nature portfolio

Peer Review File

Giant tunnel electroresistance through a Van der Waals junction by external ferroelectric polarization

Corresponding Author: Professor Bobo Tian

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This work proposes a novel memory device-vertical tunneling FeFET, in which the channel of a typical FeFET is replaced by a tunneling barrier formed by Van der Waals junction. The Fermi level of MoS_2 is bipolarly tuned by ferroelectric domains. Because the direct quantum tunneling strength across the junction is sensitive to the barrier shape that is affected by the Fermi level of MoS_2 “electrode”, the vertical tunneling FeFET yields a striking ON/OFF ratio up to 109. Furthermore, more than 20 distinct intermediate conductance states with a retention time of more than 1000 s are obtained, showing the potential for neuromorphic application.
The devices also exhibit ambipolar behavior and gate tunable operation states of output level, including positive-pass, OFF, negative-pass, and full-pass modes. These experimental results are understood well using the classical band alignment model. This work would provide readers a guidance for developing MoS_2-based reconfigurable devices.
The prototype vertical tunneling FeFETs proposed in this work will trigger great research enthusiasm for vertical tunneling channel-based memory. I would like to recommend this manuscript to be accepted for publication in Nature Communications with addressing the following issues.
1. All the output curves in the manuscript are extracted from the color mapping of transfer curves under different VDS. Have the output curves been measured under different constant gate voltages and are they consistent with the extracted data?
2. As seen in Fig. 1h, why the switching ratio for VDS=0.3 V is lower than that for VDS=-0.3 V?
3. Some abbreviations, such as Gr, are not provided with their full names. The author is requested to complete them for the convenience of the reader.
4. Some statements contain syntax errors, such as in line 200, “Figures 3d-i presents” should be “Figures 3d-i present”; in line 227, “remains towards” should be “remains toward to” and so on. Please review other similar instances in the article and make corrections accordingly.

Reviewer #2

(Remarks to the Author)
2D semiconductors are highly promising to be utilized in future transistors. So far, complementary logic components and underlying mechanisms for the polarity modulation still remain puzzling in the field, hampering design of high-performance devices. The present work is attempting to exploit and probe into ferroelectric domain-based nonvolatile modulation of Fermi level in MoS_2 and quantum tunnelling through nanoscale h-BN, which can lead to high electroresistance ratio in the vertical FeFET. The results in this work also show a novel way to design advanced ferroelectric memory. In general, the manuscript achieves the requirements of Nature Communications. However, in current version, there are several vital points that need to be clarified and corrected.

(1) There are no atomic-scale images that show the boundaries among MoS_2, graphene and BN. How do their boundaries influence the performance of the device? Did the authors control the stacking orientations of MoS_2, graphene and BN, or they just contacted randomly?

(2) What is the origin of the ferroelectricity in this device? From MoS_2 or BN? This is important for the understanding of the

underlying mechanism.

(3) For the application, devices should be stable. How about the stability of the device? Did the authors carry out the cycling test?

(4) In abstract and summary parts, the authors claim that "The Fermi level of MoS2 is bipolarly tuned by ferroelectric domains". However, there is not direct evidence showing bipolarization and the evolution process of ferroelectric domains under different electric fields.

(5) In Methods Part, there is no detailed information on MoS2 and h-BN. How did the authors obtain MoS2 and h-BN? Any further characterizations on MoS2 and h-BN? Since there are several different types of structures for MoS2 and BN, the authors should give more information on structures.

Reviewer #3

(Remarks to the Author)
The ambipolar field-effect characteristics are appealing because they enable a wide range of reconfigurable logic circuits. Experimental demonstrations of ambipolar field-effect behavior have been limited to a few 2D materials, such as MoTe2 and WSe2, while the ambipolar properties in the widely studied MoS2 remain unclear. In this manuscript, the authors demonstrated that both n-type and p-type characteristics can be achieved in the MoS2 channel via electrostatic control. The observed ambipolar field-effect characteristics in MoS2-FeFETs are well explained by a band alignment model. The experiments conducted are thorough, and the explanations provided are compelling. This study incorporates electrostatic control through non-volatile ferroelectric polarization, which introduces a memory effect in the MoS2-FeFETs. By designing a vertical tunneling barrier as the channel, the ferroelectric transistor device exhibits a large ON/OFF ratio of 10^9, making it attractive for memory applications. The manuscript is well-organized, with clear figure presentations. Below are some suggestions that may further enhance the quality of the manuscript.
1. Working mechanism: additional measurements and discussions are needed to make it more comprehensible.
1) In the vertical tunneling MoS2-FeFETs, tunnel electroresistance through the Van der Waals junction is achieved using an external ferroelectric gate. It is suggested to include a discussion comparing the ON/OFF ratio with the tunnel electroresistance that directly passes through the ferroelectric layer.
2) The modulation of the Fermi level in MoS2 plays a critical role in the resistive switching of the device. It is suggested to evaluate the change in the Fermi level of MoS2 induced by the ferroelectric domains.
3) In MoS2-based vertical tunneling FeFETs, the transfer curves demonstrate ambipolar performance, featuring a pronounced p-type branch at VDS = -0.3 V and a stronger n-type branch at VDS = 0.3 V. A more detailed explanation of this electrical behavior should be provided.

2. Performance limit:
1) In Figs. 1h and 1i, the authors present the transfer curves and retention characteristics of the MoS2-based vertical tunneling FeFET. While the authors state that "the ON/OFF ratio can reach up to 10^9," there appears to be only a three-order magnitude difference between the highest and lowest values in Figure 1i. I recommend that the authors include additional data to better demonstrate the performance limits.
2) The operating voltage of 30 V is quite high. What is the energy consumption for each operation at this voltage? From the perspective of potential practical applications, a lower operating voltage is preferable. How can you optimize your devices to achieve a smaller operating voltage?
3) The switching speed and stability are crucial for practical applications. Can the authors provide more data to illustrate these parameters?

3. Necessary comparison with the reported works
1) The ambipolar operation of MoS2 has been reported using an ionic liquid gate. It is recommended to include more discussion on the advantages of using a ferroelectric gate compared to the ionic liquid gate.

4. Some writing errors
1) In line 142, "+30V" should be changed to "+30 V," as there is typically a space between the numerical value and its unit. Please review the manuscript carefully and correct similar errors throughout.
2) Figures 2a and 3a-c contain redundant information. Please revise accordingly.
3) To maintain consistency, it is preferable to refer to "Schottky-contacted FeFET" as "asymmetric Schottky-contacted FeFET" from line 150 to line 170.
4) Reference numbers should be included in Fig. 5c to enhance the manuscript's accessibility.
5) Figures S9 and S10 clearly illustrate the full-pass, OFF to negative-pass transition, and the reverse process, respectively. The manuscript description needs to be updated to reflect this.
6) I have concerns regarding the arrangement and layout of Figures 4 and 5. First, Figure 4 appears cluttered and provides limited information. Second, I have difficulty distinguishing the differences between the left and right panels in Figures 5a and 5b. Please address these issues carefully.

Reviewer #4

(Remarks to the Author)
The paper presents a stack combining a ferroelectric and 2D materials to yield a novel transistor device design with

extremely high Ion/Ioff. The transistor uses ferroelectric polarisation to tune the Fermi level of the MoS2 channel material, while h-BN acts as an insulating barrier layer. This layer acts to enhance tunneling injection in the ON-state to improve current while acting to suppress current in the OFF-state. This is impressive and impactful work with a complete analysis of the ambipolar FETs showing a strong understanding of behaviour. I recommend publication. That being said there are some points that need to be addressed:

- The ferroelectric layer in these devices is very thick and yields a low polarisation. The material choice should be discussed. Other materials would help the scaling challenge. Applying +/-40V to switch a device is also not device-ready, a thinner ferroelectric would solve this.
- In reference to figure 1d, it is claimed that full 180degree phase contrast in the PFM image is observed. While I have no doubt this is ferroelectric, there seems to be less that 180degree switch. This could be explained by surface charging or some defect dipoles. Nevertheless, the combination of the amplitude and phase images are convincing without this claim.
- Whilst I agree that this is impressive work and promising for future devices, the repeated claims that these devices are promising for various applications including 'multibit memory and neuromorphic computing' are a little too ambitious. The ferroelectric of choice requires too high thickness for scaling, and high device operation voltage is needed. These statements need rewording to prevent misunderstanding.
- Figure 3 is not so clear, it would be helped by imrpoving the caption.
- Figure references need checking, some figures did not appear to exist.
- English quality needs to be improved.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all the concerns from this reviewer. I would like to recommend this manuscript for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)
The authors have addressed my concerns, so it is publishable on Nature Communications now.

Reviewer #3

(Remarks to the Author)
The authors addressed all the concerns. Therefore, I recommend to published in Nature Communications.

Reviewer #4

(Remarks to the Author)
All points from my first review have been addressed well, I would recommend publication while noting the following. Although voltage scaling of ferroelectric switching is well understood in the regime of 100-200nm thickness, within the useful thickness range (<20nm) for real devices, voltage scaling will undoubtedly not be linear with decreasing thickness. Interfacial strain and electrostatic boundary conditions play an increasingly dominant role, and can even increase the fields required for switching. Therefore, one should be extremely careful in stating "As shown in Fig. S13, the operating voltage decreases from 20 V for the device with a 200 nm-thick ferroelectric layer to 10 V for the device with 100 nm-thick ferroelectric layer" to imply that simply scaling thickness would work well in such a device.

Point-to-point reply letter

Response to the Reviewer #1's comments

General comments:

This work proposes a novel memory device-vertical tunneling FeFET, in which the channel of a typical FeFET is replaced by a tunneling barrier formed by Van der Waals junction. The Fermi level of MoS_2 is bipolarly tuned by ferroelectric domains. Because the direct quantum tunneling strength across the junction is sensitive to the barrier shape that is affected by the Fermi level of MoS_2 "electrode", the vertical tunneling FeFET yields a striking ON/OFF ratio up to 10^9. Furthermore, more than 20 distinct intermediate conductance states with a retention time of more than 1000 s are obtained, showing the potential for neuromorphic application.

The devices also exhibit ambipolar behavior and gate tunable operation states of output level, including positive-pass, OFF, negative-pass, and full-pass modes. These experimental results are understood well using the classical band alignment model. This work would provide readers a guidance for developing MoS_2-based reconfigurable devices.

The prototype vertical tunneling FeFETs proposed in this work will trigger great research enthusiasm for vertical tunneling channel-based memory. I would like to recommend this manuscript to be accepted for publication in Nature Communications with addressing the following issues.

Response: We appreciate Reviewer #1 for his/her comments on our manuscript. We did appropriate changes according to his/her comments. Below is a point-by-point reply to the questions raised by the Reviewer #1.

Comments 1-1: All the output curves in the manuscript are extracted from the color mapping of transfer curves under different V_{DS}. Have the output curves been measured under different constant gate voltages and are they consistent with the extracted data?

Response 1-1:

We thank Reviewer #1 for this valuable question. As seen in Fig. R1, the output curves of a vertical tunneling MoS_2-FeFET have been measured under different constant gate voltages (**Figs. R1a-c**) and they are consistent with the extracted data from transfer curves (**Figs. R1d-f**).

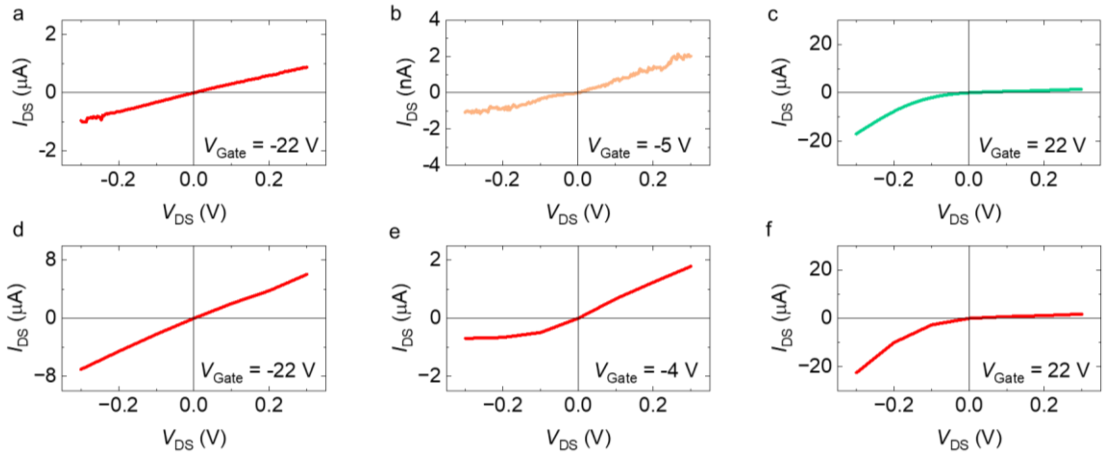

Fig. R1 a-c The output curves of a vertical tunneling MoS_2-FeFET measured under different constant gate voltages. **d-f** The extracted output curves from transfer curves that is shown in **Figs. S11c**, **d** and **f**, respectively.

Comments 1-2: As seen in Fig. 1h, why the switching ratio for V_{DS}=0.3 V is lower than that for V_{DS} =-0.3 V?

Response 1-2:

We thank Reviewer #1 for highlighting this important issue. The output curves on a semi-logarithmic scale of vertical tunneling MoS_2-FeFET are presented in **Fig. R2**, where maximum switching ratio occurs (i.e., V_{Gate} =3 V). The red and black lines correspond to downward (after V_{Gate} backward sweeping) and upward (after V_{Gate} forward sweeping) polarization states, respectively. Like the discussion of **Figs. 4c** and **4f** in our manuscript, the output curves in **Fig. R2** show np rectification for downward polarization and pn rectification for upward polarization. Given the inherent n-type nature of MoS_2, the output curve for downward polarization exceeds that for upward polarization, enabling a high switching ratio at negative V_{DS}, which reasonably explains the phenomena in **Fig. 1h**.

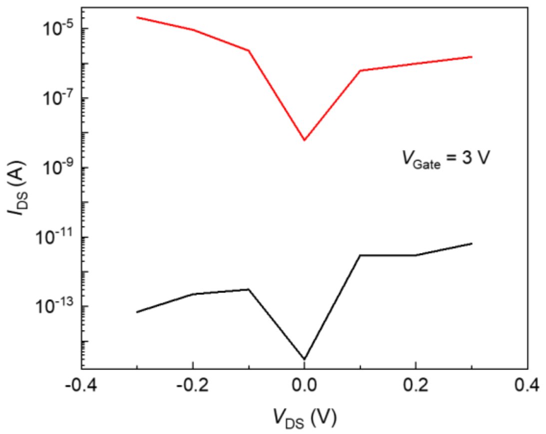

Fig. R2 The output curves of vertical tunneling MoS_2-FeFET at V_{Gate}= 3 V. The red and black curves correspond to downward (after V_{Gate} backward sweeping) and upward (after V_{Gate} forward sweeping) polarization states, respectively.

Comments 1-3: Some abbreviations, such as Gr, are not provided with their full names. The author is requested to complete them for the convenience of the reader.

Response 1-3:

We thank Reviewer #1 for this kind reminder. "Gr" has been changed into "Graphene (Gr)" in the revised manuscript. We have also carefully checked and revised our manuscript avoid any sudden abbreviations.

Comments 1-4: Some statements contain syntax errors, such as in line 200, "Figures 3d-i presents" should be "Figures 3d-i present"; in line 227, "remains towards" should be "remains toward to" and so on. Please review other similar instances in the article and make corrections accordingly.

Response 1-4:

We thank Reviewer #1 for this kind reminder. We have checked the manuscript thoroughly and corrected the syntax errors, as marked in blue in the revised manuscript.

Response to the Reviewer #2's comments

General comments:

2D semiconductors are highly promising to be utilized in future transistors. So far, complementary logic components and underlying mechanisms for the polarity modulation still remain puzzling in the field, hampering design of high-performance devices. The present work is attempting to exploit and probe into ferroelectric domain-based nonvolatile modulation of Fermi level in MoS_2 and quantum tunnelling through nanoscale h-BN, which can lead to high electroresistance ratio in the vertical FeFET. The results in this work also show a novel way to design advanced ferroelectric memory. In general, the manuscript achieves the requirements of Nature Communications. However, in current version, there are several vital points that need to be clarified and corrected.

Response:

We thank Reviewer#2 for his/her comments on our work. All these comments have been well evidenced by our further experiments in the revised manuscript. Below is a point-by-point response to the questions raised by the Reviewer #2.

Comments 2-1: There are no atomic-scale images that show the boundaries among MoS_2, graphene and BN. How do their boundaries influence the performance of the device? Did the authors control the stacking orientations of MoS_2, graphene and BN, or they just contacted randomly?

Response 2-1:

We thank Reviewer #2 for these valuable questions. During the device fabrication process, the twist angles between different layers were not considered, and the layers were directly assembled using conventional transfer techniques. The contacts among MoS_2, graphene and BN were checked using cross-sectional TEM technique. As shown in **Fig. R3**, both h-BN/MoS_2 and Gr/MoS_2 contacts show clear and sharp interfaces. The MoS_2 films are constituted by 3~4 layers with a thickness of ~2.5 nm. The BN films are constituted by 11~12 layers with a thickness of ~4 nm. The Gr films are constituted by 13~14 layers with a thickness of ~4.5 nm.

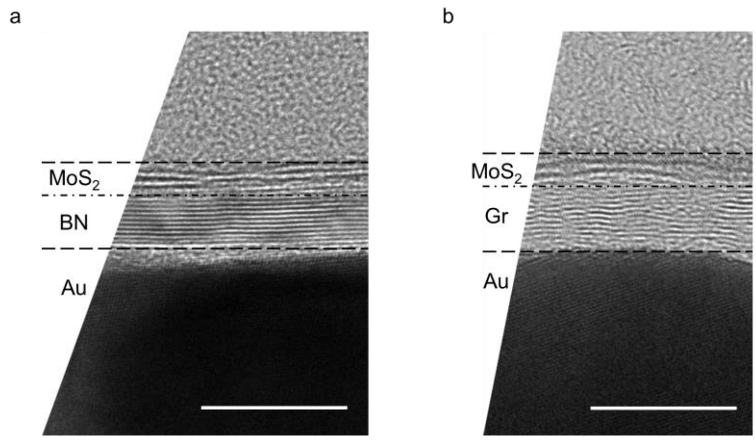

Fig. R3 a-b Cross-sectional TEM image of h-BN/MoS_2 (**a**) and Gr/MoS_2 (**b**) interfaces. Scale bar: 10 nm.

We have added these discussions to the revised manuscript. See "The boundaries among MoS_2, graphene and BN were checked using cross-sectional TEM technique. As shown in **Fig. S2**, both h-BN/MoS_2 and Gr/MoS_2 contacts show clear and sharp interfaces. The MoS_2 films are constituted by 3~4 layers with a thickness of ~2.5 nm. The BN films consist of 11~12 layers with a thickness of ~4 nm. The Gr films are made up with 13~14 layers with a thickness of ~4.5 nm." from line 3 to line 7 in page 6.

Comments 2-2: What is the origin of the ferroelectricity in this device? From MoS_2 or BN? This is important for the understanding of the underlying mechanism.

Response 2-2:

We sincerely thank Reviewer #2 for this question and apologize for the confusion caused by our unclear explanation. The ferroelectricity in our devices originates from the ferroelectric polymer P(VDF-TrFE). The local electric field, generated by the ferroelectric polarization of P(VDF-TrFE), modulates the Fermi level of MoS_2 in a nonvolatile manner, which in turn affects quantum tunneling through the underlying MoS_2/h-BN/Au junction.

Comments 2-3: For the application, devices should be stable. How about the stability of the device? Did the authors carry out the cycling test?

Response 2-3:

We thank Reviewer #2 for these valuable questions. All samples in our manuscript are covered with the ferroelectric polymer P(VDF-TrFE), which is spin-coated on top of the 2D materials and serves as both the gate dielectric and a protective layer. The transfer curves of our samples show minimal changes after one month in the air (**Fig. R4**), indicating good stability. We also performed cycling test on our devices to check the endurance behavior. As shown in **Fig. R5**, the vertical tunneling MoS_2-FeFET still work well after 10^7 cycles.

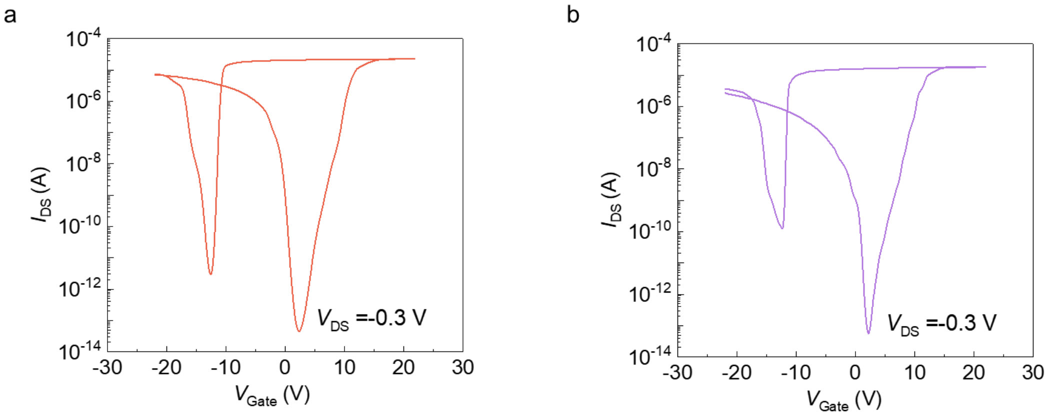

Fig. R4 a-b Transfer curves of vertical tunneling MoS_2-based FeFET at pristine state **(a)** and after one month in the air **(b)**.

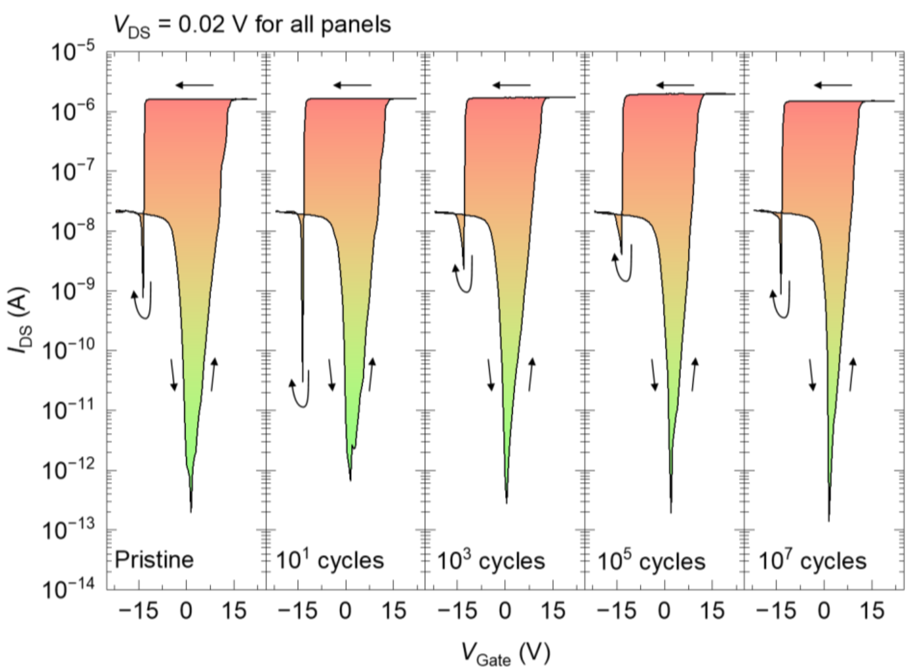

Fig. R5 Endurance behavior of vertical tunneling MoS_2-based FeFETs. The evolution of transfer curve with the cycles of voltage triangle wave with an amplitude of 30 V and frequency of 10 kHz.

We have added these discussions to the revised manuscript. See "The cycling tests are conducted to check the endurance behavior of vertical tunneling MoS_2-FeFETs. To avoid the disturbance of the joule heating effect by high channel currents during the cycling tests, a low V_{DS} of only 0.02 V is used. The transfer curve is checked after 10, 10^3, 10^5 and 10^7 cycles of voltage triangle wave with an amplitude of 30 V and frequency of 10 kHz and compared with the pristine one (**Fig. 6b**). These transfer curves, characterized by a huge ON/OFF ratio of ~7 orders with the ultralow V_{DS}=0.02 V, exhibits minimal variation during all cycling tests, implying that the device still work well after 10^7 cycles." from line 9 to line 16 in page 21.

Comments 2-4: In abstract and summary parts, the authors claim that "The Fermi level of MoS_2 is bipolarly tuned by ferroelectric domains". However, there is not direct evidence showing bipolarization and the evolution process of ferroelectric domains under different electric fields.

Response 2-4:

We appreciate Reviewer #2 for this value question. Ferroelectric materials exhibit spontaneous polarization that can be switched by an electric field. Notably, multiple stable polarization states can be configured by precisely controlling the parameters of the electric field, such as amplitude, frequency, and duration. This is evidenced by correlation experiment between polarization states and tunneling resistances (**Fig. R6a**)[1], and between polarization states and tunable pn homojunctions in our previous work (**Figs. R6b-c**)[2].

[Figure Redacted]

Fig. R6 Multiple stable polarization states can be configured by precisely controlling the parameters of the electric field. Different polarization states correspond to continuous resistances (**a**) and tunable self-rectifying *I-V* curves (**b, c**). Obtained from Ref. 1 and Ref. 2.

In our samples, the ferroelectric polarization would generate intense electric field and enable substantial modulation of carrier concentration and band structure within MoS_2. Specifically, the downward ferroelectric polarization of P(VDF-TrFE) would effectively prompt n-type (or highly n-type doping) behavior in MoS_2. Conversely, the upward ferroelectric polarization would deplete electrons and accumulate holes in MoS_2, with the Fermi level approaching the top of valence band and lightly p-type doping characteristic. The bipolar tunning of MoS_2 is supported by the ambipolar behavior in transfer curves of vertical tunneling MoS_2-based FeFET (**Fig. R7**) and hall measurements (**Fig. R8**).

To delve into the underlying mechanisms of our findings, the hall measurements were performed on a MoS_2 flake that is covered by ferroelectric polymer films. The hall measurements tell the information of carriers type and density which reflects the influence of ferroelectric polarization on the energy band alignment of MoS_2. The dominated carrier of MoS_2 is electron with a density of $1.2\times10^{18}/cm^3$ for a pristine ferroelectric state, hole with a density of $6.7\times10^{15}/cm^3$ for a upward ferroelectric state, and electron with a density of $4.5 \times 10^{18}/cm^3$ for a downward ferroelectric state respectively (**Fig. R8**).

Based on the energy band model, the carrier density can be calculated using below formulas[3]:

$$n_0 = N_\mathrm{C} \exp(-\frac{E_\mathrm{C}-E_\mathrm{F}}{k_0 T}) \qquad (1)$$

$$N_C = \frac{2\,(2\pi m_\mathrm{n}^* k_0 T)^{\frac{3}{2}}}{h^3} = 4.82 \times 10^{15} T^{\frac{3}{2}} (\frac{m_\mathrm{n}^*}{m_0})^{3/2} \qquad (2)$$

$$p_0 = N_\mathrm{V} \exp(-\frac{E_\mathrm{F}-E_\mathrm{V}}{k_0 T}) \qquad (3)$$

$$N_V = \frac{2\,(2\pi m_\mathrm{p}^* k_0 T)^{\frac{3}{2}}}{h^3} = 4.82 \times 10^{15} T^{\frac{3}{2}} (\frac{m_\mathrm{p}^*}{m_0})^{3/2} \qquad (4)$$

where n_0 and p_0 are density of electron and hole carriers respectively. The E_C, E_F and E_V are the bottom of conductance band, Femi level and top of valence band respectively. m_n^* and m_p^* are effective mass of electron and hole carriers while m_0 is the free electron rest mass. k_0, h and T are Boltzmann's constant, Pruck constant and temperature set at 300 K, respectively.

To distinguish the Femi level of MoS_2 under upward and downward polarization states, here we define E_{Fn} of MoS_2 for downward polarization state and E_{Fp} for upward polarization state respectively. Based on equation (1) and (3), one can obtain: E_{Fn}-E_{Fp}=(E_C-E_V)+$k_0 T \times ln\frac{n_0 \times p_0}{N_\mathrm{C} \times N_\mathrm{V}}$. The E_g=(E_C-E_V) is the bandgap of MoS_2 which is ~1.8 eV for layers of MoS_2 films. The N_C and N_V can be calculated based on equations (2) and (4) respectively. According to the literature, the m_n^* and m_p^* of MoS_2 are in the range of 0.37-0.97 m_0 and 0.44-2.8 m_0 respectively[4]. The $N_C \times N_V$ value of MoS_2 can be evaluated to be in the range of 4.12×10^{37}-2.81×10^{39}, accords well with previous reports[3]. Then, based on the hall measurement result, the E_{Fn}- E_{Fp} is calculated to be in the range of 1.50-1.61 eV. It should be noted that the E_{Fn} is nearly overlaps the conduction band edge[5], it means the $E_{Fp} \approx E_g$-(E_{Fn}- E_{Fp}) is 0.18-0.3 eV higher than the valence band edge. These energy band alignments of MoS_2 under different polarization states results accord well with previous reports[6].

We have added these discussions to the revised supplementary information. See “hall measurements were performed on a MoS_2 flake that is covered by ferroelectric polymer films. The hall measurements provide the information of carriers type and density, reflecting the influence of ferroelectric polarization on the energy band alignment of MoS_2. The dominated carrier of MoS_2 is electron with a density of $1.2\times 10^{18}/cm^3$ for pristine ferroelectric state, hole with a density of $6.7\times 10^{15}/cm^3$ for upward ferroelectric state, and electron with a density of $4.5\times 10^{18}/cm^3$ for downward ferroelectric state, respectively (**Table S1**). Based on the energy band model, the Femi level of MoS_2 nearly overlaps the conduction band edge for the downward polarization state and is 0.18-0.3 eV above the valence band edge for the upward polarization state, according well with previous reports[36].” from line 15 of page 12 to line 3 of page 13.

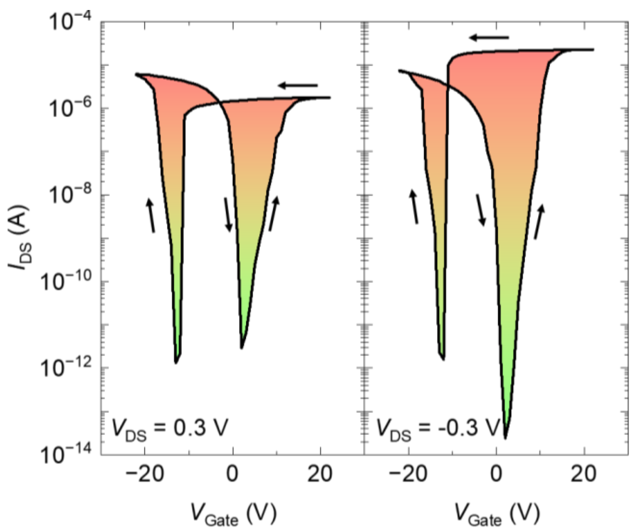

Fig. R7 Transfer curves of vertical tunneling MoS_2-based FeFET in a semilog plot, measured at $V_{DS} = \pm 0.3$ V.

Polarization state	Carrier type	Carrier density
Unpolarized	electron	$1.15723\times10^{18}/cm^3$
Upward polarization	hole	$6.72812\times10^{15}/cm^3$
Downward polarization	electron	$4.49665\times10^{18}/cm^3$

Fig. R8 The hall measurement results for pristine, upward polarization and downward polarization states respectively.

Reference:

1. Giant Electroresistance of Super-tetragonal BiFeO3 Based Ferroelectric Tunnel Junctions. ACS Nano 7, 5385 (2013);

2. Ferroelectric-defined reconfigurable homojunctions for in-memory sensing and computing. Nature Materials, 22, 1499 (2023);

3. The physics of semiconductors. 7th edition, Chapter 4, pages 56-63, Publishing house of electronics industry, Beijing, 2017

4. Effects of strain on band structure and effective masses in MoS_2. Physical Review B 86, 241401(R) (2012)

5. Two-dimensional electronic transport and surface electron accumulation in MoS_2. Nature Communications 9, 1442 (2018)

6. Measuring Band Modulation of MoS_2 with Ferroelectric Gates. Nano Lett. 23, 2114 (2023)

Comments 2-5: In Methods Part, there is no detailed information on MoS_2 and h-BN. How did the authors obtain MoS_2 and h-BN? Any further characterizations on MoS_2 and h-BN? Since there are several different types of structures for MoS_2 and BN, the authors should give more information on structures.

Response 2-5:

We thank Reviewer #2 for these valuable questions. The h-BN and MoS_2 flakes were exfoliated directly onto Polyvinyl Alcohol (PVA) and Polydimethylsiloxane (PDMS), respectively, using Scotch tape from single crystals purchased from HQ Graphene. Raman spectroscopy was performed on both MoS_2 and h-BN, as shown in **Fig. R9**. The characteristic peaks are in excellent agreement with previous reports on 2H-MoS_2 and h-BN[1].

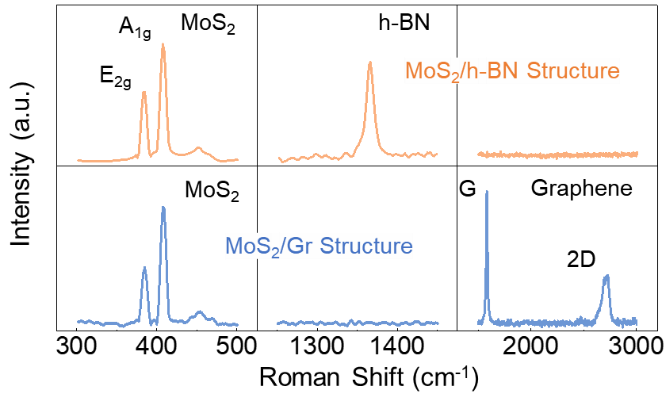

Fig. R9 Raman spectra for MoS_2/h-BN and MoS_2/Gr heterostructures.

Reference:

1. Application of Raman spectroscopy to probe fundamental properties of two-dimensional materials. npj 2D Materials and Applications 4, 13 (2020);

Response to the Reviewer #3's comments

General comments:

The ambipolar field-effect characteristics are appealing because they enable a wide range of reconfigurable logic circuits. Experimental demonstrations of ambipolar field-effect behavior have been limited to a few 2D materials, such as $MoTe_2$ and WSe_2, while the ambipolar properties in the widely studied MoS_2 remain unclear. In this manuscript, the authors demonstrated that both n-type and p-type characteristics can be achieved in the MoS_2 channel via electrostatic control. The observed ambipolar field-effect characteristics in MoS_2-FeFETs are well explained by a band alignment model. The experiments conducted are thorough, and the explanations provided are compelling. This study incorporates electrostatic control through non-volatile ferroelectric polarization, which introduces a memory effect in the MoS_2-FeFETs. By designing a vertical tunneling barrier as the channel, the ferroelectric transistor device exhibits a large ON/OFF ratio of 10^9, making it attractive for memory applications. The manuscript is well-organized, with clear figure presentations. Below are some suggestions that may further enhance the quality of the manuscript.

Response:

We thank Reviewer #3 for his/her valuable comments on our work. We did appropriate modifications in our revised manuscript to clarify all points raised by Reviewer #3. Below is the point-by-point reply to these questions.

Comments 3-1: Working mechanism: additional measurements and discussions are needed to make it more comprehensible.

Comments 3-1-1: In the vertical tunneling MoS_2-FeFETs, tunnel electroresistance through the Van der Waals junction is achieved using an external ferroelectric gate. It is suggested to include a discussion comparing the ON/OFF ratio with the tunnel electroresistance that directly passes through the ferroelectric layer.

Response 3-1-1:

We sincerely thank Reviewer #3 for this constructive suggestion to compare our vertical tunneling FeFET with Ferroelectric Tunneling Junction (FTJ). In an FTJ, where two electrodes sandwich a ferroelectric tunnel barrier, the barrier profile can be modulated by ferroelectric polarization reversal, resulting in tunnel electroresistance (TER). FTJ takes advantage of direct quantum tunneling effect through the ferroelectric layer, which typically require the ferroelectric layer to be only a few nanometers. However, the coercive electric field in nano-scale ferroelectric thin films is significantly higher than that in bulky films, suffering from poor fatigue performance (<10^6 cycles)[1]. In our vertical tunneling MoS_2-FeFETs, TER is achieved through the Van der Waals MoS_2/h-BN/metal junction that is controlled by an external ferroelectric gate. Unlike FTJs, the ferroelectric layer in our device does not function as a tunneling layer but as a third control terminal. This removes the thickness constraint imposed by quantum tunneling, effectively mitigating the fatigue issues associated with FTJs. We have performed cycling test our devices to check the endurance behavior. As shown in **Fig. R10**, the vertical tunneling MoS_2-FeFET still work well after 10^7 cycles. Moreover, nonvolatile modulation of the Fermi level in MoS_2 via ferroelectric domains, combined with quantum tunneling through the nanoscale h-BN, has demonstrated an impressive TER of up to 10^9 at room temperature-surpassing the TER values reported for FTJs[1]. Besides, the leakage currents in a vertical tunneling FeFET that go through a thick insulative ferroelectric gate is much lower than the inevitable tunneling currents in an FTJ, which pioneers several orders of magnitude lower energy consumption in the vertical tunneling MoS_2-FeFET. The energy consumption is calculated using the formula $E=UIt$, where U, I and t are the operating voltage amplitude, the leakage current and operating speed respectively. The gate leakage current of the vertical tunneling MoS_2-FeFETs is at the picoampere level, as seen in **Fig. S13**. The energy consumption for opening an ON/OFF ratio of more than 10^4 by the 22 V (1 μs) and 31 V (500 ns) operations is of ~0.22 fJ and ~0.16 fJ, respectively.

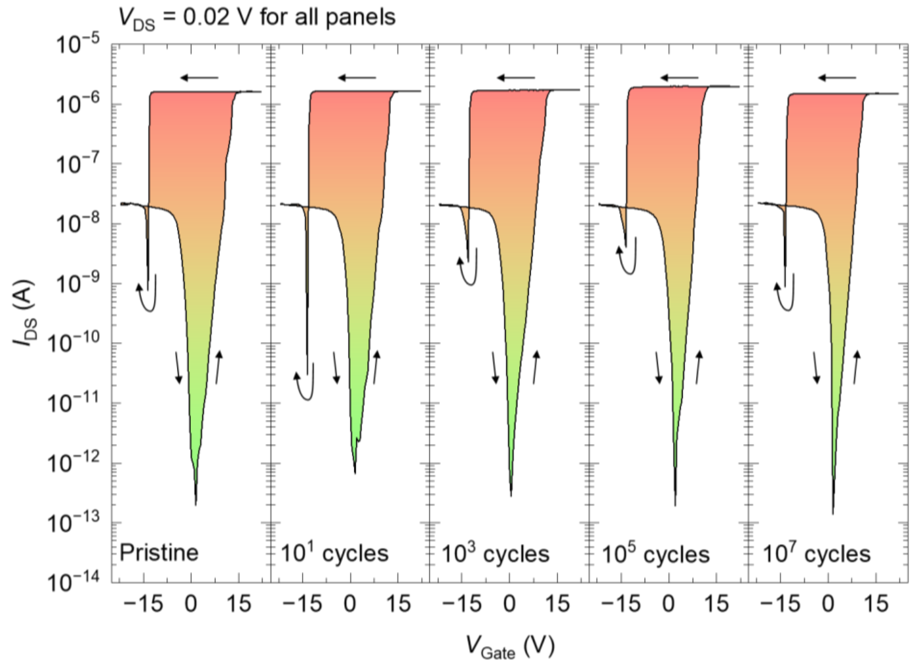

Fig. R10 Endurance behavior of vertical tunneling MoS_2-based FeFETs. The evolution of transfer curve with the cycles of voltage triangle wave with an amplitude of 30 V and frequency of 10 kHz.

We have added these discussions to the revised manuscript. See "The energy consumption is calculated using the formula $E=UIt$, where U, I and t are the operating voltage amplitude, the leakage current and operating speed respectively. The gate leakage current of the vertical tunneling MoS_2-FeFETs is at the picoampere level, as seen in **Fig. S12**. The energy consumption for opening an ON/OFF ratio of more than 10^4 by the 22 V (1 μs) and 31 V (500 ns) operations is of ~0.22 fJ and ~0.16 fJ, respectively. Note that this is the record low energy consumption of memory device to the best of our knowledge. The cycling tests are conducted to check the endurance behavior of vertical tunneling MoS_2-FeFETs. To avoid the disturbance of the joule heating effect by high channel currents during the cycling tests, a low V_{DS} of only 0.02 V is used. The transfer curve is checked after 10, 10^3, 10^5 and 10^7 cycles of voltage triangle wave with an amplitude of 30 V and frequency of 10 kHz and compared with the pristine one (**Fig. 6b**). These transfer curves, characterized by a huge ON/OFF ratio of ~7 orders with the ultralow V_{DS}=0.02 V, exhibits minimal variation during all cycling tests, implying that the device still work well after 10^7 cycles." from line 1 of page 21 to line 14 of page 21, and "It is worthy to compare the vertical tunneling FeFET with the Ferroelectric Tunneling Junction (FTJ) which takes advantage of direct quantum tunneling effect through the ferroelectric layer. In FTJ device, it typically requires the ferroelectric layer to be only a few nanometers. However, the coercive electric field in nano-scale ferroelectric thin films is significantly higher than that in bulky films, suffering from poor fatigue performance in FTJs (<10^6 cycles)[55]. Unlike FTJs, the ferroelectric layer in vertical tunneling FeFETs does not function as a tunneling layer but as a third control terminal, that is, the tunnel electroresistance through the below Van der Waals junction is achieved by modulating the Femi level of 2D semiconductor electrode by an external ferroelectric gate. This removes the thickness constraint imposed by quantum tunneling, effectively mitigating the fatigue issues associated with FTJs. As shown in **Fig. 6b**, the vertical tunneling MoS_2-FeFET still work well after 10^7 cycles. Besides, the leakage currents in a vertical tunneling FeFET that pass through thick and insulative ferroelectric gate are much lower than the inevitable tunneling currents in FTJ, pioneering energy consumption as low as 0.16 fJ per operation." from line 5 to line 19 of page 22.

Comments 3-1-2: The modulation of the Fermi level in MoS_2 plays a critical role in the resistive switching of the device. It is suggested to evaluate the change in the Fermi level of MoS_2 induced by the ferroelectric domains.

Response 3-1-2:

We sincerely thank Reviewer #3 for this constructive suggestion to evaluate the change in the Fermi level of MoS_2 induced by the ferroelectric domains. The hall measurements were performed to confirm the switch of carriers type and to obtain the carrier density (**Fig. R11**).

Polarization state	Carrier type	Carrier density
Unpolarized	electron	$1.15723\times10^{18}/cm^3$
Upward polarization	hole	$6.72812\times10^{15}/cm^3$
Downward polarization	electron	$4.49665\times10^{18}/cm^3$

Fig. R11 The hall measurement results for pristine, upward polarization and downward polarization states respectively.

To delve into the underlying mechanisms of our findings, the hall measurements were performed on a MoS_2 flake that is covered by ferroelectric polymer films. The hall measurements tell the information of carriers type and density which reflects the influence of ferroelectric polarization on the energy band alignment of MoS_2. The dominated carrier of MoS_2 is electron with a density of $1.2\times10^{18}/cm^3$ for a pristine ferroelectric state, hole with a density of $6.7\times10^{15}/cm^3$ for a upward ferroelectric state, and electron with a density of $4.5\times10^{18}/cm^3$ for a downward ferroelectric state respectively (**Fig. R11**). Based on the energy band model, the carrier density can be calculated using below formulas[1]:

$$n_0 = N_{\mathrm{C}} \exp\left(-\frac{E_{\mathrm{C}}-E_{\mathrm{F}}}{k_0 T}\right) \qquad (1)$$

$$N_C = \frac{2\,(2\pi m_{\mathrm{n}}^* k_0 T)^{\frac{3}{2}}}{h^3} = 4.82\times10^{15} T^{\frac{3}{2}} \left(\frac{m_{\mathrm{n}}^*}{m_0}\right)^{3/2} \qquad (2)$$

$$p_0 = N_{\mathrm{V}} \exp\left(-\frac{E_{\mathrm{F}}-E_{\mathrm{V}}}{k_0 T}\right) \qquad (3)$$

$$N_V = \frac{2\,(2\pi m_{\mathrm{p}}^* k_0 T)^{\frac{3}{2}}}{h^3} = 4.82\times10^{15} T^{\frac{3}{2}} \left(\frac{m_{\mathrm{p}}^*}{m_0}\right)^{3/2} \qquad (4)$$

where n_0 and p_0 are density of electron and hole carriers respectively. The E_C, E_F and E_V are the bottom of conductance band, Femi level and top of valence band respectively. m_{n}^* and m_{p}^* are effective mass of electron and hole carriers while m_0 is the free electron rest mass. k_0, h and T are Boltzmann's constant, Pruck constant and temperature set at 300 K, respectively.

To distinguish the Femi level of MoS_2 under upward and downward polarization states, here we define E_{Fn} of MoS_2 for downward polarization state and E_{Fp} for upward polarization state respectively. Based on equation (1) and (3), one can obtain: E_{Fn}-E_{Fp}=(E_C-E_V)+$k_0 T \times ln\frac{n_0\times p_0}{N_{\mathrm{C}}\times N_{\mathrm{V}}}$. The E_g=(E_C-E_V) is the bandgap of MoS_2 which is ~1.8 eV for layers of MoS_2 films. The N_C and N_V can be calculated based on equations (2) and (4) respectively. According to the literature, the m_{n}^* and m_{p}^* of MoS_2 are in the range of 0.37-0.97 m_0 and 0.44-2.8 m_0 respectively[2]. The $N_C\times N_V$ value of MoS_2 can be evaluated to be in the range of 4.12×10^{37}-2.81×10^{39}, accords well with previous reports[3]. Then, based on the hall measurement result, the E_{Fn}- E_{Fp} is calculated to be in the range of 1.50-1.61 eV. It should be noted that the E_{Fn} is nearly overlaps the conduction band edge[3], it means the $E_{Fp}\approx E_g$-(E_{Fn}- E_{Fp}) is 0.18-0.3 eV higher than the valence band edge. These energy band alignments of MoS_2 under different polarization states results accord well with previous reports[4].

We have added these discussions to the revised supplementary information. See "hall measurements were performed on a MoS_2 flake that is covered by ferroelectric polymer films. The hall measurements provide the information of carriers type and density, reflecting the influence of ferroelectric polarization on the energy band alignment of MoS_2. The dominated carrier of MoS_2 is electron with a density of $1.2\times10^{18}/cm^3$ for pristine ferroelectric state, hole with a density of $6.7\times10^{15}/cm^3$ for upward ferroelectric state, and electron with a density of $4.5\times10^{18}/cm^3$ for downward ferroelectric state, respectively (**Table S1**). Based on the energy band model, the Femi level of MoS_2 nearly overlaps the conduction band edge for the downward polarization state and is 0.18-0.3 eV above the valence band edge for the upward polarization state, according well with previous reports[36]." from line 15 of page 12 to line 3 of page 13.

Reference:

1. The physics of semiconductors. 7th edition, Chapter 4, pages 56-63, Publishing house of electronics industry, Beijing, 2017

2. Effects of strain on band structure and effective masses in MoS_2. Physical Review B 86, 241401(R) (2012)

3. Two-dimensional electronic transport and surface electron accumulation in MoS_2. Nature Communications 9, 1442 (2018)

4. Measuring Band Modulation of MoS_2 with Ferroelectric Gates. Nano Lett. 23, 2114 (2023)

Comments 3-1-3: In MoS_2-based vertical tunneling FeFETs, the transfer curves demonstrate ambipolar performance, featuring a pronounced p-type branch at V_{DS} =0.3

V and a stronger n-type branch at V_{DS} = -0.3 V. A more detailed explanation of this electrical behavior should be provided.

Response 3-1-3:

We sincerely thank Reviewer #3 for this constructive suggestion. In the case of vertical tunneling MoS_2-FeFET, the carrier transport properties are governed by asymmetric Van der Waals MoS_2/h-BN/metal tunnel junction. As seen in **Figs. 4c** and **4f**, for V_{DS}=0.3V, the electrons tunnel from MoS_2 to the electrode when the ferroelectric polarization points downward and the holes tunnel in the reverse path when the ferroelectric polarization points upward. Ascribed to the disparity in density of states between MoS_2 and metal electrodes, the electron tunnelling current for downward polarization is significantly diminished relative to the hole tunnelling current for upward polarization, thereby tilting the transfer curve towards more pronounced p-type characteristic. Conversely, when V_{DS} is -0.3V, the situation is reversed, with the n-type behavior being more evident due to the dominant tunneling of electrons from the electrode into the MoS_2 channel.

We have added these discussions to the revised manuscript. See "because the carriers' density in the metal is much higher than that in the MoS_2, at V_{DS}=0.3 V, the current for electrons tunnelling from MoS_2 to the electrode is significantly diminished relative to the tunneling current of holes in the reverse path, thereby tilting the transfer curve towards more pronounced p-type characteristic. Conversely, when V_{DS} is -0.3 V, the situation is reversed, with the n-type behavior being more evident due to the dominant tunneling of electrons from the electrode into the MoS_2 channel. This dual nature of the transfer curves highlights the effectiveness of the tunneling junction as channel and accentuates the pivotal role of V_{DS} polarity in dictating the operative regime of semiconductor, thereby dynamically steering the device between n-type and p-type conduction modes." from line 9 to line 18 in page 17.

Comments 3-2: Performance limit:

Comments 3-2-1: In Figs. 1h and 1i, the authors present the transfer curves and retention characteristics of the MoS_2-based vertical tunneling FeFET. While the authors state that "the ON/OFF ratio can reach up to 10^9," there appears to be only a three-order magnitude difference between the highest and lowest values in Figure 1i. I recommend that the authors include additional data to better demonstrate the performance limits.

Response 3-2-1:

We thank Reviewer #1 for this kind reminder and recommendation. As can be seen from **Fig. 1h**, a negative V_{DS} give much higher ON/OFF ratio than a positive V_{DS}. We remeasured the retention behavior using a negative V_{DS} (V_{DS}=-0.2 V). As shown in **Fig. R12**, it demonstrates 22 distinct conductance states with minor variation over a period of 10^3 s except the gradual rising in the ultralow conductance state. We have updated the **Fig. 1i** in the revised manuscript.

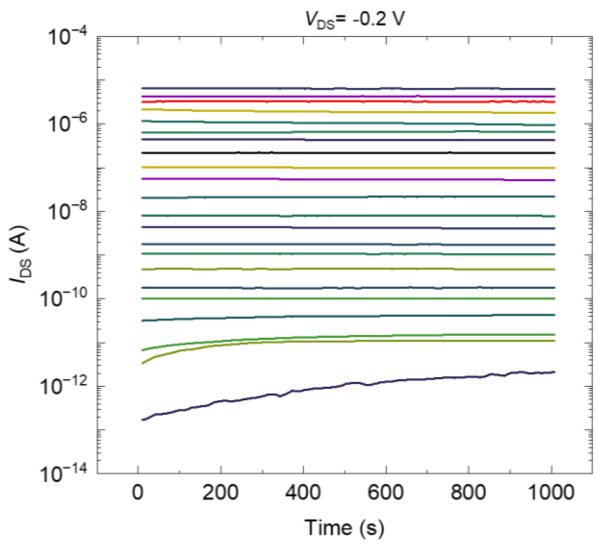

Fig. R12 The retention characteristics of 22 intermediate conductance states in vertical tunneling MoS_2-FeFET that is measured at V_{DS} =-0.2 V.

Comments 3-2-2: The operating voltage of 30 V is quite high. What is the energy consumption for each operation at this voltage? From the perspective of potential practical applications, a lower operating voltage is preferable. How can you optimize your devices to achieve a smaller operating voltage?

Response 3-2-2:

We appreciate Reviewer #2 for this value question. To evaluate the energy consumption, the operating speed was measured and shown in **Fig. R13**. The device is programmed to OFF states by applying constant negative V_G pulses (-14 V, 5 ms) and to ON states by applying positive V_G pulses whose amplitude and width are in a range of 14 V to 31 V and 1 ms to 500 ns respectively. Each programming voltage is followed by a constant V_d=-0.2 V to verify the conductance state of the Van der Waals junction. As shown in **Fig. R13**, despite of the increasing voltage amplitude, the ON/OFF ratio gradually decay with the decrease of width of operating voltage pulse. The achieved speed of the vertical tunneling MoS_2-FeFET can be as fast as 500 ns for a 31 V pulse which still produces an ON/OFF ratio of more than 10000.

The energy consumption is calculated using the formula $E=UIt$, where the leakage current is of ~2 nA (**Fig. S5**). The energy consumption for opening an ON/OFF ratio of more than 10000 by the 22 V (1 μs) and 31 V (500 ns) operations is of 0.044 fJ and 0.031 fJ respectively.

We agree with the reviewer that a lower operating voltage is preferable from the view of practical application. A smaller operating voltage can be obtained by reducing the thickness of ferroelectric layer in the vertical tunneling MoS_2-FeFET device. As shown in **Fig. R14**, the operating voltage is reduced to 10 V for the device with a 100 nm-thick ferroelectric layer from 20 V for the device with a 200 nm-thick ferroelectric layer. Further work is needed to optimize the ultrathin and high-quality ferroelectric polymer films for an operating voltage that is small enough to be compatible with mature complementary metal oxide semiconductor (CMOS) techniques. On the parallel, other ferroelectrics such as ultrathin hafnium-based ferroelectric is a good candidate that is worthy to be further explored in this novel memory structure.

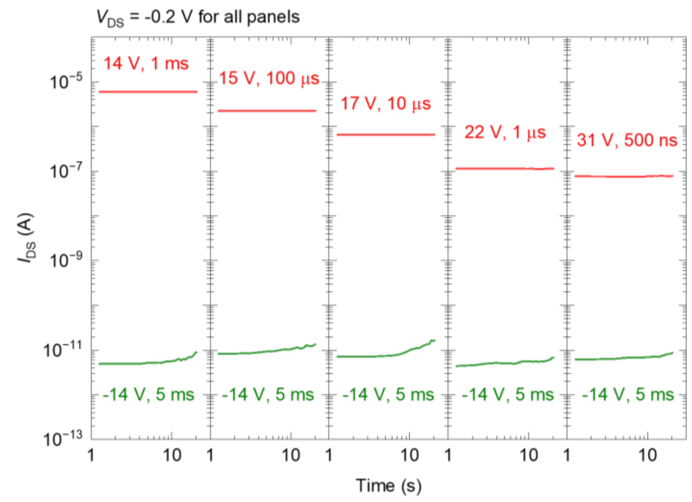

Fig. R13 Switching speed test for vertical tunneling MoS_2-FeFET.

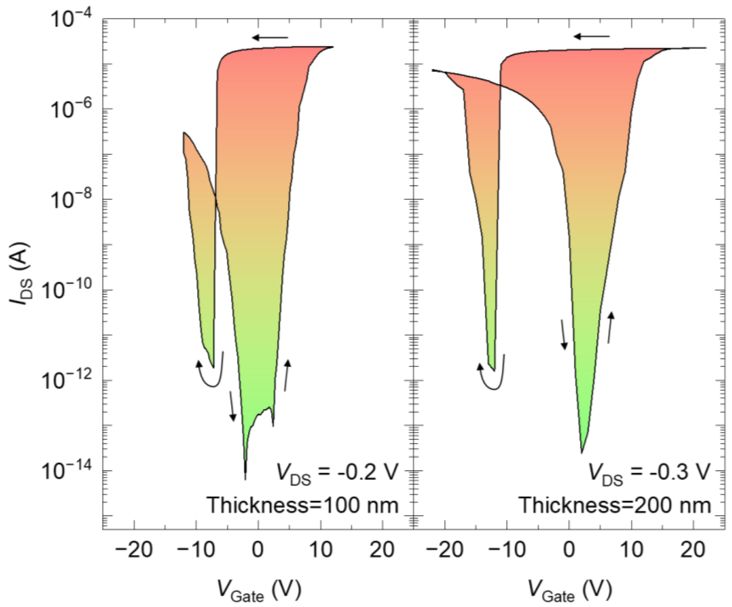

Fig. R14 Transfer curves of vertical tunneling MoS_2-FeFET with a sthickness of 100 nm (left panel) and 200 nm (right panel) respectively.

We have added these discussions to the revised manuscript. See "As a potential memory device, key memory characteristics such as operating speed, energy consumption and endurance behavior are tested for vertical tunneling MoS_2-FeFETs. The device is programmed to OFF states by applying constant negative V_{Gate} pulses (-14 V, 5 ms) and to ON states by applying positive V_{Gate} pulses with amplitudes ranging from 14 V to 31 V and pulse widths between 1 ms and 500 ns. Each programming voltage is followed by a constant V_d=-0.2 V to verify the conductance state of the Van der Waals junction. As shown in **Fig. 6a**, despite of the increasing voltage amplitude, the ON/OFF ratio gradually decays with the decrease of operating voltage pulse width. The vertical tunneling MoS_2-FeFET achieves a switching speed as fast as 500 ns by a 31 V pulse, while still maintaining an ON/OFF ratio of more than 10^4.

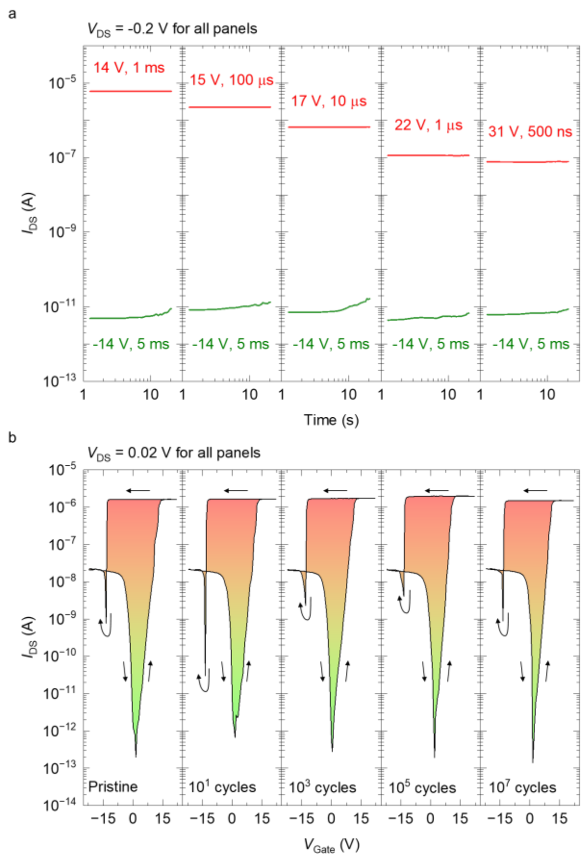

Fig. 6 | The switching speed and endurance behavior of vertical tunneling MoS_2-FeFET. a The evolution of I_{DS} with time after programing the device using constant negative V_{Gate} pulses (-14 V, 5 ms) and positive V_{Gate} pulses with amplitudes ranging from 14 V to 31 V and pulse widths between 1 ms and 500 ns, respectively. The V_{DS}=-0.2 V. **b** The evolution of transfer curves with the cycles of voltage triangle wave with an amplitude of 30 V and frequency of 10 kHz for a vertical tunneling MoS_2-FeFET.

The energy consumption is calculated using the formula $E=UIt$, where U, I and t are the operating voltage amplitude, the leakage current and operating speed respectively. The gate leakage current of the vertical tunneling MoS_2-FeFETs is at the picoampere level, as seen in **Fig. S12**. The energy consumption for opening an ON/OFF ratio of more than 10^4 by the 22 V (1 μs) and 31 V (500 ns) operations is of ~0.22 fJ and ~0.16 fJ, respectively. Note that this is the record low energy consumption of memory device to the best of our knowledge. The cycling tests are conducted to check the endurance behavior of vertical tunneling MoS_2-FeFETs. To avoid the disturbance of the joule heating effect by high channel currents during the cycling tests, a low V_{DS} of only 0.02 V is used. The transfer curve is checked after 10, 10^3, 10^5 and 10^7 cycles of voltage triangle wave with an amplitude of 30 V and frequency of 10 kHz and compared with the pristine one (**Fig. 6b**). These transfer curves, characterized by a huge ON/OFF ratio of ~7 orders with the ultralow V_{DS}=0.02 V, exhibits minimal variation during all cycling tests, implying that the device still work well after 10^7 cycles.

A lower operating voltage is preferable from the view of practical application. This can be obtained by reducing the thickness of ferroelectric layer in the vertical tunneling MoS_2-FeFET device. As shown in **Fig. S13**, the operating voltage decreases from 20 V for the device with a 200 nm-thick ferroelectric layer to 10 V for the device with 100 nm-thick ferroelectric layer. Further work is needed to optimize the ultrathin and high-quality ferroelectric polymer films to achieve operating voltages low enough for compatibility with mature complementary metal-oxide-semiconductor (CMOS) technology. On the parallel, other ferroelectrics, such as ultrathin hafnium-based ferroelectrics, present promising alternatives that warrant further exploration in this novel memory structure." from line 16 of page 19 to line 4 of page 22.

Comments 3-2-3: The switching speed and stability are crucial for practical applications. Can the authors provide more data to illustrate these parameters?

Response 3-2-3:

We appreciate Reviewer #3 for this valuable question. As mentioned in Response 3-2-2, the achieved speed of the vertical tunneling MoS_2-FeFET is measured to be 500 ns for pulse with amplitude of 31 V (**Fig. R13**). Besides, the transfer curve of this device shows minimal changes after one month (**Fig. R15**), indicating its good stability in the air atmosphere.

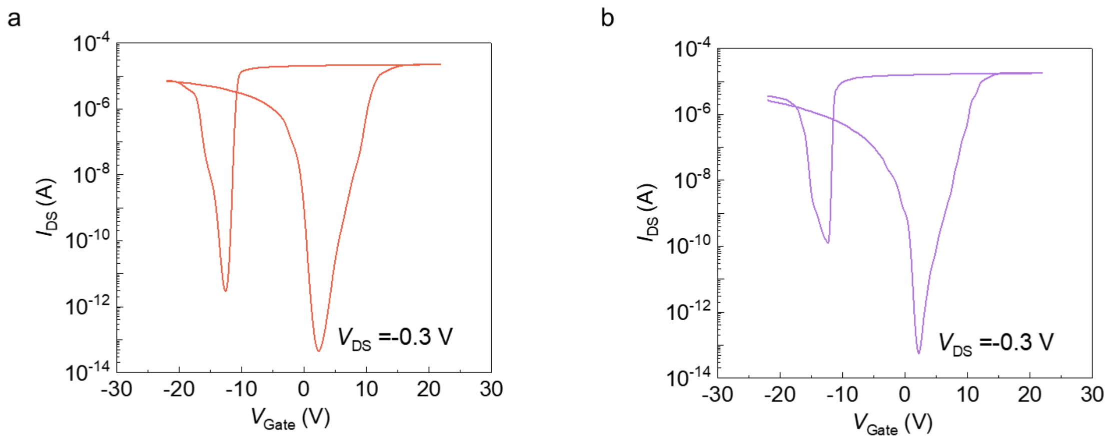

Fig. R15 Transfer curves of vertical tunneling MoS_2-based FeFET at pristine state **(a)** and after one month **(b)**.

Comments 3-3: Necessary comparison with the reported works

Comments 3-3-1: The ambipolar operation of MoS_2 has been reported using an ionic liquid gate. It is recommended to include more discussion on the advantages of using a ferroelectric gate compared to the ionic liquid gate.

Response 3-3-1:

We thank Reviewer #3 for this kind suggestion. In addition to ferroelectric gating, the electrolyte gating is another effective approach to provide strong local electric field. The application of voltage across electrolyte results in migration of ions towards the channel. The accumulation of ions at the electrolyte-channel interface, creating an electric field and electrostatically inducing carriers of opposite charge to accumulated ions on the channel side at the interface. The electric double layer formed by the ions and carriers is essentially nanometer-scale parallel-plate capacitor, resulting in very large specific capacitance up to 100 μF cm^{-2} and corresponding to giant induced charge carrier densities up to 10^{15} cm^{-2}. However, electrolyte gating has poor performance in respect to operating speed (more than 1 ms), retention performance (short-term memory) and device integration[1]. Ferroelectrics exhibit spontaneous polarization below Curie temperature, and the ferroelectric polarization can be reversed by external electric field in low-power (~1 fJ), high-speed (less than 1 μs) and nonvolatile manner (long-term memory)[2,3]. The Ferroelectric gating can enable high electrostatic doping concentrations due to their strong localized electric fields. Analog polarization switching can be achieved by precisely controlling the applied electric field, which does not evoke the localized migration of ions or defects and ensure high endurance[2,3].

Reference:

1. Flexible Vertical Photogating Transistor Network with an Ultrashort Channel for In-sensor Visual Nociceptor, Advanced Functional Materials, 31, 2104327 (2021);

2. Ferroelectric-defined reconfigurable homojunctions for in-memory sensing and computing, Nature Materials, 22, 1499 (2023);

3. A ferroelectric fin diode for robust non-volatile memory, Nature Communications, 15, 513 (2024);

Comments 3-4: Some writing errors

Comments 3-4-1: In line 142, "+30V" should be changed to "+30 V," as there is typically a space between the numerical value and its unit. Please review the manuscript carefully and correct similar errors throughout.

Response 3-4-1:

We thank Reviewer #3 for this kind reminder. We have carefully checked our manuscript and corrected typographical errors throughout, which are highlighted in blue in the revised version.

Comments 3-4-2: Figures 2a and 3a-c contain redundant information. Please revise accordingly.

Response 3-4-2:

We appreciate Reviewer #3's valuable suggestion. To avoid redundancy with Figure 2a-c, we have removed original Figures 3a-c in the revised manuscript.

Comments 3-4-3: To maintain consistency, it is preferable to refer to "Schottky-contacted FeFET" as "asymmetric Schottky-contacted FeFET" from line 150 to line 170.

Response 3-4-3:

We thank Reviewer #3 for this suggestion. "Schottky-contacted FeFET" has been changed into "asymmetric Schottky-contacted FeFET" in the revised manuscript.

Comments 3-4-4: Reference numbers should be included in Fig. 5c to enhance the manuscript's accessibility.

Response 3-4-4:

We thank Reviewer #3 for this kind reminder. Reference numbers have been added in Fig. 5c to improve the manuscript's accessibility in the revised manuscript.

Comments 3-4-5: Figures S9 and S10 clearly illustrate the full-pass, OFF to negative-pass transition, and the reverse process, respectively. The manuscript description needs to be updated to reflect this.

Response 3-4-5:

We thank Reviewer #3 for this kind reminder. "full-pass to negative-pass transition" has been changed into "full-pass, OFF to negative-pass transition" in the revised manuscript.

Comments 3-4-6: I have concerns regarding the arrangement and layout of Figures 4 and 5. First, Figure 4 appears cluttered and provides limited information. Second, I have difficulty distinguishing the differences between the left and right panels in Figures 5a and 5b. Please address these issues carefully.

Response 3-4-6:

We thank Reviewer #3 for these constructive suggestions and feel sorry for the unclear description, which led to misunderstanding. Figure 4 clarifies the band information of three devices (i.e., symmetric Schottky-contacted MoS_2-FeFET, asymmetric Schottky-contacted MoS_2-FeFET and vertical tunneling MoS_2-FeFET) under various polarization states and the resulting differences in output curves. The left and right panels in Figs. 5a and 5b present the band alignments for ON-state with the Fermi level of MoS_2 residing near the conduction band edge of MoS_2 (left panels) and OFF-state with the Fermi level of MoS_2 positioned in the middle of bandgap (right panels).

We have added more cues to avoid misunderstandings in the revised manuscript. See “The band alignments for ON-state with the Fermi level of MoS_2 residing near the conduction band (left panel) and OFF-state with the Fermi level of MoS_2 positioned in the middle of bandgap (right panel) are shown in **Figs. 5a** and **5b**, corresponding to asymmetric Schottky-contacted MoS_2-FeFET and vertical tunneling MoS_2-FeFET, respectively.” from line 1 to line 5 in page 18.

Response to the Reviewer #4's comments

General comments:

The paper presents a stack combining a ferroelectric and 2D materials to yield a novel transistor device design with extremely high I_{on}/I_{off}. The transistor uses ferroelectric polarisation to tune the Fermi level of the MoS_2 channel material, while h-BN acts as an insulating barrier layer. This layer acts to enhance tunneling injection in the ON-state to improve current while acting to suppress current in the OFF-state. This is impressive and impactful work with a complete analysis of the ambipolar FETs showing a strong understanding of behaviour. I recommend publication. That being said there are some points that need to be addressed:

Response:

We thank Reviewer #4 for his/her recommendation for publication and for the valuable comments that will help improve the quality of this manuscript. Below is our point-by-point response to the questions raised by Reviewer #4.

Comments 4-1: The ferroelectric layer in these devices is very thick and yields a low polarisation. The material choice should be discussed. Other materials would help the scaling challenge. Applying +/-40V to switch a device is also not device-ready, a thinner ferroelectric would solve this.

Response 4-1:

We sincerely appreciate Reviewer #4 for pointing out this highly important issue. In our work, organic P(VDF-TrFE) is adopted as the ferroelectric gate due to its easy processing, low cost, and inherent flexibility. To emphasize the versatility of our device structure and further reduce the operating voltage, inorganic ferroelectrics with a moderate coercive field and low critical thickness will be explored as gate dielectrics in future work. For example, ultrathin hafnium-based ferroelectric is a good candidate that is worthy to be further explored in this novel memory structure.

In additionally, we fully agree with Reviewer #4 that lower operation voltage is more preferred for device application. A smaller operating voltage can be obtained by reducing the thickness of ferroelectric layer in the vertical tunneling MoS_2-FeFET device. As shown in **Fig. R16**, the operating voltage is reduced to 10 V for the device with a 100 nm-thick ferroelectric layer from 20 V for the device with a 200 nm-thick ferroelectric layer. Further work is needed to optimize the ultrathin and high-quality ferroelectric polymer films for an operating voltage that is small enough to be compatible with mature complementary metal oxide semiconductor (CMOS) techniques.

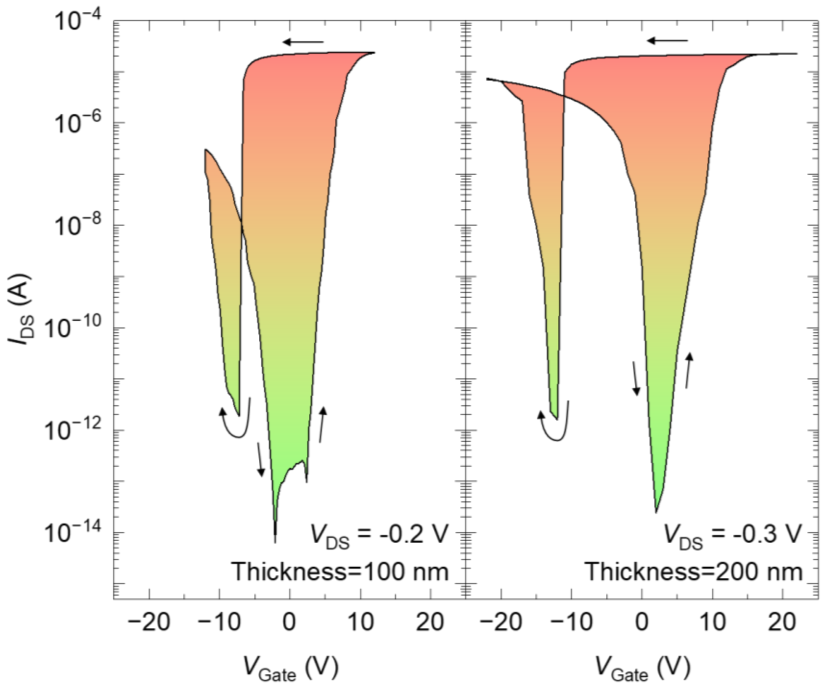

Fig. R16 Transfer curves of vertical tunneling MoS_2-FeFET with a thickness of 100 nm (left panel) and 200 nm (right panel) respectively.

We have added these discussions to the revised manuscript. See "A lower operating voltage is preferable from the view of practical application. This can be obtained by reducing the thickness of ferroelectric layer in the vertical tunneling MoS_2-FeFET device. As shown in **Fig. S13**, the operating voltage decreases from 20 V for the device with a 200 nm-thick ferroelectric layer to 10 V for the device with 100 nm-thick ferroelectric layer. Further work is needed to optimize the ultrathin and high-quality ferroelectric polymer films to achieve operating voltages low enough for compatibility with mature complementary metal-oxide-semiconductor (CMOS) technology. On the parallel, other ferroelectrics, such as ultrathin hafnium-based ferroelectrics, present promising alternatives that warrant further exploration in this novel memory structure."

from line 17 of page 21 to line 4 in page 22.

Comments 4-2: In reference to figure 1d, it is claimed that full 180 degree phase contrast in the PFM image is observed. While I have no doubt this is ferroelectric, there seems to be less that 180degree switch. This could be explained by surface charging or some defect dipoles. Nevertheless, the combination of the amplitude and phase images are convincing without this claim.

Response 4-2:

We sincerely thank Reviewer #4 for this valuable question and apologize for not providing direct evidence of the 180° phase contrast in the PFM image. We agree with Reviewer #4 that some extrinsic factors such as surface charging or defect dipoles may result in a phase switch of less than 180°. As shown in **Fig. R17**, the PFM phase signals exhibit nearly 180° phase contrast between opposite domains in the P(VDF-TrFE) films.

[Figure redacted]

Fig. R17 PFM phase (**a**) and amplitude (**b**) images of P(VDF-TrFE) films after writing a "panda" shape with biased conductive tip. (**c**)The profile of the black line labeled in phase image (**a**) shows nearly 180° phase contrast between opposite domains.

Comments 4-3: Whilst I agree that this is impressive work and promising for future devices, the repeated claims that these devices are promising for various applications including 'multibit memory and neuromorphic computing' are a little too ambitious. The ferroelectric of choice requires too high thickness for scaling, and high device operation voltage is needed. These statements need rewording to prevent misunderstanding.

Response 4-3:

We sincerely appreciate Reviewer #4 for pointing out this important issue. To avoid any potential misunderstandings, "indicating great potential for robust multi-bit memory and neuromorphic computing applications." has been changed into "indicating possible potential for robust multi-bit memory and neuromorphic computing applications" in the revised manuscript.

Comments 4-4: Figure 3 is not so clear, it would be helped by improving the caption.

Response 4-4: We acknowledge Reviewer #4 for this kind suggestion. In the caption of Figure 3, "Color mapping of I_{DS} in MoS_2-FeFETs with different contacts" has been changed into "Color mapping of I_{DS} with evolution of V_{GS} and V_{DS}" in the revised manuscript.

Comments 4-5: Figure references need checking, some figures did not appear to exist.

Response 4-5:

We appreciate Reviewer #4's thoughtful reminder. To avoid redundancy with Figures 2a-c, we have removed Figures 3a-c in the revised manuscript. Additionally, we have thoroughly checked the revised manuscript to ensure that all figures and panels in these figures are appropriately addressed.

Comments 4-6: English quality needs to be improved.

Response 4-6:

We thank Reviewer #4 for this suggestion. We have carefully reviewed and polished the English writing and highlighted the changes in blue in the revised manuscript.

Point-to-point reply letter

Response to the Reviewer #1's comments

Comments:

The authors have addressed all the concerns from this reviewer. I would like to recommend this manuscript for publication in Nature Communications.

Response:

We appreciate Reviewer #1 for his/her positive comments that "I would like to recommend this manuscript for publication in Nature Communications".

Response to the Reviewer #2's comments

Comments:

The authors have addressed my concerns, so it is publishable on Nature Communications now.

Response:

We appreciate Reviewer #2 for his/her positive comments that "The authors have addressed my concerns, so it is publishable on Nature Communications now".

Response to the Reviewer #3's comments

Comments:

The authors addressed all the concerns. Therefore, I recommend to published in Nature Communications.

Response:

We appreciate Reviewer #3 for his/her positive comments that "I recommend to published in Nature Communications".

Response to the Reviewer #4's comments

Comments:

All points from my first review have been addressed well, I would recommend publication while noting the following.

Response:

We appreciate Reviewer #4 for his/her positive comments that "I would recommend publication while noting the following". We did appropriate changes according to his/her comments. Below is a point-by-point reply to the questions raised by the Reviewer #1.

Comments 4-1: Although voltage scaling of ferroelectric switching is well understood in the regime of 100-200nm thickness, within the useful thickness range (<20nm) for real devices, voltage scaling will undoubtedly not be linear with decreasing thickness. Interfacial strain and electrostatic boundary conditions play an increasingly dominant role, and can even increase the fields required for switching. Therefore, one should be extremely careful in stating "As shown in Fig. S13, the operating voltage decreases from 20 V for the device with a 200 nm-thick ferroelectric layer to 10 V for the device with 100 nm-thick ferroelectric layer" to imply that simply scaling thickness would work well in such a device.

Response 4-1:

We thank Reviewer #4 for this valuable reminder. We agree with Reviewer #4 for his/her point that "voltage scaling will not be linear with decreasing thickness within the small thickness range (<20nm) and the interfacial strain and electrostatic boundary conditions play an increasingly dominant role, and can even increase the fields required for switching". We added this discussion into revised our manuscript. See "It should be noted that the voltage scaling is not always linear with decreasing thickness when the thickness approaches nanoscale. The interfacial strain and electrostatic boundary conditions may play an increasingly dominant role and can even increase the fields required for switching." from line 9 to line 12 in page 17.