Supporting Information

HfO$_x$/AlO$_y$ Superlattice-Like Memristive Synapse

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1. The binary switching behavior of HfO$_x$-based memristor

![Graph](image)

**Figure S1.** Long-term synaptic plasticity of Ti/HfO$_x$/TiN memristor. The device was programmed by 50 depression pulses of -1.3V (100ns) for the LTD process and 50 potentiation pulses of 1.4V (100ns) for the LTP process. An abrupt switch occurred during the LTD process.
Figure S2. Schematic illustration of the dynamic evolution of V<sub>O</sub> CFs for Ti/HfO<sub>x</sub>/TiN memristor under the continuous programming pulses. a) Post-Forming state, there is a robust CF formed during the forming process. b) There is a large gap formed between the top electrode (TE) and CF after the application of the first RESET pulse, which is corresponding to the abrupt decrease of conductance with the first RESET pulse applied as shown in Figure S1. c) d) Once the large gap formed, the following RESET pulses are hard to enlarge it and the decrease of conductance will be slower. Thus, the linearity of LTD for the Ti/HfO<sub>x</sub>/TiN memristor is non-ideal. For the LTP process, e) after the first SET pulse is applied, a weak CF will form between the residual robust CF and TE and the conductance will increase gradually. f) g) h) With the subsequent series of SET pulses applied, the width of the weak CF will increase until becomes a strong CF again and the conductance will increase gradually at the same time.
2. Calculation of $V_0$ formation energy

**Figure S3.** Primitive cell structures of 6 common binary metal oxide memristive materials. a) Structure of m-HfO$_2$. b) Structure of m-ZrO$_2$. c) Structure of $P4_2/mnm$-TiO$_2$. d) Structure of $P6_3mc$-ZnO. e) Structure of $R̅3c$-Al$_2$O$_3$. f) Structure of $γ$-phase Ta$_2$O$_5$. 
Figure S4. $V_0$ formation energy of 6 binary metal oxide memristive materials, where HfO$_2$, Ta$_2$O$_5$ and ZrO$_2$ own oxygen vacancies with different positions.

To screen out the suitable combination of materials for SLL switching layer, the $V_0$ formation energies of 6 common binary metal oxide memristive materials were calculated, including m-HfO$_2$, m-ZrO$_2$, TiO$_2$, ZnO, Al$_2$O$_3$, and $\gamma$-phase Ta$_2$O$_5$, as described in Figure S3. The $V_0$ formation energy represented the difficulty of generating $V_0$ in the oxide materials, which can partly reflect the difficulty of $V_0$ migration. The $V_0$ formation energy was calculated by the Vienna Ab initio Simulation Package (VASP), where the generalized gradient approximation (GGA) was used for the exchange-correlation energy, within the Perdew–Burke–Ernzerhof (PBE) functional. For each structure, a supercell of at least 10Å×10Å×10Å was established for the calculation of $V_0$ formation energy. A constant 500 eV plane-wave kinetic energy cutoff was used throughout the calculations. The valence electron configurations are 5p, 5d and 6s for Hf and Ta, 3s and 3p for Al, 3p, 3d and 4s for Ti, 3p and 3d for Zn, 4s, 4p, 5d and 5s for Zr, 2s and 2p for O. In the self-consistent calculation, the convergence precision
of the total system energy is less than $10^{-6}$ eV/Å. The V-O formation energy is calculated from equation S1:

$$E_f = (E_v - E_p) + \mu_O$$  \hspace{1cm} (S1)$$

where $E_f$ represents the formation energy of V-O, $E_v$ is the energy of a supercell with an V-O, $E_p$ is the energy of a supercell without V-O, and $\mu_O$ is the chemical potential of oxygen atom (-4.96 eV).\cite{1}

The calculated results are presented in Figure S4, where $E_f(\text{Al}_2\text{O}_3)>E_f(\text{HfO}_2)>E_f(\text{ZrO}_2)>E_f(\text{Ta}_2\text{O}_5)>E_f(\text{TiO}_2)>E_f(\text{ZnO})$, consistent with the previous reports.\cite{2, 3} Hence, if we choose HfO$_2$ as the basic resistive switching material, only Al$_2$O$_3$ can be used as the barrier layer. According to the calculated results, Al$_2$O$_3$ is suitable to be used as a barrier layer for its highest $E_f$, and the blocking effect would be more significant when combined with the materials with lower $E_f$ such as TiO$_2$ or ZnO.

3. Composition Optimization of HfO$_x$/AlO$_y$ SLL film

![Figure S5](image)

**Figure S5.** Forming process comparison of thick SLL memristor (4 cycles of 15 atomic layers of HfO$_x$ and 5 atomic layers AlO$_y$) and thin SLL memristor (13 cycles of 3 atomic layers of HfO$_x$ and 1 atomic layer AlO$_y$). a) Post-forming state of two memristors, the thick SLL memristor is prone to thermal breakdown during the forming process. b) Forming process comparison, the initial resistance of thick SLL memristor is 6 orders of magnitude higher than that of thin SLL memristor, in addition, the forming voltage of thick SLL memristor is about 4.8V and that of thin SLL memristor is 1.25V.
Figure S6. Multi-level resistance comparison of SLL memristor with different HfO$_x$/AlO$_y$ SLL film compositions. a) SLL device with 5 cycles of 9 atomic layers of HfO$_x$ and 1 atomic layer AlO$_y$, b) 5 cycles of 9 atomic layers of HfO$_x$ and 2 atomic layers AlO$_y$, c) 4 cycles of 12 atomic layers of HfO$_x$ and 1 atomic layer AlO$_y$.

According to the optimization results, when the thickness of AlO$_y$ barrier layers is thick, the initial resistance and forming voltage ($V_F$) of the SLL memristor will become too high, the $V_F$ close to 5V is adverse for the integration of transistors. Meanwhile, the high $V_F$ also increases the possibility of thermal breakdown during the forming process, as shown in Figure S3. When the thickness of AlO$_y$ layers decreases to only one atomic layer, the forming voltage will be reduced to 1.25 V and the device is less prone to thermal breakdown. In addition, reducing the thickness of AlO$_y$ layers can decrease the $V_F$, and increasing the number of cycles can improve the number of conductance states, which are consistent with our design expectation. As illustrated in Figure S4 there are trip points for the SLL memristors with thick HfO$_x$ layers and thin AlO$_y$ layers. When the composition of HfO$_x$ is much higher than that of AlO$_y$ and each AlO$_y$ layer is just one or two atomic layers, the ability of AlO$_y$ barrier layers to regulate the CFs will be weakened leading to the abrupt switching behavior.
4. Atomic concentration of HfOₓ/AlOᵧ SLL film and HfOₓ film

**Table S1.** The atomic concentration of HfOₓ/AlOᵧ SLL film and HfOₓ film

| Atomic Concentration% | Hf   | Al   | O    | C     |
|----------------------|------|------|------|-------|
| (HfOₓ/AlOᵧ)ₜ𝑖𝑛/TiN | 24.96| 15.25| 58.12| 1.67  |
| HfOₓ/TiN            | 37.53| 0    | 58.97| 3.49  |

X-ray photoelectron spectroscopy (XPS) spectra were obtained with AXIS-ULTRA DLD-600W equipment to determine chemical binding states and atomic ratio of different elements in HfOₓ/AlOᵧ SLL film and HfOₓ film. The binding energy was calibrated with the position of the C1s peak at 285 eV. As shown in **Table S1**, the atomic ratio of Hf and Al is about 5:3 in HfOₓ/AlOᵧ SLL film, and both these two films are non-stoichiometric which means there are numbers of Vₒ formed in the as-deposited film.

**Figure S7.** The element profile along the thickness direction of (30HfOₓ/10AlOᵧ)ₓ5 layer by EDX analysis.
Figure S8. a) The element profile along the thickness direction of the HAO SLL memristor, by energy dispersive X-ray spectroscopy (EDX) analysis. b) EDX mapping of HAO SLL memristor.

EDX line scanning and mapping were employed to check the element distribution in the HfO<sub>x</sub>/AlO<sub>y</sub> SLL memristor and stratification of HfO<sub>x</sub>/AlO<sub>y</sub> SLL film, results are shown in Figure S7, S8.
5. Operating speed of HfO$_x$/AlO$_y$ SLL memristor

**Figure S9.** Resistance of HfO$_x$/AlO$_y$ SLL memristor versus the voltage pulse amplitude and width, a) and c) are reset process, b) and d) are set process. The inset shows the waveform of the applied pulse.

By applying a series of voltage pulses with increasing amplitude or width, we further investigated the response of HfO$_x$/AlO$_y$ SLL memristor to V pulse. **Figure S7a, b** show the response of resistance to increasing amplitude $V_{\text{pulse}}$ with a fixed pulse width of 10ns, which means that the operating speed of the memristor is $\leq$ 10ns. **Figure S7c, d** show the response of resistance to increasing width $V_{\text{pulse}}$ with a fixed pulse amplitude of 2.5V, which means that the operating power consumption of the memristor is <0.25nJ.
Table S2. Comparison of main performance indicators between this work and memristive synapses with fixed programming pulse

| Type of memristive synapses | Program time/spike | LTP nonlinearity | LTD nonlinearity | Retention | Reference |
|-----------------------------|-------------------|-----------------|-----------------|-----------|-----------|
| LiSiOx                      | 200ns             | 1.03            | 4.58            | $10^4s@125^\circ C$ | [4]       |
| PCMO                        | 100$\mu$s         | 5.5             | 4               | N/A       | [5]       |
| Ag/GeSe                     | 60$\mu$s          | N/A             | N/A             | $3 \times 10^3 s@25^\circ C$ | [6]       |
| AlOx/TaOx                   | 10$\mu$s          | N/A             | N/A             | $10^4s@25^\circ C$ | [7]       |
| TaOx/Al$_2$O$_3$            | 10$\mu$s          | 2.41            | 2.77            | $10^4s@25^\circ C$ | [8]       |
| TaOx/TiO$_2$                | 40ms              | 0.66            | 0.69            | N/A       | [9]       |
| Ag:a-Si                     | 300$\mu$s         | 2.4             | 4.88            | N/A       | [10]      |
| OCG-HfOx                    | 100ns             | N/A             | N/A             | $10^4s@85^\circ C$ | [11]      |
| Al:HfO$_2$                  | 100$\mu$s         | 1.94            | 0.61            | $10^4s@120^\circ C$ | [12]      |
| ETML/HfOx                   | 50ns              | 0.04            | 0.63            | $6 \times 10^3 s@125^\circ C$ | [13]      |
| HfOx/AlO$_y$ SLL            | 30ns              | 1.06            | 5.43            | $10^4s@85^\circ C$ | This work |

This work
6. Calculation results of bonding for HfOx/AlOy SLL film

![Diagram of bonding at the interface of HfOx layer and AlOy layer.](image)

**Figure S10.** Differential charge density at the interface of the HfOx layer and AlOy layer.

To investigate the bonding situation at the interface of the HfOx layer and AlOy layer, we established an interface model between HfOx layer and AlOy layer and calculated the differential charge density at the interface. **Figure S8** shows the *ab initio* calculation results, compared with Hf atoms, Al atoms at the interface have stronger electron-withdrawing ability and the Al-O bond has higher bond energy than the Hf-O bond, which is consistent with the XPS results as shown in **Figure 2b,c.**
7. Fitting results of conduction mechanism

**Figure S11.** Conduction mechanism fitting results of HfO$_x$/AlO$_y$ SLL memristor. a) LRS of SET process (0~0.2 V) follows Ohmic conduction. b) LRS of the SET process (0.2~0.6 V) follows Schottky conduction. c) LRS of SET process (0.6~0.8 V) follows SCLC. d) LRS of RESET process (0~0.1 V) follows Ohmic conduction. e) LRS of RESET process (-0.1~0.6 V) follows Schottky conduction. f) LRS of RESET process (-0.6~0.8 V) follows SCLC. g) HRS of SET process (0.1~0.8 V) follows Poole-Frenkel emission. h) HRS of RESET process (-0.2~1.2 V) follows Poole-Frenkel emission.

Fitting expression of conduction mechanisms$^{[14]}$:

**Schottky Emission:** \( I_{SE} = \alpha T^{3/2} E \mu \left( \frac{m^*}{m_0} \right)^{3/2} \exp \left[ -q \left( \phi_B - \sqrt{qE/4\pi\varepsilon} \right) / kT \right] \) \( \ln I \propto V^{1/2} \) (S2)

**Poole-Frenkel Emission:** \( I_{PF} = q \mu N_c \exp \left[ -q \left( \phi_T - \sqrt{qE/4\pi\varepsilon} \right) / kT \right] \ln(I/V) \propto V^{1/2} \) (S3)

**Space-charge-limited Conduction (SCLC):** \( I_{SCLC} = \frac{q}{\theta} \varepsilon_i \mu \theta \frac{V^2}{d^3} \ln I \propto \ln V \) (S4)
Ohmic Conduction: \[ J_{ohmic} = \sigma E = q \mu N_c E \exp \left( \frac{-(E_c - E_F)}{kT} \right) \ln I \propto \ln V \] (S5)

Figure S12. Conduction mechanism fitting results of HfO\(_x\) memristor. a) LRS of SET process (0~0.44 V) follows Ohmic conduction. b) HRS of SET process (0.143~0.44 V) follows Schottky conduction. c) LRS of RESET process (0~0.58 V) follows Ohmic conduction. d) HRS of RESET process (-0.14~1 V) follows Schottky conduction.

The piecewise fitting results show that, for LRS, there are numerous primary carriers in HfO\(_x\) switching layer leading to the Ohmic conduction, indicating the existence of robust CF. When it comes to HRS, the device follows Schottky emission conduction mechanism, which illustrates the drastic rupture of CF during the RESET process.
8. Migration energy of oxygen atoms in HfO\textsubscript{x}/AlO\textsubscript{y} SLL film

![Diagram](image)

**Figure S13.** Migration energy of oxygen atoms in HfO\textsubscript{x}/AlO\textsubscript{y} (3 cycles/1 cycles) SLL film. a) Atomic layers model of SLL switching layer with 3 HfO\textsubscript{x} cycles and 1 AlO\textsubscript{y} cycle. 3 different migration paths of oxygen atoms cross the AlO\textsubscript{y} layer in HfO\textsubscript{x}/AlO\textsubscript{y} SLL film, the migration process is divided into 3 steps of HfO\textsubscript{x}-AlO\textsubscript{y}-HfO\textsubscript{x}, and each path is constituted of 18 points. The migration energy of each step of oxygen atoms migrating along b) path 1, c) path 2, d) path 3. For each path, the migration barrier of oxygen atoms cross the AlO\textsubscript{y} layer is higher than that of the HfO\textsubscript{x} layers.
**Figure S14.** Migration energy of oxygen atoms in HfO$_x$/AlO$_y$ (3 cycles/3 cycles) SLL film. a) Migration paths of oxygen atom in the HfO$_x$/AlO$_y$ SLL film. (Path 1 is from interface to Al$_2$O$_3$, path 2 is from interface to HfO$_2$, path 3 is inside the Al$_2$O$_3$, path 4 and 5 are inside the HfO$_2$ with different coordination numbers.) b) The energy barrier to be overcome for oxygen atoms migrating along different paths in the HfO$_x$/AlO$_y$ SLL film.

Comparing these two SLL models, the migration energy of the film with 1 AlO$_y$ cycle is lower than that of the film with 3 AlO$_y$ cycles, especially for the energy to cross the AlO$_y$ layer. The reduction in migration energy is mainly due to the reduction in the thickness of AlO$_y$ layer, which enlarges the atom spacing of O at the interface because of the interface mismatch. The calculated results of the SLL model with 1 AlO$_y$ cycle demonstrated the blocking effect of AlO$_y$ layer and the speed advantage of the device, in the meantime, the stronger blocking effect of the thicker AlO$_y$ layer illustrated the reason for the higher operating voltage and the deteriorative performance of the corresponding device.
9. Calculation result of DOS for HfOx/AlOy SLL film

Figure S15. Electronic density of states for HfOx/AlOy (3 cycles/1 cycles) SLL film, where the red data is the density of state (DOS) of AlOy layer and the blue data is the DOS of HfOx layer. The abnormally tiny DOS for the "conduction band" at the AlOy layer actually reflects the impact of adjacent HfOx states, while the hide band gap of AlOy serves as a barrier for electron conduction.
10. Statistical analysis of device-to-device variation for HfO\textsubscript{x}/AlO\textsubscript{y} SLL memristor

**Figure S16.** Resistance statistical results of 15 independent HfO\textsubscript{x}/AlO\textsubscript{y} SLL memristor samples, and each cell was operated for 10 cycles. The mean value of LRS is 2.6 k\(\Omega\) and of HRS is 59.2 k\(\Omega\), the standard deviation of LRS (\(\sigma_{\text{LRS}}\)) is 1.1 k\(\Omega\) and \(\sigma_{\text{HRS}}\) is 7.8 k\(\Omega\). Due to the analog switching behavior, the distribution of resistance state is uneven.

**Figure S17.** DC characteristics of 5 HfO\textsubscript{x}/AlO\textsubscript{y} SLL memristor samples operated for 10 cycles, all the cells exhibited bidirectional analog switching behavior.
Figure S18. The device-to-device variation of HfO$_x$/AlO$_y$ SLL memristor’s conductance update, where the data of LTD and LTP process were acquired from 5 samples with the 30ns operating pulse. The mean coefficient of variation of LTD (CV$_{\text{LTD}}$) is 8.38% and the mean CV$_{\text{LTP}}$ is 12.08%, which were from calculating the CV of conductance corresponding to each pulse and averaging.

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