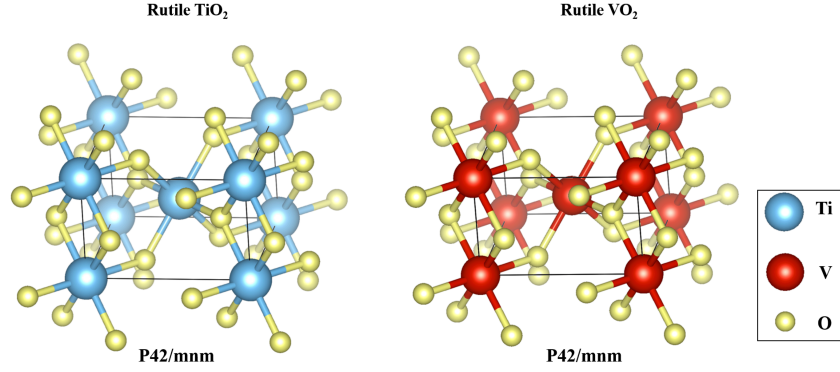
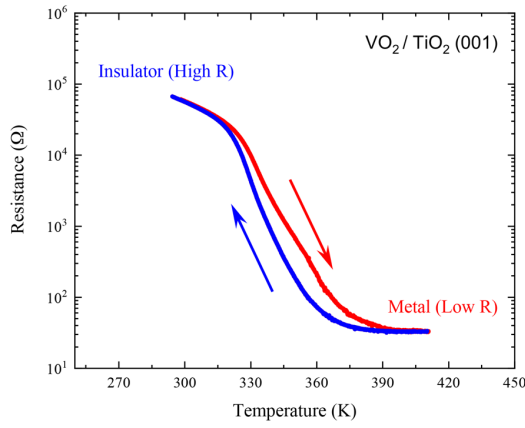


Figure 3.2 Atomic models for R TiO_2 (left) and R VO_2 (right). The lattice parameters for R TiO_2 are $a=b=4.59 \text{ \AA}$, $c=2.96 \text{ \AA}$. The lattice constants for R VO_2 are $a=b=4.55 \text{ \AA}$, $c=2.86 \text{ \AA}$.

(a)



(b)

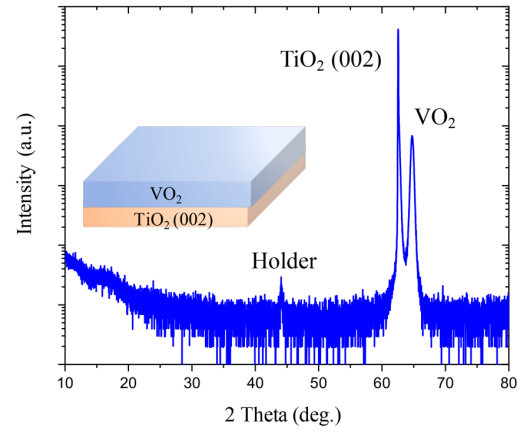


Figure 3.3 Basic characterizations of VO_2/TiO_2 thin film. (a) R-T curve for 150 nm VO_2 thin film. (b) XRD result showing the coherent growth of VO_2 film.

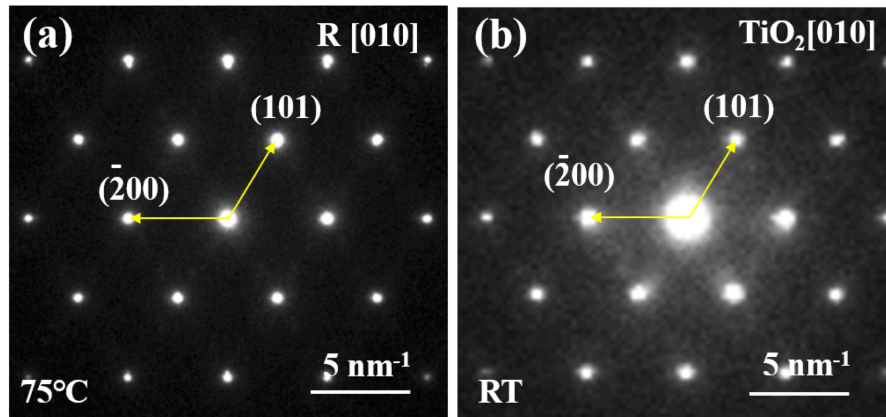


Figure 3.4 Selected area electron diffraction (SAED) pattern for R VO_2 (a) and R TiO_2 (b) along $[010]$ direction.

Figure 3.1(a) illustrates the VO₂/TiO₂ system. The 150 nm VO₂ thin film grows epitaxially on the (001) TiO₂ substrate by rf magnetron sputtering, since rutile VO₂ (R VO₂) and rutile TiO₂ (R TiO₂) share very close in-plane lattice constants (1% lattice mismatch, as illustrated in Figure 3.2). This system is therefore suitable for in-situ TEM measurements. The R-T curve of as-deposited VO₂ shows a metal-insulator transition at T_{MIT} ~340 K, with at least 3 orders of magnitude change in the electrical resistance. (Figure 3.3a). The single-phase growth of the VO₂ thin film on (001) TiO₂ is consistent with the XRD scan shown in Figure 3.3b. The selected area electron diffraction patterns for R VO₂ and R TiO₂ are shown in Figure 3.4 and also demonstrate the single-phase growth of the VO₂ film. SiO₂ layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) method on the top of VO₂ as an insulating protection layer for TEM measurements. The thickness of each layer is indicated in Figure 3.3a. The in-plane VO₂ devices for *operando* TEM studies were prepared by standard focused ion beam (FIB) lift-out method. To apply electrical stimuli through the planar VO₂ devices, 3 mm diameter semicircle chips with Au pads were used, as shown in the lower panel of Figure 3.3a. By wire bonding, the Au pads on the chip are connected to the electrical feedthroughs on our custom biasing TEM holder. The electric field was applied on VO₂ along in-plane direction via two Pt electrodes, which were deposited during the FIB sample preparation process. Figure 3.1b presents the *ex-situ* R-T measurement of the TEM device by using a probe station. This clearly shows that the VO₂ layer conserves its IMT behavior with a transition temperature ~ 335 K after FIB milling. The current-voltage (I-V) measurement displayed in Figure 3.1c shows a volatile resistive switching at room-temperature. The I-V curves were measured at least 150 times to confirm the device endurance. Our TEM device demonstrates a very stable volatile resistive switching behavior at room temperature. Statistical results of the threshold voltage (V_{th})

distribution are shown in Figure 3.1d. The slight V_{th} difference between each IV cycles shows that the stochasticity during the MIT within the VO_2 TEM device. In addition, it is known that VO_2 will change from its M1 phase to its R phase under heating and/or biasing conditions. We found that there were some variations between each cycle in I-V curves. To elucidate this, we extracted the initial resistance of M1 VO_2 at room temperature between each IV switching (as shown in Figure 3.1e). Interesting effects were observed: the initial resistance of M1 VO_2 varies slightly for each IV cycles. The mean value is about $5020\ \Omega$ with $\pm 30\ \Omega$ variance. Based on the *operando* TEM measurements, which will be discussed later, we attribute this variance to randomly formed insulating M1 VO_2 domains after each IV measurements. The structural stochasticity places an important effect on the electronic properties of VO_2 due to the coupling between IMT and structural phase transition.

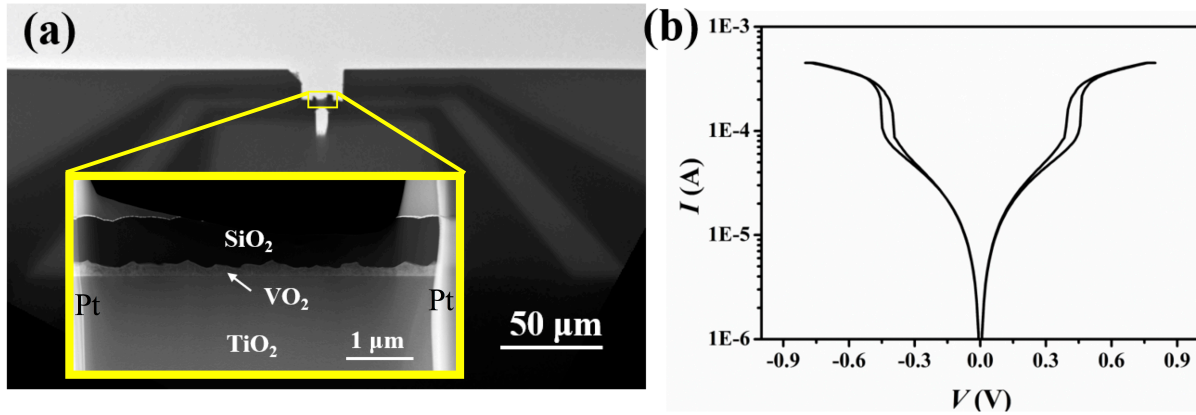


Figure 3.5 TEM characterizations of the VO_2/TiO_2 planar device. (a) Low-magnification TEM image of the chip configuration. The sample is in the yellow rectangle area. Insert, HAADF-STEM image of the FIB TEM device. The electric field was applied on the VO_2 along in-plane direction via two Pt electrodes. (b) The measured IV curves during *in-situ* TEM experiments for the VO_2/TiO_2 planar device.

To understand the underlying physics behind the volatile switching and the resistance variance, transmission electron microscopy (TEM) characterizations have been carried out. The low magnification TEM image in Figure 3.5a shows the device configuration. The insert figure is

the magnified high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image from the yellow rectangle area in Figure 3.5a. *In-situ* biasing TEM experiments were carried out on this planar VO₂ device at room temperature. The IV curve in Figure 3.5b clearly shows the volatile switching of the VO₂ device. The structural changes under external voltage biasing was captured with simultaneous I-V measurement while the sample is in the TEM (shown in Figure 3.6a). The selected area electron diffraction (SAED) pattern acquired from the yellow circle area in Figure 3.6a before conducting the biasing experiments is shown in Figure 3.6b. Using the (20 $\bar{1}$) from [102]_{M1} zone axis (as indicated by red arrow), the DF-TEM image is shown in Figure 3.6a. In the following, we simultaneously acquire SAED pattern of the yellow area while applying a voltage bias. With 1 V biasing across the planar VO₂ device (above the threshold), the diffraction pattern changes from Figure 3.6b to Figure 3.6d, which corresponds to the diffraction pattern from Rutile VO₂ [100] direction. The lack of obvious contrast in the acquired DF-TEM image as shown in Figure 3.6c is due to the position of the objective-lens aperture. After removing the external biasing, the VO₂ returns to a monoclinic phase as the diffraction pattern in Figure 3.6e-f demonstrates. Two mirror patterns along [010]_{M1} direction can be observed and the distribution of M1 VO₂ phase along [102] zone axis has changed. Another set of experiment has been conducted and the results are shown in Figure 3.6g-j. The diffraction pattern in Figure 3.6j is similar to that of Figure 3.6b with a changed distribution of [102] domains. Based on the analyses, we demonstrate that the orientation of the M1 VO₂ can be changed and stabilized in a random orientation.

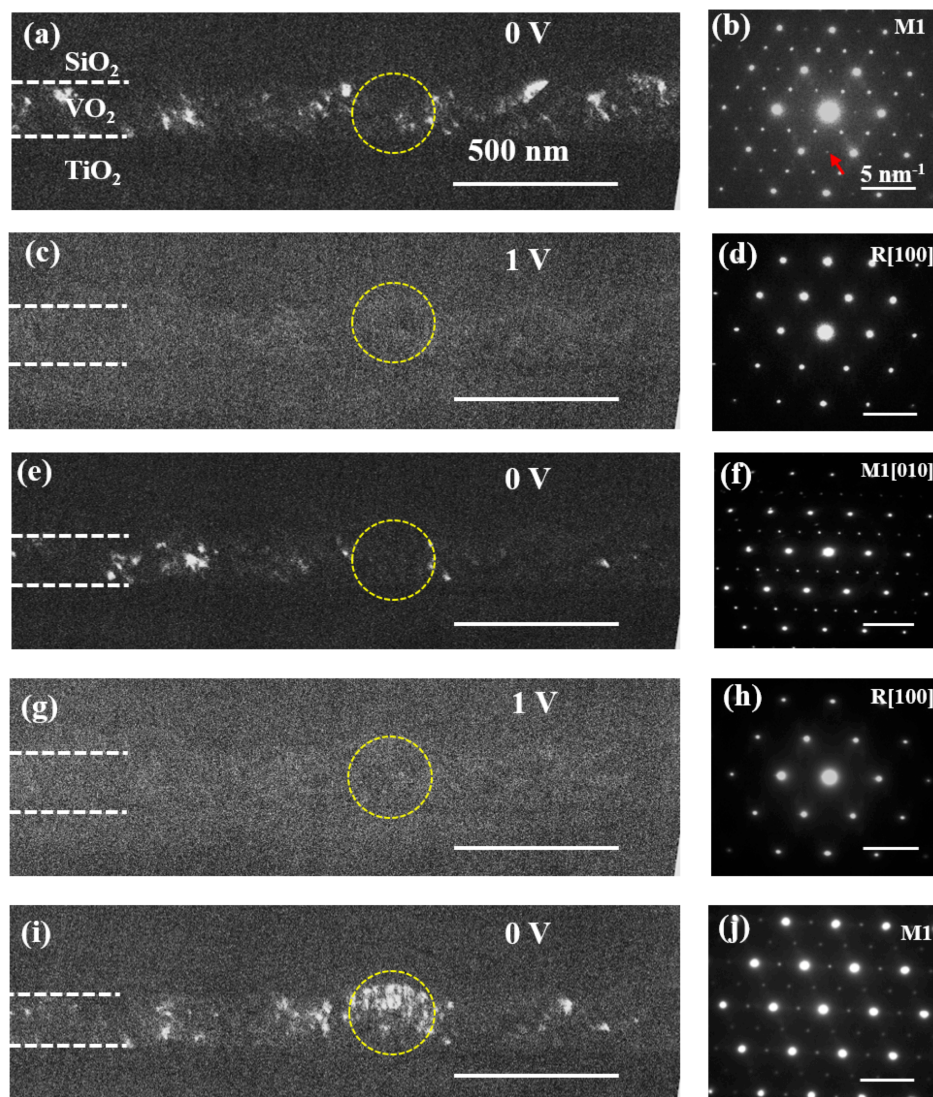


Figure 3.6 Operando dark field TEM (DF-TEM) studies for the VO₂ monoclinic/rutile domain evolution during volatile resistive switching. (a) DF-TEM image using the diffraction spot ($(20\bar{1})$ from $[102]_{M1}$ zone axis) indicated by the red arrow in (b) before bias is applied. (b) SAED pattern acquired from the yellow dotted areas in (a). (c) DF-TEM image with 1 V electric biasing applied. (d) SAED pattern under 1V biasing demonstrating that M1 VO₂ changed to R VO₂. (e) DF-TEM image taken after the removal of the biasing. (f) SAED pattern showing the VO₂ changed to M1 $[010]$. (g) DF-TEM with 1 V electric biasing and M1 VO₂ changed to R VO₂ as indicated in (h). (i) DF-TEM taken after removing external biasing. (j) SAED pattern acquired from the yellow region. The same diffraction spot and objective-lens aperture position in (a) are used for all the DF-TEM images.

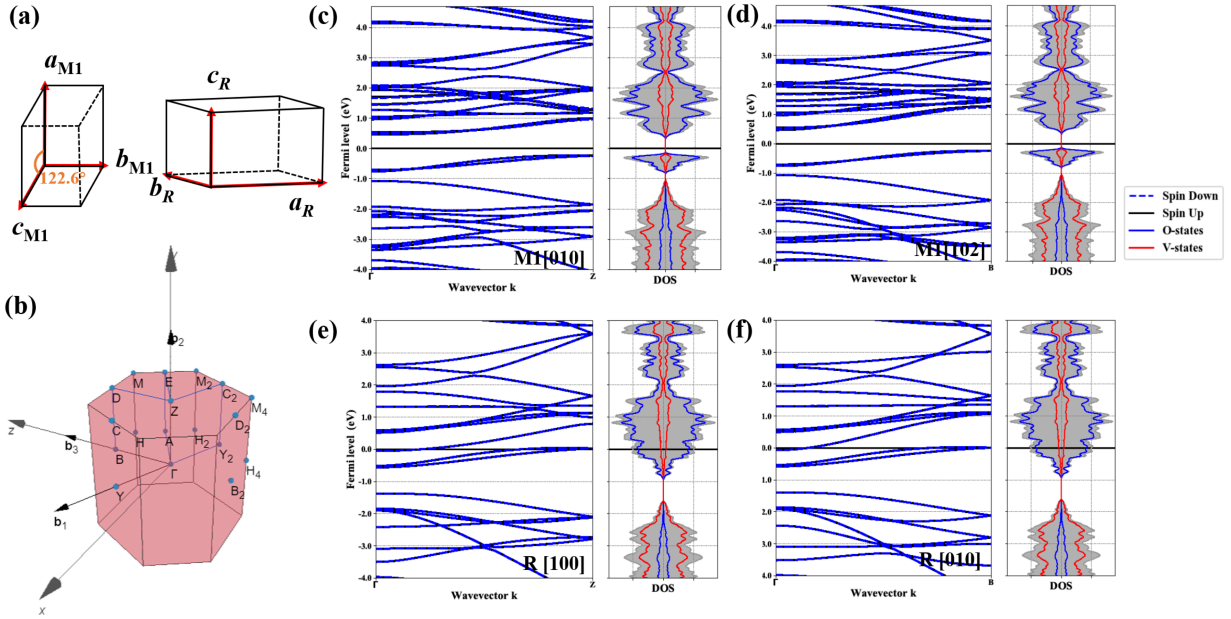


Figure 3.7 The calculated band structures of M1 VO₂ and R VO₂. (a) The relative coordination systems for M1 VO₂ and R VO₂. The [010]_{M1} is parallel to the [100]_R. (b) The first Brillouin zone of M1 VO₂. The critical points are indicated. Γ -B and Γ -Z corresponding to [102]_{M1} and [010]_{M1}, respectively. Band structures and project DoS for M1 VO₂ along the (c) [010]_{M1} and (d) [102]_{M1} directions and R VO₂ along the (e) [100]_R and (f) [010]_R directions. A legend is provided with the blue dashed and black solid lines being the down and up spin states of the band structure respectively and the blue solid and red solid lines being the O and V states of the DoS, respectively

The initial resistance variance shown in Figure 3.1 and the in-plane structural variation of M1 VO₂ structure have been further verified by density functional theory (DFT) calculations. The critical points of M1 VO₂ first Brillouin zone are shown in Figure 3.7b [14,15]. The [010]_{M1} and [102]_{M1} are along Γ -Z and Γ -B, respectively. To maintain a consistent k-point density, we relaxed the high-temperature rutile phase with a monoclinic basis based on the low temperature phase. The band structure and density of states (DoS) along Γ -Z and Γ -B for both M1 VO₂ and R VO₂ are shown in Figure 3.7c-f. The band gaps along [010]_{M1} and [102]_{M1} are 0.689 eV and 0.702 eV, respectively, while there is no band gap for R VO₂.

The difference of the band gaps along [010] M1 and [102] M1 also explain the variance of the resistance shown in Figure 3.1e. It is known that the conductivity of an intrinsic semiconductor is related to the band gap. The intrinsic conductivity given in terms of the band gap E_g as $\sigma(T) = \sigma_0 \exp(-E_g/2k_bT)$. From this, the calculated conductivity ratio is $\sigma[102]_{M1}/\sigma[010]_{M2} \sim 1.286$. Here we neglect the resistance change at the domain walls (including twinning planes), because the domain walls are more metallic than the domain. Since the resistances of [102]_{M1} and [010]_{M1} are different, the different ratio of M1 domains among the crystallographic variants could lead to resistance variation in the insulating state of the VO₂ planar device. This what produces the stochasticity in electronic and structural properties.

3.4 Conclusion

Transmission electron microscopy, electrical transport measurements, and density functional theory calculations have been combined to successfully reveal the nanoscale phase transition during the volatile switching in VO₂ based planar devices. Both *in-situ* TEM studies and *ex-situ* device measurements were carried out, for the first time, on the same TEM nano-chips. We show that during volatile resistive switching in VO₂, the monoclinic domains will change its orientations, imposing non-negligible influence on the electrical properties, which could have important implications for the electronic performance in bio-inspired neuromorphic computing.

3.5 Supplementary Information – Methods

3.5.1 Thin film growth and Device Fabrication

150 nm epitaxial VO₂/TiO₂ (001) thin films were deposited using rf magnetron sputtering from a V₂O₃ target. A 3.6-mtorr Ar/O₂ mix (8% O₂) was used during thin film deposition, and the substrate was ~ 615°C during the growth. X-ray diffraction (XRD) measurements were performed using Rigaku SmartLab with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The SiO₂ was deposited by Trion Orion III PECVD system at 400°C for 5 min. The thickness of SiO₂ was measured to be 700 nm via TEM. The Au and Pt layers were deposited by sputtering and FIB, respectively.

3.5.2 Electrical measurements

Temperature dependent electrical transport measurement and resistive switching measurements of VO₂ TEM devices were performed in a Lakeshore TTPX probe station with a Keithley 6221 current source and a Keithley 2182A nanovoltmeter in a two-point probe configuration.

3.5.3 In-situ TEM measurements

The dark field TEM images and electron energy loss spectroscopy spectra were acquired by a FEI Talos F200X TEM operated under 200 kV. The *in-situ* biasing holder was STM Nanofactory *in-situ* biasing holder with slight customization. The wire bonding connecting chip and holder were conducted by a wedge bonder Kulicke & Soffa 4526.

3.5.4 DFT calculations

All density functional theory (DFT) [16] calculations were performed using the Vienna Ab initio Simulation Package (VASP) within the projector augmented wave (PAW) approach. [17] The exchange-correlation effects were modeled using the Perdew-Berke-Ernzerh of (PBE) generalized gradient approximation (GGA) functional. [18] The GGA functional is unable to

correctly predict electronic properties such as the band structure, bandgap and DoS due to the strong correlation in VO₂. [19] We circumvent this by introducing the Hubbard U parameter with U=3.06 eV to all calculations of the high temperature R and low temperature M1 VO₂ phases. The Hubbard U was fitted to obtain a band gap of 0.6 eV in the low temperature monoclinic phase of VO₂ in accordance with experimentally observed band gaps. [20] The pseudopotentials used are similar to those used in the Materials Project. [21] The energies and atomic forces of all calculations were converged within 10⁻⁵ eV and 0.01 eVÅ⁻¹ respectively and a plane wave cutoff energy of 900 eV was used. Γ -centered k-point meshes of 9×9×9 were used in calculating the DoS. Analysis of density of states (DoS) and band structure was performed with the aid of the Python Materials Genomics (Pymatgen) materials analysis library. [22] The high-symmetry K-path of the band structure was obtained using the method described by Setyawan and Curtarolo. [23]

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Chapter IV – Formation and relaxation of conductive filament through non-volatile resistive switching in VO₂

4.1 Overview

Having discussed the volatile resistive switching mechanisms in VO₂ in previous chapter, we will now focus on the non-volatile resistive switching properties of the VO₂ two-terminal devices and the oxygen vacancies filament formation mechanism. VO₂, as one of the only two VO_x members with a IMT above room temperature ($T_{\text{IMT}} \sim 340$ K) has attracted much attention for developing novel hardware for neuromorphic computing. The electrically induced volatile resistive switching can be observed when the device temperature is close to T_{IMT} . The mechanism behind the volatile switching in VO₂ is believed to be a combination of thermal and/or electrical field induced IMT in response to external stimuli. Despite this interest, the mechanisms for non-volatile switching functioning as synapse in this oxide remain not understood. In this work, we use electrical transport measurements, in-situ transmission electron microscopy on Au/VO₂/Ge vertical devices to study the electroforming process. We discovered the formation of Magnéli V₅O₉ phase conductive filaments with a pronounced metal-insulator transition and that vacancy diffusion can erase the filament, allowing for the system to “forget”. It is possible to induce the oxygen vacancy diffusion and non-volatile filament formation at low temperature regime. Thus, both volatile and non-volatile switching can be achieved in VO₂, useful to emulate neuronal and synaptic behaviors, respectively. Our systematic operando study of the filament provides a more comprehensive understanding of resistive switching, key in the development of resistive switching based neuromorphic computing.

4.2 Introduction

The development of smaller, faster and more energy-efficient resistive switching devices with multi-functions is crucial for realizing neuromorphic computing systems. In these, “neurons” (neuristors) are active components which produce non-linear electric signals under external excitations, while the “synapses” (synaptors) control the connectivity between active elements [1]. The challenge in developing a brain-like computing hardware is to mimic and integrate these active components and their interconnections using electronic devices. Two different classes of materials are generally proposed to emulate neurons and synapses. Correlated insulators with metal-insulator transitions (such as VO_2 or NbO_2) commonly feature threshold or volatile resistive switching: the transition to the metallic state can be induced by applying a voltage, and the device returns to the insulating state once the stimulus is removed. This makes them ideal candidates for reproducing neural spiking [2]. On the other hand, many non-correlated systems, such as TiO_2 , HfO_x or phase change materials, are well known for having reversible non-volatile resistive switching, very promising for implementing synaptic behavior [3]. In the case of oxides, this switching is due to the drift of oxygen vacancies under strong electric fields. Moreover, to improve the processing speed, scalability, device density and connectivity like those in biological systems, the development of 3D crossbar circuit is necessary [4, 5]. However, fabrication of 3D stacked arrays is difficult and further studies on vertical resistive switching devices will be required.

Among the different materials, VO_2 has attracted much attention because of its threshold switching behavior and its insulator-metal transition (IMT) near room-temperature [6-11]. The mechanism behind the volatile switching in VO_2 is believed to be a combination of thermal and/or electrical field induced IMT in response to an external voltage/current input [12-15].

However, unlike other transition-metal oxides such as TiO_2 [16, 17], the microscopic nature of the electroforming process and non-volatile switching behavior in the Mott insulator VO_2 has not yet been explored [18]. Interestingly, this provides the opportunity to realize non-volatile resistive switching (caused by oxygen vacancy migration) coexisting with volatile resistive switching. This is of great potential, since the same material can show both neuron-like and synapse-like functionalities. The nanoscale nature of the conductive filament poses a major challenge to the study of the non-volatile switching mechanism [19]. Here, combining operando transmission electron microscopy (TEM), electrical transport measurements, we elucidate the electroforming process in $\text{Au}/\text{VO}_2/\text{Ge}$ vertical devices. The operando TEM studies allow to conduct simultaneous structural and transport characterizations. The atomic structure of the nanoscale conductive filament was unambiguously determined and a filament relaxation/recovery mechanism has been demonstrated. Our study unveiled the essential role of oxygen defects in the filament formation and relaxation during resistive switching.

4.3 Results and discussion

4.3.1 Non-volatile resistive switching

Figure 4.1a shows a 150-nm VO_2 thin film deposited onto a Ge substrate by magnetron sputtering. The single-phase growth of the (011) VO_2 thin film was confirmed by X-ray diffraction (see Figure 4.2) [20]. The Ga-doped Ge substrate has p-type conductivity with a room temperature resistivity of 0.001 Ohms-cm. To investigate the resistive switching behavior, a VO_2 layer sandwiched between two electrodes (Au as top electrode and highly doped Ge as bottom electrode as shown in Figure 4.1a) was fabricated. Figure 4.1b shows the thermal-induced IMT for one of the $\text{Au}/\text{VO}_2/\text{Ge}$ devices with a transition temperature, $T_{\text{IMT}} \sim 345$ K. This device

exhibits a nearly three order of magnitude resistance change with a 10 K heating-cooling thermal hysteresis. The atomic unit cell of the low temperature monoclinic insulating phase (noted as M1 phase) and the high temperature rutile metallic phase are shown in the insets. Volatile resistive switching can be found for the Au/VO₂/Ge devices when their temperature is raised close to the T_{IMT} (in Figure 4.3). The VO₂ returns to the insulating state upon removing the external current. The mechanism of this switching has been studied earlier and is due to a combination of thermal [12-14] and/or non-thermal [15] switching depending on the details of the defects present.

Figure 4.1c shows the I-V curve measured at room-temperature, featuring clear non-volatile resistive switching. As the current increases to the threshold value, a large drop of the voltage indicates the formation of the low resistance state between the two electrodes. The subsequent temperature-dependent transport measurement of this device reveals another insulator-metal transition around 140 K with a 50 K-wide thermal hysteresis. Moreover, the low temperature IMT (Figure 4.1d) shows a resistive asymmetry between the heating and cooling branches. The broadening of the hysteresis and the asymmetry in the R-T curve have been observed in many one-dimensional correlated oxide systems with first order phase transition like VO₂ and V₂O₃ [21, 22]. In addition, like other transition-metal oxides [1, 18, 23], oxygen migration in VO₂ may lead to the formation of oxygen-deficient filaments. Thus, the pronounced IMT with several orders of magnitude resistance change might be associated with an oxygen deficient vanadate phase within the VO₂ film. Due to the multiple possible vanadium oxidation states, a whole oxide family known as Magnéli (V_nO_{2n-1}) and Wadsley phases (V_nO_{2n+1}) [24] are stable. Among these compounds, only V₂O₃, V₅O₉ and V₆O₁₁ have lower oxygen/vanadium ratios than VO₂ with an IMT near 140 K. This implies that these VO_{2-x} phases are possibly formed during the resistive switching within the VO₂ film.

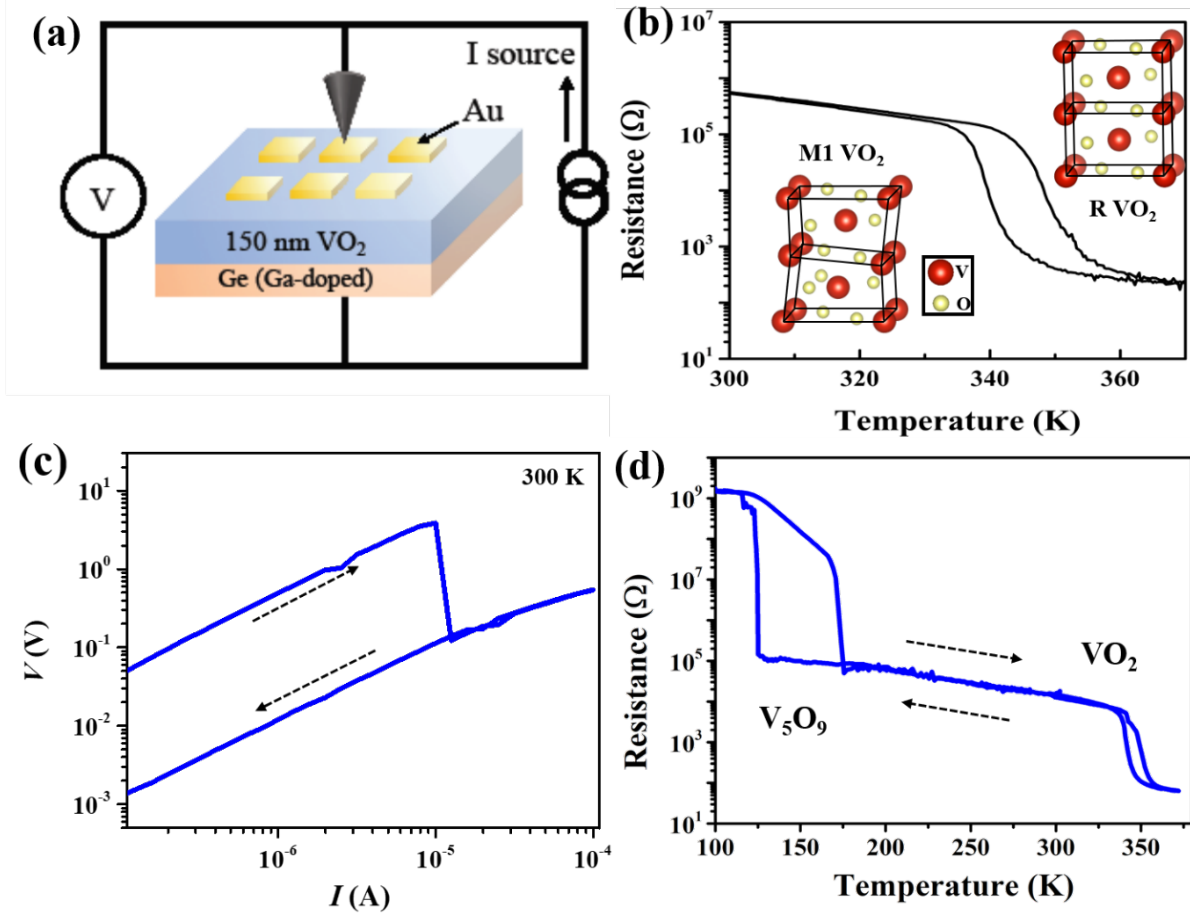


Figure 4.1: Non-volatile resistive switching in Au/VO₂/Ge vertical devices at room temperature. (a) Schematic illustration of the out-of-plane VO₂ device and the measurement set-up. The Au and highly doped Ge are top and bottom electrodes, respectively. (b) Resistance as a function of temperature of 150 nm VO₂ film. Inset, low temperature insulating VO₂ monoclinic phase (M1 VO₂) and high temperature metallic VO₂ rutile phase (R VO₂). (c) Room temperature I-V curve. The non-volatile resistive switching can be induced at room temperature. (d) After electroforming, the R-T curve of the VO₂ device shows another insulator-metal transition behavior at low temperatures. Based on the operando TEM measurements, which will be discussed later, we attribute this low temperature phase transition to the formation of V₅O₉ phase.

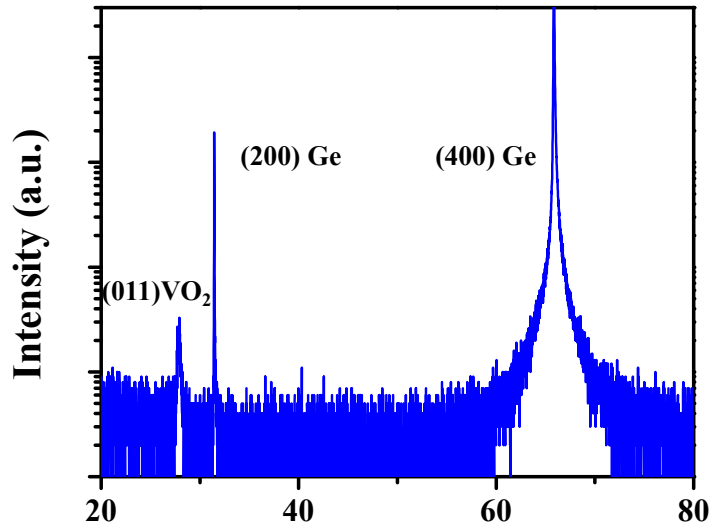


Figure 4.2: Room-temperature XRD scans for vanadium oxide films on (100) Ge substrate.

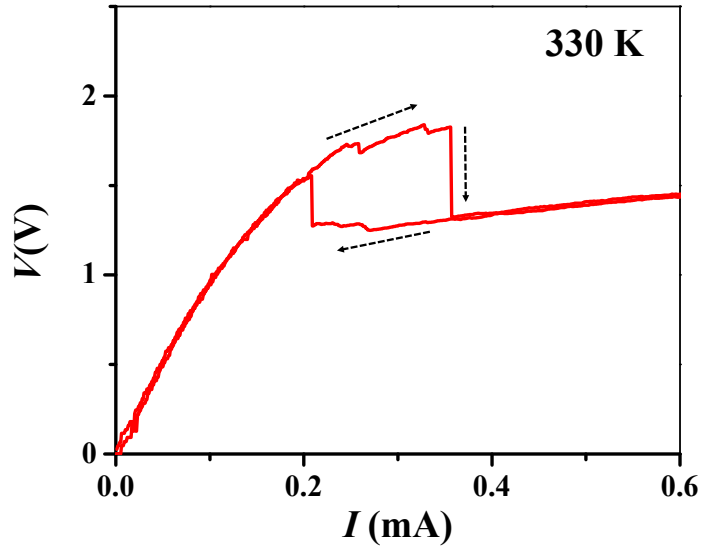


Figure 4.3: Typical volatile resistive switching in VO₂. I-V curve measured at 330K for one of the Au/VO₂/Ge devices. The volatile resistive switching can be induced when the device temperature is close to T_{IMT} (~340 K).

4.3.2 Operando TEM studies

To understand the non-volatile switching mechanism and gain insights into the filament formation, in-situ biasing TEM experiments were carried out. The experimental set-up is shown in Figure 4.4. All the experimental images in Figure 4.4 are scanning transmission electron microscopy, high-angle, annular dark field (STEM-HAADF) images, which are sensitive to the atomic weight in the sample [25].

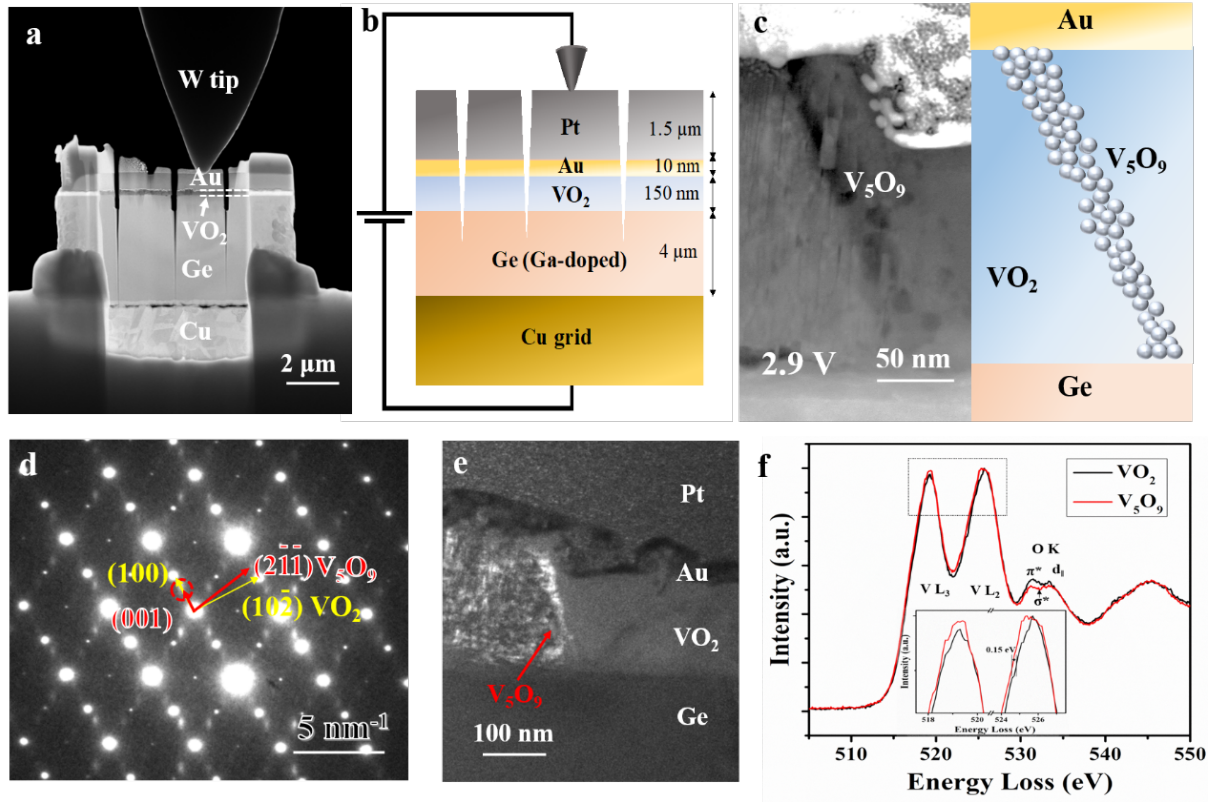


Figure 4.4: Operando TEM studies showing the formation of conductive filament. (a), (b) HAADF image and schematic diagram of the experimental setup of the VO_2 device. Each FIB sample has three vertical cuts, making two out-of-plane devices. (c) Experimental image and the corresponding schematic illustration of the conductive filament. (d) Selected area electron diffraction acquired from the conductive filament area. (e) Dark field image using the diffraction spot marked by red circle ((001) of V_5O_9) in (d). (f) Core-loss EELS spectra for VO_2 and V_5O_9 . Approximately 0.15 eV energy shift is found for the V_5O_9 .

Figure 4.4b shows the top Au and Pt layers are the protection layers deposited during FIB (focused ion beam) process and used as top electrode in the biasing experiments. The sample was separated into two independent out-of-plane devices by three vertical FIB cuts. The piezo-controlled W tip was grounded and made a contact with the top Pt layer.

While sweeping the voltage from 0 V to 3 V, the conductive filament becomes visible as the dark regions in the image. Figure 4.4c depicts the morphology of the conductive filament and the corresponding schematic illustration of the conductive filament is shown. The STEM images show the changes of the sample with increasing the voltage in Figure 4.5. The selected area electron diffraction (SAED) pattern acquired from the filament area (the actual selected area on the sample is about 100 nm in diameter) is shown in Figure 4.4d. Together with the electron diffraction peaks from the M1 VO₂ phase (the electron diffraction pattern for the pure M1 VO₂ can be found in Figure 4.8), an additional set of diffraction peaks with about 1/3 of the reciprocal lattice spacing of VO₂ along the a-axis (indicated by red arrows) is observed. This is identified as the V₅O₉ phase. The simulated SAED patterns for M1 VO₂ [010] and [102], as well as V₅O₉ [120] are shown in the Figure 4.8, which match well with the experimental diffraction pattern in Figure 4.4d. Considering the lattice symmetry, both the M1 VO₂ and V₅O₉ phases have structural variants, i.e., twinning. A diffraction mirror plane can be identified. Using the diffraction spot from the V₅O₉ phase, as indicated by the red circle in Figure 4.4d, a dark field TEM image was acquired, showing the distribution of the newly formed V₅O₉ phase. The shape of the conductive filament is consistent with that shown in Figure 4.4c, showing that the conductive filament is composed of V₅O₉ phase. The high resolution TEM image acquired from the filament area is shown in Figure 4.6. The dark field TEM image also shows some isolated V₅O₉ nano-grains (within tens of nanometer in size) near the conductive filament formed during the electroforming

process. The region identified as conductive filament is within a VO_2 matrix. It is noteworthy to mention that V_5O_9 phase also shows a first order IMT (the transition temperature is about 135 K), consistent with the low temperature IMT shown in Figure 4.1d [26, 27]. Electron energy loss spectroscopy (EELS) results also reveal the change of V valence state in the conductive filament area [28]. Since the $L_{2,3}$ edges of V are very close to the O K edge, L_3 and L_2 area ratios in EELS cannot be used to extract the valence state of V [10]. However, the change of valence states could affect the number of screening electrons around the nucleus, thus resulting in a change in the onsite energy of the L_3 edge. Furthermore, considering the VO_6 octahedral coordination, the lowest unoccupied state should change as well, which should be reflected in the oxygen K edge. Figure 4.4f shows a 0.15 eV red-shift in energy for the V_5O_9 phase, which is an indication for the decrease of the V valence state and the stoichiometry change (27). The energy positions for π^* , σ^* , $d//$ orbitals in the VO_2 EELS spectrum can be identified in oxygen K edge, which is consistent with X-ray results [29]. In V_5O_9 phase, the formation of oxygen vacancy increases the occupation of the π^* orbital and thus the first peak in the oxygen K edge should decrease. Since V_5O_9 is conductive at room temperature, its orbital diagram can be deduced from an analysis of the orbital hybridization (Figure 4.7) [10].

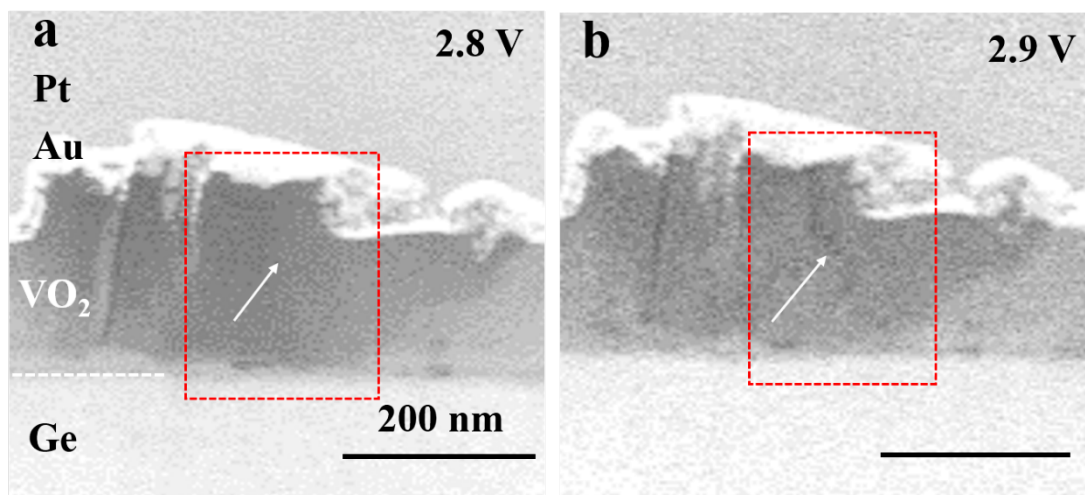


Figure 4.5: (a) Before and (b), after the formation of the conductive filament. The position of the conductive filament is indicated by the white arrow.

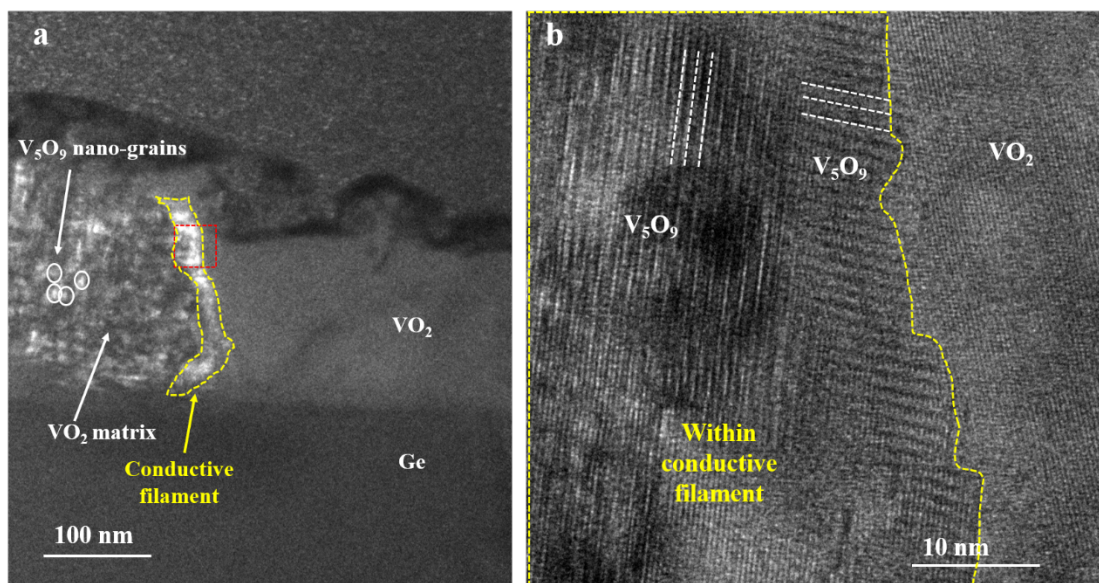


Figure 4.6: TEM studies on the conductive filament area. (a) Dark field TEM images showing the V_5O_9 conductive filament (in yellow). Some V_5O_9 nano-grains within VO_2 matrix have been encircled. (b) High resolution TEM image acquired from the red rectangle area in (a), showing the twin structure of V_5O_9 phase.

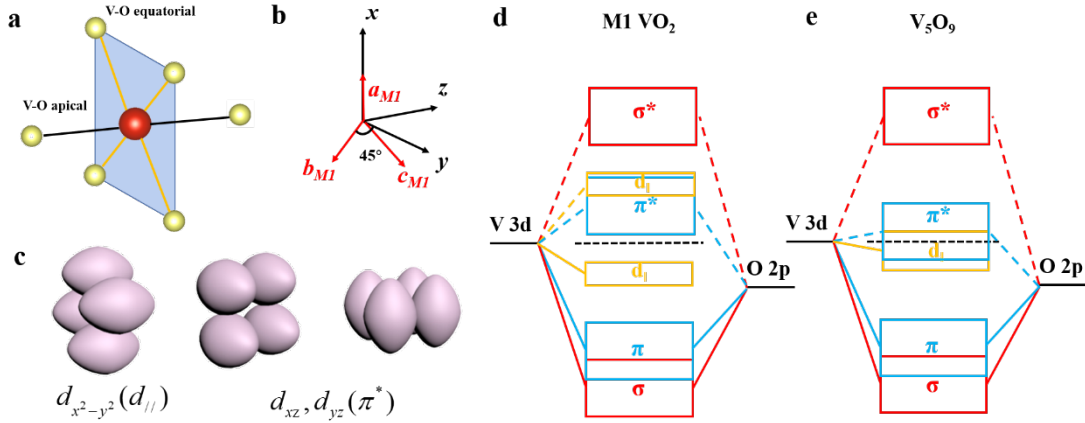


Figure 4.7: Orbital hybridization analyses for two relevant vanadium oxides. (a) Schematic diagram showing the VO₆ octahedron. The apical and equatorial V-O bonds are indicated in black and orange colors. (b) The relationship between the geometric axis (red arrows) and the coordination axis of M1 phase VO₂. (c) The illustration of vanadium t_{2g} d orbitals. (d), (e) Schematic of the orbital band structure of M1 phase VO₂ and V₅O₉ phase, deduced from the measured EELS result.

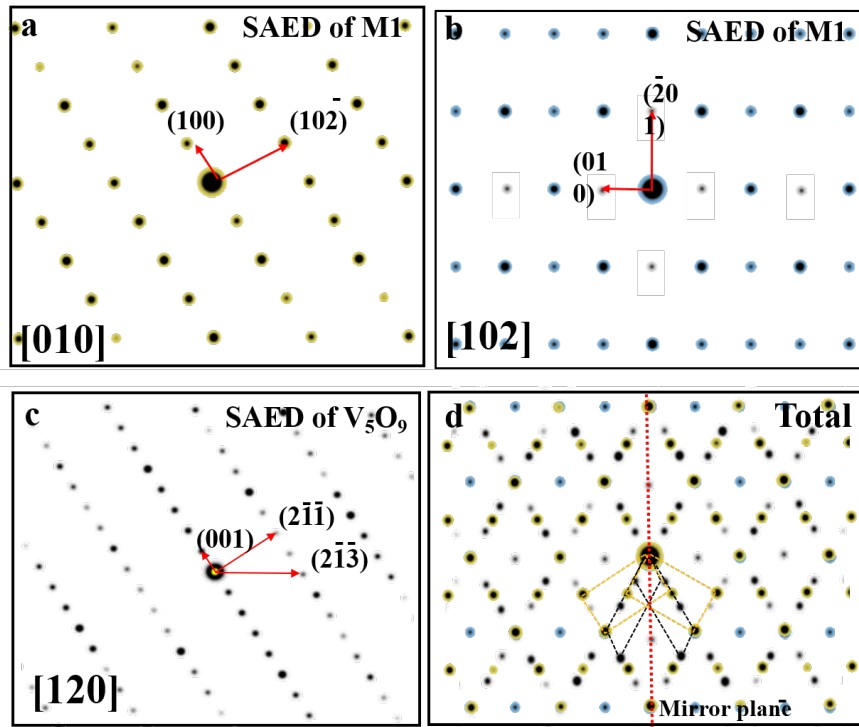


Figure 4.8: Simulated electron diffraction patterns. (a-c) Simulated electron diffraction patterns for M1 VO₂ from [010] and [102], and V₅O₉ from [120], respectively. (d) The combination of M1 VO₂ [102] diffraction, two sets of twinned V₅O₉ from [102] and M1 VO₂ from [010], which matches well with the experimental results shown in the main text. The mirror plane of twins is shown in red. The yellow parallelograms mark the base vectors for M1 VO₂ in reciprocal space, while the black parallelograms show those of V₅O₉.

4.3.3 Relaxation of the nanoscale V_5O_9 filament

The mechanism of oxygen migration and the switching reversibility can be further studied by thermally annealing the device after the non-volatile filament formation. Transport properties of strongly correlated oxides, such as VO_2 and V_5O_9 , are extremely sensitive to the variation in oxygen content, carrier density and structural disorder [30]. Figure 4.9a shows the R-T curve of the V_5O_9 filament after the IV switching (blue curve), after annealing in air for 30 min (green) and 1 h (red) at 400 K. The R-T curve changes dramatically, showing the recovery from V_5O_9 to the original VO_2 state as a result of the re-oxidation of the filament during annealing. The resistance in the low temperature region increases with longer annealing time associated with a degradation of the V_5O_9 IMT, indicating the disappearance of this Magnéli phase. It may worthwhile to mention that small change along the filament length could result in a large change in the total resistance, making the low temperature IMT signal appear to be strong. The R-T measurements at high temperature reveal the VO_2 IMT, as shown in Figure 4.9b. After the V_5O_9 filament forming, the magnitude of the VO_2 IMT is slightly reduced. This electroforming process is likely to increase the density of oxygen vacancies and lead to oxygen loss from the VO_2 monoclinic structure. These vacancies behave as electron donors in the original VO_2 , thereby increasing the number of free charge carriers and leading the IMT degradation. After annealing, the VO_2 will partially recover to the original state. The reduced resistive change and the decrease in the hysteresis loop width across the IMT indicate further the presence of the oxygen deficient phase.

The breakdown electric field of the non-volatile filamentary switching is temperature independent at nearly ~ 28 MV/m (Figure 4.9c). Moreover, the power needed to induce non-volatile switching increases with increasing device temperature (Figure 4.9d). This is

inconsistent with pure Joule heating-triggered behavior and indicates the presence of oxygen migration, as described before [31]. On the other hand, triggering the volatile resistive switching at high temperature ($\sim T_{\text{MIT}}$) may be dominated by local Joule heating. In this case, the power dissipation and threshold voltage are expected to decrease with increasing device temperature [32]. The temperature dependence of the breakdown electric field will be significant. These results show that both volatile and nonvolatile resistive switching can be realized, but as evidenced by the very different T dependence, caused by different mechanisms in the Au/VO₂/Ge vertical geometry.

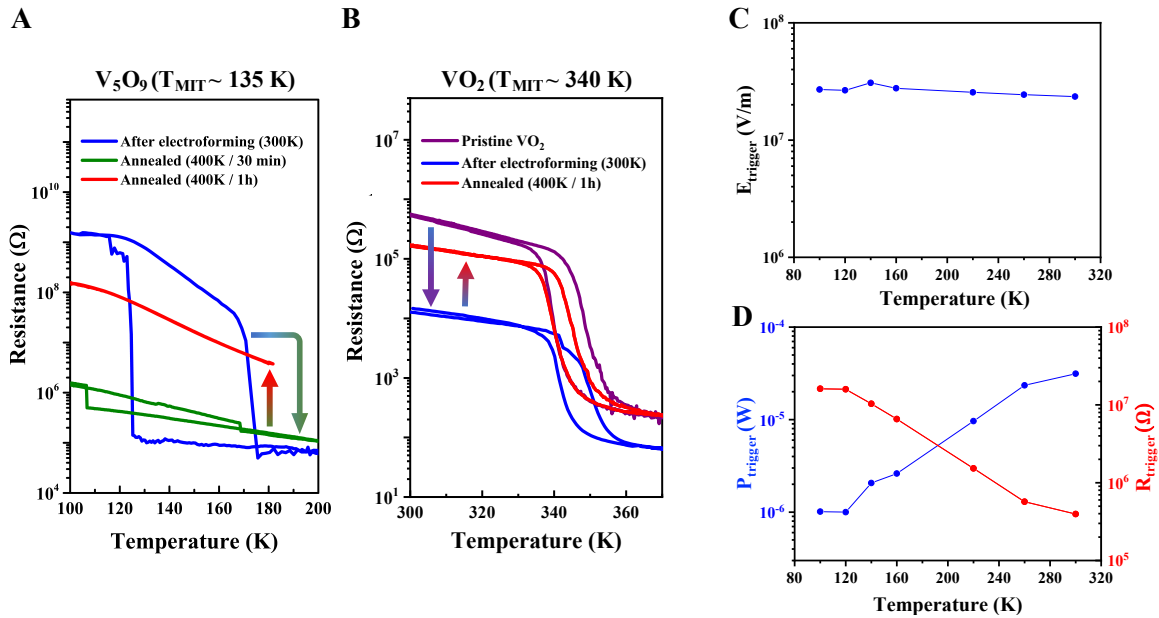


Figure 4.9: Relaxation of the nanoscale filament in VO₂. (a) R vs T for a device at low temperatures: after the non-volatile resistive switching (blue); after thermal annealing for 30 min at 400 K in air (green); after thermal annealing for 1 hour at 400 K in air (red). (b) R vs. T curve for a device at high temperature: Pristine VO₂ device (purple); after non-volatile resistive switching (blue); after thermal annealing for 1 hour at 400K in air (red). (c) Breakdown electrical field as a function of device temperature. (d) Power dissipation (P_{trigger}) and switching resistance (R_{trigger}) as a function of device temperature for VO₂ non-volatile switching.

Using the experimental set-up shown in Figure 4.10a, the reversibility of the conductive filament in Au/VO₂/Ge vertical device was studied in TEM. The compliance current was limited to 0.1 mA and the first “set process” is shown in black in Figure 4.10d. The IV curve was measured simultaneously while recording the TEM images, as shown in Figure 4.4. The device has high resistance initially and the current increases sharply with the application of 2.8 V. The sample resistance decreases markedly with the formation of the conductive filament as illustrated in Figure 4.10 (e and f). This in-situ biasing measurement agrees well with the ex-situ device measurement shown in Figure 4.1c. After the biasing experiments, the sample was annealed in air at 400 K for 30 min to test its reversibility. Figure 4.10b shows the morphology of conductive filament after partial recovery. The dark areas clearly decreased compared with those shown in Figure 4.4c. The V₅O₉ phase returns to VO₂ during annealing in air, showing the reversibility of the non-volatile resistive switching. The second test was applied under the same condition on the recovered sample, and the IV curve is shown in red in Figure 4.10d. Similar to the first measurement, the sample shows high resistance state and changes to low resistance state at 2.6 V. The change of voltage decreases slightly, due to the remaining V₅O₉ phase in the recovered sample, as illustrated in Figure 4.10g. The snapshot after the second switching experiment is shown in Figure 4.10c, showing the formation of the conductive filament. The new filament appears at the same position of the old one, indicating that the filament has a “memory effect”. However, the diameter of the filament becomes bigger, as illustrated in Figure 4.10h, which is consistent with the lower resistance state in the second measurement. From the TEM measurements, we found that the conductive filaments form in a randomly fashion between the top and bottom parallel electrodes. It is possible that the local defects, such as oxygen vacancies,

grain boundaries, domain boundaries may facilitate filament formation, and further exploration is needed.

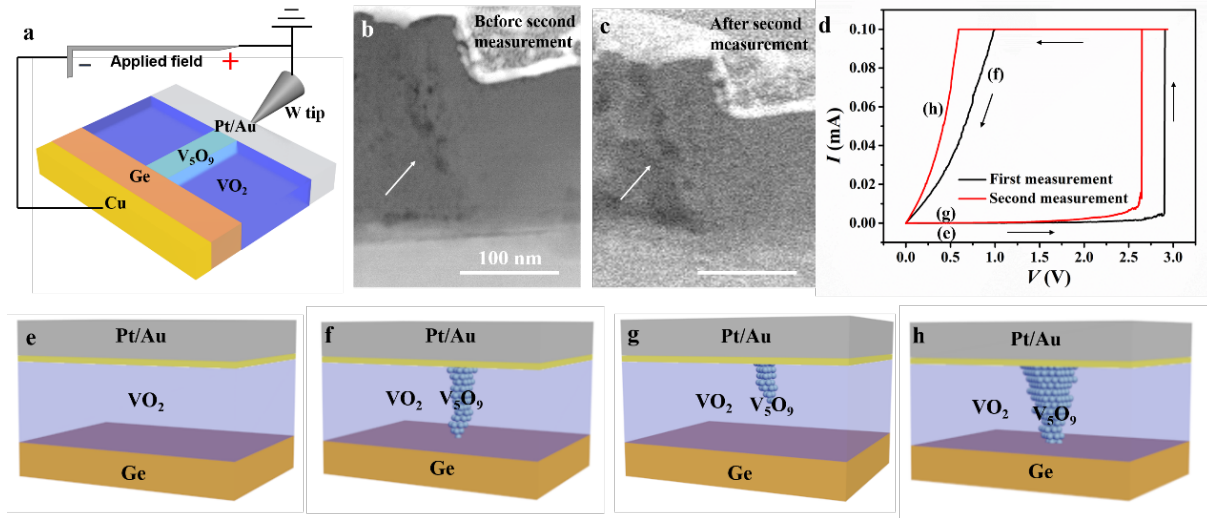


Figure 4.10: Reversibility of the non-volatile resistive switching. (a) The schematic showing the formation of V_5O_9 conductive filament under external bias. (b) HAADF-STEM showing the morphology of the conductive filament after recovery. (c) Formation of the conductive filament at the same position after second biasing experiment. (d) IV curve measured in-situ in the TEM. The black and red curves show the IV results for the first and second measurement, respectively. For the first measurement, the initial state is illustrated in (e). The low resistance state after electroforming process is shown in (f). After the recovery, the partially-survived filament is plotted in (g), which is the starting state for the second measurement. The final state with the formation of thicker conductive filament after second switching is demonstrated in (h).

Unlike TiO_2 [16], VO_2 exhibits the insulator-metal transition above room temperature. In TiO_2 , a large reset current can be used to disrupt the conductive filament by Joule heating. However, for VO_2 , it will be difficult to reset the conductive path using electrical stimuli after the electroforming process. The surrounding areas of V_5O_9 conductive filament will be heated up by the current, leading to the formation of metallic rutile-phase VO_2 . The large current will flow through the metallic rutile phase VO_2 rather than accumulating enough heat for oxygen migration to disrupt the filament.

Based on our experimental results, filament formation process can be understood by this scenario: (1) During the initial switching stage (electroforming), the oxygen vacancies start moving under the external field. Above certain oxygen vacancy level, the isolated V_5O_9 nano-grains will form in some part of the VO_2 thin film. (2) Once the V_5O_9 nano-grains connect between two electrodes, large current will naturally flow through the conductive pathway. The filament is shorting the rest parts of the VO_2 film which are highly insulating. The voltage/electric field will be significantly reduced after the switching and prevent further formation of other V_5O_9 conductive filament.

In conclusion, we show the formation of V_5O_9 conductive filaments in VO_2 devices using in-situ TEM and ex-situ electrical transport experiments. Besides the intrinsic volatile switching of VO_2 , the non-volatile switching can be attributed to the appearance and disappearance of the V_5O_9 Magnéli phase. Our study identified the essential role played by the Magnéli filament within the VO_2 device. This is supported with detailed characterizations of the insulator-metal transition, phase composition, lattice structure and its relation to the surrounding VO_2 . We demonstrated that two different resistive switching behaviors can be induced using $\text{Au}/\text{VO}_2/\text{Ge}$ vertical resistive switching device. For volatile resistive switching at high temperature regime,

the transition to the metallic state can be induced by applying an electric field, and the device returns to the insulating state once the stimulus is removed. Interestingly, at lower temperature regime, the non-volatile switching triggered by ion migration will maintain the metallic state and show memory effect. This is of great interest to emulate both neuronal and synaptic behaviors on the same material. Moreover, we have identified the V_5O_9 filament relaxation effect that allows the system to “forget”. This could have crucial implications in the implementation of oxide-based devices for neuromorphic computing. Our findings could be applied to a broad range of interdisciplinary fields, including strongly correlated materials, complex oxides with IMT behavior. Also, the second IMT of the Magnéli V_5O_9 filaments is an excellent candidate for low temperature applications. We believe this work is likely to be of great interest to researchers exploring new resistive switching oxide devices with different memory effects and modulating transport properties across metal-insulator transitions in oxide-based technology.

4.4 Supplementary Information – Methods

4.4.1 Thin film growth and Device Fabrication

150 nm thick VO_2 thin films were grown on (100) oriented P-type Ga-doped Ge substrates by RF magnetron sputtering from a V_2O_3 target. The growth of VO_2 was done at a substrate temperature of 445 °C using an Ar/ O_2 mixture (8% O_2) at 3.7 mTorr. Single phase growth of VO_2 was confirmed by room-temperature θ -2 θ x-ray diffraction (XRD) using Rigaku SmartLab with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and transmission electron microscopy. 100 nm Au top electrodes for electrical transport measurements were fabricated using e-beam evaporation and a shadow mask. The Pt layers were deposited by FIB.

4.4.2 Electrical measurements

Temperature dependent electrical transport measurement of Au/VO₂/Ge devices were performed in a Lakeshore TTPX probe station with a Keithley 6221 current source and a Keithley 2182A nanovoltmeter in a two-point probe configuration.

4.4.3 In-situ TEM

The TEM studies were carried out on a FEI Talos microscope at 200 kV accelerating voltage. The in-situ biasing study was carried out with STM Nanofactory in-situ biasing holder. TEM samples were fabricated by a FEI Helios dual beam system. The samples were polished at low voltages to remove the surface damage layers at the last step of the sample preparation. The EELS was acquired with 0.1 eV/ch dispersion. To satisfy the selection rule, the convergence angle was 19.1 mrad and the collection angle was 39.6 mrad. The energy resolution was estimated to be 0.7 eV.

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Shaobo Cheng*, Min-Han Lee* (*equal contribution), Xing Li, Lorenzo Fratino, Federico Tesler, Myung-Geun Han, Javier del Valle, R. C. Dynes, Marcelo J. Rozenberg, Ivan K. Schuller, Yimei Zhu. “Operando characterization of conductive filament during resistive switching in Mott VO₂” Proc. Natl. Acad. Sci. U.S.A. 118, e2013676118 (2021) The dissertation author was the co-first author/ principal investigator of this paper. The dissertation author conceived and designed the project, fabricated the devices, performed the electrical transport measurements, analyzed the data and co-wrote the paper.

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Chapter V – Volatile Resistive Switching in V_3O_5 Magnéli Phase

5.1 Overview

In previous work (Chapter 2), we have developed the novel gas evolution technique to modify the oxygen stoichiometry in vanadium oxide thin films. We demonstrate an effective pathway to strategically stabilize any Magnéli phases thin film despite their extremely narrow phase stability range. This chapter focuses on the resistive switching phenomena in V_3O_5 , one of the promising Magnéli phases for use in the oxide electronic applications and neuromorphic computing. Our technique can provide excellent control over a wide range of thermodynamic phase diagram, allow us to explore new oxide materials with pronounced insulator-metal transition (IMT). V_3O_5 , a compound of the vanadium oxide Magnéli series, is one of the rare materials to exhibit an insulator-metal transition (IMT) above room temperature ($T_{\text{IMT}} \sim 415$ K). The nanoscale switching mechanisms of the electrically triggered IMT in this material are still not clear. Here we demonstrate, for the first time, both volatile resistive switching (RS) and fast oscillatory spiking regimes in V_3O_5 devices at room temperature (120 K below the phase transition temperature) by applying an electric field. We use *operando* optical imaging to track a reflectivity change during the RS and find that a percolating high temperature metallic phase filament is formed. This demonstrates that the electrically induced VRS triggers the phase transition. Furthermore, we capture optically the spiking oscillations and the filament formation to understand the switching behavior. Our studies play an important role in understanding the volatile resistive switching mechanisms and demonstrate that V_3O_5 can be a key vanadium oxide for neuromorphic computing.

5.2 Introduction:

Resistive switching in materials that undergo an insulator to metal phase transition (IMT) is the subject of intense fundamental research¹⁻⁵ and it could enable a variety of novel applications, ranging from optoelectronic devices,^{6,7} oxide electronics,^{8,9} to artificial neurons and synapses for hardware-level neuromorphic computing.¹⁰⁻¹⁵ From the practical point of view room temperature operation of devices is highly desirable. The number of materials with the IMT above room temperature, however, is rather limited.¹⁶ At present, most research focuses on resistive switching in VO_2 ($T_{\text{IMT}} \approx 340 \text{ K}$) and NbO_2 ($T_{\text{IMT}} \approx 1080 \text{ K}$). When resistive switching is realized at temperatures far below the phase transition, it is not always clear whether or how the switching is related to it. Several explanations for the origin of the resistive switching have been proposed: triggering of the IMT by Joule heating, doping of the insulating phase by the high electric field, and the so called “thermal runaway”. In the first case, the electrical triggering of the IMT via Joule self-heating, leads to the formation of a high temperature phase metallic filament.^{5,17} In the second case, the high electric field promotes charges from a low lying state into the conduction band thus electrically doping and destabilizing the Mott material.³ “Thermal runaway” occurs by the formation of a low resistance filament at an intermediate temperature (that is below the high temperature metallic phase), which is possible because of a rapid decrease of resistance with increasing temperature in the insulating phase. It is rather well-established that the switching in pristine VO_2 ^{3,5,17} at room temperature (i.e. $\sim 50 \text{ K}$ below T_{IMT}) can be driven by local Joule heating across the IMT. On the other hand, in V_2O_3 (and also radiation damaged VO_2), resistive switching can be accomplished by destabilization of the Mott state by charge injection.³ In NbO_2 , Joule heating has been claimed to be the cause of both, local heating across the IMT^{18,19} and “thermal runaway”²⁰⁻²³ for resistive switching well below the T_{IMT} . This variety

of possibilities illustrates that observation of resistive switching in a IMT material does not automatically indicate the triggering mechanism. It is therefore of critical importance to establish the physical driving force behind the switching, especially if the transition temperature is far from the room temperature.

Here we focus on the physical nature of the resistive switching in V_3O_5 thin films. Recently, resistive switching was demonstrated in V_3O_5 bulk crystals at room temperature (i.e. 120 K below T_{IMT}).²⁴ It was not clear, however, whether this switching was produced by inducing the phase transition or by a thermal runaway in the insulating phase similar to NbO_2 . By combining electrical transport measurements and direct optical imaging, we show that the resistive switching originates from a coupled thermo-electric triggering of the phase transition along a filamentary conductive path. This conclusion is further supported by numerical simulations that describe the physical mechanism in detail. Quite remarkably, we achieve control of the filamentary structure that we imaged in both, static I-V measurements and in a dynamic self-oscillating "spiking" regime. Furthermore, our results demonstrate that the phase transition could be induced even when operating at a temperature well below T_{IMT} , which is relevant for potential neuromorphic hardware applications.

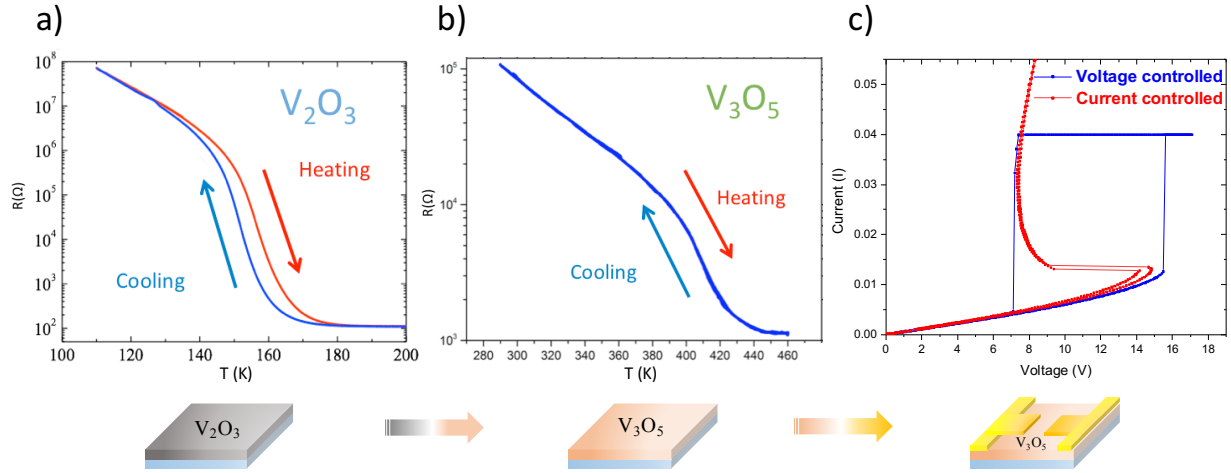


Figure 5.1: Temperature dependent electrical transport properties of (a) as-deposited V_2O_3 thin film; (b) transformed V_3O_5 thin film. The high quality V_3O_5 thin film with an IMT above room temperature, together with the absence of thermal hysteresis in the $R(T)$, is an excellent material for volatile resistive switching applications. (c) Voltage-controlled & current-controlled I-V curves showing a volatile resistive switching behavior in the two-terminal V_3O_5 device.

5.3 Volatile Resistive Switching in V_3O_5 :

The synthesis of pure phase V_3O_5 is challenging because the required stoichiometric range is very narrow (with an O/V ratio between 1.666 and 1.668 ± 0.002).²⁵⁻²⁷ In this work, we obtained V_3O_5 films by transforming V_2O_3 films in a high-temperature well-controlled oxygen environment. The details of the annealing process are available in previous chapter (Chapter 3).²⁷ Two Ti/Au electrodes were patterned on top of the film to make planar two terminal devices for resistive switching measurements. (Figure 5.1) The planar device configuration enables an easy access to probe the optical response of V_3O_5 simultaneously with the electrical properties, which allowed us to detect the triggering of the phase transition during resistive switching.

We observed a clear signature of the phase transition in our V_3O_5 devices, by using two independent techniques, resistance (R) and optical reflectivity (Ref) vs. temperature measurements (Figure 5.2a). Around $T_{IMT} \approx 415$ K, the resistance rapidly changes by about a factor of three. At the same time, the devices display a significant reduction of the optical

reflectivity. Both $R(T)$ and $\text{Ref}(T)$ show a continuous, non-hysteretic evolution near T_c , which is expected for a 2nd order phase transition.^{28,29} There is an important difference, however, between the $R(T)$ and $\text{Ref}(T)$. $R(T)$ shows a strong nonlinear (exponential) temperature decrease in the insulating state, below $T < 400$ K. Because of this, the relative resistance change from room temperature to the onset of the phase transition is comparable to the relative resistance change across the IMT. As a consequence, the observation of a resistance change during current induced resistive switching in a room temperature experiment, does not necessarily imply that T_{IMT} is exceeded and that the phase transition has been triggered. The resistance is not a reliable way to track the onset of the IMT. In contrast, since the optical reflectivity is nearly independent of temperature in the insulating state (below ~ 360 K) and shows a change only at the onset of the IMT (close to 415 K), the observation of a change in the reflectivity would present a definitive evidence that the IMT transition has been triggered under the external stimuli and suggesting that T_{IMT} has been exceeded.

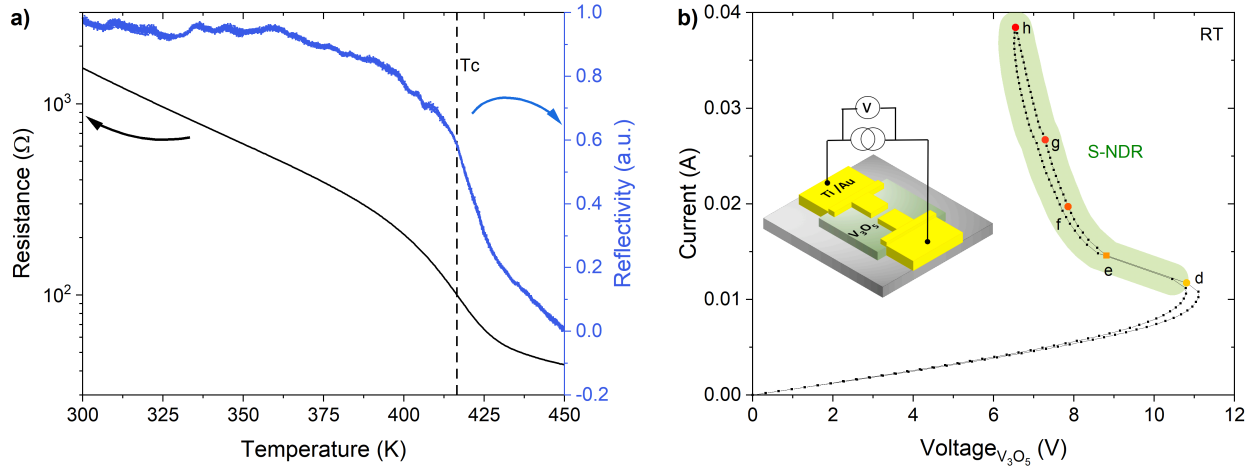


Figure 5.2: Resistance and reflectivity characteristics of a V_3O_5 device. (a) The resistance vs. temperature ($R(T)$) (in black) and the reflectivity vs. temperature ($\text{Ref}(T)$) (in blue) curves clearly show an insulator to metal transition (IMT) around 415 K. No thermal hysteresis is observed in either curves indicating a 2nd order transition. (b) Room temperature (RT) current - voltage characteristic. Above an ~ 12 mA threshold current, the V_3O_5 device switches into a low resistance state, through an S-shaped NDR ($dV/dI < 0$) regime. Insert, V_3O_5 two-terminal device.

V_3O_5 devices showed a pronounced resistive switching at room temperature. Above a certain threshold, the current-controlled I-V characteristics develop an S-type negative differential resistance (S-NDR),³⁰ i.e. a region where the slope, dV/dI , is negative. The NDR corresponds to the onset of the resistive switching: as the current increases, the voltage drop across the device becomes smaller, indicating that the resistance suddenly decreases. The NDR first appears under a power ~ 120 mW, dissipated in the device. Such power is expected to cause a significant Joule self-heating, which most likely drives the observed resistive switching. However, as mentioned before, this observation alone does not unambiguously imply that the device has overcome the phase transition temperature. Another important observation is that the I-V characteristics do not show any significant hysteresis. This is in stark contrast with the previously reported measurements in V_3O_5 bulk crystals that a clear hysteresis could be observed during the I-V loops.²⁴ We attribute the absence of the I-V hysteresis in our devices to the thin film geometry. The good thermal coupling between the Al_2O_3 substrate and the V_3O_5 film allows a fast steady-state temperature distribution in the device, that is established rapidly upon changing the applied voltage/current. The efficient thermal coupling in thin film devices allows fast speed operation, which we demonstrate next by probing the self-oscillation regime in V_3O_5 .

5.4 Fast Spiking Oscillation Behavior:

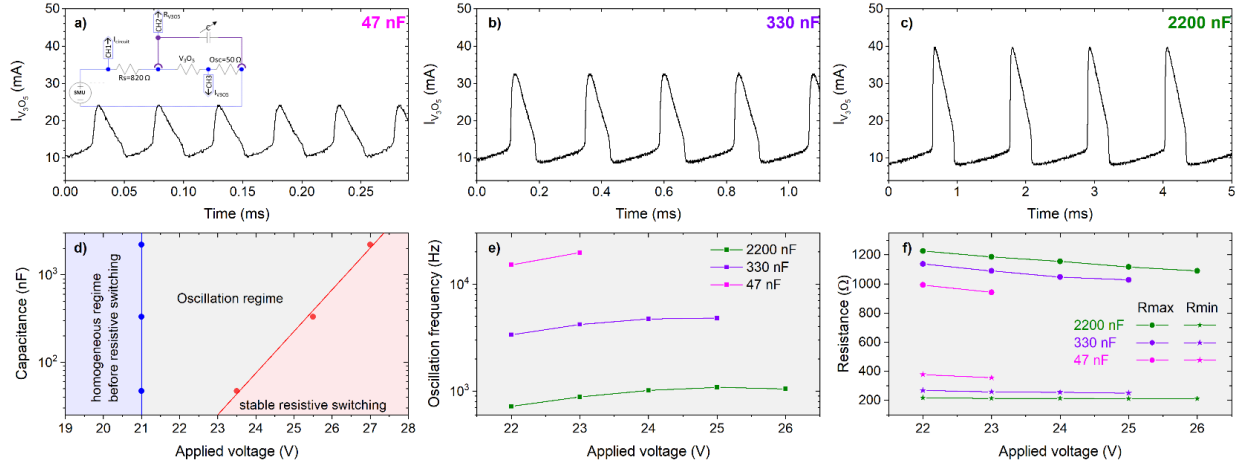


Figure 5.3: Self-oscillation regime in V_3O_5 . (a-c) Time dependence of the current through the V_3O_5 device for different capacitances: 47 nF in (a), 330 nF in (b), and 2200 nF in (c). In inset, Pearson-Anson circuit. (d) Summary of the three different regimes as function of the capacitance and the applied voltage. For voltages below 21 V (blue area), the resistive switching has not happened, and therefore the device is in a homogeneous regime, independently of the capacitance. Above 21V, the device enters in an oscillation regime (grey area) that ends at higher voltages (red area) where the resistive switching state is stable. (e) Oscillation frequency as a function of the applied voltage for different capacitance. The frequency decreases substantially as the capacitance increases, but increases slightly with the voltage. Neither the homogeneous regime nor the stable resistive switching regime are shown. (f) Minimum and maximum resistances of the V_3O_5 device during the oscillation regime as a function of the voltage and for different capacitances. Both the amplitude of the resistance change and the extrema resistance values depends on the capacitance. The maximum resistance decreases slowly with the applied voltage independently of the capacitance, the minimum resistance is nearly independent of the voltage.

Inducing dynamic self-oscillating resistive switching regime in IMT materials allows mimicking the spiking behavior of biological neurons, which could find applications in hardware-level implementation of neuromorphic computing.^{31,32} We realized self-oscillation in V_3O_5 by assembling a Pearson-Anson-type circuit (Figure 5.3a inset).³³ We connected a series resistor and a parallel capacitor to the V_3O_5 device and monitored the instantaneous voltage and current using an oscilloscope.

We observed persistent, fast current oscillations at room temperature when the circuit is biased with a dc voltage (Figure 5.3a-c). The oscillation regime appears within a certain dc bias

range that depends on the parallel capacitance value. The larger the capacitor, the wider the dc bias range where the oscillating regime can be induced (Figure 5.3d). The oscillation frequency also depends strongly on the capacitance, ranging from hundreds of Hz to several tens of kHz (Figure 5.3e). We also find a strong capacitance dependence for the amplitude and the extreme values of the self-oscillations (Figure 5.3f). As an example, the resistance change obtained with the 2200 nF capacitor is almost twice the one obtained with the 47 nF capacitor. Although the low resistance state is nearly independent of the applied voltage, the resistance in the high resistive state slightly decreases when increasing the applied voltage. As the voltage increases, the RC constant decreases in the insulating state (due to larger current densities and increased self-heating effect) leading to shorter oscillation periods. On the other hand, the relative fraction of time spent in the filamentary state increases with voltage. Consequently, above a certain voltage the time spent in the filamentary state becomes equal to the oscillation period itself, and the oscillations stop, driving the system into a stable resistive switching regime. When comparing the extreme values of the self-oscillations to the dc I-V curve in Figure 5.2b, we find that the state of V_3O_5 alternates between points before the onset of NDR and points deep into the NDR region. This suggests that the two resistive switching modes, the static dc switching and the dynamic self-oscillating switching, originate from the same physical mechanism, which we investigate using coupled electrical and optical measurements.

5.5: Operando Optical Imaging During Resistive Switching:

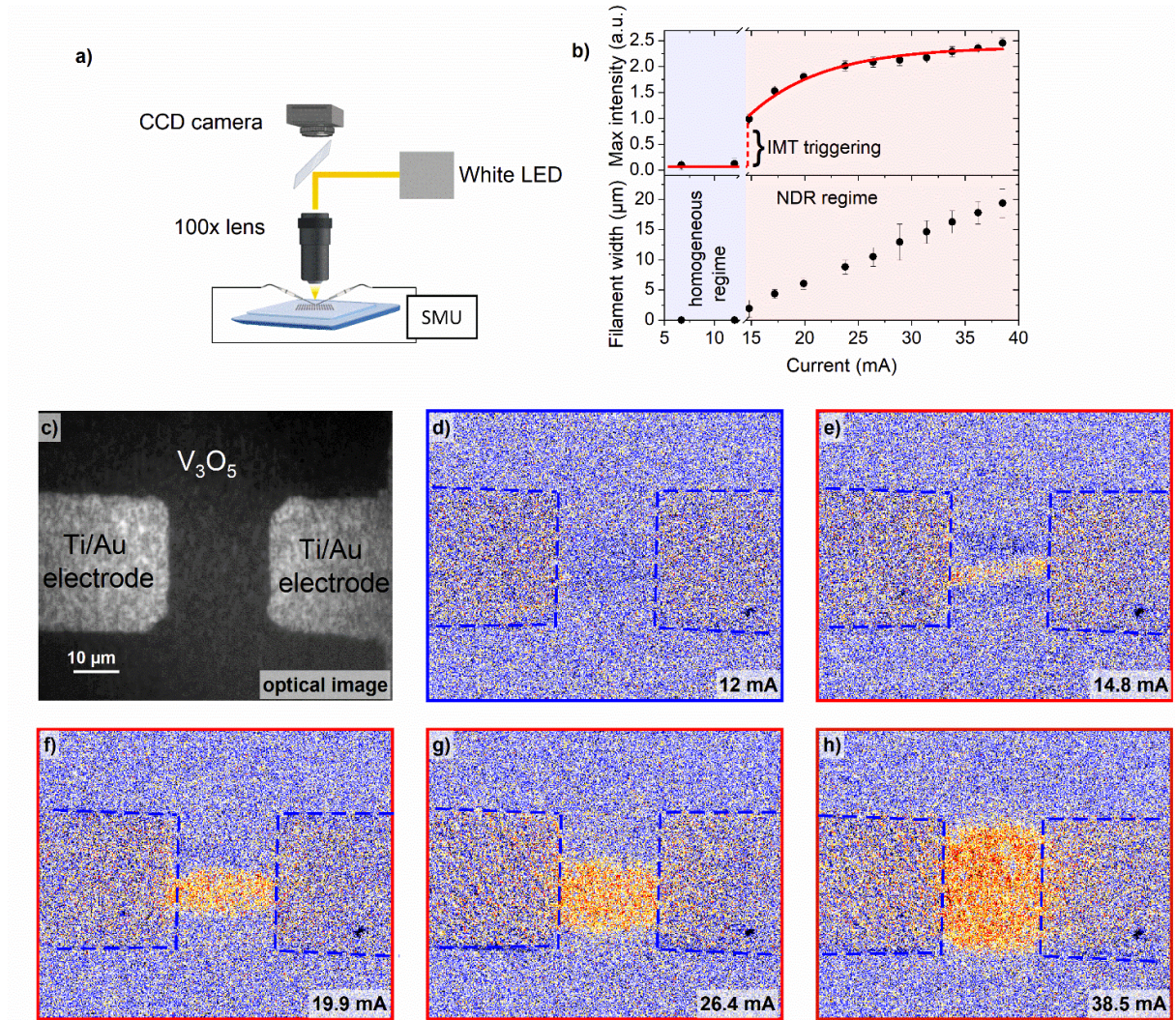


Figure 5.4: Optical imaging of the resistive switching in V_3O_5 . (a) Measurement setup used to optically image the V_3O_5 device during resistive switching. A white LED is used to illuminate the sample through a 100x objective. A CCD camera images the device as shown in (c). (b) Current dependence of the maximum intensity and the filament width. The light blue and red areas correspond to the regimes before and during NDR respectively. (c) Optical image of the V_3O_5 device. The dark area is the V_3O_5 film, the two bright regions are the electrodes. The gap separating the two electrodes is $\sim 20 \mu m$. (d- h) Differential contrast images of the resistive switching in V_3O_5 . The images show the formation of the filament that percolates between the electrodes. This filament is the high-temperature low-resistance phase of V_3O_5 . (d-h) correspond to 12 mA (yellow “d” point in Figure 5.2b)), 14.8 mA (orange “e” point in Figure 5.2b)), 19.9 mA (dark orange “f” point in Figure 5.2b)), 26.4 mA (light red “g” point in Figure 5.2b)), and 38.5 mA (red “h” point in Figure 5.2b)) respectively.

We observed clear evidence that voltage induced resistive switching in V_3O_5 is caused by the IMT and not by a “thermal runaway” high conductance filament, which would still be within the insulating phase. This is found by simultaneously combining two independent techniques, optical reflectivity, and resistance measurement, during the resistive switching. We used an optical microscope to track the reflectivity changes while performing the switching measurements in current control mode (Figure 5.4a). To improve the signal to noise and contrast, we show the difference between a reference image recorded at zero current and the images acquired as the device is subject to various currents (Figure 5.4 d-h). This way we obtain differential images of the optical reflectivity change from the unperturbed state, which allows a reliable detection of the phase transition with spatial resolution.

No reflectivity change was found for the applied electric currents in 0 - 12 mA range, i.e. below the onset of the NDR (Figure 5.4d, light blue area in Figure 5.4b). However, as soon as the current drives the device into the NDR region, the reflectivity change shows an abrupt jump (Figure 5.4b) resulting in the appearance of a filament that percolates between the device electrodes (Figures 5.4 e-h).

Filamentary switching is a very common phenomenon that has been observed in a variety of systems,^{2,3,34–38} extending far beyond IMT materials. In our case, the important point is that the filament appears as the change of the optical reflectivity, which, according to our equilibrium $R(T)$ and $Ref(T)$ measurements (Figure 5.4a), implies that the IMT has been triggered during the resistive switching. Thus, a sufficiently large dc current drives V_3O_5 into the high-temperature metallic phase even at room temperature, i.e. 120 K below T_{IMT} (295 K vs. 415 K).

From the optical imaging of the V_3O_5 devices in the self-oscillation regime, we found evidence that the phase transition is triggered in each oscillation period. By using an exposure

time of 55 ms, we were able to acquire images that correspond to temporal averages of 38-55 oscillation event per image (oscillation frequency of 0.7-1 kHz in the case of 2200 nF capacitor). When the applied bias drives the V_3O_5 device into the oscillation regime, a wide but a low-intensity filament appears in the images (Figure 5.5 b and c). Because this filament corresponds to the optical reflectivity change, we can immediately conclude that the V_3O_5 in the oscillation regime, undergoes the phase transition following the same argument as in the case of the static resistive switching (see the discussion in the previous paragraph). As the bias is increased, causing faster oscillation, the reflectivity change becomes more intense, but the filament width remains unchanged. When the bias becomes large enough to drive the device out of the oscillation regime and induces a stable resistive switching, the wide, low-intensity filament abruptly collapses into a narrow high-intensity filament which continues to widen with further bias increase (Figure 5.5 d-f).

To identify the origin of the wide filament in the oscillation regime, we compared the filament intensity to the time fraction that the device spends in the low-resistance filamentary state (extracted from the time-dependency of the resistance measurements). We find a linear correlation between the intensity and the time (Figure 5.5g). This implies that the observed apparent wide low-intensity filament results from the temporal averaging done by our acquisition system. In fact, it results from the average of the rapid evolution of the system between two extreme states: the filamentary one when V_3O_5 has low resistance, and the homogeneous non-filamentary state when V_3O_5 recovers its high resistance. This conclusion is further supported by the fact that the width of the low-intensity filament during the oscillations is approximately the same as the filament width in the stable switching regime under the maximum current of the oscillations (compare Figure 5.5 c and e). Consequently, we find that despite the device base

temperature being at 120 K below T_{IMT} , a filamentary phase transition in V_3O_5 is triggered in each oscillation cycle and the current discharge is intense and fast enough so to make the filament grow as wide as it would be in a stable dc switching under similar conditions.

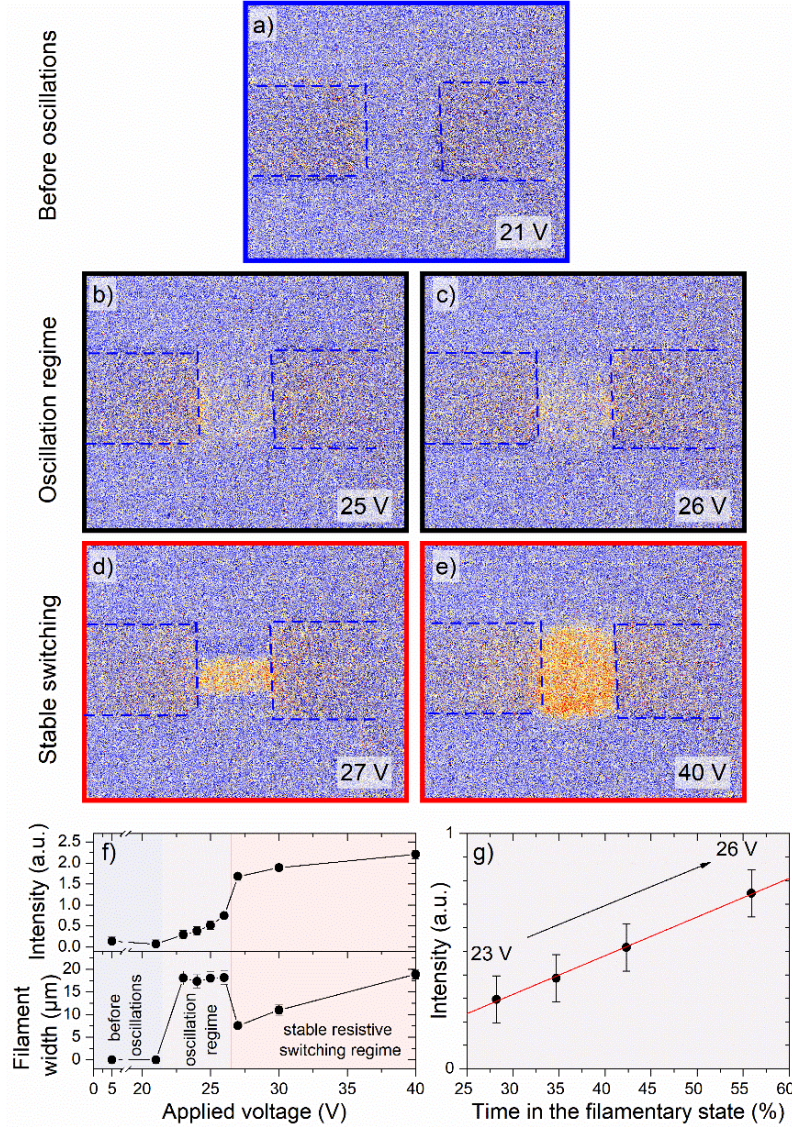


Figure 5.5: Optical imaging of the self-oscillation regime in V_3O_5 . (a-e) Differential contrast images of the resistive switching in V_3O_5 acquired at the different voltages, corresponding to the homogeneous regime before oscillations in (a), the oscillation regime in (b) and (c), and during the stable resistive switching regime after the oscillations in (d) and (e). (f) Applied voltage dependence of the maximum intensity and width of the filament. The light blue, grey, and red areas correspond to the before oscillations, oscillations, and stable resistive switching regime, respectively. (g) Intensity of the reflectivity change vs. time spent in the filamentary state during the oscillation regime. The time spent in the filamentary state is extracted from the electrical measurement for each voltage.

In summary, we demonstrated that V_3O_5 Magnéli Phases exhibits volatile resistive switching both in static and in fast spiking oscillatory modes. This switching can be induced at room temperature, more than 120 K below the equilibrium IMT temperature of V_3O_5 . Using a combination of transport and optical measurements, we showed that the resistive switching is triggered by the phase transition, which occurs via the formation of a percolating metallic-phase filament. The phase transition is triggered on a short time scale enabling the dynamics of filament creation and annihilation during each cycle in the fast oscillation regime. Because of the relatively low resistivity of V_3O_5 in the insulating state ($\sim 10^{-2} \Omega \cdot \text{cm}$) the phase transition can be driven far below T_{IMT} without causing the device degradation. As a consequence, large power can be supplied to the device using moderate voltages which do not induce electric fields strong enough to initiate ion migration and/or dielectric breakdown. This feature may be important for applications, since V_3O_5 devices may have a better performance compared to VO_2 , whose extremely large insulating state resistivity ($> 10 \Omega \cdot \text{cm}$) often leads to the device breakdown before the electric triggering of the IMT. In addition, the T_{IMT} of V_3O_5 is much lower compared to NbO_2 , 420 K vs. 1080 K. This implies that the resistive switching in V_3O_5 has a substantially better energy efficiency than NbO_2 . Overall, V_3O_5 displays a similar set of functionalities as VO_2 and NbO_2 (transitions in resistivity and optical reflectivity, resistive switching, fast spiking behavior), therefore using V_3O_5 could enable further improvement of a wide range of potential applications based on the IMT materials.

5.6 Supplementary Information – Methods

5.6.1 Thin film growth and device fabrication

In this work, V_3O_5 thin films are synthesized from 100 nm thick V_2O_3 thin film (grown by magnetron sputtering) using the gas evolution technique described earlier (Chapter 2).²⁷ By tuning very precisely the oxygen partial pressure and the temperature, we are able to control the oxygen stoichiometry of the thin film and therefore transforming the V_2O_3 into V_3O_5 . 20 μm wide Ti/Au electrodes were patterned on top of the film separated by a 20 μm gap to create devices, so that an electric field triggered resistive switching can be induced.

5.6.2 Electrical measurements:

Temperature dependent electrical transport measurement (R-T curves) were performed in a Lakeshore TTPX probe station with a Keithley 6221 current source and a Keithley 2182A nanovoltmeter in a two-point probe configuration. Resistive switching measurements were carried out using a Keithley 2450 Source Meter Unit. To develop spiking dynamics, sought in neuromorphic applications, an oscillatory regime has been generated in the NDR region by adding a capacitor in parallel to the V_3O_5 device, as shown in the circuit in inset of Figure 5.2b. The oscillatory spiking behavior is measured as function of time, by using three channels of an oscilloscope. CH1 allows a measurement of the current through the series resistor (I_{circuit}) which give an oscillatory behavior for a certain voltage range. These oscillations are used to determine the frequency (Figure 5.3e). CH2 provides the voltage across the capacitor, which allows determination of the resistance of the device. CH3 gives a measurement of the current flowing through the V_3O_5 device ($I_{V_3O_5}$), which produces the spiking behavior (Figure 5.3a-c).

5.6.2 Optical imaging measurements:

The spatial dependence of the optical reflectivity of the V_3O_5 device was tracked as a function of applied voltage using an optical microscope. Figure 5.4a illustrates the setup used for the experiment. The device was illuminated with a white LED (400-700 nm) through a 100x lens of an optical microscope and imaged using a CCD camera.

5.7: Acknowledgement

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Chapter VI – Conclusion and Future Perspectives

6.1 Conclusion

In the dissertation, we demonstrated that vanadium oxides such as VO_2 , V_2O_3 and V_3O_5 are great candidates for resistive switching and neuromorphic computing applications. In Chapter 2, we developed a gas evolution technique to study the effect of oxygen stoichiometry as well as the electrical, structural and chemical states properties in these strongly correlated oxide. In Chapter 3 & 4, we studied the mechanisms of volatile and non-volatile resistive switching in VO_2 two-terminal devices. We found that the volatile resistive switching behavior is due to the electrically induced metal-insulator transition under an applied electric field. In addition, we demonstrate that different monoclinic structural orientations could lead to intrinsic variability of the electronic properties. On the other hand, we found that when triggering the resistive switching far below the transition temperature, a non-volatile behavior could be observed. This switching is due to the oxygen vacancies migration and oxygen deficient phase filament formation. We found that both volatile and non-volatile switching can be achieved in single Mott material, depending on the device temperature. In Chapter 5, we studied the electrically induced metal-insulator transition in V_3O_5 Magnéli Phases. This exotic phase was stabilized using gas evolution technique described in Chapter 2. We optically capture the spiking neuron oscillations and the metallic filament formation to understand the volatile switching behavior. Our results suggest that next-generation memory and energy-efficient computing devices could be designed and implemented using these materials.

6.2 Future Perspectives

Many open questions remain unanswered in these strongly correlated materials. From the materials science point of view, the complex phase diagram in the V-O system has drastically hindered the development of thin film & device applications. Using the gas evolution technique, it might be possible to stabilize any Magnéli (V_nO_{2n-1}) and Wadsley phases (V_nO_{2n+1}). This will open a new way to study other exotic phase oxide thin films & devices. In addition, this technique can be applied to other complex oxide systems. For instance, complex oxides including $La_{0.7}Sr_{0.3}CoO_3$ (LSCO), $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), $La_{0.7}Sr_{0.3}FeO_3$ (LSFO) and rare-earth nickelate $RNiO_3$ (La, Pr, Nd, Sm...) could be potential candidates for next generation neuromorphic devices due to a variety of electronic, structural, optical and magnetic properties. The physics of these materials are still being investigated. Their physical properties and oxygen stoichiometry might be effectively controlled by gas evolution technique as well. On the other hand, many resistive switching devices rely on the conductive filament formation in insulating materials. These may be due to an intrinsic metal-insulator transition, structural phase transition, or ion diffusion under an electric field. Understanding the switching mechanisms during the filament formation and recovery is important for practical applications. The nanoscale nature of the ion migration process causes a great challenge to study its mechanism. At macroscopic level, these phase transition or switching phenomena may be well studied. However, when scaling down to the microscopic or atomic level, there might be new physics or new phenomena in these materials. New in-situ characterization techniques will be needed to study the defect migration mechanisms and the electronic structure of strongly correlated oxides under electric field.

Appendix

1. Gas evolution system

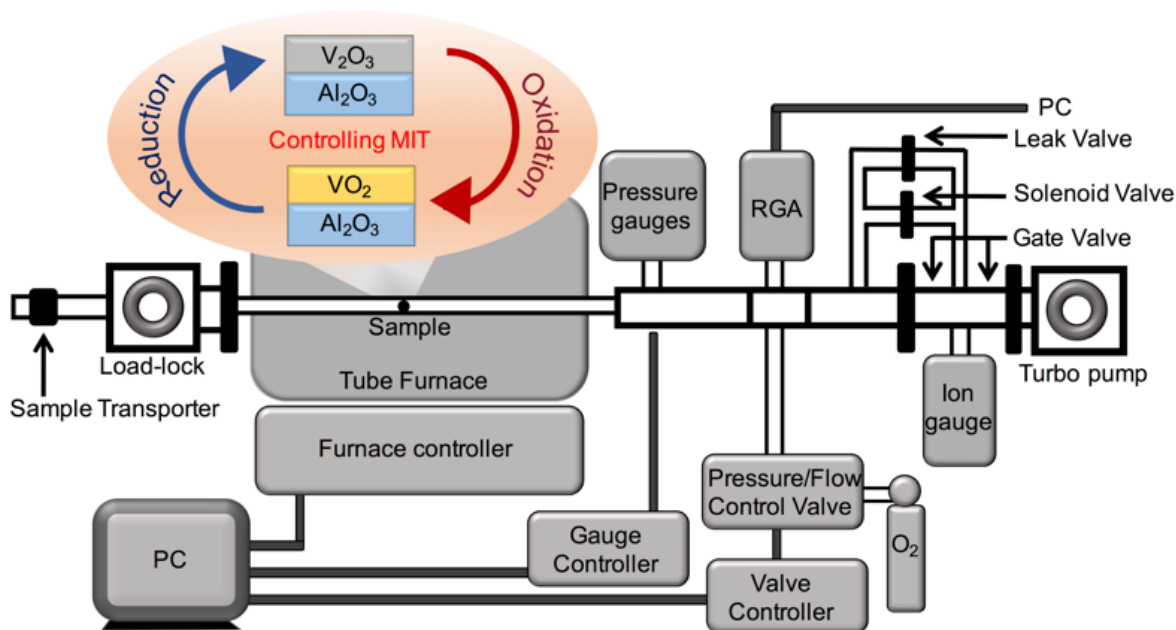


Figure A1. Schematic illustration of the gas evolution setup used to control the oxygen stoichiometry in complex oxide thin films.

A high-vacuum oxygen annealing method was developed to synthesize complex oxide thin films with controlled oxygen stoichiometry. The experimental setup is shown in Figure A1. The base pressure in the high vacuum system is $\sim 1 \times 10^{-7}$ Torr. Thin film samples were placed into the center of a Lindberg/Blue MTM 1200°C tube furnace for heat treatment under different oxygen atmospheres. The PO_2 was measured using a 100 amu SRS Residual Gas Analyzer equipped with a quadrupole mass spectrometer (UHV to 10^{-4} torr) and two capacitance manometers (10^{-4} torr to 1000 torr). A MKS Series 245 pressure/flow control valve, a variable leak valve and a solenoid valve were used to carefully control the PO_2 . High purity oxygen (>99.99%) was introduced into the annealing chamber using the computer-controlled metal-

seated valve. This gas evolution setup provides a wide pressure range (UHV to 1000 torr) and allows for the continuous variation of the PO_2 under high vacuum conditions.

2. General Information

2.1 When using the gas evolution system, make sure to fill out the lab book and log sheet with all experimental information.

2.2 System Specifications:

2.2.1 Process gases: O_2 , Ar/ O_2 mixture, H_2 , N_2 or other gases (If needed). The vacuum system and the main chamber pumps are specially designed for processing highly corrosive gases.

2.2.2 Tube furnace temperature: RT-1000°C (Recommend: < 1000°C; for safety concern).

2.2.3 Partial pressure range: UHV- 1000 Torr.

2.2.4 Functionalities:

A. Controlling the oxygen stoichiometry in complex oxide thin films such as YBCO and VO_x .

[1-3]

B. Temperature Programmed Desorption. (To heat thin films under high vacuum and measure the spectra of gas desorption using quadrupole mass spectrometry)

C. Differentiating gas isotope using Residual Gas Analyzer based on partial pressure measurements. [4]

2.2.5 Materials limitations: please do not process any materials which would decompose during the gas evolution treatment under high temperature. In addition, any fragile substrate should be avoided. Any material which will contaminate the system should be avoided.

3. Operating Procedures

3.1 Thin film sample loading

3.1.1 Close the valve between the tube furnace and the load-lock chamber, vent the load-lock vacuum chamber (turning off the turbo pump power, close the valve between turbo and mechanical pump, open the vent valve when the turbo stops spinning). Be careful to turn off the ion gauge before venting the chamber. In addition, vent the load-lock very slowly using N₂ inert gas till at atmospheric pressure to prevent any adsorption of water in the chamber.

3.1.2 Open the load-lock chamber and put the sample in the sample holder on the transfer arm. Make sure to wear gloves to prevent any contamination during sample loading. Common system contamination and damage will be caused by inappropriate samples and handling.

3.1.3 Close the load-lock cover and pump the chamber. Open the valve between turbo and mechanical pump, turn on the turbo pump power when the pressure in the chamber below 50 mTorr. It will take 15-20 min to reach $< 1 \times 10^{-6}$ Torr. If there are any problems during pumping down, please check the leaking issues. Then, transfer the sample into the center of the high vacuum tube furnace for heat treatment.

3.2 Tube Furnace:

3.2.1 Turn on furnace controller with switch and the Eurotherm iTool software.

3.2.2 Click “Scan” and “Scan all device addresses” to find the tube furnace control system.

3.2.3 Set the temperature program for the annealing. (Ramping rate, set point, dwell time, etc.)

Different heat treatments and functionalities can be achieved through this program.

Detailed manual could be found below:

Eurotherm iTool: <https://www.eurotherm.com/products/power-control/power-control-software/eurotherm-itools/>

3.2.4 Ramping rate limitations: Recommend: $< 20\text{ }^{\circ}\text{C}/\text{min}$; for safety concern).

3.2.5 Wait until the furnace temperature at or below $100\text{ }^{\circ}\text{C}$. Turn off the furnace program and power after the annealing process.

3.3 Pressure controller:

3.3.1 Open the LabVIEW program “651basic_com”.

3.3.2 Find the correct VISA resource number (default “COM 17”) and check the communication light.

3.3.3 Set the values for pressure/flow control valve to control the gas partial pressure in the system. Make sure the status of the pressure/flow control valve is fully closed before any processing. Before opening the valves, turn off the ion gauge first. Try to increase the gas flow and valve position from the minimum value (0.1% opening). The system pressure should be below 1×10^{-4} Torr when RGA is running.

3.3.4 Close the pressure/flow control valve after the gas evolution process.

3.3.5 Turn on the ion gauges.

3.4 SRS Residual Gas Analyzer:

3.4.1 Turn on the RGA controller and Open the RGA program.

3.4.2 Connecting to RGA head: click “Head”, “Connector list setup” and find the RGA port.

3.4.3 Select the display mode (Analog, Histogram, Pressure vs Time, etc.)

3.4.4 Turn on the RGA filament.

3.4.5 Set the scan parameters (elements, mass, speed, etc.) and start the scan.

3.4.6 Measure the RGA analog scan for wide mass range to check the residual gas compositions in the gas evolution system before each measurement.

Detailed manual for the RGA could be found below:

SRS RGA manual: <https://www.thinksrs.com/downloads/pdfs/manuals/RGAm.pdf>

3.4.7 Stop the scan and turn off the filament.

3.4.8 Save the file by clicking the “Save”.

3.4.9 Disconnect the RGA head in the “Connector list setup” and close the program.

3.4.10 Turn off the RGA controller power.

3.5 Thin film sample unloading:

3.5.1 Transfer the thin film to the load-lock chamber gently. The vacuum degree between the main chamber and the load lock should be similar.

3.5.2 Close the valve between the tube furnace and the load-lock chamber, vent the load-lock vacuum chamber (turning off the ion gauge and the turbo pump power, close the valve between turbo and mechanical pump, open the vent valve when the turbo stops spinning). In addition, vent the load-lock very slowly using N₂ inert gas till at atmospheric pressure.

3.5.3 Open load-lock chamber and carefully remove the thin film sample.

3.5.4 Pump down the load-lock chamber after experiments in order to keep the system under high vacuum at all times. Please make sure the system pressure is under high vacuum before the user leaves the room.

3.6 Fill out the lab notebook and log sheet with all experimental information.

4. Acknowledgements

Some parts of the appendix are incorporated into the following publication:

Min-Han Lee*, Yoav Kalcheim, Javier del Valle, and Ivan K. Schuller “Controlling Metal-Insulator Transitions in Vanadium Oxide Thin Films by Modifying Oxygen Stoichiometry” *ACS Applied Materials & Interfaces*, **13**, 887 (2021). The dissertation author was the principal investigator/author on this paper. All experiment parts and corresponding writing were performed by the author.

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