Ferroelectric Memristors Based Hardware of Brain Functions for Future Artificial Intelligence

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Abstract. Brain-inspired neuromorphic computing systems have long attracted significant interests to replace the conventional Von-Neumann systems because of the development of big data analysis and artificial intelligence has put forward higher requirements for computing speed and energy consumptions. Memristive devices are known as one of the most significant candidates to implement brain-inspired neuromorphic computing systems due to their special properties to emulate biological synapses of human brains. Ferroelectric material is a breakthrough for the resistive-switching layer of memristors due to their continuously tunable resistive switching behaviors. However, the application of ferroelectric memristors is limited by unstable performance and the low switching ratio. In this work, ferroelectric memristors have been fabricated and two-dimensional (2D) material MXene (Ti₃C₂) has been firstly introduced to the Cu/PZT/Pt devices. The insertion of MXene can enhance the performance of the devices by boosting the formation of conductive filaments of oxygen vacancies. The Cu/MXene/PZT/Pt devices exhibit stable resistive switching phenomena and have a high switching ratio about 10⁶. The resistance of Cu/MXene/PZT/Pt memristors can be regulated under continuous voltage pulses. More interestingly, some synaptic functions have been successfully mimicked using Cu/MXene/PZT/Pt memristors. This work will pave the way for the development of the implementation of brain-inspired computing systems.

1. Introduction
In this era of big data, the conventional Von-Neumann computing systems have begun to encounter some technical bottlenecks, e.g., separation of storage and computing, huge energy consumption, and poor computing ability [1, 2]. As a consequence, brain-inspired computing systems, which can perform massive parallel operating and solve complex problems without consuming too much energy, have attracted great interests [3, 4]. Various kinds of new electronic devices have been explored to mimic biological synapses, which is the most important learning behavior of human brains [5]. Memristors are one of the most important candidates because of their excellent properties, e.g., impacted structure, tunable resistance states, fast switching speed, and low operating voltage [6, 7].

Ferroelectric tunnel junction (FTJ) has become excellent competitors of the resistive-switching layer of memristors for mimicking artificial synaptic devices [8, 9]. FTJ can be gradually modified by the modulation of the height of the interface barrier [10], which may give rise to a continuously...
tunable resistive switching behavior [11]. However, the application of FTJ memristors are limited by the high operating voltage, the low switching ratio, and slow write/read speed [12]. It has been widely accepted that the resistance of memristors can be controlled by the growth and dissolution of conductive filaments between two metal electrodes [10]. It will be useful to improve the performance of FTJ memristors by controlling the growth of conductive filaments [13].

In this work, high-performance ferroelectric memristors based on a novel Cu/MXene/PZT/Pt structure have been successfully fabricated, which exhibit excellent reproducing bipolar resistive-switching properties, high switching ratio of current, and low operation voltage. MXene (Ti$_3$C$_2$) has been firstly introduced to the resistive-switching layer of FTJ memristors [6]. The conduction mechanisms of Cu/Ti$_3$C$_2$/PZT/Pt have been investigated in details. In addition, the conductivity of Cu/Ti$_3$C$_2$/PZT/Pt memristors can be modulated by pulses of voltage. More interestingly, the biological responses have been simulated, e.g., paired-pulses facilitation (PPF) behavior and spike time-dependent plasticity (STDP). This work will further promote the application of FTJ memristors in brain-inspired semiconductor devices.

2. Results and Discussions

The successful preparation of Ti$_3$C$_2$ powder was firstly investigated by scanning electron microscope (SEM) as shown in figure 1a. It vividly shows an accordion-like nanostructure. The structure of Cu/MXene/PZT/Pt memristors is shown in figure 1b. Based on the silicon wafer, the device stacks consist of 100 nm platinum (Pt) bottom electrode and 40 nm PZT layer, which were deposited by sputtering. Next, Ti$_3$C$_2$ was deposited on the PZT layer by spinning coating. Finally, 80 nm Cu was sputtered as top electrodes.

![Figure 1. (a) The morphology of MXene (Ti3C2). (b) 3D structure of the Cu/MXene/PZT/Pt memristor.](image)

A double-voltage-sweep was applied to Cu/MXene/PZT/Pt memristors to measure its $I$-$V$ characteristic. As the process ∘-⊙ shown in figure 2a, the Cu/MXene/PZT/Pt memristors exhibit an excellent resistive-switching. When a positive voltage sweeps from 0 V to 1.5 V, the resistance of the devices shifts from the high resistance state (HRS) to the low resistance state (LRS) accompanied by a conspicuous rise in working current. The process is called the SET process. When the sweeps from 1.5 V to 0 V, the working current drops proportionally, which indicates that the device maintains at LRS. When the negative voltage sweeps from 0 V to -1.5 V, the resistance of the device is shifted from the LRS to the HRS. In order to observe the stability of the Cu/MXene/PZT/Pt memristors, retention of the devices have been measured. As shown in figure 2b, the red and the blue lines represent the values of resistance of on state ($R_{on}$) and the values of resistance of off state ($R_{off}$), respectively. The switching value of the devices can up to $10^6$ for 3000 s.

The possible mechanisms of Cu/MXene/PZT/Pt memristors have been shown in figure 3. The realization of resistive-switching can be concluded to the growth and dissolution of conductive filaments of oxygen vacancies. When the positive voltage was applied to Cu electrode, Cu + O$^{2-}$ = CuO$_x$ is the critical oxidation reaction to form the oxygen vacancies in the PZT layer [12]. In addition,

$$\text{Cu} + \text{O}^{2-} = \text{CuO}_x$$
the effects of polariton charges may affect the resistive-switching of Cu/MXene/PZT/Pt memristors. As is shown in the schematic diagram of figure 3b, when the orientation of ferroelectric polariton of points to the PZT/Pt interface under positive voltage pulses, the height of the junction barrier of PZT/Pt will be lower [10, 12, 14]. On the contrary, the ferroelectric barrier will be raised when the negative voltage pulses are applied to the memristor. The variations of the ferroelectric barrier will affect the transition of oxygen vacancies. As is shown in figure 3a, the insertion of 2D materials may accelerate the oxidation rate of Cu in this process, which will further strengthen the formation of conductive filaments [13]. Thus, excellent performance of the Cu/MXene/PZT/Pt memristors is reasonable, and the mechanisms of the device are different from the ferroelectric memristors, which are based on the initial polariton of ferroelectric films.

Figure 2. (a) The typical I-V hysteretic curve of Cu/MXene/PZT/Pt memristor. (b) The retention of Cu/MXene/PZT/Pt memristors.

Figure 3. (a) The schematic diagram of the formation of conductive filaments of Cu/MXene/PZT/Pt memristors. (b) The schematic diagram of changes of Schottky barriers of Cu/MXene/PZT/Pt memristors by the variations of the applied bias voltages.

In biological synapse, upon the arrival of simulation to pre-synapse, the influx of calcium ions (Ca$^{2+}$) will induce the release of neurotransmitters to the post-synapse. These are the internal mechanisms of excitatory and inhibitory of brain functions. In this ferroelectric memristors-based artificial synapse, the top and bottom electrode can serve as the input of pre-synaptic and output of post-synaptic, while the conductance of ferroelectric memristors is regarded as the synaptic weight [15]. In order to mimic the brain functions for the development of future artificial intelligence, a series
of voltage pulses have been applied to the Cu/MXene/PZT/Pt memristors to observe the continuously tunable performance of conductance. In this work, the value of the pulse interval is fixed as 20 ms. The PPF is one of the important parameters which can affect the neural computation of biological synapses. As is shown in figure 4a, when the two voltage pulses with the same amplitude of 4 V are applied to the Cu/MXene/PZT/Pt memristors, the current of the second pulse is larger than the current generated by the first pulse. The PPF index of this memristor is about 2. This result indicates that the memristive devices can be able to mimic the paired-pulse facilitation of synapses successfully. In addition, the relationship of the PPF index and pulse interval is shown in figure 4b. The pulses with an amplitude of 4 V were applied to the Cu/MXene/PZT/Pt devices. It can be concluded that the PPF index \((G_2 - G_1) / G_1\) will increase with the decrease of the pulse intervals. In this equation, \(G_1\) and \(G_2\) are the conductance values after the first and the second pulse, respectively. This relationship can be fitted by the function of \(y = A_1 \times \exp\left(-\Delta t / t_1\right) + y_0\) (\(t_1\) corresponds to the decaying time, is equal to 1.027, and the \(\Delta t\) is a time interval variable). It can be explained that the smaller pulse intervals result in more effectively forming of conductive filaments. This is similar to the biological synapse, when the interval of the pulse of perception decrease, the memory effects can be reinforced.

![Figure 4](image-url)

**Figure 4.** (a) Typical PPF behavior induced by a pair of pre-synaptic spikes. (b) The relationship between the double pulse facilitation index and the pulse interval and the fitting map. (c) Illustration of spike signals and STDP function of Cu/MXene/PZT/Pt memristor. \(\Delta W\) can be calculated as \((I_2 - I_1) / I_1\), where the \(I_2, I_1\) refer to the current measured before and after the pair-voltage application.

The pre- and postsynaptic stimulations can be able to modulate the synaptic connections by temporal interaction. The STDP, an important fact of biological neural networks, describes the temporal modification of synaptic weight. This is related to the time \((\Delta t = t_{\text{pre}} - t_{\text{post}})\) between the presynaptic and postsynaptic spike. When a postsynaptic event occurs \((\Delta t > 0)\), the synaptic weight will decrease and bring out the results of long-time depression (LTD). When an event occurs in presynaptic \((\Delta t < 0)\), the weight of synapse will increase and bring out the results of long-time
potentiation (LTP). For simulating STDP behavior, a pair of pulses with positive voltage (4 V) and negative voltage (-4 V) were applied to Cu/MXene/PZT/Pt memristors. Figure 4c shows the changes of synaptic weight (∆W) along with the changes of ∆t. ∆W can be calculated as (I₂ - I₁) / I₁, where the I₂, I₁ refer to the current measured before and after the pair-voltage application. An increase (or decrease) in synaptic weight before (or after) a presynaptic event can be seen from figure 4c. As ∆t becomes smaller, the value of ∆W has become greater. All the above results demonstrate that the STDP behavior can be successfully simulated by the Cu/MXene/PZT/Pt memristors.

3. Conclusion
In summary, the Cu/MXene/PZT/Pt memristive devices have been successfully fabricated, which exhibit excellent bipolar resistive-switching properties, high switching ratio of current, and low operation voltage. It can be concluded that the insertion of MXene (Ti₃C₂) can improve the performance of devices by boosting the formation of oxygen vacancies. The biological responses of human brains have been successfully mimicked by the devices. This work will provide a promising approach for building efficient human-brain computing systems.

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