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Chapter 1

Synaptic Behavior in Metal Oxide-Based Memristors

Ping Hu, Shuxiang Wu and Shuwei Li

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Abstract

With the end of Moore’s law in sight, new computing paradigms are needed to fulfill the increasing demands on data and processing potentials. Inspired by the operation of the human brain, from the dimensionality, energy and underlying functionalities, neuromorphic computing systems that are building upon circuit elements to mimic the neurobiological activities are good concepts to meet the challenge. As an important factor in a neuromorphic computer, electronic synapse has been intensively studied. The utilization of transistors, atomic switches and memristors has been proposed to perform synaptic functions. Memristors, with several unique properties, are exceptional candidates for emulating artificial synapses and thus for building artificial neural networks. In this paper, metal oxide-based memristor synapses are reviewed, from materials, properties, mechanisms, to architecture. The synaptic plasticity and learning rules are described. The electrical switching characteristics of a variety of metal oxide-based memristors are discussed, with a focus on their application as biological synapses.

Keywords: memristor, metal oxide, synapse, neuromorphic computing, synaptic plasticity

1. Introduction

With the aid of modern technology, human society has entered into a new big data era. Meanwhile, it brings a new challenge to humans for data processing. Despite the great success in the past decades, the traditional computer based on Von Neumann architecture and complementary metal oxide semi-conductor (CMOS) technology is still suffering limitations of dealing with big data while it can only deal with well-defined data. These machines cannot compete with the biological system in solving the imprecisely specified problems of the real world which are very simple for biological beings [1, 2]. Even though the digital computers can emulate some functionality...
of certain animals with comparable speed and complexity, the energy consumptions increase exponentially as the animal hierarchy becomes higher with a very huge volume. Conversely, the biological brain is a compact dense system which can offer parallel processing, self-learning, and adaptivity with a combination of storage and computation in very low power consumption [3]. In these decades, the implementation of Von Neumann architecture computers to mimic biological systems has been in the form of software but such simulations are not comparable to biological systems in terms of efficiency and speed due to the physical limitation of those digital computers. Even the artificial neural networks based on CMOS-integrated circuits are far inadequate for constructing bionic systems. The truly reason for this drawback is the need to transfer data between a memory(storing data) and a processor(computing based on the data). This requirement of data transfer generates an intrinsic delay and inefficiency, which is a bottleneck for all CMOS-based neural networks [4]. In the past decades, the semi-conductive technology has led to great progress under the aid of the rapid development of the electronic industry, which has promoted the steps forward to develop artificial neural networks. In 2011, the supercomputer Watson, with 2880 computing cores [5], won the human-machine contest which proved that supercomputers have their advantages in some aspects [6]. But the important point that has been ignored in this comparison is the energy consumption and the physical volume of the computers. Watson has thousands of cores and requires about 80 kW of power and 20 tons of air-conditioned cooling capacity [7], while the human brain occupies space like a soda bottle and consumes power of 10 W.

Therefore, an alternative approach to building a brain-like or neuromorphic computational system with distributed computing and localized storage in networks becomes an attractive option [1, 8–11]. The brain-like computational system can outperform conventional computers with good performance in handing the real-time processing of unstructured sensory data, such as image, video or voice recognition, navigation, etc. [12–17]. Also, the brain-like computational system has the advantages of architecture and function compared to conventional computers, offering massive parallelism, small area, scalability, power efficiency, the combination of memory and computation, self-learning and adaptivity [3]. Many researches have helped us understand how neurons and synapses function and revealed how essential synapses are to biological computations, especially in memorizing and learning [18–21]. However, building compact neuromorphic computing systems remains as a challenge, especially for the lack of electronic elements which could mimic the biological synapses. In recent decades, the research of neuromorphic systems is renewed by the understanding of biological neural networks and the emergence of new nanodevices. Particularly, the emergence of the fourth electronic element, memristor [22–28], makes it feasible to construct bionic hardware which will lead to effective, high-performance neuromorphic computing hardware.

In this chapter, we will discuss synaptic devices and summarize the recent progress in neuromorphic hardware, which is based on memristors. In particular, we will focus on a few typical devices based on metal oxides and their key properties served as synapses. We will start with a brief description of memory and the learning of synapses in Section 2. In Section 3, we will elaborate more on these oxide-based memristors (TiO\textsubscript{x}, WO\textsubscript{x}, HfO\textsubscript{x}, TaO\textsubscript{x}, NiO\textsubscript{x}, etc.) with an emphasis on resistive switching (RS) characteristics, which is followed by neuromorphic computing applications and the underlying physical mechanism. We limit this review to metal oxide-based memristive devices for the emulation of synaptic functionalities and will not cover the literature on neuromorphic circuits.
2. Plasticity and learning of the synapse

In the nervous system, neurons and synapses are the basic units for transit information to the whole biological body. In the human brain, it consists of ~$10^{11}$ neurons and an extremely large number of synapses, ~$10^{15}$, which act as a highly complex interconnection network among the neurons [29]. Neurons consist of three main parts: a soma, dendrites, and an axon. Neurons generate action potentials (spikes), with amplitudes of approximately 100 mV and durations in the range of 0.1–1 ms in their soma. The spikes propagate through the axon and are transmitted to the next neuron through the synapses. A synapse [30] is a 20–40 nm junction between the axon and the dendrites (shown in Figure 1) that permits a neuron (or nerve cell) to pass an electrical or chemical signal to another neuron or to the target efferent cell. Each neuron connects with other neurons through $10^{3}$–$10^{4}$ synapses to form a complex network. The information transmission between neurons with the synapses is very complicated which
is excited by the surroundings. At the synapse, the plasma membrane of the signal-passing neuron (the presynaptic neuron) comes into close apposition with the membrane of the target (postsynaptic) cell. Both the presynaptic and postsynaptic sites contain extensive arrays of molecular machinery that links the two membranes together and carries out the signaling process. The presynaptic neuron will open the voltage-gated calcium channels as the action potentials arrive, and then the diffusion of Ca\(^{2+}\) ions will make the synaptic vesicle release neurotransmitters to the synaptic junction. Released neurotransmitters bind with their receptor sites of the Na\(^{+}\) gated ion channels at postsynaptic neurons, which lead them to open and allow Na\(^{+}\) ions to diffuse inside the cell. When the aggregated membrane potential reaches a certain threshold, the neuron generates a spiking. The activation either potentiates or inhibits the postsynaptic neuron. The action potentials propagation, the neurotransmitters release and diffusion, and the neurons spiking activity constitute the ways whereby neurons communicate and transmit information to one another and to nonneuronal tissues [31].

In the biological brain, neurons and synapses are the two basic computational elements connected to each other. To perform different functions including visual, auditory, olfactory, gustatory and tactile means, as well as modulating and regulating a multitude of other physiological processes, the neuron system operates computation by integrating the inputs coming from other neurons and generating spikes across the synapses. In neuron computation, the synapses change their connection strength as a result of neuronal activity, which is known as synaptic plasticity. It is widely accepted that synaptic plasticity is the key mechanism of learning and memorizing for the biological brain [32]. In Hebbian's theory, both pre- and postsynaptic cells are activated coincidently, which results in modifications of synaptic strength between the two cells, thereby creating associative links between them [33]. In other words, the synapse plasticity is triggered by release of neurotransmitters of the presynaptic neurons and by diffusion of calcium ions into postsynaptic neurons, through excitatory amino-acid receptors and possibly voltage-gated calcium channels (VGCCs).

How the brain can achieve learning and memory is a critical question in neuroscience. In 1949 [34], Hebbian postulated a concept of spike-timing-dependent plasticity (STDP), firstly, as a synaptic learning rule which has been demonstrated in various neural circuits over a wide spectrum including insects, animals, and humans, even plants [35–37]. It has attracted considerable interest in neuroscience from experiment to computation [38–41]. According to the asymmetric window of STDP, the synaptic plasticity depends on the order of pre- and postsynaptic spiking within a window of tens of milliseconds. Over the past decades, much progress has been made in understanding the mechanism of STDP. In general, the synapse will be excited (increases in synaptic strength or weight) if repeated presynaptic spikes arrive a few milliseconds before postsynaptic spikes, whereas the synapse will be inhibited (decreases in synaptic strength or weight) if repeated spikes arrive after postsynaptic spikes. In [35], Bi and Poo have plotted a figure of the synaptic weight change as a function of relative timing of pre- and postsynaptic spikes which is called the STDP function or learning window and varies in synapse types. The change of synaptic weight $\Delta w$ depends on the relative timing between presynaptic spike and postsynaptic spikes. A smaller spike timing difference results in a larger increase in synaptic weight. The total weight change $\Delta w$ induced by an impulse with pairs of pre- and postsynaptic spikes is considered as a function [42, 43]:
\[
\Delta w_i = \sum_{j=1}^{N} \sum_{n=1}^{N} W(t_j^n - t_i')
\]  

where \(W(x)\) denotes the STDP function, \(i,j\) are the notes of the pre- and postsynapses, and \(t_i' (t_j^n)\) labels the firing times of the pre/post-synaptic neuron. An acceptable form of STDP function \(W(x)\) is given as

\[
W(x) = \begin{cases} 
A_+ \exp(-x/\tau_+) & x > 0 \\
-A_- \exp(x/\tau_-) & x < 0 
\end{cases}
\]

The parameters \(A_+\) and \(A_-\) depend on the current value of the synaptic weight \(w\), where \(\tau_+\) and \(\tau_-\) are the time constants in the order of 10 ms for biological synapses [36]. Several recent reports have shown the STDP dependencies on rate, higher-order spiking motifs, and dendritic location [39]. This timing-centric view of plasticity is not meant to imply that spike rate is irrelevant. However, this timing-centric view of plasticity is not the only form responsible for synaptic learning in the biological brain. The learning rules may vary with different factors, such as the type, location of a synapse, firing rate, and spiking orders. Several other fundamental learning rules including rate-dependent synaptic plasticity, frequency-dependent synaptic plasticity, and cooperativity have also been studied extensively and believed to be very critical for biological neuron computation.

### 3. Synaptic devices based on metal oxide memristors

To imitate the learning and memorization of the biological system, new materials as well as architectures exhibiting memristive behavior fit the need well. Memristor, an abbreviation of memory and resistor, is the fourth fundamental passive circuit elements, the others being the resistor, the capacitor, and the inductor, which were proposed theoretically by Professor Leon Chua [22]. It is a kind of a nonlinear, two-terminal element that cannot be replicated with any combination of other fundamental electrical elements. Memristors behaves like a resistor with resistance depending on the history of the current passing through. In fact, it maintains a relationship between the time integrals of current and voltage across a two-terminal element, and the resistance remains in the value as it had earlier when the current stopped. In other words, the memristor has a memory of the current that was last turned on. In 2008, HP Labs realized memristors physically in nanoscale titanium dioxide cross-point resistive switches [24]. In this operation, the device exhibits pinched current-voltage(I-V) hysteresis indicating a resistive memory effect, and the conductive area is adjusted by the concentration of oxygen vacancies, which determine the whole conductive states (resistive switching state), that is, high resistance state (HRS) and low resistance state (LRS). This work invoked a renewable research of new materials and devices that have memristive effects, such as NiO, WO\(_3\), ZrO\(_2\), ZnO, HfO\(_2\), TaO\(_2\), and TiO\(_2\) [44-50] binary oxides, BiFeO\(_3\), SrTiO\(_3\), ZnSO\(_4\), and LiNbO\(_3\) [51–54] ternary oxides, and CuO/ZnO, HfO\(_2\)/TiO\(_2\), and TaO\(_2\)/NiO\(_2\) [55–57] heterostructures. Table 1 gives a summary of the recent work of oxide-based memristors including memristive properties.
Nowadays, the memory is usually referred to as resistive random-access memory (RRAM) devices which can be traced as early as the 1960s [58]. In general, these devices are nanoscale in dimensions and offer excellent performance for data storage in terms of operation speed, nonvolatility, and read/write cycling [59]. Amounts of work have been performed to elucidate types of switching mechanisms that underlie resistive switching phenomena in a

<table>
<thead>
<tr>
<th>Material (architecture)</th>
<th>Endurance (cycles)</th>
<th>Retention</th>
<th>On/off ratio</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Pt/TiO₂/Pt</td>
<td>83</td>
<td>10⁴ s</td>
<td>2</td>
<td>[69]</td>
</tr>
<tr>
<td>Pt/TiO₂/Pt</td>
<td>8000</td>
<td>—</td>
<td>1.2</td>
<td>[50]</td>
</tr>
<tr>
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<td>1000</td>
<td>10 years</td>
<td>10²</td>
<td>[49]</td>
</tr>
<tr>
<td>Ti/Ta₂O₅/Pt</td>
<td>120</td>
<td>10⁴ s</td>
<td>65</td>
<td>[50]</td>
</tr>
<tr>
<td>ITO/WO₃/ITO</td>
<td>320</td>
<td>2 × 10⁴ s</td>
<td>10</td>
<td>[45]</td>
</tr>
<tr>
<td>Al/WO₃/Pt</td>
<td>200</td>
<td>3 × 10⁴ s</td>
<td>~50</td>
<td>[79]</td>
</tr>
<tr>
<td>Cu/WO₃/Pt</td>
<td>150</td>
<td>3 × 10⁴ s</td>
<td>~10</td>
<td>[79]</td>
</tr>
<tr>
<td>Pt/WO₃/Pt</td>
<td>50</td>
<td>3 × 10⁴ s</td>
<td>~100</td>
<td>[79]</td>
</tr>
<tr>
<td>Cu/WO₃/ITO</td>
<td>1000</td>
<td>5 × 10⁴ s</td>
<td>10³</td>
<td>[80]</td>
</tr>
<tr>
<td>Al/ZrO²/Al</td>
<td>5</td>
<td>—</td>
<td>54.8</td>
<td>[47]</td>
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<tr>
<td>Al/ZrO₂-x/Al</td>
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<td>—</td>
<td>4.8</td>
<td>[47]</td>
</tr>
<tr>
<td>Ag/ZrO/Pt</td>
<td>100</td>
<td>10⁵ s</td>
<td>10³</td>
<td>[106]</td>
</tr>
<tr>
<td>Ti/ZrO/Pt</td>
<td>1000</td>
<td>—</td>
<td>100</td>
<td>[107]</td>
</tr>
<tr>
<td>Al/ZrO/Pt</td>
<td>300</td>
<td>10⁵ s</td>
<td>10³</td>
<td>[108]</td>
</tr>
<tr>
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<td>10⁵ s</td>
<td>162</td>
<td>[44]</td>
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<td>30</td>
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<tr>
<td>Ti/ZrO₂/Pt</td>
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<td>—</td>
<td>10³</td>
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<td>~7</td>
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<tr>
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<td>10⁵ s</td>
<td>40</td>
<td>[110]</td>
</tr>
<tr>
<td>Ta/HfO₂/Pt</td>
<td>10¹</td>
<td>10 years</td>
<td>~100</td>
<td>[111]</td>
</tr>
<tr>
<td>TiN/HfO₂/Pt</td>
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<td>10⁵ s</td>
<td>~15</td>
<td>[112]</td>
</tr>
<tr>
<td>Ti/HfO₂/Pt</td>
<td>50</td>
<td>3 × 10⁴ s</td>
<td>100</td>
<td>[100]</td>
</tr>
<tr>
<td>Pt/HfO₂/HfO₂-x/TiN</td>
<td>100</td>
<td>—</td>
<td>1000</td>
<td>[103]</td>
</tr>
<tr>
<td>Pt/BiFeO₃/Pt</td>
<td>50</td>
<td>2 × 10⁴ s</td>
<td>~100</td>
<td>[51]</td>
</tr>
<tr>
<td>Pt/TiNb:5SrTiO₃/Pt</td>
<td>100</td>
<td>10⁵ s</td>
<td>~10³</td>
<td>[105]</td>
</tr>
<tr>
<td>Cu/HfO₂/TiO₂/Pt</td>
<td>1000</td>
<td>10⁵ s</td>
<td>10</td>
<td>[56]</td>
</tr>
<tr>
<td>Pt/NiO/TiO₂/FTO</td>
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<td>10⁵ s</td>
<td>100</td>
<td>[104]</td>
</tr>
<tr>
<td>Pt/Ti/Ta₂O₅/HfO₂/Pt</td>
<td>50</td>
<td>2 × 10⁴ s</td>
<td>650</td>
<td>[102]</td>
</tr>
</tbody>
</table>

Table 1. Recent work on metal oxide-based memristors.

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broad spectrum of material systems [25–28, 60–62]. According to the switching mechanism, the memristors can be categorized into phase change, valence change, conductive bridge, electrochemical metallization, and ferroelectric devices. Due to the simple structure, biological plausibility, and excellent properties for memory, the scientific researchers explored the application of memristors from data storage to analogy neuromorphic computing for spatial-temporal pattern recognition, sequence learning, navigation, and direction selectivity. As for the human brain-like characteristics, memristor technology could one day lead computer systems to a new state that can remember and associate patterns in a way similar to how people do. Next, we will focus on several kinds metal oxide-based memristors with analog synaptic behavior which are intensively studied for neuromorphic computing.

3.1. TiO$_2$- and WO$_3$-based memristors

The first physical instantiation of the memristor was generally acknowledged that was made from TiO$_2$ by Strukov et al. [24], but as early as in 1968, it was found that the TiO$_2$ thin-film device shows memristive properties [63]. In literature [63], the work demonstrated that thin films exhibited resistive switching (RS) effects with pinched hysteretic current-voltage (I–V) curves during repeated tests. And also, there are several experimental researches on the RS effect of TiO$_2$-based devices before 2008, such as Pt/TiO$_2$/Ru [64] and sputter-deposited Pt/ TiO$_2$/Pt [65] devices. For memristors, the distinctive property is the pinched hysteretic loop indicating no energy dissipation. In [62], the prototype of memristor showed bipolar RS I–V curves with pinched points, which are a result of local stoichiometric change caused by the migration of oxygen vacancies. As oxygen vacancies act as donors in the TiO$_2$ layer in the depletion zone, the conductance of the device could be modulated by the depletion or accumulation of Vos. Specifically, when the device undergoes a set process from a high resistance state to a low resistance state by the external electric field, the Vos will accumulate resulting in an increase of the conductive layer width. When applying electric pulse with reverse polarity, the Vos will be driven back thereby the conductive layer will become thin. Later it was demonstrated in some studies that the accumulation of Vos in TiO$_2$ may cause the formation of a new Magneli phase (Ti$_{4n}$O$_{7n}$) that is metallic and directly studied by TEM [66, 67]. In 2009 [68], a flexible Al/TiO$_2$/Al memristor fabricated by solution processing was reported. In this work, it showed that oxygen vacancies were introduced by the aluminum electrodes, and if a noble metal (Au) electrode was used, the form and reversibility of switching will change. The mechanism of the memristive effect strongly depends on the synthesis method, the choice of metal electrodes, and their interfacial properties. Many suggested that an understanding has been put forward through a series of experimental analyses from the view of film composition, microcrystalline structure, and switching zones. It also should be noted that the RS effect of the devices will be affected by device architecture, electrode materials, and layer stacks.

As a prototype of the memristor, TiO$_2$-based devices show their potential in neuromorphic computing. Seo et al. [69] used titanium oxide as the active material to perform synaptic behavior in the context of analog memory, synaptic plasticity and STDP function. A bilayer of TiO$_x$ and TiO$_y$ structure was fabricated by atomic layer deposition and the sol-gel method, respectively. In the device, the titanium oxide bilayer works as a progressive resistance-changing medium with Al and W as the top and bottom electrodes. The multilevel conductance states were achieved by
the movement of oxygen between the TiO\(_2\) and the TiO\(_x\) layer. In the report, the thickness of the less conductive layer TiO\(_x\) was controlled by the applied bias which finally resulted in multilevel conductance and analog memory characteristics. As a positive bias was applied to the top electrode, the oxygen ions were driven from TiO\(_x\) to TiO\(_2\) and the effective thickness of the TiO\(_2\) layer is reduced, which resulted in an increased conductance. Conversely, by applying negative bias to the device, the oxygen ions are moved from TiO\(_2\) to TiO\(_x\), which caused a reduction of conductance. Due to the easy controlling of conductance, the analog characteristics of this device have been intensively studied. By applying sets of identical positive (negative) pulses, conductance can be progressively increased (decreased) as well as the potentiation (depression) in biological synapse. Figure 2 illustrated the continuous potentiating and depressing characteristics of the device which were extremely useful for precisely modulating the device’s synaptic weight. Also, the prior conductance state dependence of the subsequent conductance change is shown in Figure 2b. The results confirmed that the device showed the behavior as in the biological synaptic STDP model [70]: prior synaptic weight states affect the subsequent weight change. Furthermore, the time dependence of the device conductance change was studied which resembled that of the biological synapse. This indicated the titanium oxide bilayer’s resistive switching device had great potential for mimicking biological synapses.

In 2012 [71], Yu fabricated TiO\(_2\)/HfO\(_x\)/TiO\(_2\)/HfO\(_x\) multi-layer RRAM stacks and showed that the resistance states of the stacks could be gradually modulated by using identical pulses. The gradual resistance modulation behavior is useful for learning with high fault tolerance. Berdan in 2016 [72] demonstrated that TiO\(_2\) memristors can exhibit non-associative plasticity. The transition between long-term plasticity (LTP) and short-term plasticity (STP) of this device was presented. The rate-limiting volatility in TiO\(_2\) RRAM devices was very essential to capture short-term synaptic dynamics. In addition to Seo’s works on the bilayer TiO\(_2\)/TiO\(_x\) device [69], Bousoulas studied the role of interfaces in TiO\(_2\)/TiO\(_x\) RRAM structures for high multilevel switching and synaptic properties [73]. A CMOS-memristor architecture composed of the 8*8 array of the neuron was demonstrated by Mostafa [74]. The proposed system comprises CMOS neurons interconnected through TiO\(_{2-x}\) memristors and spike-based learning circuits which modulate the conductance of

**Figure 2.** (a) The potentiation and depression for the device and (b) conductance dependence on history. Reprinted with permission from [69].
the memristive synapse elements according to a spike-based perceptron plasticity rule. In 2016, Park developed a Mo-/TiOx-based interface RRAM with 64-level conductance states and proposed a hybrid pulse mode for the synaptic application [75]. Under the stimuli of the hybrid pulse mode, the TiO$_2$-based devices show good performance and enhanced pattern recognition accuracy, which was confirmed through synaptic simulation.

Although many investigations have been carried out on the resistive switching mechanism of the TiO$_2$-based memristor, the demonstration of TiO$_2$-based memristor for the artificial synapse is still limited when compared to PCMO, HfO$_x$, and TaO$_x$ materials. In most situations, TiO$_x$ is used in bilayer or multi-layer stacks’ synaptic device to optimize the performance. Another great candidate for memristors as artificial synapses is tungsten oxides (WO$_x$) because of their high endurance, CMOS compatibility, and memorization and learning functions. Similar to TiO$_2$, WO$_x$ is also extensively studied as a memristor due to its CMOS compatibility into standard manufacturing processes [76]. Additionally, WO$_x$ is a kind of transition metal oxide and can be served as n-type semiconductors depending on its stoichiometry and morphology. Due to its attractive properties, it has been studied for both digital and analog memory. Liu et al. [77] have fabricated Cu/WO$_3$/Pt structure devices and demonstrated multilevel storage properties by the application of suitable compliance current values. In that study, the device exhibited pronounced RS effects with an endurance of over 10 cycles and a retention of over $10^4$ s. During the set process, the conductive filament is modulated by the compliance current between the Cu and WO$_3$ interface. In addition to the work of Celano [78], the applied positive bias will aid the creation of oxygen vacancies resulting in conductive filaments. The applied negative bias will drive back the oxygen ions to recombine with the vacancies, making the device turn OFF. Meanwhile, the role of electrodes on RS effect has also been studied, such as Ag/WO$_3$/ITO, W/WO$_3$/Pd, and Pt/WO$_3$/ITO [79, 80]. In these studies, no matter the material of the electrodes, the RS effects originate from the formation or annihilation of oxygen vacancies. Under positive bias, the non-inert electrode is oxidized and the ions diffuse toward another electrode to expand a conductive filament and vice versa. That is to say, a continuous concentration gradient of oxygen vacancies will be introduced during the oxidation process for the inert electrodes, which can result in low or high resistance states of the devices. In addition, the temperature and humidity impact on the performance of WO$_x$ memristors were studied [81, 82]. The conductance will decrease as the temperature increases due to higher oxygen vacancies’ diffusion. In addition to the temperature, the memristive effects of tungsten oxide are also highly humidity dependent. The adsorbed moisture on the surface of WO$_x$ has resulted in decreasing conductances as the H cation induces an increase in barrier heights.

Synaptic behaviors and modeling of WO$_x$ memristors were reported by Chang [83]. The Pd/WO$_3$/W memristor shows reliable synaptic operations with robust endurance behavior. The devices can endure at least $10^5$ potentiation/depression pulses without degradation which is a necessary characteristic for practical applications in neuromorphic systems. Furthermore, the conductance change is governed by the history of the applied voltage signals, leading to synaptic behaviors including long-term potentiation and depression. The memristor behavior was explained by a novel model that takes both drift and diffusion effects into consideration. Figure 3 presents the retention loss curve and memory loss in a human memory curve of the Pd/WO$_3$/W memristor [84]. It was found that the memristor device retention can be
improved with the application of repeated stimulations and bears remarkable similarities to the STM-to-LTM transition in biological systems. Among other transition metal oxides, WO$_x$ is a great candidate material for synaptic device application. For further exploring its applications in neuromorphic computing, the enhancement of synaptic operation time (endurance) is of importance.

### 3.2. Other metal oxide memristor-based synaptic devices

Besides titanium oxide- and tungsten oxide-based memristors discussed above, a variety of other materials has been studied to implement the neural network as a synaptic device. Similar to TiO$_x$ NiO$_x$ is one of the earliest materials found to exhibit resistive switching behavior. Although NiO$_x$-based RRAM devices have been reported with high endurance ($10^6$) and retention, its application for neuromorphic computing is restricted due to poor uniformity. Akoh fabricated synaptic devices with bipolar NiO$_x$ memristors [85]. This device also has the ability to update the synaptic conductance according to the difference of pre- and post-neuron spike timing. Hu et al. studied the paired-pulse-induced response of an NiO$_x$-based memristor, which is similar to the paired-pulse facilitation (PPF) of biological synapse [86]. In addition to PPF, the synaptic LTP of NiO$_x$-based memristors was also studied by Hu et al. [87]. The LTP effect of the memristor has a dependence on pulse height, width, interval, and number of pulses. An artificial neural network is constructed to realize the associative learning and LTP behavior in the extinction of association in Pavlov’s dog experiment.

AlO$_x$ is of interest in memristor materials due to its large band gap (~9 eV) and low RESET current (~μA). For neuromorphic application, AlO$_x$ can also be used alone or stacked with other RRAM materials to improve the uniformity of the synaptic device characteristics. A GdO$_x$ and Cu-doped MoO$_x$ stack with platinum top and bottom electrodes was reported by Choi [88]. The weighted sum operation was carried out on an electrically modifiable synapse array circuit based on the proposed stacks [89]. The biological synaptic behavior was demonstrated by Chang through integrating SiO$_x$-based RRAM with Si diodes. The proposed one-diode-one-resistor (1D-1R) architecture not only avoids sneak-path issues and lowers standby power consumption but also helps to realize STDP behaviors [90]. VO$_x$ is a well-known Mott material,

![Figure 3](image)

**Figure 3.** (a) Retention loss curve of Pd/WO$_x$/W-based memristor and (b) forgetting memory of the human memory curve. Reprinted with permission from [44].
which experiences sharp and first-order metal-to-insulator transition (MIT) at the around 68°C [91]. The application of VOₓ as RRAM materials had been explored by Drisoll et al. [92] through the sol-gel technique. Nevertheless, most researches on VOₓ so far focus on its use for select devices, which can be integrated with the RRAM device to mitigate sneak-path current. The Pt/VOₓ/Pt selector has been integrated with NiO unipolar RRAM by Lee et al. [93] in 2007 and ZrOₓ/HfOₓ bipolar RRAM by Son et al. [94] in 2011. In 2016, 1S-1R configuration of W/VOₓ/Pt selection device and Ti/HfOₓ/Pt RRAM was demonstrated by Zhang et al. [95]. However, thermal instability is a major challenge with VOₓ for practical applications [13].

3.3. Mechanisms

The modulation of the device resistance with memory effects is essential to mimic biological synapse. And the understanding of switching mechanism is also important to incorporate memristors as a bionic synapse into the neuromorphic computing system. Many suggestions have been put forward to elucidate the causes of resistive memory effects of those oxide-based memristors. The most popular views on RS mechanism are taken as ionic diffusion and thermal effect.

For the mechanism of ionic drift and diffusion, under the stimulation of applied bias, the ions will migrate, and the conductance of memristors will be enhanced or depressed [96–98]. Actually, there are two types of ionic drift: cation and anion drift, which depends on the materials used for active layers and electrodes. For example, for Strukov’s [24] TiO₂ memristor, both electrodes have inert Pt; the movement of oxygen vacancies causes the whole active TiO₂ layer to separate into two parts, with one part rich in oxygen vacancies and being more conductive. Hence, the difference in the concentration of oxygen vacancies leads to oxygen ion (anions) diffusion. Oxygen ions move to the anode and more oxygen vacancies are created. The increase of oxygen vacancies then makes the device more conductive to a low resistance state. Meanwhile, there is some evidence that the noninert electrode can hinder the combination of oxygen ions and serve as an oxygen vacancy reservoir. In the set process, the metal is oxidized and the metal ions diffuse into the insulating layer to develop a conducting filament. Under negative bias, the filaments are ruptured by the increase of the electric field.

The second mechanism is about the heating effect [99, 100]. In the set or reset process, the active layer material is changed by the application of an electric field and flowing current heat. As the current is applied, the heat is released and the ions drift, forming an electron path to develop the conductive filament. At the same time, due to the collision of electrons, a new boundary may be created that inhibits the formation of the filament with excess heat [100]. Joule heating effects have been credited both in unipolar and in bipolar switching memories. In unipolar switching, under the high current passing through the memory devices, the heating fuses the conductive filaments in the reset process which is similar to that in bipolar switching. In bipolar switching, Joule heating dissolves the filament when sufficiently high current flows through the device. If this rupture happens in the SET process, it becomes a valid operation since the resistance did not stay in LRS and result in threshold switching [101]. However, large current should be avoided in the device which will introduce bad effects to performance or lead to a permanent failure because large current flowing through the filament will generate severe Joule heating, and a steep increase of the temperature in the filament will finally melt the filament.
Generally, the physical origin of the switching effect in memristors depends on architectures, materials, and interfaces. The comprehensive study of the mechanism is very helpful to the manipulation of memory and to extend the application of memristors. In terms of conductance modulation in memristors, many metal oxide-based memristors can perform not only on digital memory but also on analog memory which is similar to biological functions.

4. Conclusion

In this review, we have outlined an overview of memristor-based synaptic devices, especially for the metal oxide memristors. The neuromorphic approach with oxide-based RRAM devices is promising. Focusing on TiO$_x$, WO$_x$ based memristor, the electrical switching characteristics are reviewed. Exploiting the physical mechanisms, the synaptic behaviors of those devices are also discussed. Owing to the magnificent increased computational efficiency, and also increasing compatibility in computer technology and CMOS technology, metal oxide-based synaptic devices are gaining prominent interest. The progress of neuromorphic engineering on devices confirms that the memristive synapses can meet the demand of low energy consumption, high connectivity, and density in neuromorphic devices for efficiently encoding, storing, and processing information. However, challenges still remain for overall oxide-based RRAM materials. Although the inherent fault tolerance of neural network models is able to mitigate the impact of device variation to some extent, the improvement of spatial variation and temporal variation turns out to be one of the greatest challenges on a long-term basis. In addition, the improvement of reliability characteristics of the memristor synaptic devices is another key challenge which is not well studied.

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