Controlling Resistance Switching Performances of Hf$_{0.5}$Zr$_{0.5}$O$_2$ Films by Substrate Stress and Potential in Neuromorphic Computing

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Ferroelectric Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO) thin films have attracted wide attention in terms of potential applications of nonvolatile ferroelectric memories. However, the effect of strain on the resistance switching characteristics of the ferroelectric HZO thin-film memristors has not been fully studied so far. In this work, the strain effects on the HZO thin-film memristors are investigated. HZO films with different resistance properties are also prepared by controlling the value of oxygen pressure. Based on the testing results, it is proposed that the resistance switching behavior of HZO films may be caused by the joint participation between ferroelectricity and oxygen vacancy migration. The study also found that HZO films can successfully simulate learning behavior similar to the human brain. The applied pulses with a width of tens of nanoseconds timescale are beneficial to realize fast learning and computing. These results provide a fundamental and deep insight on HZO-based ferroelectric semiconductor oxide thin-film memristors and their potential applications in next-generation artificial electronic synaptic devices.

1. Introduction

Neuromorphic computing, or brain-inspired computing, integrating electronic devices which emulate the electrical behavior of neural networks, has emerged as a new strategy with great potential to enable information processing at a low energy cost.$^{[1,2]}$ Ferroelectric materials, in which spontaneous polarization are switchable, are ideal candidates for the basic active electronic devices due to their excellent resistive switching properties and biosynaptic simulation capabilities.$^{[3-6]}$ By electrically modulating the potential barriers associated with polarization reversal, resistive switching in ferroelectric thin films can be achieved.$^{[5-10]}$ In addition, spontaneous polarization and domain switching are closely related to strain in ferroelectric thin films.$^{[11]}$ To date, the intensely studied materials are BaTiO$_3$ and PbZr$_x$Ti$_{1-x}$O$_3$ and it has been reported that the ferroelectric properties of the two ferroelectric films are affected by strain.$^{[12-16]}$ However, due to their complex structure and difficulty to expand, these materials are difficult to integrate into the current semiconductor technology. Lead-free ferroelectric HfO$_2$-based thin films to provide a broad new prospect in this field because of their excellent properties, chemical simplicity, complementary metal–oxide–semiconductor (CMOS) compatibility, and strong ferroelectric properties even if the ultrathin thickness is less than 10 nm.$^{[17-20]}$ Very recently, Hafnia-based thin films (Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO)) stand out due to its robust ferroelectric polarization even at the ultrathin limit and excellent compatibility with silicon devices.$^{[21-23]}$ It is necessary to study how strain would affect HZO ferroelectric memristor and the corresponding resistive switching process.

Furthermore, defects such as oxygen vacancies are often present in ferroelectric oxide thin films.$^{[24]}$ Theoretically, the vacancy generation ($G$) in the resistive process obeys the following relationship$^{[25]}$

$$G = G_0 e^{-\frac{E_a + \beta E}{K_b T}}$$  \hspace{1cm} (1)$$

where $K_b$ is Boltzmann constant, $T$ is Kelvin temperature, $G_0$ and $\beta$ are fixed constants, $E_a$ and $E$ are defect activation energy and electric field strength, respectively. In addition, oxygen partial pressure during deposition affects the crystal structure, charge transport properties, and ferroelectricity of the film.$^{[26,27]}$
Therefore, the coexistence of oxygen vacancy migration (OVM) and ferroelectricity are expected in a memory, which has been reported recently.\cite{24,28–31}

In this work, strain induced by different substrates on HZO films memristors were studied and the related epitaxial properties of HZO films were reported in previous work.\cite{32} Three different substrates were chosen: LaAlO$_3$ (LAO), (La,Sr)(Al,Ta)O$_3$ (LSAT), and SrTiO$_3$ (STO). HZO layer was sandwiched between Pd and LaSrMnO$_3$ (LSMO), which were the top and bottom electrodes, respectively. The deposition details can be found in the experimental part. The ferroelectric properties were studied by Piezoresponse force microscopy (PFM). In addition, Pd/HZO/LSMO/LAO devices grown with different oxygen pressures were prepared. Based on the testing results, it is proposed that the resistance switching behavior of HZO films may be caused by the joint participation between ferroelectricity and oxygen vacancy migration, which is consistent with the conclusions of related reports.\cite{30} More importantly, this study showed that the HZO devices can emulate learning behaviors similar to the brain, such as spike-timing-dependent plasticity (STDP), and paired-pulse facilitation (PPF). It is expected that these experimental results can promote the research of HZO films memristors and promote their application in electronics.

2. Results and Discussion

First, two characteristic peaks belonging to m(111) and o(200) planes of HZO\cite{33} films grown on three different substrates are identifiable in Figure 1a–c, indicating that HZO films can be crystallized under the same film growth conditions. The crystallinity of the orthorhombic phase of HZO thin films in different devices can be roughly calculated by formulas:

\[
R = \frac{A}{A + B},
\]

where \(A\) is the orthorhombic phase intensity and \(B\) is the monoclinic phase intensity. It can be known from the calculation that the orthorhombic crystal orientation intensity ratios of the devices based on LAO, LSAT, and STO substrate are 0.432, 0.382, and 0.361, respectively, as shown in Table S1, Supporting Information. It can be shown that the HZO/LSMO/LAO device has relatively excellent orthorhombic crystallinity of HZO thin film. Next, substrate-induced strains were investigated. It is known that lattice mismatch between substrate and thin film could induce strain during film growth. The lattice misfit \(\varepsilon\) is commonly defined as:

\[
\varepsilon = \frac{a_{\text{sub}} - a_{\text{film}}}{a_{\text{film}}},
\]

where \(a_{\text{sub}}\) and \(a_{\text{film}}\) are the bulk values of the lattice parameters of the substrate and thin-film material, respectively. The lattice mismatch between LSMO thin film and different substrates has been calculated as shown in Table S2, Supporting Information. The lattice
parameters for substrates are the same as in the previous case and it has been explained that LSMO can be fully strained to the substrate.\cite{12} Apparently, HZO films grown on LAO and LSAT substrates are under different strains. It is worth noting that the previous work has shown that our HZO films are completely relaxed with respect to the substrate and LSMO layer, so the strain effect should apply equally to HZO film.\cite{12}

Figure 1d,e demonstrated the PFM phase and amplitude hysteresis loops. The coercive voltage ($V_c$) is represented by the two minimum values in the amplitude loop. $V_c$ for HZO/LSMO/LAO device are 1 and $-1.8$ V, $V_c$ for HZO/LSMO/LSAT device are 0.2 and $-1.6$ V, and $V_c$ for HZO/LSMO/STO device are 0 and $-1.5$ V. The strain dependence observed in Figure 1d,e is in good agreement with previous work,\cite{14–16} where the value of $V_c$ in HZO film is affected by different strains. In addition, it can be seen that the PFM phase hysteresis loop of the HZO/LSMO/LAO device shows the relatively sharpest ferroelectric switch of 180°, which indicates that the device can have better ferroelectricity and reversible polarization switch.\cite{37} and the ferroelectricity of the device is further confirmed in Figure S1, Supporting Information. In this study, the device with LAO as the substrate has a relatively better ferroelectric performance because the stress caused by the lattice mismatch between LSMO/LAO can make the crystallinity of the orthorhombic phase of the HZO/LSMO/LAO device increased under our experimental conditions. Because it is known that the origin of the ferroelectricity of HZO films is the orthorhombic phase\cite{38} and the strain caused by the larger lattice mismatch in a certain range may be conducive to the enhancement of thin-film ferroelectric properties.\cite{12–16} Figure 1f–k show the PFM phase and amplitude images for $-3$ and $+3$ V polarizations on regions of $2 \times 2 \mu$m$^2$ and $1 \times 1 \mu$m$^2$, respectively. The results show that the polarization direction of the unpolarized region is the same as that of the $+3$ V region, which indicates that the pristine HZO film has a preferred downward polarization.

Figure 2a–c represents the $I$–$V$ curves of Pd/HZO/LSMO/S, where S denotes different substrates. For Pd/HZO/LSMO/LAO, the switching voltage distribution is concentrated and the $I$–$V$ curves window is larger, which indicates good information storage. In contrast, the switching voltage distribution of the other two devices is scattered and the $I$–$V$ curves window is smaller, which indicates poor memory of the devices. The better ferroelectricity of the HZO/LSMO/LAO device may be beneficial to the storage performance of the device, which is consistent with previous reports.\cite{15} Figure S2 and S3, Supporting Information, are statistics of HRS/LRS and switching voltage of HZO thin-film devices with different substrates, respectively.

Now we look into the oxygen partial pressures during film growth. Figure S4, Supporting Information, shows the XRD pattern of the HZO film grown under different oxygen pressures and the results indicate that the device prepared under the oxygen pressure of 13 Pa has the best crystallinity. Figure 3a,b shows PFM phase and amplitude hysteresis loops of HZO/LSMO/LAO devices grown under different oxygen pressures. It can be seen that the device has relatively good ferroelectricity under 13 Pa oxygen pressure, which is consistent with the above XRD test results. Figure 3e,f shows 100 consecutive cycles of the $I$–$V$ characteristics of HZO/LSMO/LAO devices grown under 0.5 and 26 Pa oxygen pressures. In general, during the film deposition process, the lower the oxygen pressure is, the more oxygen vacancies\cite{39–41} At the same time, there are reports that more oxygen vacancies will enhance the mobility of oxygen ions, which may become a favorable condition for resistance switching properties.\cite{39,42} However, Figure 3c and 3e,f shows that the resistance switching characteristics of the devices grown under the lowest oxygen pressure are not enhanced (compared with the device under 0.5 Pa oxygen pressure, the switching characteristics of the device under 13 Pa oxygen pressure are better), indicating that apart from oxygen vacancies, there may be other factors. It can reasonably be inferred that the RS behavior of the devices may be caused by the synergy between ferroelectricity and oxygen vacancies, which is consistent with what has been reported.\cite{39} Figure 3d,g,h shows the amplitude and phase images upon electrical poling of $+3$ V at $1 \times 1 \mu$m$^2$ region and $-3$ V at $2 \times 2 \mu$m$^2$ region of HZO films grown on LAO under the oxygen partial pressures of 0.5 Pa, 26 Pa, respectively, which can also indicate that the pristine HZO film has a preferred downward polarization.

Figure S5, Supporting Information, shows the high and low resistance of 100 sets of the resistive cycle of Pd/HZO/LSMO/LAO devices grown under different oxygen pressures. Compared with the low resistance value, the high resistance value has more sharp feedback on the change of oxygen partial pressure. With the increase in oxygen pressure, and the initial film resistivity increases and the corresponding high resistance value also shows an increasing trend. To compare more clearly the dependence of different switching voltages on oxygen pressure, Figure S6, Supporting Information, shows switching voltages with different oxygen partial pressures. Both Figure S5 and S6, Supporting
Information, show that HRS and V_{set} exhibit the same trend, and both increase with increasing oxygen partial pressure. From Equation (1), it is easy to infer that the generation of defects is affected by the electric field. The switch from HRS to LRS requires defects assisted oxygen vacancy migration inside the film induced by V_{set}. Therefore, a higher HRS requires a stronger electric field, i.e., a larger V_{set} value.

Several models have been reported to explain the ferroelectric and semiconductor characteristics induced ferroelectric resistive switching (FE-RS) effects.\textsuperscript{[44]} To better understand the bipolar resistance switching in Pd/HZO/LSMO/LAO, linear fitting curves of \(\log(I) - \log(V)\) are depicted in Figure 4a. The change in slope can be separated into two stages. As the applied positive bias increases, the slope of the HRS first changes from 1.11 to 1.90, which can be explained by the space charge limited current (SCLC) mechanism of the injection process. Then, the slope becomes 7.39, indicating that injected electrons quickly occupy the shallow traps. The high bias portion almost reaches the region of Child’s law (\(I \propto V^2\)).\textsuperscript{[45]} So SCLC model for \(I-V\) curve of the HRS part may be applicable to our observations, which is consistent with previous reports.\textsuperscript{[45-48]} As shown in Figure 4b, the \(I-V\) curve of the LRS part can be fitted as a functional formula: \(I = A \sinh(BV)\), where the fitting constants \(A = 0.43\) and \(B = 3.55\). This functional relationship is consistent with the characteristics of the electron-tunneling model.\textsuperscript{[49,50]} In addition, the RS process is understood by the schematic diagram of the device resistance switching process under positive voltage shown in Figure 4c.d. When a positive voltage is applied to the top Pd electrode, the width of the depletion layer and the barrier height of the bottom HZO/LSMO interface will be reduced due to the downward polarization,\textsuperscript{[50]} so that the device is in the LRS state. In contrast, a negative voltage applied to the top electrode will cause upward polarization and a depleted charge region will appear in the LSMO region. This will cause the height and width of the barrier at the bottom interface to increase,\textsuperscript{[30]} so the device is in the HRS state. At the same time, when a positive voltage is applied to the device, positively charged oxygen vacancies migrate from the HZO film to the HZO/LSMO interface. With the accumulation of oxygen vacancies at the interface, the barrier height also decreases.\textsuperscript{[30]} The electrons can easily tunnel through the interface barrier, and the device is thus located at LRS. When a reverse voltage is applied, this process is reversed, the oxygen vacancies are pulled away from the HZO/LSMO interface and returned to the inside of the HZO film, the HZO/LSMO interface barrier is restored,\textsuperscript{[30]} and the device returns to HRS. It is worth noting that when the device is in an LRS state, the Schottky barrier is narrower and lower and the electrons can easily tunnel,\textsuperscript{[50,51]} which is in good agreement with the electron-tunneling model as shown in Figure 4b. In addition, there is a report that the reduction of the barrier height is caused by polarization and the further reduction is driven by the accumulation of oxygen vacancies,\textsuperscript{[52]} which further confirms the rationality of our proposed model that ferroelectricity and oxygen vacancies jointly adjust the interface barrier to cause resistance switching of the memristor.

Plasticity is an important factor in biology\textsuperscript{[53]} and STDP is a form of the Hebbian learning rule that changing the time interval between presynaptic and postsynaptic peaks can change the synaptic weight.\textsuperscript{[54]} Here, the interval between the terminal of the pre-synaptic (post-synaptic) spike and the beginning of the post-synaptic (pre-synaptic) spike can be defined as \(\Delta t\).\textsuperscript{[54]} To reproduce the STDP behavior, we used a pair of pulses with an amplitude of 5 V with different \(\Delta t\) ranging between 300 and 0 ns. The HZO films performed long-term potentiation (LTP) and long-term depression (LTD) and realized the STDP function\textsuperscript{[54]} as shown in Figure 5a. The STDP behavior can be simplified by the exponential function in the mathematical model: \(W = A \times e^{(-\Delta t/\tau)}\), where \(A\) and \(\tau\) represent the scale
factor and time constant in the STDP function, respectively.\textsuperscript{[55,56]} In this study, $A = 81.93$ and $\tau = 62$ ns, respectively. $\Delta W$ is a constant that represents the nonlinear component of synaptic changes. Therefore, it can be reasonably concluded that the study successfully simulated the STDP behavior of biological synapses, which is consistent with other work.\textsuperscript{[37]} The type of STDP forms is demonstrated by applying programmed pre- and post-spiking pulse pairs in different interval time windows between 300 and 0 ns, which is undoubtedly much faster than the speed of STDP in the human brain (about $10^5$ times) and other ferroelectric memristors (as shown in Table S3, Supporting Information).\textsuperscript{[32,58–61]} Therefore, the ferroelectric memristor based on HZO thin films presents a promising potential in ultrafast neuromorphic chips application.

Furthermore, when a neuron is subjected to two consecutive stimuli, the PPF phenomenon refers to an increase in the synaptic weight upon reducing the interval between two consecutive potentiating pulses.\textsuperscript{[62]} Figure 5b shows that the sample successfully simulated the PPF phenomenon. The formula for PPF is as follows.
PPF = \frac{G_2 - G_1}{G_1} \times 100\% = C_1 \times e^{\tau_1} \times C_2 \times e^{\tau_2} \tag{2}

G_1 and G_2 represent the conductance of the device after the first and second pulses, respectively.\[^{[54]}\] Similar to the characteristic relaxation times observed in biological synapses, the two fitting time constants (\(\tau_1\) and \(\tau_2\)) correspond to fast and slow decay terms, respectively. In this study, \(\tau_1\) is 5.2 ns and \(\tau_2\) is 137 ns. It can be concluded that shortening the pulse interval can improve the storage property of the HZO film devices, which is consistent with the biological synaptic function realized by controlling the pulse pair. The PPF behavior is successfully simulated in our samples, which is consistent with the reported results.\[^{[35,56,63]}\]

Similar to biological synapses, spike parameters (such as pulse amplitude, width, and interval) will affect the conductance modulation of HZO films under an electric field. In the experimental samples, nanosecond positive pulses were used for modulation. The device pulse test circuit diagram is shown in Figure S7a, Supporting Information. First, the influence of the amplitude of the pulse train on the resistance is studied when the pulse train is applied to the sample. In this work, the pulse width and interval are 50 and 50 ns, respectively. Figure S7b, Supporting Information, shows the dependence of the sample resistance on the pulse amplitudes. As we increase the positive pulse amplitudes, the resistance changes faster. Then we studied the effect of pulse width on HZO films. The 40, 50, and 60 ns wide voltage pulse were applied to the device with a fixed 6 V amplitude and 50 ns interval. The relationship between device conductance and pulse width is shown in Figure S7c, Supporting Information. For both potentiating and depressing processes, as the pulse width increases, the device conductance changes faster. Finally, this study demonstrates how the pulse interval tunes the memristor conduction. The intervals of voltage pulses are 40, 50, and 60 ns, with a fixed 6 V amplitude and 50 ns width. As shown in Figure S7d, Supporting Information, the increase in pulse interval leads to less conduction variation in potentiating and depressing processes. It is worth noting that as the number of pulses increases, the current becomes saturated, which is consistent with the biological synaptic weight modulation.\[^{[64]}\] In the neuromorphic system, continuous learning increases the weight of synapses, but the inherent limitation of the modulation Hebbian rule leads to limited values of synaptic weights. In summary, the result is that the spikes in the pulse train will sustain synaptic stimulation but the conduction has reached saturation.\[^{[65]}\]

### 3. Conclusions

In summary, the polarization inversion voltage and storage performance of HZO thin-film memristor differ due to different substrate strains. The results indicated it is necessary to further study the effect of strain on composite oxide ferroelectric thin-film memristors to design excellent memory devices. It can be reasonably concluded that the RS behaviors for HZO-like ferroelectric semiconducting oxide films can be due to the joint participation of ferroelectric and VO\(_x\). This study showed that the HZO films can also simulate learning behaviors similar to the brain, such as STDP and PPF, and so on. Moreover, the device can achieve fast learning and computing speed by applied pulse with tens of nanosecond timescale. These results can help promote basic research on HZO-based ferroelectric semiconductor oxide thin-film memristor and their potential applications in next-generation artificial electronic synaptic devices.

### 4. Experimental Section

For Pd/HZO/LSMO/S devices, where S stands for different substrates: LAO, STO, and LSAT, LSMO (10 nm) was grown at 750 \(^\circ\)C under the oxygen pressure of 26 Pa, followed by HZO (10 nm) prepared at 450 \(^\circ\)C and oxygen pressure of 13 Pa. The film was then cooled down to room temperature in a pure oxygen environment at 130 Pa. The laser luminous flux was 1.25 J cm\(^{-2}\) and the repetition frequency was 3 Hz. At last, the diameter of 90 \(\mu\)m of Pd electrodes was deposited on HZO using a shadow mask by magnetron sputtering under the Ar pressure of 1.0 Pa. For Pd/HZO/LSMO/LAO samples grown under different oxygen pressures, oxygen pressures of 0.5, 13, and 26 Pa were used, respectively.

**Supporting Information**

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

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\), oxygen vacancies, resistance switching, substrate stress, synaptic bionics

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