Hf_{0.5}Zr_{0.5}O₂-based ferroelectric memristor with multi-level storage potential and artificial synaptic plasticity

Tianqi Yu^{1†}, Fuchao He^{2†}, Jianhui Zhao¹, Zhenyu Zhou¹, Jingjing Chang^{2*}, Jingsheng Chen^{3*} and Xiaobing Yan^{1,3*}

ABSTRACT Memristors are designed to mimic the brain's integrated functions of storage and computing, thus breaking through the von Neumann framework. However, the formation and breaking of the conductive filament inside a conventional memristor is unstable, which makes it difficult to realistically mimic the function of a biological synapse. This problem has become a main factor that hinders memristor applications. The ferroelectric memristor overcomes the shortcomings of the traditional memristor because its resistance variation depends on the polarization direction of the ferroelectric thin film. In this work, an Au/Hf_{0.5}Zr_{0.5}O₂/P⁺-Si ferroelectric memristor is proposed, which is capable of achieving resistive switching characteristics. In particular, the proposed device realizes the stable characteristics of multi-level storage, which possesses the potential to be applied to multi-level storage. Through polarization, the resistance of the proposed memristor can be gradually modulated by flipping the ferroelectric domains. Additionally, a plurality of resistance states can be obtained in bidirectional continuous reversibility, which is similar to the changes in synaptic weights. Furthermore, the proposed memristor is able to successfully mimic biological synaptic functions such as long-term depression, long-term potentiation, paired-pulse facilitation, and spike-timing-dependent plasticity. Consequently, it constitutes a promising candidate for a breakthrough in the von Neumann framework.

Keywords: ferroelectric memristor, multi-level storage, resistive switching, neuromorphic network, synaptic plasticity

INTRODUCTION

In today's big data era, collection and storage of information are of particular importance. Although software technology has been greatly improved in recent years and people can use software to process information, the development of storage hardware, especially in the field of multi-level storage and neural networks, requires a strong research effort. The use of hardware can eliminate the impact of software vulnerabilities on simulation. In this way, data can be processed and stored faster and more accurately. So far, one of the most suitable devices to implement the above functions is the memristor (or called resistive random access memory (RRAM)) [1–6]. The metal-insulator-metal-based architecture of a traditional memristor has resulted in a miniaturized size, low power consumption, high response speed, and simple manufacturing requirements. Experiments have indicated that the formation and fracture of the conductive wire inside a traditional memristor are unstable, resulting in a random distribution of the threshold voltage. In many RRAMs, switching between low-resistance state (LRS) and high-resistance state (HRS) is only allowed to represent the “0” and “1” states, respectively. However, these two storage levels are insufficient for the increasing demand for large-capacity storage in big data. In addition, many memristors can hardly achieve bidirectional analog resistance modulation [7]. These kinds of memristor devices have gradual conductance changes only at one side, and cannot faithfully simulate the potentiation and de-

¹ Key Laboratory of Brain-like Neuromorphic Devices and Systems of Hebei Province, College of Electronic Information Engineering, Hebei University, Baoding 071002, China

² School of Microelectronics, Xidian University, Xi'an 710071, China

³ Department of Materials Science and Engineering, National University of Singapore, Singapore 117576, Singapore

[†] These authors contributed equally to this work.

* Corresponding authors (emails: yanxiaobing@ime.ac.cn (Yan X); msecj@nus.edu.sg (Chen J); jjingchang@xidian.edu.cn (Chang J))

pression of biological synapse function [8,9]. Thus, the performance of the memristor is undoubtedly impaired, making it a difficult-to-control device. To overcome these problems, the development of new types of memristors is on the agenda [3].

As a new type of memristor, the ferroelectric memristor has the potential to be applied to multi-level storage and the function of simulating biological synapses [4]. Unlike conventional memories, the ferroelectric memristor does not require an electroforming process during its fabrication. Thus, the stability of the ferroelectric memristor's resistance state during operation is ensured. At the same time, it exhibits a non-destructive operating mode. Through polarization, the ferroelectric domain in the ferroelectric thin film can be reversed, so that the resistance of the device continuously changes in the positive and negative voltage polarity directions. Interestingly, the device's resistance can be changed by pulse parameters and formulated to simulate the "synaptic weight" in biological synaptic behavior, which is consistent with the Hebbian theoretical framework [10]. This behavior can be used for neuromorphic calculations by changing the weight of the connections between two neurons [11]. According to previous reports, ferroelectric memristors are usually fabricated using perovskite metal oxide materials. However, a memristor consisting of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) as a functional layer has recently been realized by using an atomic layer deposition (ALD) process [12–14]. The chemical and physical properties of Zr are very similar to those of Hf, and the ferroelectric properties of HZO can be obtained at a lower temperature [15]. It has been reported that the ferroelectric HZO-based films can be incorporated into field-effect transistors and are compatible with complementary metal-oxide-semiconductor technology, which can be accurately controlled. These results paved the way for the resistance switching mechanism for high-density memories and faster-operating ferroelectric memristors. They have also stimulated further investigation into the properties of ferroelectric HZO films.

In this work, a ferroelectric memristor based on $\text{Au}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2(\text{HZO})/\text{p}^+\text{-Si}$ which has the potential of multi-level storage and applications in biological synapses is reported. The reason is that when $\text{Zr}/[\text{Hf}+\text{Zr}]$ is 0.5, the $\text{H}_x\text{Zr}_{1-x}\text{O}_2$ film can obtain the strongest ferroelectric characteristics [15]. Experimental results show that the proposed device exhibits gradual change during the process of resistance switching. Also, multiple stable resistance states are possible (highlighting the potential of multi-level storage), and the device can achieve bidirec-

tional voltage regulation under positive and negative pulses. Moreover, its resistance exhibits continuously adjustable characteristics, and the device is able to mimic biological synapses such as long-term depression (LTD), long-term potentiation (LTP), paired-pulse facilitation (PPF), and spike-timing-dependent plasticity (STDP) [16–18]. The proposed device has two polarization states. HZO film up-polarization will gradually increase the resistance of the device and eventually put it in the HRS. The downward polarization of the HZO film causes the resistance of the device to gradually decrease and eventually put it in the LRS. This phenomenon of switching the resistance of the device by ferroelectric polarization can be used to mimic the change of biological synaptic weight, which explains the changes in the weight of the presynaptic and postsynaptic membranes due to the transport of K^+ , Ca^{2+} , and Na^+ during the reaction [18–20].

EXPERIMENTAL SECTION

Device preparation

The heavily doped $\text{p}^+\text{-Si}$ substrate was ultrasonically cleaned with acetone, ethanol and deionized water successively at room temperature for 10 min. Then the substrate was dried using pure nitrogen. Prior to deposition, an O_2 plasma treatment (10 min, 20 W) was carried out to remove the surface residues and promote the formation of metal oxide thin film. After that, the ALD process was carried out at 300°C . Argon was used as gas carrier and purge gas. Tetrakis (diethylamino) zirconium (TDMAZr)/purge/ H_2O /purge/tetrakis (diethylamino) hydrazine (TDMAHf)/ H_2O /purge were sequentially cycled 200 times with a deposition rate of 0.1 nm per cycle. Consequently, a 20-nm HZO film was deposited on the substrate. The three groups of HZO films were prepared in this way. Finally, the devices were completed by thermally evaporating a 300-nm-thick Au electrode (with different radius of 100, 200 and 300 μm) on top of the each group film with patterned shadow masks.

Characterizations

The piezoresponse force microscopy (PFM) measurements were conducted using a commercial atomic force microscopy (AFM) system (Cypher-S, Asylum Research, USA). The sample was grounded through a bottom electrode. The polarization state of HZO film was observed by supplying a small alternating current (AC) bias *via* a conductive probe (PPP-EFM, Nanosensors, Netherlands). Resonance enhanced technique (DART, Dual AC

Resonance Tracking) was used to ensure better response and minimize topographic crosstalk. The electric poling was performed by scanning a specific region while applying a large direct current (DC) bias to the tip. The PFM hysteresis loops were acquired at a fixed location while applying gradually increased switching DC bias and a constant small probing AC bias. The remnant polarization was used to plot the hysteresis loops. A cross-section of a crystalline film-based junction was obtained by a transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

A schematic diagram of a device based on the Au/HZO/ p^+ -Si structure is given in Fig. 1a, where p^+ -Si serves as the bottom electrode, the HZO film is grown as the functional layer, and Au serves as the top electrode of the device. A TEM image is presented in Fig. 1b. TEM analysis of the Au/HZO/ p^+ -Si cross-section sample shows that at the interface between HZO and p^+ -Si. There is a natural SiO_x intermediate layer with a thickness of about 2 nm. The HZO thin film with a thickness of 20 nm is in a polycrystalline state. The morphology scan of the sample across a $10\ \mu\text{m} \times 10\ \mu\text{m}$ region is shown in Fig. 1c, where a relatively smooth surface can be observed. A hysteresis loop of PFM is presented in Fig. 1d, which shows the ferroelectric properties of the HZO film [4, 21–

23]. The minimum value of the amplitude loop obtained from the testing results indicates that the coercive voltage of the portion is about -3.0 and 1.0 V. Amplitude and phase images of the out-of-plane PFM written to the HZO surface are presented in Fig. 1e and f, respectively. According to the amplitude image of the PFM (shown in Fig. 1e), the local polarization direction of the HZO is downward. The device responds when an excitation voltage is applied [11]. When a -5 V bias is applied, the HZO film is polarized in the upward direction; when a $+5$ V bias is applied, the polarization direction of the HZO film is downward. Phase comparison in Fig. 1f indicates that by inverting the ferroelectric domain, the polarization is antiparallel in these two regions, and the ferroelectric domain in the HZO film can be completely inverted [24,25].

The influence of the size of Au electrode on the stability and reversibility of the ferroelectric memristor was investigated using three Au electrode radii of 300, 200 and $100\ \mu\text{m}$, named as A-, B-, and C-type, respectively. In order to explain the size effect of the ferroelectric memristor, while avoiding the influence of unnecessary factors in each of the three devices [19], one size was randomly selected and then measured at room temperature in a dry environment. A classic I - V measurement of 50 cycles was initially performed, as shown in Fig. 2a, e and i. For the A-type device, the $0 \rightarrow 9 \rightarrow 0 \rightarrow -9 \rightarrow 0$ V scan mode was

Figure 1 Schematic of the device structure, PFM and TEM measurements of the HZO film. (a) Device structure diagram. (b) TEM image of the cross-section structure of the grown Au/HZO/ p^+ -Si. (c) Morphological scan of HZO grown on p^+ -Si over a $10\ \mu\text{m} \times 10\ \mu\text{m}$ area. (d) PFM hysteresis loop. (e) PFM amplitude image. (f) PFM phase image.

Figure 2 *I-V* curves, resistance switching voltages, high and low resistance distributions of A- (a–d), B- (e–h) and C-type (i–l) devices. (a, e, i) Classic *I-V* curves in 50 cycles. (b, f, j) Distribution histograms and Gaussian fitting curves of set voltages. (c, g, k) Distribution histograms and Gaussian fitting curves of reset voltages. (d, h, l) Statistical high- and low-resistance profiles.

used, $0 \rightarrow 8 \rightarrow 0 \rightarrow -6 \rightarrow 0$ V for the B-type device, and $0 \rightarrow 6 \rightarrow 0 \rightarrow -4 \rightarrow 0$ V for the C-type device. The testing results indicate that all the devices have obvious resistance switching characteristics. However, compared with the A- and B-type devices, the *I-V* window of the C-type device has no obvious fluctuation, indicating stable resistance switching characteristics. Therefore, the *I-V* characteristics of the device become more stable when the size decreases.

To further explore the relationship between the device size and stability, the threshold voltage, HRS, and LRS distribution of the three types of devices were calculated [5,19]. The results are shown in Fig. 2b and c, f and g, j and k, respectively. It can be observed that for the A-, B- and C-type devices, the set voltage distributions are 1.4 to 2.8 V, 1.7 to 2.5 V, 1.5 to 2.3 V, respectively, and the corresponding Gaussian fitting values are (2.089 ± 0.114) V, (2.041 ± 0.091) V, and (1.848 ± 0.065) V, respectively. Their reset voltage distributions are -3.0 to -1.6 V, -2.8 to -1.6 V, and -2.1 to -1.3 V, respectively,

and the corresponding Gaussian fitting values are (-2.269 ± 0.144) V, (-2.099 ± 0.137) V, and (-1.764 ± 0.063) V, respectively. According to the testing data, the set and reset voltages for the A-, B- and C-type devices are about 2.1 and -2.3 V, 2.0 and -2.1 V, 1.8 and -1.8 V, respectively. By comparison, it can be observed that a smaller-sized device has a smaller threshold voltage, which is advantageous for reducing the power consumption of the device. The distribution of HRS and LRS for the three types of devices are shown in Fig. 2d, h, and l [26]. The high resistance of the devices is distributed on the order of $10^5 \Omega$, and the low resistance is distributed on the order of $10^4 \Omega$. However, compared with the A- and B-type devices, the resistance of the C-type device exhibits a more stable resistance switching, which fluctuates only in a small range. Therefore, it can be found that the C-type device has the most stable and largest $R_{\text{off}}/R_{\text{on}}$ ratio. Most importantly, it was found by comparison that a device can be impressed by decreasing its size. Therefore, C-type devices are used for the following testing. At the same

time, the $R_{\text{off}}/R_{\text{on}}$ ratios for the three types of devices were also calculated. Details are displayed in Fig. S1 of the Supplementary information. In addition, the structure, resistance switching ratio, and the synaptic plasticity function of the proposed devices were compared with those of the HfO_2 -based devices reported in previous studies (Table 1).

It was reported in a previous study that when the thickness of the HZO film exceeds 5 nm, the limited conduction mechanism at the interface is likely to be the main mechanism for the resistance switching of the ferroelectric film. In this work, the thickness of the grown HZO film was 20 nm, and therefore the direct tunneling model was not applicable. Compared with the Fowler-Nordheim tunneling model, the thermionic emission (TE) model might be more reasonable [12,27]. For the proposed Au/HZO/ p^+ -Si devices, the functional layer is HZO, with a band gap of 5.8 eV, and electron affinity of 2.8 eV; the bottom electrode is Si, with a work function of 4.85 eV. From these parameters, it can be concluded that the Schottky barrier across the HZO/ p^+ -Si interface is reasonable for the TE mechanism so that electrons can overcome the barrier [28,29]. The change in the potential barrier of the device is shown in Fig. S2a. This model was used to fit the I - V curve. From the fitted I - V characteristic curve shown in Fig. S2b, it is observed that when a positive voltage is applied, the device is turned on (ON), and when a negative voltage is applied, the device is turned off (OFF). Under ferroelectric polarization, the height of the barrier changes significantly. This causes the resistance to change between a high resistance and a low resistance. The parameter information used for the I - V fitting, as

shown as Table S1.

It is well known that memristors have simulating synaptic function characteristics. Therefore, their adjustability and stability are very important. The I - V curves under five positive and negative voltage scans, with amplitude gradients, are shown in Fig. 3a and c [30]. As shown in Fig. 3a, unlike devices with a sudden change in conductance, the application of the positive excitation voltage causes a gradual increase in the conductance of the proposed device. Also, the loop of each I - V curve is higher than the loop of the previous I - V curve. As shown in Fig. 3c, the application of a negative excitation voltage causes a gradual decrease in the conductivity of the device, and the loop of each I - V curve is lower than the loop of the previous I - V curve. Therefore, a DC scan mode can be used to fine-tune the device. Continuity and adjustability prove the excellent memristive characteristics of the proposed device. This is a necessary feature of the memristive device for simulating the behavior of the biological synapse.

At the same time, the stability and repeatability of the proposed device's resistance changes were also examined by performing retention measurements for each adjustable state of the device. These results are shown in Fig. 3b and d, respectively. For the Au/HZO/ p^+ -Si device, each state of the positive and negative voltage sweep was performed for 7200 s [31]. Although resistance fluctuations are observed for each controllable state, the amplitude of these fluctuations is very small, and no jump occurs in the resistance state. Thus, the performance of the device is hardly affected. Based on this, it shows that the proposed device exhibits good stability and repeat-

Table 1 Statistics of this work and previous reports on dopants used for doping HfO_2 thin films, characterization methods, device switching resistance ratio, and synaptic plasticity behavior

Structure	Dopant	Characterization method	$R_{\text{off}}/R_{\text{on}}$	Synaptic plasticity	Refs.
Au/HZO/Si	Zr	TEM, PFM	1500%	Yes	Our work
TiN/ HfO_2 /TiN	No	N. A.	1000%	Yes	[29]
Ti/ HfO_2 /TiN	No	N. A.	1000%	Yes	[34]
Au/HZO/TiN	Zr	GIXRD	166%	No	[41]
TiN/HZO/TiN	Zr	HR-TEM	N. A.	N. A.	[50]
Ti/ HfO_2 /TiN	No	N. A.	N. A.	Yes	[45]
TiN/ HfO_2 /TiN	No	XRD	1000%	No	[32]
TiN/HfO/TiN	La	GIXRD	N. A.	N. A.	[42]
TiN/HZO/TiN	Zr	N. A.	N. A.	N. A.	[14]
Pt/HZO/TiN	Zr	GIXRD	N. A.	N. A.	[37]
TiN/Gd: HfO_2 /TiN	Gd	XRD	N. A.	N. A.	[30]
TiN/ HfO_2 /TiN	No	XRD	N. A.	N. A.	[33]
TiN/HZO/Si	Zr	TEM	800%	Yes	[46]

Figure 3 Continuous regulatable and retentive testing of the devices. (a, c) The positive and negative portions of the I - V curves indicate that the device can simulate fluctuations in biological synapses, i.e., the continuously adjustable performance of the device. (b, d) Positive and negative regulatable resistance state retention testing.

ability. This indicates that each of the controllable resistance states of the proposed device can be maintained for a long time, which suggests a great potential for multi-level and long-term storage applications [5]. In addition to the voltage changes, the increase in conductance (decrease in resistance) can be explained more clearly by calculating the conductance and current values (both measured at the end of each scan), which shows the change in conductance with the scan period. As shown in Fig. S3, these gradual changes in conductance (resistance) further reflect the continuously changing characteristics of the device.

As described above, since the function of a memristor is similar to that of a biological synapse, memristors have a great potential for application in the field of biological synapses. For devices based on the Au/HZO/ p^+ -Si structure, the effect of the device on the resistance change under the application of a driving voltage pulse train was initially investigated [32,33]. Therefore, the programming voltage was set as follows: the negative voltage pulse section was $-8 \rightarrow 0$ V, and the set step voltage was -0.2 V; the positive voltage pulse section was $0 \rightarrow 8$ V, and the set step voltage was 0.2 V. The width of each pulse was 1 ms,

and the pulse interval was 1 ms. The change in the device's resistance is presented in Fig. 4a. In the negative pulse section, where the absolute value of the voltage gradually increases, the device's resistance increases as the negative voltage decreases. In the positive pulse section, where the absolute value of the voltage gradually increases, the device's resistance decreases as the positive voltage increases [12,16,34]. Thus, modulations in biological synaptic weights (changes in the strength of the connection between biological synapses) can be simulated by changes in the resistance of a memristive device. This shows that by applying positive and negative pulses onto the device, the device exhibits bidirectional resistance adjustment characteristics. This is an important prerequisite for simulating biological synapses and for applications to neural networks [35,36]. So far, although conventional RRAM is regarded as the devices most likely to implement synaptic functions, their instability of conductive filaments and the randomness of resistance switches hinder their applications [23,37]. Therefore, the proposed Au/HZO/ p^+ -Si devices have opened up new avenues for their successful application in the field of biological synapses.

Figure 4 Characteristics and memristive behavior of the ferroelectric memristor devices. (a) Memristive behavior produced by the classic pulsed application of the device. Applying a negative pulse/positive pulse to the device causes the conductance to decrease/increase, representing synaptic weight modulation due to boosting or suppressing the pulse. (b) Typical R - V hysteresis loop measured by increasing the negative voltage pulse from -6 to 7 V. (c) Change in the resistance state when a pulse width of 1 ms, an interval of 1 ms, and a reset voltage of 6.5 V were applied to the device. (d) Change in the resistance state when a pulse width of 1 ms, an interval of 1 ms, and a reset voltage of -5 V were applied to the device. (e, f) The changes of resistance state of the Au/HZO/Si device with the pulse amplitude and pulse duration.

In the previous work on ferroelectric memristors, it has been reported that the continuous switching behavior of the device's resistance states may be caused by the following reasons: ferroelectric modulation channel conductance in a ferroelectric gate field-effect transistor, ferroelectric field-effect modulation of carrier concentration, and height change of the ferroelectric barrier [3]. The observed continuous resistance switching may be derived from the charge concentration modulation of the ferroelectric field-effect, as observed in previous work by our group [35]. The possible origin of the memristive behavior of the proposed HZO thin film is further discussed in Fig. S4.

Next, the device's typical non-volatile resistance-switch R - V curve was also measured to verify the device's memristive switching characteristics [3,22,38–41]. The scan drive voltage sequence was set to $-6 \rightarrow 0$ V, $0 \rightarrow 7$ V, and finally back to -6 V from 7 V. The width of each pulse and the pulse interval were both

1 ms. As shown in Fig. 4b, by applying a drive voltage sequence, the device is able to achieve a continuous change between the LRS and the HRS. A series of resistance states between HRS and LRS can also be obtained by applying different voltages [11]. When the applied voltage is 7 and -6 V, respectively, the maximum $R_{\text{off}}/R_{\text{on}}$ ratio can be obtained. In general, various resistance states are possible in a ferroelectric memristor because of the different degrees of inversion of the ferroelectric domains in the HZO film [23]. According to the PFM data, the polarization direction of the local HZO thin film domain is downward, that is, uniformly directed to p^+ -Si [42]. When a driving voltage is applied, the memristor's ferroelectric domain begins to flip. Starting from the uniform downward ferroelectric polarization state in the HZO layer, the ratio of the lower and upper polarization regions is gradually increased from 0 to 100% (uniformly upward polarization) by applying a set of negative voltage pulses or by applying a positive voltage pulse to perform

the reverse process.

The process of applying a different drive voltage sequence to the device to make it evolve from an LRS to an HRS and from HRS to LRS is also demonstrated [23]. In order to measure the results shown in Fig. 4c and d, the drive voltage pulse sequence is set as follows: pulse duration and pulse interval are both 1 ms; positive voltage amplitude is 6.5 V, negative voltage amplitudes are -3.5 , -4 , -4.5 and -5 V. The negative voltage amplitude is -5 V, and the positive voltage amplitudes are 5, 5.5, 6 and 6.5 V. Based on these settings, it is found that the final resistance state of the Au/HZO/ p^+ -Si device depends on the negative (Fig. 4c) and positive voltage pulse sequences (Fig. 4d) applied. Therefore, the device can be regulated.

In the proposed devices, the resistance can be adjusted by changing the voltage amplitude and pulse width of the applied driving voltage. As shown in Fig. 4e and f, the tendency of the device to gradually transition from HRS (LRS) to LRS (HRS) under the application of different voltage amplitudes and pulse widths has been statistically analyzed [23]. The interval of the pulse sequence is set to 1 ms. As can be seen from Fig. 4e and f, several intermediate resistance states can be obtained by adjusting the parameters of the drive pulse sequence, which is consistent with the results presented in Fig. 4a and b. Therefore, multiple resistance states can be obtained for

the Au/HZO/ p^+ -Si devices by applying a voltage pulse sequence. This result agrees well with the results obtained by the continuous scanning described above, indicating the potential for multi-level storage [43]. In addition, we also found that the device has good endurance, as shown in Fig. S5.

The multi-level resistance characteristics of the Au/HZO/ p^+ -Si devices (for the regulation of different resistance states) were further verified. To this purpose, in the process of setting and resetting, three series of pulse sequences with different pulse widths, different pulse intervals, and different pulse amplitudes were applied to regulate the device. Detailed information is presented in Fig. S6.

In the current research, the application of memristive devices to the field of artificial synapses is one of the hottest topics. The device is required to mimic the function of the neuromorphology [43,44]. One of its most important functions is its ability to receive external stimuli (input signals) in a timely manner and to respond accordingly (response). In this work, a sequence of voltage pulses applied to the device was generally selected as an input signal. Simulating the intensity of bio-synchronous learning, the response intensity of the proposed devices depends on the amount of voltage applied to the voltage pulse train (Fig. 5). As shown in Fig. 5a, a pulse

Figure 5 Au/HZO/ p^+ -Si device response to the application of an input pulse sequence. (a) A sequence of excitation pulses for applying different voltage amplitudes to the device, from 4.5 to 8 V, where the pulse width and spacing of the control pulses are kept at 1 ms. (b) For the action response, it shows the current response of the device after applying a pulse sequence of different voltage amplitudes, while observing the incubation time under different conditions (the number of pulse sequences required). The black arrow indicates the incubation time produced when a voltage amplitude of 6 V is applied to the device.

sequence with a pulse width of 1 ms and an interval of 1 ms was applied to different voltage amplitudes, and the testing results (output current) were recorded. According to the results, after a certain number of applied pulses, as the voltage amplitude increases, the incubation time of the Au/HZO/p⁺-Si device gradually decreases, and the conductance of the device begins to change (Fig. 5b). Therefore, the incubation time of the device can be reduced by increasing the voltage amplitude of the pulse sequence applied to the device. At the same time, for three (high voltage) pulse sequences with voltage amplitudes of 8, 7 and 6.5 V, the switching event of the device only occurs when the first pulse is applied. This indicates that the incubation time of the device is extremely small (it happens within 2 ms) [43]. Therefore, the less incubation time, the fewer voltage pulse sequences are required to turn the device on. The incubation time of the device can be adjusted by adjusting the voltage amplitude of the applied pulse sequence and judging whether the device has reached its incubation time by the number of pulses. The existence of incubation time indicates that the device needs a certain response time to be turned on during the process (there is a certain time difference between the application of the excitation voltage and the

formation of the response current). This lays a solid foundation for the successful application of the device to simulate the function of biological synapses and calculation of neuromorphic network.

From a biological point of view, since the device exhibits bidirectional continuous adjustable characteristics, it can be applied to a wide range of neural network systems. Therefore, it is possible to further explore synaptic plasticity functions [18,20,43,45–48]. A schematic representation of a synapse, which is the interconnection between two neurons, is depicted in Fig. 6a. In this study, the focus was placed on the bio-synaptic STDP, which is one of the most classical learning rules in Hebbian's law. According to the STDP learning rule, the presynaptic membrane is stimulated earlier than the postsynaptic membrane ($\Delta t > 0$), indicating that the bio-synaptic connections between the two neurons will be increased, causing LTP. If the presynaptic membrane is stimulated later than the postsynaptic membrane ($\Delta t < 0$), the synaptic connection strength between the two neurons will be decreased, causing LTD. The biological neuron is composed of a synaptic front end and a synaptic rear end, which is similar to the sandwiched structure of the memristor's top electrode-HZO layer-bottom electrode.

Figure 6 Biological synaptic diagram and learning characteristics. (a) Schematic representation of the neuronal synaptic structures, including presynaptic, postsynaptic, cell and nucleus, axons and dendrites. (b) STDP characteristics of the ferroelectric memristors. As Δt increases, the ΔW of LTP and LTD gradually decreases. The green lines indicate the fitting results of the data. (c, d) Characteristic curves of PPF. As the time interval increases, the rate of change of its PPF gradually decreases. The green lines indicate the fitting results of the data.

The resistance of the device changes because of the polarization of the HZO film, and thus, changes in biological synaptic weights can be simulated. Therefore, the biosynthesis characteristics of memory and learning can be simulated by regulating the resistance of the memristor, which has great research value [12]. The STDP rule is an important learning rule in artificial neural networks. The simulation of the synaptic learning function often requires the implementation of STDP rules. In the proposed device, the presynaptic and postsynaptic peaks were applied to the bottom and top electrodes of the device, respectively. The Au/HZO/p⁺-Si device can simulate well the STDP learning rule, as shown in Fig. 6b. Therefore, for the regulation of synaptic weights, changing of the pulse interval between the front and back peaks can be selected [16,20]. In the calculation of neuromorphology, for the analysis of Hebbian learning rules, the exponential function $\Delta W = Ae^{-\Delta t/\tau} + w_0$ can be used to fit the STDP. In this formula, ΔW is the relative change in synaptic weight, A is the scale factor, τ is the time constant, and w_0 is a constant representing the non-association component of the synaptic change. From Fig. 6b, it can be concluded that by changing the pulse interval (i.e., changing $[\Delta t]$), a successful fit for the change in the synaptic weight can be obtained using the above exponential function. For biological synapses, the time constant is generally about 10 ms. Therefore, it is believed that the memristor, based on the Au/HZO/p⁺-Si structure, has the potential to be applied in fast neural computing chips [19]. The information on specific fitting parameters can be found in Table S2.

In biological synapses, PPF is another important learning rule that has received widespread attention in the field of synaptic learning. PPF operates as a sum of time applied to biological synapses. Reducing the time interval between two consecutive enhancement pulses increases the synaptic weight [16,19,49,50]. This simulates the process of learning and forgetting in biological synapses. This feature can correspond to the sensitivity to information processing. The results of the PPF measurement for the Au/HZO/p⁺-Si device are shown in Fig. 6c and d. The formula for calculating PPF is [16]

$$\text{PPF} = (G_2 - G_1) / G_1 \times 100\% \\ = C_1 \exp(-t / \tau_1) + C_2 \exp(-t_2 / \tau_2), \quad (1)$$

where G_1 and G_2 are the conductance after the first and second pulses, respectively, τ_1 and τ_2 are time constants. By fitting the results, it can be seen that relatively speaking, a smaller time interval will cause the device to be placed at high conductance, while a larger time interval

will place the device at low conductance. When the time interval is large enough, there will be no further change in the device's conductance. This result is in complete agreement with the characteristics of biological synaptic learning and forgetting. We also counted the error bars of STDP and PPF. We can see that although all the measured values have fluctuations, they all fluctuate in a small range around the average. Specific information on the fitting parameters for the PPF measurement can also be found in Table S2. In addition, the results also show that the proposed device has the ability to simulate homeostatic plasticity, details is shown in Fig. S7.

CONCLUSIONS

In this work, Au/HZO/p⁺-Si-based ferroelectric memristors were successfully manufactured. These devices are non-volatile and have a high-to-low resistance ratio of $R_{\text{off}}/R_{\text{on}} \sim 1500\%$. They also maintain excellent stability in resistive switching performance. The ferroelectric domains in the HZO film are gradually reversed due to ferroelectric polarization, and the resistance can be gradually switched. At the same time, due to their bidirectional gradual resistance modulation characteristics, the devices exhibit great potential for successful application in multi-level storage systems. Through in-depth analysis, it was found that the resistance switching behavior of the Au/HZO/p⁺-Si devices can be used to simulate changes in biological synaptic weights, i.e., biological synaptic learning and forgetting processes such as LTP/LTD, STDP, and PPF. Therefore, the proposed device can play an important role in the field of multi-level storage, while also opening up new avenues for the next generation of non-volatile memory and neuromorphic network.

Received 13 March 2020; accepted 29 June 2020;
published online 25 September 2020

- 1 Chua L. Memristor-the missing circuit element. *IEEE Electr Device L*, 1971, 18: 507–519
- 2 Strukov DB, Snider GS, Stewart DR, *et al.* The missing memristor found. *Nature*, 2008, 453: 80–83
- 3 Chanthbouala A, Garcia V, Cherifi RO, *et al.* A ferroelectric memristor. *Nat Mater*, 2012, 11: 860–864
- 4 Kim DJ, Lu H, Ryu S, *et al.* Ferroelectric tunnel memristor. *Nano Lett*, 2012, 12: 5697–5702
- 5 Goswami S, Matula AJ, Rath SP, *et al.* Robust resistive memory devices using solution-processable metal-coordinated azo aromatics. *Nat Mater*, 2017, 16: 1216–1224
- 6 Sangwan VK, Lee HS, Bergeron H, *et al.* Multi-terminal memtransistors from polycrystalline monolayer molybdenum disulfide. *Nature*, 2018, 554: 500–504
- 7 Yi W, Savel'Ev SE, Medeiros-Ribeiro G, *et al.* Quantized conductance coincides with state instability and excess noise in tan-

- talum oxide memristors. *Nat Commun*, 2016, 7: 11142
- 8 Yan X, Zhao Q, Chen AP, *et al.* Vacancy-induced synaptic behavior in 2d WS₂ nanosheet-based memristor for low-power neuromorphic computing. *Small*, 2019, 15: 1901423
 - 9 Kim KH, Gaba S, Wheeler D, *et al.* A functional hybrid memristor crossbar-array/CMOS system for data storage and neuromorphic applications. *Nano Lett*, 2012, 12: 389–395
 - 10 Soni R, Petraru A, Meuffels P, *et al.* Giant electrode effect on tunnelling electroresistance in ferroelectric tunnel junctions. *Nat Commun*, 2014, 5: 5414
 - 11 Guo R, Wang Y, Yoong HY, *et al.* Effect of extrinsically introduced passive interface layer on the performance of ferroelectric tunnel junctions. *ACS Appl Mater Interfaces*, 2017, 9: 5050–5055
 - 12 Yoong HY, Wu H, Zhao J, *et al.* Epitaxial ferroelectric Hf_{0.5}Zr_{0.5}O₂ thin films and their implementations in memristors for brain-inspired computing. *Adv Funct Mater*, 2018, 28: 1806037
 - 13 Yoon C, Lee JH, Lee S, *et al.* Synaptic plasticity selectively activated by polarization-dependent energy-efficient ion migration in an ultrathin ferroelectric tunnel junction. *Nano Lett*, 2017, 17: 1949–1955
 - 14 Müller J, Böske TS, Schröder U, *et al.* Ferroelectricity in simple binary ZrO₂ and HfO₂. *Nano Lett*, 2012, 12: 4318–4323
 - 15 Kim SJ, Mohan J, Summerfelt SR, *et al.* Ferroelectric Hf_{0.5}Zr_{0.5}O₂ thin films: A review of recent advances. *JOM*, 2018, 71: 246–255
 - 16 Yan X, Zhao J, Liu S, *et al.* Memristor with Ag-cluster-doped TiO₂ films as artificial synapse for neuroinspired computing. *Adv Funct Mater*, 2018, 28: 1705320
 - 17 Boyn S, Grollier J, Lecerf G, *et al.* Learning through ferroelectric domain dynamics in solid-state synapses. *Nat Commun*, 2017, 8: 14736
 - 18 Oh S, Kim T, Kwak M, *et al.* HfZrO_x-based ferroelectric synapse device with 32 levels of conductance states for neuromorphic applications. *IEEE Electron Device Lett*, 2017, 38: 732–735
 - 19 Yan X, Pei Y, Chen H, *et al.* Self-assembled networked PbS distribution quantum dots for resistive switching and artificial synapse performance boost of memristors. *Adv Mater*, 2019, 31: 1805284
 - 20 Yin YW, Burton JD, Kim YM, *et al.* Enhanced tunnelling electroresistance effect due to a ferroelectrically induced phase transition at a magnetic complex oxide interface. *Nat Mater*, 2013, 12: 397–402
 - 21 Chanthbouala A, Crassous A, Garcia V, *et al.* Solid-state memories based on ferroelectric tunnel junctions. *Nat Nanotech*, 2011, 7: 101–104
 - 22 Wen Z, Li C, Wu D, *et al.* Ferroelectric-field-effect-enhanced electroresistance in metal/ferroelectric/semiconductor tunnel junctions. *Nat Mater*, 2013, 12: 617–621
 - 23 Luo ZD, Peters JJP, Sanchez AM, *et al.* Flexible memristors based on single-crystalline ferroelectric tunnel junctions. *ACS Appl Mater Interfaces*, 2019, 11: 23313–23319
 - 24 Wang ZJ, Bai Y. Resistive switching behavior in ferroelectric heterostructures. *Small*, 2019, 15: 1805088
 - 25 Yan X, Zhou Z, Ding B, *et al.* Superior resistive switching memory and biological synapse properties based on a simple TiN/SiO₂/p-Si tunneling junction structure. *J Mater Chem C*, 2017, 5: 2259–2267
 - 26 Ambriz-Vargas F, Kolhatkar G, Broyer M, *et al.* A complementary metal oxide semiconductor process-compatible ferroelectric tunnel junction. *ACS Appl Mater Interfaces*, 2017, 9: 13262–13268
 - 27 Pantel D, Alexe M. Electroresistance effects in ferroelectric tunnel barriers. *Phys Rev B*, 2010, 82: 134105
 - 28 Pantel D, Goetze S, Hesse D, *et al.* Room-temperature ferroelectric resistive switching in ultrathin Pb(Zr_{0.2}Ti_{0.8})O₃ films. *ACS Nano*, 2011, 5: 6032–6038
 - 29 Matveyev Y, Egorov K, Markeev A, *et al.* Resistive switching and synaptic properties of fully atomic layer deposition grown TiN/HfO₂/TiN devices. *J Appl Phys*, 2015, 117: 044901
 - 30 Hoffmann M, Schroeder U, Schenk T, *et al.* Stabilizing the ferroelectric phase in doped hafnium oxide. *J Appl Phys*, 2015, 118: 072006
 - 31 Li C, Hu M, Li Y, *et al.* Analogue signal and image processing with large memristor crossbars. *Nat Electron*, 2017, 1: 52–59
 - 32 Shosuke F, Yuuichi K, Tsunehiro I, *et al.* First demonstration and performance improvement of ferroelectric HfO₂-based resistive switch with low operation current and intrinsic diode property. In: Proceedings of the IEEE Symposium on VLSI Technology. Honolulu, 2016
 - 33 Sang X, Grimley ED, Schenk T, *et al.* On the structural origins of ferroelectricity in HfO₂ thin films. *Appl Phys Lett*, 2015, 106: 162905
 - 34 Covi E, Brivio S, Fanciulli M, *et al.* Synaptic potentiation and depression in Al:HfO₂-based memristor. *Microelectron Eng*, 2015, 147: 41–44
 - 35 Guo R, Zhou Y, Wu L, *et al.* Control of synaptic plasticity learning of ferroelectric tunnel memristor by nanoscale interface engineering. *ACS Appl Mater Interfaces*, 2018, 10: 12862–12869
 - 36 Yang R, Huang HM, Hong QH, *et al.* Synaptic suppression triplet-STDP learning rule realized in second-order memristors. *Adv Funct Mater*, 2018, 28: 1704455
 - 37 Park MH, Kim HJ, Kim YJ, *et al.* Study on the degradation mechanism of the ferroelectric properties of thin Hf_{0.5}Zr_{0.5}O₂ films on TiN and Ir electrodes. *Appl Phys Lett*, 2014, 105: 072902
 - 38 Jin Hu W, Wang Z, Yu W, *et al.* Optically controlled electroresistance and electrically controlled photovoltage in ferroelectric tunnel junctions. *Nat Commun*, 2016, 7: 10808
 - 39 Garcia V, Bibes M. Ferroelectric tunnel junctions for information storage and processing. *Nat Commun*, 2014, 5: 4289
 - 40 Li C, Huang L, Li T, *et al.* Ultrathin BaTiO₃-based ferroelectric tunnel junctions through interface engineering. *Nano Lett*, 2015, 15: 2568–2573
 - 41 Fan Z, Xiao J, Wang J, *et al.* Ferroelectricity and ferroelectric resistive switching in sputtered Hf_{0.5}Zr_{0.5}O₂ thin films. *Appl Phys Lett*, 2016, 108: 232905
 - 42 Kozodaev MG, Chernikova AG, Korostylev EV, *et al.* Ferroelectric properties of lightly doped La:HfO₂ thin films grown by plasma-assisted atomic layer deposition. *Appl Phys Lett*, 2017, 111: 132903
 - 43 Milano G, Luebben M, Ma Z, *et al.* Self-limited single nanowire systems combining all-in-one memristive and neuromorphic functionalities. *Nat Commun*, 2018, 9: 5151
 - 44 Yoon JH, Wang Z, Kim KM, *et al.* An artificial nociceptor based on a diffusive memristor. *Nat Commun*, 2018, 9: 417
 - 45 E. Covi SB, A. Serb, T. Prodromakis, *et al.* HfO₂-based memristors for neuromorphic applications. In: Proceedings of the IEEE International Symposium on Circuits and Systems (ISCAS). Montreal, 2016. 393–396
 - 46 Mikheev V, Chouprik A, Lebedinskii Y, *et al.* Ferroelectric second-order memristor. *ACS Appl Mater Interfaces*, 2019, 11: 32108–32114
 - 47 Yan X, Wang K, Zhao J, *et al.* A new memristor with 2D Ti₃C₂T_x MXene flakes as an artificial bio-synapse. *Small*, 2019, 15: 1900107
 - 48 Wang G, Yan X, Chen J, *et al.* Memristors based on the hybrid

structure of oxide and boron nitride nanosheets combining memristive and neuromorphic functionalities. *Phys Status Solidi RRL*, 2019, 14: 1900539

- 49 Yan X, Zhang L, Chen H, *et al.* Graphene oxide quantum dots based memristors with progressive conduction tuning for artificial synaptic learning. *Adv Funct Mater*, 2018, 28: 1803728
- 50 Zarubin S, Suvorova E, Spiridonov M, *et al.* Fully ALD-grown TiN/Hf_{0.5}Zr_{0.5}O₂/TiN stacks: Ferroelectric and structural properties. *Appl Phys Lett*, 2016, 109: 192903

Acknowledgements This work was supported by the National Natural Science Foundation of China (61674050 and 61874158), the Outstanding Youth Project of Hebei Province (F2016201220), the Outstanding Youth Cultivation Project of Hebei University (2015JQY01), the Project of Science and Technology Activities for Overseas Researcher (CL 201602), the Project of Distinguished Young of Hebei Province (A2018201231), the Support Program for the Top Young Talents of Hebei Province (70280011807), the Training and Introduction of High-level Innovative Talents of Hebei University (801260201300), the Hundred Persons Plan of Hebei Province (E2018050004 and E2018050003), and the Supporting Plan for 100 Excellent Innovative Talents in Colleges and Universities of Hebei Province (SLRC2019018).

Author contributions Yan X conceived the idea and revised the paper. Yu T fabricated the samples, finished the test data and prepared the manuscript. Chang J and Chen J coordinated this study. This article was discussed with contributions from all authors. All authors have approved the final version of this article.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

Xiaobing Yan is currently a professor at the College of Electronic Information Engineering, Hebei University. He received his PhD degree from Nanjing University in 2011. From 2014 to 2016, he held the Research Fellow position at the National University of Singapore. His current research interest is in the field of memristors.

Tianqi Yu received a bachelor's degree from Henan University of Science and Technology in 2018. He is a graduate student at the College of Electronic Information Engineering, Hebei University. His current research focuses on ferroelectric materials for memristor applications.

Hf_{0.5}Zr_{0.5}O₂基铁电忆阻器的多级存储潜力以及人工突触可塑性

于天奇^{1†}, 何付超^{2†}, 赵建辉¹, 周振宇¹, 常晶晶^{2*}, 陈景升^{3*}, 闫小兵^{1,3*}

摘要 忆阻器能够模拟人脑兼具存储和计算的功能, 从而突破冯·诺依曼框架。然而, 传统忆阻器内部导电细丝的形成和断裂是不稳定的, 因此难以真实地模仿生物突触的功能, 这个问题已成为阻碍忆阻器模拟神经突触应用的主要因素。铁电忆阻器克服了传统忆阻器的缺点, 因为它的电阻变化取决于铁电薄膜的极化翻转。本工作中, 我们提出了一种具有Au/Hf_{0.5}Zr_{0.5}O₂/p⁺-Si结构的铁电忆阻器, 能够实现电阻开关特性。重要的是, 该器件能够实现多级存储的稳定特性, 具有应用于多级存储的潜力。同时通过调控铁电极化, 忆阻器的电阻可由铁电畴的翻转来逐步调节。同时, 我们可以获取具有双向连续可逆性的多个电阻状态, 这类似于神经突触权重的变化。我们还成功模拟了生物学突触功能, 例如长期抑制, 长期促进, 双脉冲易化和尖峰时间依赖可塑性。因此, 该器件是一种有希望突破冯·诺依曼框架的候选者。