The Flexible Aluminum-doped Hafnium Oxide ferroelectric synapse device for neuromorphic computing

The supporting information includes:

Fig. S1 EDS mapping image of the Au/Ti/HfAlO/Pt/Ti/Mica devices.

Fig. S2 (a) and (b) PFM amplitudes and phase for the HfAlO thin films with -10 V and +10 V, respectively. (c) XPS survey spectra of the initial form of the HfAlO thin films.

Fig. S3 The effect of bending diameter of (a) 22 mm, (b) 15 mm, (c) 12 mm and (d) bending times of 500 times at bending diameter of 12 mm on the ferroelectric characteristics, respectively.

Fig. S4 Finite element analysis model of the devices.

Fig. S5 SEM images of HfAlO films bent diameter of (a) flat, (b) 22 mm (c) 15 mm and (d) 12 mm, respectively. SEM images of HfAlO films bent times of (e) 500 and (f) 1000, respectively.

Fig. S6 Stress as a function of bending diameter at the (a) path2, (b) path3, (c) path4 and (d) path5, respectively.

Fig. S7 (a) EPSC triggered by a pulse (3.5 V, 100 ns), (b) and (c) the relationship between response current and pulse width (pulse amplitude=3 V) and pulse amplitude (pulse width=100 ns), respectively. (d) LTP/LTD characteristics simulated by applying consecutive different pulses width.
Fig. S8 Average confusion matrix of training results under (a) 200, (b) 300, (c) 400, (d) 500, (e) 600, (f) 700, (g) 800 and (h) 1000th epoch, respectively.

Table S1 Comparison of flexible Hf-based ferroelectric devices

Table S2 Material parameter of modeling materials

S1 EDS mapping image of the devices.

Fig. S1 EDS mapping image of the Au/Ti/HfAlO/Pt/Ti/Mica devices.

Fig. S1 the cross sectional image of the Au/Ti/HfAlO/Pt/Ti/Mica ferroelectric tunnel junctions is clear. In order to obtain the element
distribution, energy dispersive spectrometer mapping images are used as the measurement method. The constituent elements of Hf, O, Ti, Au, Al and Pt are uniformly distributed in the films.

**S2 (a) and (b) PFM amplitudes and phase for the HfAlO thin films (c)**

XPS survey spectra of the initial form of the HfAlO thin films.

Fig. S2 (a) and (b) PFM amplitudes and phase for the HfAlO thin films with -10 V and +10V, respectively. (c) XPS survey spectra of the initial form of the HfAlO thin films.

To demonstrate the presence of the ferroelectric characteristics in the HfAlO thin films, the HfAlO films are observed by applying a large electrical field in PFM. As shown in Fig. 2S (a), the bright and dark regions indicated upward and downward ferroelectric polarization. The PFM images of the HfAlO films show uniform responses. Fig.2S (b) shows that the PFM response was equal for +P and –P poled regions with ~440° phase change, which shows the excellent ferroelectric characteristics. Fig. 2S(c) shows the XPS profiles of the HfAlO thin films with the Hf/Al cycle ratio of 34:1, which comprised Hf (16.5%), Al (1.7%) and O.
S3 The effect of bending diameter of and bending times on the ferroelectric characteristics, respectively

Fig. S3 The effect of bending diameter of (a) 22 mm, (b) 15mm, (c) 12mm and (d) bending times of 500 times at bending diameter of 12 mm on the ferroelectric characteristics, respectively.

Fig. S3 (a)-(c) show the P-E curves of the devices at bending diameter of 22, 15 and 12 mm, respectively. Fig. S3 (d) shows the P-E curves of the devices after 600 bending times at bending diameter of 12 mm.
Table S1 Comparison of flexible Hf-based ferroelectric devices with Mica substrates.

For the Hf-based ferroelectric devices, the film thickness is about 10 nm, as shown in Table S1. The bending times can reach $10^3$ times, which benefit for the high-density integration of flexible electronic devices.

S4 finite element analysis model of the devices

Fig. S4 finite element analysis model of the devices

To understand stress effects on the crack formation, the finite element studies are performed using the software ABAQUS. A two-dimensional model is built in consideration of the film stacked structure (see Fig. S4). The model assumes perfect bonding at the interface.
Table S2 material parameter of modeling materials

<table>
<thead>
<tr>
<th>materials parameters</th>
<th>HfAlO</th>
<th>Pt</th>
<th>Au</th>
<th>Mica</th>
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<tr>
<td>Poisson’s ratio (GPa)</td>
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<td>169</td>
<td>120</td>
<td>120</td>
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<tr>
<td>Elastic modulus</td>
<td>0.25</td>
<td>0.38</td>
<td>0.44</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table S2 the Elastic modulus and poisson's ratio for HfAlO thin films, Pt, Au and Mica.

As shown in Table S1, the elastic modulus of HfAlO, Pt, Au and Mica are 43, 169, 120 and 120 GPa, respectively. The poisson's ratio HfAlO, Pt, Au and Mica are 0.25, 0.38, 0.44 and 0.31, respectively.

S5 SEM images of HfAlO films different bent diameter

Fig. S5 SEM images of HfAlO films bent diameter of (a) flat, (b) 22 mm (c) 15 mm and (d) 12mm, respectively. SEM images of HfAlO films bent times of (e) 500 and (f) 1000, respectively.

As seen in Fig. S5, there is hardly any crack on the surface of unbent samples. When the bending diameters are 22 mm, Fig. S5(b) shows that irregular micro cracks appear on the surface. The cracks begin to form when the bending diameter is 15 mm (see the fig. S5(c)). With further
decrease in bending times, the films suffer from severe cracking problem, as shown in Fig. S5 (d). The formation and expansion of cracks may consequently affect the ferroelectric characteristics. With the increase of bending times, Fig. S5 (e) and (f) show that the crack further extend and reaches saturation.

**S6 Stress as a function of different bending diameter**

![Stress plots](image)

Fig. S6 Stress as a function of bending diameter at the (a) path2, (b) path3, (c) path4 and (d) path5, respectively. (e) Crack propagation path of the films.
Fig. S6(a) and (b) clearly show that the stress concentration is easily encountered round middle parts of the HfAlO films. When the devices are bent, the great stress causes the part films destroyed, i.e., the crack formation. However, the stress is smaller than that of Path1, which cannot be the crack formation. As the stress is transferred, the stress becomes smaller, which makes crack formation more difficult, as shown in Fig. S6 (c) and (d). As shown in Fig. S6(e), the stress concentration at the crack tip A may accelerate the crack propagation towards the substrate, generating the tensile region B. In the expansion process of tensile region, the crack spacing continues to increase and thus causes the fatigue fracture.

S7 (a) EPSC triggered by a pulse, (b) and (c) the relationship between response current and pulse width and pulse amplitude respectively. (d) LTP/LTD characteristics simulated by applying consecutive different pulses width
Fig. S7 (a) EPSC triggered by a pulse (3.5V, 100 ns), (b) and (c) the relationship between response current and pulse width (pulse amplitude=3 V) and pulse amplitude (pulse width=100 ns), respectively. (d) LTP/LTD characteristics simulated by applying consecutive different pulses width

Fig. S7 (a) shows the process of simulating short-term synaptic plasticity. EPSC was excited by an electric pulse with an amplitude of 3.5 V and a width of 10ns. A pulse applied to HfAlO devices resulting in a change in conductance. EPSC increased sharply and then gradually decreased after being stimulated, which corresponds to the performance of the HfAlO FTJs when subjected to a single stimulus. With the pulse width increasing from 50 to 250 nm, the EPSC of HfAlO FTJ increases from 50 to 200 pA (Fig.S7 (b)). For the voltage amplitude change, Fig. S7(c) shows the similar trend. Fig. S7 (d) shows that the synaptic weights
gradually increased and decreased, indicating HfAlO FTJ can contribute to the development of bioelectronics.

S8  Average confusion matrix of training results.

Fig. S8 Average confusion matrix of training results under (a) 200, (b) 300, (c) 400, (d) 500, (e) 600, (f) 700, (g) 800 and (h) 1000th epoch, respectively.

Fig. S8 shows the training progresses of HfAlO ferroelectric synapses. The diagonal color is changed into the yellow in the output matrix, and all patterns (“0-9”) are successfully identified, which demonstrate the great potential of the HfAlO artificial synapses in information processing.