

Symmetry breaking induces room-temperature interface ferroelectricity in two-dimensional metastable mosaic-like heterostructures

Corresponding Author: Dr Yao Wen

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 manuscript reports metastable SmO₂/Sm₂O₃ lateral heterostructures grown by molten eutectic salt, and claims that interfacial symmetry breaking gives rise to room-temperature ferroelectricity and to high-performance memristive switching governed by oxygen-vacancy migration along a vertical heterointerface. The topic is potentially interesting. However, in my view the manuscript does not provide sufficiently rigorous evidence for its claims, and I therefore cannot support publication in Nature Communications in its present form.

The main issue is that the strongest claims of the paper are substantially overinterpreted relative to the data. In particular, both the origin of the ferroelectricity and the origin of the memristive switching remain insufficiently demonstrated.

Major comments

1. The claim that ferroelectricity originates from the SmO₂/Sm₂O₃ interface is not convincingly established: The SHG data demonstrate non-centrosymmetry, but SHG alone does not prove ferroelectricity, and certainly not that the switchable polarization is localized at the interface. The ferroelectric evidence relies essentially on PFM box-in-box writing and local phase/amplitude hysteresis loops from only a very limited number of flakes. This is insufficient for such a strong claim. The manuscript lacks critical controls such as spatially resolved demonstration that the PFM response is confined to the interface. In addition, no independent macroscopic ferroelectric measurements (e.g., P–E loops or PUND protocol) are provided to corroborate the local PFM observations.
2. The proposed memristive switching mechanism is largely speculative: The manuscript attributes the resistive switching to oxygen-vacancy migration along a vertical SmO₂/Sm₂O₃ heterointerface, coupled to reversible oxygen exchange with the Ti electrode. However, no direct evidence is provided for this mechanism. In particular, there is no direct observation of oxygen redistribution, no spectroscopic demonstration of reversible Ti oxidation/reduction, no post-switching interfacial chemical analysis, and no nanoscale current mapping showing that conduction is confined to the proposed interface. As presented, this is a plausible scenario, but not a demonstrated mechanism.
3. The transport analysis does not uniquely support the claimed valence-change mechanism: The supplementary transport analysis is not sufficiently compelling or self-consistent. For the Au-bottom-electrode devices, the authors invoke Ohmic conduction in LRS and SCLC-like behavior in HRS; for the Gr-bottom-electrode devices, the reported power-law exponents are different and the interpretation appears less clear. These analyses do not provide a unique fingerprint of interfacial oxygen-vacancy-guided switching, nor do they rule out other switching mechanisms.
4. Device robustness and reproducibility are not at the level expected for the claims made: The graphite-based devices are tested for only 85 cycles, while the Au-based devices show endurance of only 10 cycles and substantial cycle-to-cycle variability. Moreover, the device-to-device on/off ratio spans several orders of magnitude. This degree of dispersion is difficult to reconcile with the manuscript's repeated emphasis on a highly controlled interface-governed mechanism and undermines the claim of robust high-performance memristors.

5. The material is introduced as a lateral heterostructure, but this is not supported by the displayed TEM measurement. The structural characterization is inherently local, and the TEM analysis does not demonstrate that the SmO₂/Sm₂O₃ interface extends continuously across the full thickness of the nanosheet. In particular, there is no direct evidence that such an interface forms a vertically connected pathway between the top and bottom electrodes. This point is critical, as the proposed memristive mechanism relies on a vertically continuous interfacial channel for ionic and electronic transport.

Minor comments

6. The manuscript contains numerous grammatical issues and awkward phrasing, including several statements in the abstract and main text that are overstated relative to the evidence. Expressions such as “unambiguous evidence,” “robust room-temperature ferroelectric polarization,” and “the switching mechanism originates from...” should be softened unless substantially stronger evidence is provided.

7. Quantitative statistics for the ferroelectric measurements are missing. It would be important to know how many flakes/devices were tested and how reproducible the PFM response is.

8. The phase characterization would benefit from valence-sensitive spectroscopy and more direct mapping of phase purity and interface distribution.

Recommendation

Overall, while the system may be of interest, the manuscript does not presently provide sufficiently rigorous evidence for its key claims regarding interfacial ferroelectricity and the microscopic origin of memristive switching. The conclusions are significantly overinterpreted relative to the data. I therefore recommend rejection.

Reviewer #2

(Remarks to the Author)

In the manuscript entitled "Symmetry breaking induces room-temperature ferroelectricity in two-dimensional metastable heterostructures" Yang et al. explore the SHG and ferroelectric properties of the SmO₂/Sm₂O₃ interface, which displays a switchable polarization due to oxygen vacancy migration. The work is technically sound and the results are interesting. However, several clarifying edits are required before the work is suitable for publication.

1. Figure 2(g) shows a SHG signal that completely disappears at a temperature around 700 K. Is this change reversible? If it occurs due to a phase transformation of the metastable SmO₂ to Sm₂O₃, then it likely is not. Is the measurement shown in 2(g) taken on heating or cooling?

2. How is in-plane PFM data taken? Is a nanosheet measured that is on its side? Or perhaps one with a different out-of-plane direction? Does the interface occur in one plane in a nanosheet or is the interface 3-dimensional?

3. SHG can be used to measure water/mica interfaces, which is essentially a mica/oxide interface as is obtained during SmO_x growth. How can one be certain that the SHG line shown in Figure 2(f) is indeed from the SmO₂/Sm₂O₃ interface, when a response may be expected from a mica/oxide interface? Was the SHG measured following exfoliation onto a different substrate?

4. How are plots in Fig4(f) and 4(g) calculated? Is DFT used in these cases?

5. It is shown in Figure 4(h) that illumination with an electron beam results in a transformation to the more stable Sm₂O₃ phase due to mass transport. This implies that the SHG and ferroelectric properties are irreversibly changed during heating (see comment 1). This characteristic should be discussed, especially considering that component electronics are generally expected to heat during operation.

6. It is not clear based upon the microscopy present in the manuscript - does the SmO₂ Sm₂O₃ form a smooth interface with the Sm₂O₃? For example, can this be considered a bilayer? Or are there regions of SmO₂ within the Sm₂O₃ nanosheets? The image in figure 3(a) (as well as supplementary figure 6) implies the latter of these options.

7. The analysis of the mechanism driving the difference between LHS and RHS is slightly difficult to understand. Based upon the symmetry arguments given, the expectation would be that the center of symmetry is broken at any SmO₂/Sm₂O₃ interface. However, the explanation given around lines 340 - 352 centers around the formation of conductive filaments, which should be a mechanism separate from ferroelectric switching. Do these two mechanisms coexist? This seems reasonable based upon the cyclical IV curves, however the discussion perhaps needs more clarity in articulating this and connecting this with the IV curves.

8. There are several typographical errors that require attention for readability:

- Line 71 - Perhaps the word 'ionic' should be removed?
- Line 139 - 140 - Only half of a sentence.
- Line 145 - 147 - Only half of a sentence.
- Line 150 - Perhaps the ', is helpful.' should be removed?
- Line 342 - 345 This sentence needs to be rewritten.

- f. Supplementary figures 11 and 12 are mentioned in the main text before supplementary figure 10.
- g. Figure 2(d) is poor resolution and the step height inset is not readable.
- h. Figure 4(e) (and in the text) uses the phrase 'in-of-plane', where typically 'in-plane' is used.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I appreciate the authors' thorough and constructive response to the reviewers' comments. The revised manuscript has been substantially strengthened through the addition of macroscopic ferroelectric measurements, additional PFM characterization, cross-sectional TEM-EELS analysis, and C-AFM current mapping. These new results significantly reinforce the proposed physical picture and the authors have also moderated several mechanistic claims, making the interpretation more balanced and consistent with the available evidence.

While some aspects of the microscopic mechanism remain inferential—as is often the case in oxide memristive systems—I consider that the conclusions are now adequately supported by the experimental data presented. I therefore recommend publication in its present form.

Reviewer #2

(Remarks to the Author)

The authors have addressed many of the comments provided, clarifying the structural organization of the films and origin of transport signals, as well as providing additional details regarding modeling and characterization. Below is provided an additional comment that will be necessary to address ahead of publication:

1. Based upon the irreversibility observed using T-resolved SHG, it is evident that there is no intrinsic ferroelectricity in this structure (i.e. a thermodynamically stable unit cell with a stable field-dependent dipole switching mechanism). Instead, broken symmetry and reversible, field-dependent oxygen transport at the interface between the Sm oxides gives the appearance of ferroelectricity. This detail should be clarified in the title, and elsewhere in the manuscript. As read, the title implies that the Sm oxide interface constitutes a 2D ferroelectric, such as MoS₂/WS₂, or In₂Se₃. However, in these two other cases, the polarization mechanism involves reversible movement of constitutive species and not charged defects.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have sufficiently addressed my comments.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

1 Reviewers' Comments:

2 **Reviewer #1 (Remarks to the Author):**

3 This manuscript reports metastable $\text{SmO}_2/\text{Sm}_2\text{O}_3$ lateral heterostructures grown by
4 molten eutectic salt, and claims that interfacial symmetry breaking gives rise to
5 room-temperature ferroelectricity and to high-performance memristive switching
6 governed by oxygen-vacancy migration along a vertical heterointerface. The topic is
7 potentially interesting. However, in my view the manuscript does not provide
8 sufficiently rigorous evidence for its claims, and I therefore cannot support
9 publication in Nature Communications in its present form.

10 The main issue is that the strongest claims of the paper are substantially
11 overinterpreted relative to the data. In particular, both the origin of the ferroelectricity
12 and the origin of the memristive switching remain insufficiently demonstrated.

13 Comments:

14 1. The claim that ferroelectricity originates from the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface is not
15 convincingly established: The SHG data demonstrate non-centrosymmetry, but SHG
16 alone does not prove ferroelectricity, and certainly not that the switchable polarization
17 is localized at the interface. The ferroelectric evidence relies essentially on PFM
18 box-in-box writing and local phase/amplitude hysteresis loops from only a very
19 limited number of flakes. This is insufficient for such a strong claim. The manuscript
20 lacks critical controls such as spatially resolved demonstration that the PFM response
21 is confined to the interface. In addition, no independent macroscopic ferroelectric
22 measurements (e.g., P-E loops or PUND protocol) are provided to corroborate the
23 local PFM observations.

24 2. The proposed memristive switching mechanism is largely speculative: The
25 manuscript attributes the resistive switching to oxygen-vacancy migration along a
26 vertical $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterointerface, coupled to reversible oxygen exchange with the
27 Ti electrode. However, no direct evidence is provided for this mechanism. In
28 particular, there is no direct observation of oxygen redistribution, no spectroscopic
29 demonstration of reversible Ti oxidation/reduction, no post-switching interfacial
30 chemical analysis, and no nanoscale current mapping showing that conduction is

31 confined to the proposed interface. As presented, this is a plausible scenario, but not a
32 demonstrated mechanism.

33 3. The transport analysis does not uniquely support the claimed valence-change
34 mechanism: The supplementary transport analysis is not sufficiently compelling or
35 self-consistent. For the Au-bottom-electrode devices, the authors invoke Ohmic
36 conduction in LRS and SCLC-like behavior in HRS; for the Gr-bottom-electrode
37 devices, the reported power-law exponents are different and the interpretation appears
38 less clear. These analyses do not provide a unique fingerprint of interfacial
39 oxygen-vacancy-guided switching, nor do they rule out other switching mechanisms.

40 4. Device robustness and reproducibility are not at the level expected for the claims
41 made: The graphite-based devices are tested for only 85 cycles, while the Au-based
42 devices show endurance of only 10 cycles and substantial cycle-to-cycle variability.
43 Moreover, the device-to-device on/off ratio spans several orders of magnitude. This
44 degree of dispersion is difficult to reconcile with the manuscript's repeated emphasis
45 on a highly controlled interface-governed mechanism and undermines the claim of
46 robust high-performance memristors.

47 5. The material is introduced as a lateral heterostructure, but this is not supported by
48 the displayed TEM measurement. The structural characterization is inherently local,
49 and the TEM analysis does not demonstrate that the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface extends
50 continuously across the full thickness of the nanosheet. In particular, there is no direct
51 evidence that such an interface forms a vertically connected pathway between the top
52 and bottom electrodes. This point is critical, as the proposed memristive mechanism
53 relies on a vertically continuous interfacial channel for ionic and electronic transport.

54 6. The manuscript contains numerous grammatical issues and awkward phrasing,
55 including several statements in the abstract and main text that are overstated relative
56 to the evidence. Expressions such as "unambiguous evidence," "robust
57 room-temperature ferroelectric polarization," and "the switching mechanism
58 originates from..." should be softened unless substantially stronger evidence is
59 provided.

60 7. Quantitative statistics for the ferroelectric measurements are missing. It would be

important to know how many flakes/devices were tested and how reproducible the PFM response is.

8. The phase characterization would benefit from valence-sensitive spectroscopy and more direct mapping of phase purity and interface distribution.

Reviewer #2 (Remarks to the Author):

In the manuscript entitled "Symmetry breaking induces room-temperature ferroelectricity in two-dimensional metastable heterostructures" Yang et al. explore the SHG and ferroelectric properties of the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface, which displays a switchable polarization due to oxygen vacancy migration. The work is technically sound and the results are interesting. However, several clarifying edits are required before the work is suitable for publication.

1. Figure 2(g) shows a SHG signal that completely disappears at a temperature around 700 K. Is this change reversible? If it occurs due to a phase transformation of the metastable SmO_2 to Sm_2O_3 , then it likely is not. Is the measurement shown in 2(g) taken on heating or cooling?

2. How is in-plane PFM data taken? Is a nanosheet measured that is on its side? Or perhaps one with a different out-of-plane direction? Does the interface occur in one plane in a nanosheet or is the interface 3-dimensional?

3. SHG can be used to measure water/mica interfaces, which is essentially a mica/oxide interface as is obtained during SmO_x growth. How can one be certain that the SHG line shown in Figure 2(f) is indeed from the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface, when a response may be expected from a mica/oxide interface? Was the SHG measured following exfoliation onto a different substrate?

4. How are plots in Fig4(f) and 4(g) calculated? Is DFT used in these cases?

5. It is shown in Figure 4(h) that illumination with an electron beam results in a transformation to the more stable Sm_2O_3 phase due to mass transport. This implies that the SHG and ferroelectric properties are irreversibly changed during heating (see comment 1). This characteristic should be discussed, especially considering that component electronics are generally expected to heat during operation.

6. It is not clear based upon the microscopy present in the manuscript - does the SmO_2 Sm_2O_3 form a smooth interface with the Sm_2O_3 ? For example, can this be considered a bilayer? Or are there regions of SmO_2 within the Sm_2O_3 nanosheets? The image in figure 3(a) (as well as supplementary figure 6) implies the latter of these options.

7. The analysis of the mechanism driving the difference between LHS and RHS is slightly difficult to understand. Based upon the symmetry arguments given, the expectation would be that the center of symmetry is broken at any $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface. However, the explanation given around lines 340 - 352 centers around the formation of conductive filaments, which should be a mechanism separate from ferroelectric switching. Do these two mechanisms coexist? This seems reasonable based upon the cyclical IV curves, however the discussion perhaps needs more clarity in articulating this and connecting this with the IV curves.

8. There are several typographical errors that require attention for readability:

a. Line 71 - Perhaps the word 'ionic' should be removed?

b. Line 139 - 140 - Only half of a sentence.

Response to Reviewer #1:

This manuscript reports metastable SmO₂/Sm₂O₃ lateral heterostructures grown by molten eutectic salt, and claims that interfacial symmetry breaking gives rise to room-temperature ferroelectricity and to high-performance memristive switching governed by oxygen-vacancy migration along a vertical heterointerface. The topic is potentially interesting. However, in my view the manuscript does not provide sufficiently rigorous evidence for its claims, and I therefore cannot support publication in Nature Communications in its present form.

The main issue is that the strongest claims of the paper are substantially overinterpreted relative to the data. In particular, both the origin of the ferroelectricity and the origin of the memristive switching remain insufficiently demonstrated.

Our reply: We sincerely appreciate the Reviewer's critical evaluation of the manuscript and acknowledgment that "The main issue is that the strongest claims of the paper are substantially overinterpreted relative to the data". We also thank the reviewer for the constructive suggestions that are important for the improvement of the manuscript. We have addressed the reviewer's questions and revised our manuscript accordingly. Our point-by-point responses are stated as below.

Comment 1. *The claim that ferroelectricity originates from the SmO₂/Sm₂O₃ interface is not convincingly established: The SHG data demonstrate non-centrosymmetry, but SHG alone does not prove ferroelectricity, and certainly not that the switchable polarization is localized at the interface. The ferroelectric evidence relies essentially on PFM box-in-box writing and local phase/amplitude hysteresis loops from only a very limited number of flakes. This is insufficient for such a strong claim. The manuscript lacks critical controls such as spatially resolved demonstration that the PFM response is confined to the interface. In addition, no independent macroscopic ferroelectric measurements (e.g., P-E loops or PUND protocol) are provided to corroborate the local PFM observations.*

Our reply: Thanks again for the reviewer's very constructive suggestion. The

macroscopic ferroelectric hysteresis loop (P - E loop, where E is the electric field) obtained in Fig. R1a demonstrates the ferroelectricity of the sample, with the black arrow indicating the presence of polarization switching current. To provide a further quantitative evolutionary analysis of the ferroelectric performance under varying electric field intensities, the field-dependent behavior of the hysteresis loops is presented in Fig. R1b. Based on these observations, the remnant polarization (P_r) values were extracted from the hysteresis loops, yielding a maximum $2P_r$ of $2.97 \mu\text{C cm}^{-2}$ and a coercive field (E_c) of 0.22 MV cm^{-1} .

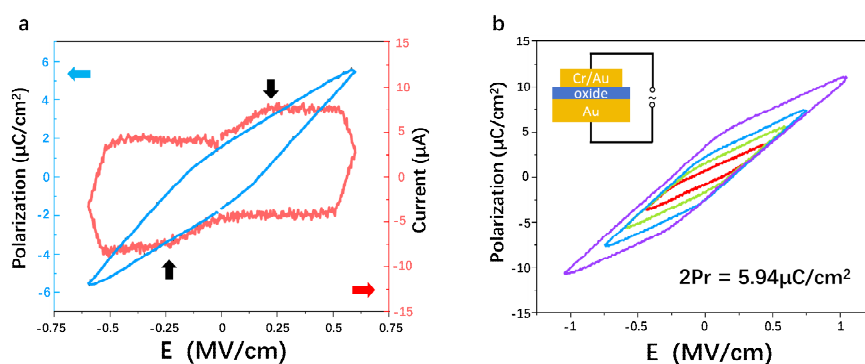


Figure R1 (a) Polarization and current versus electric field for the $\text{SmO}_2/\text{Sm}_2\text{O}_3$. (b) Polarization measured under increasing maximum electric field.

We have added relevant content to the manuscript and added new figures in Supporting Information (Supplementary Fig. 10). “To evaluate the ferroelectric properties, polarization-electric field (P - E) hysteresis loop measurement was performed. The loop exhibits a hysteretic switching response, with the black arrow indicating the polarization switching current. From these measurements, a double remnant polarization ($2P_r$) of $\sim 2.97 \mu\text{C}\cdot\text{cm}^{-2}$ and a coercive field (E_c) of $\sim 0.22 \text{ MV}\cdot\text{cm}^{-1}$ were extracted (Supplementary Fig. 10).”(pages 10, lines 235)

As shown in Fig. R2, the PFM phase and amplitude images reveal contrast variations that are spatially correlated with the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ hetero-interface (marked by dashed lines). The phase contrast exhibits a reversal across the putative interface region, while the surrounding regions show relatively weak or negligible response.

The corresponding amplitude map shows that the piezoresponse signal is primarily distributed near the interfacial region, with the signal intensity gradually diminishing away from the interface. These observations indicate a spatial correlation between the PFM response and the interface location, suggesting that the switching behavior is associated with the heterointerface rather than uniformly distributed across the oxide.

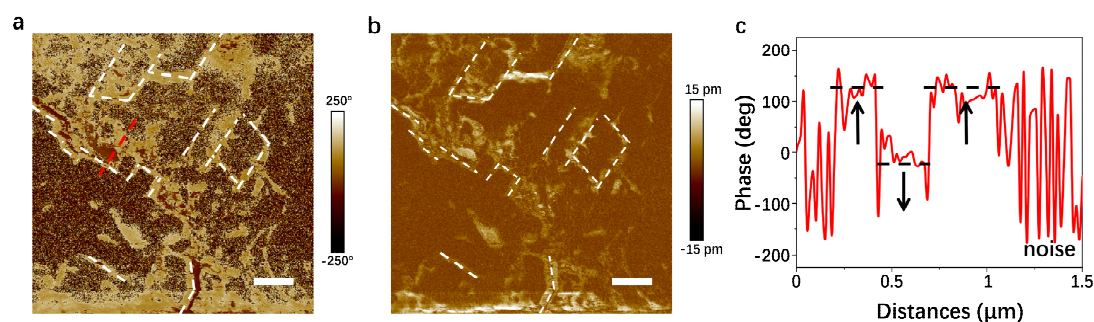


Figure R12 Phase characterization (a) PFM phase image. Scale bar, 1 μm. (b) PFM amplitude image. Scale bar, 1 μm. (c) The PFM phase profile along the red dash line shown in a.

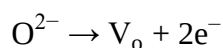
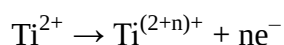
We have added new figure to Supporting Information (Supplementary Fig. 12).

Comment 2. *The proposed memristive switching mechanism is largely speculative: The manuscript attributes the resistive switching to oxygen-vacancy migration along a vertical $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterointerface, coupled to reversible oxygen exchange with the Ti electrode. However, no direct evidence is provided for this mechanism. In particular, there is no direct observation of oxygen redistribution, no spectroscopic demonstration of reversible Ti oxidation/reduction, no post-switching interfacial chemical analysis, and no nanoscale current mapping showing that conduction is confined to the proposed interface. As presented, this is a plausible scenario, but not a demonstrated mechanism.*

Our reply: We thank the reviewer for the critical and constructive assessment of the switching mechanism. We fully agree that direct experimental evidence is essential to substantiate the proposed oxygen-vacancy migration model. We have performed

comprehensive cross-sectional TEM combined with electron energy-loss spectroscopy (EELS) on devices in both the HRS and LRS, providing direct evidence for the proposed mechanism on multiple fronts.

Figure R2b displays the Ti L-edge EELS spectra across the Ti electrode for both the HRS and LRS. In the LRS, the splitting into four peaks is more pronounced in the EELS curves corresponding to the region near the interface, whereas spectra obtained far from the interface exhibit a doublet structure where the spectral features converge toward those of the HRS, thereby reflecting the spatial distribution of the Ti valence state. To further examine these valence changes, Figure R2c provides a direct comparison of the total Ti L-edge spectra between the two states. In the HRS, the Ti L-edge exhibits two characteristic peaks, consistent with the Ti^{2+} oxidation state. Upon applying a positive bias to switch the device from HRS to LRS, the Ti L-edge at the interface evolves into four distinct peaks, indicative of an increased oxidation degree of the electrode. This spectral evolution provides direct spectroscopic evidence for the oxidation state change of Ti, supporting the interpretation that reversible redox reactions at the electrode interface are intimately linked to the resistance switching process.



The spatial variation of the relative oxygen signal, as traced by the O K-edge intensity in Fig. R3, offers a semiquantitative measure of changes in local oxygen content. Critically, the observed change in Ti valence state, as shown in Fig. R2a and R2b, is intrinsically linked to this spatial redistribution of oxygen. We interpret the decreased oxygen signal in specific regions as being indicative of a locally increased oxygen-vacancy concentration. This spatial correlation between the oxygen-depleted profile and the physical location of the conductive filament provides strong support for the proposed mechanism. Within this framework, the field-driven redistribution of oxygen, resulting in a vertical accumulation of oxygen vacancies, is posited to facilitate the formation of the conductive filament that defines the LRS.

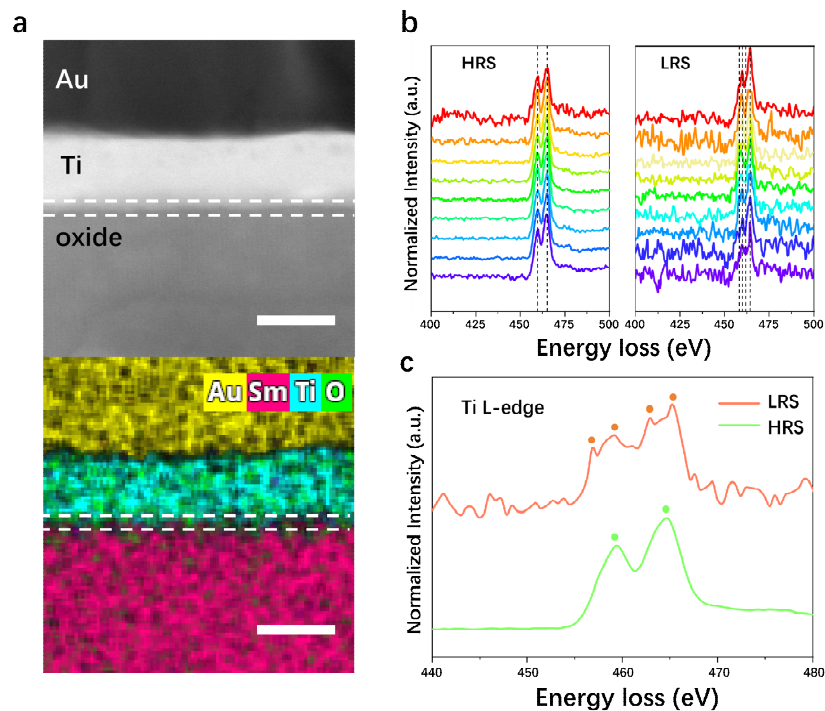


Figure R3 Cross-sectional TEM-EELS chemical analysis of Ti at the electrode interface in HRS and LRS (a) TEM image and EDS mapping of the interface. Scale bar, 10nm. (b)Ti L-edge EEL spectra as a function of position for the device in the HRS and LRS. The spectra were acquired across the Ti electrode from the bottom to the top. (c) Comparison of Ti L-edge EEL spectra between HRS and LRS. (c) O K-edge normalized intensity for the same region in the HRS and LRS.

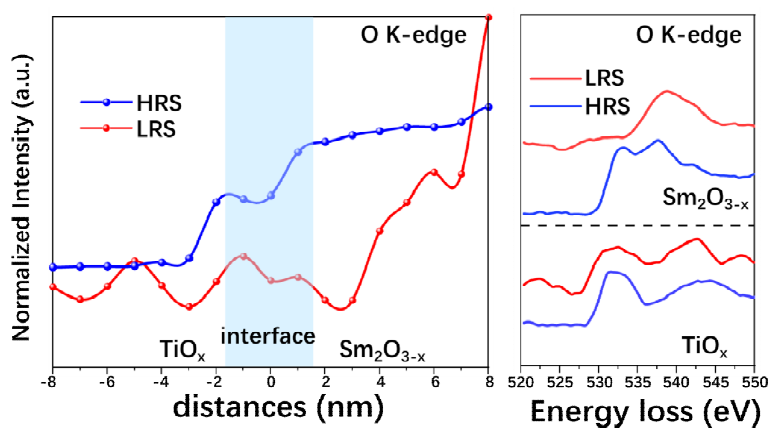


Figure R4 Cross-sectional TEM-EELS chemical analysis of O at the electrode interface in HRS and LRS

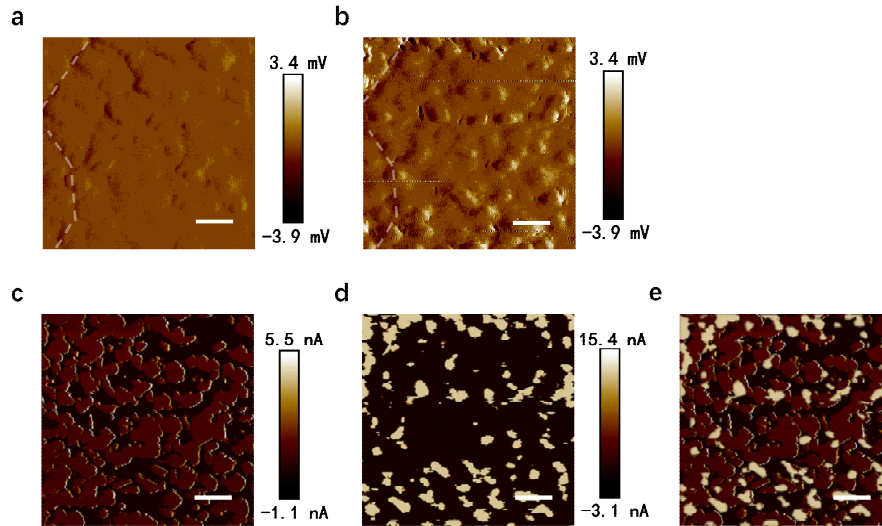


Figure R18 C-AFM characterization of the memristive device in HRS and LRS. (a) The C-AFM surface deflection at HRS. (b) The C-AFM surface deflection acquired immediately after the forming process. (c) The C-AFM current mapping images of device at HRS. (d) The C-AFM current mapping images of device at LRS. (e) Spatially superimposed C-AFM current maps acquired from the same device region in the HRS and LRS. All scale bar, 200nm.

Conductive Atomic Force Microscopy (C-AFM) images display Nanoscale current mapping information in Fig. R5. Surface topography maps of the device in the HRS (Fig. R5a) and immediately after the electroforming process (Fig. R5b) were acquired from an identical scanning area to ensure consistency in the C-AFM testing positions, thereby enabling direct spatial correlation between HRS and LRS conduction pathways. The HRS current map (Fig. R5d) reveals a non-uniform current distribution across the scanned region, where spot-like regions of relatively high current intensity are scattered rather than a homogeneous background. These localized spots indicate preferential leakage pathways in the HRS, likely attributed to the inherent spatial inhomogeneity of phases within the nanosheet region. Upon switching the device to the LRS, the current map (Fig. R5e) shows sharp and localized high-current filamentary regions with intensity significantly exceeding that of the HRS. As shown in Fig. R5c, these filaments mostly appear at a position that corresponds to the boundary between the distinct conductivity regions observed in the HRS. This

observation is consistent with the scenario in which conduction is preferentially localized at the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterointerface, although we recognize that direct confirmation would require higher-resolution spatial mapping and will be pursued in future work.

We have added relevant content to the manuscript and added new figures to Supporting Information (Supplementary Fig. 25, 26 and 27). *“This mechanism is substantiated by experimental findings. Cross-sectional EELS was performed at the Ti electrode interface in both HRS and LRS (Supplementary Fig. 25). Near the interface, the Ti L-edge spectra evolve from a doublet in the HRS to a four-peak structure in the LRS, indicating a locally increased Ti oxidation state upon switching. Spatially resolved O K-edge intensity further reveals a pronounced oxygen depletion near the interface in the LRS (Supplementary Fig. 26). The spatial overlap between the Ti valence change and the oxygen-depleted region provides direct evidence that the conductive filament is formed via field-driven oxygen migration, accompanied by reversible redox reactions at the Ti electrode. To directly visualize the conduction pathways, we performed conductive atomic force microscopy (C-AFM) current mapping on the same scanning area in both HRS and LRS (Supplementary Fig. 27). In the HRS, the current map reveals a non-uniform distribution with scattered high-current spots, suggesting preferential leakage paths within the nanosheet. Upon switching to the LRS, sharp and highly localized high-current filaments emerge, with intensities markedly higher than those in the HRS. Notably, these filaments predominantly appear at positions corresponding to the boundary between distinct conductivity regions observed in the HRS, suggesting that the conductive filament is preferentially localized near the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterointerface.”*(pages 16, lines 406)

Comment 3. *The transport analysis does not uniquely support the claimed valence-change mechanism: The supplementary transport analysis is not sufficiently compelling or self-consistent. For the Au-bottom-electrode devices, the authors invoke Ohmic conduction in LRS and SCLC-like behavior in HRS; for the*

Gr-bottom-electrode devices, the reported power-law exponents are different and the interpretation appears less clear. These analyses do not provide a unique fingerprint of interfacial oxygen-vacancy-guided switching, nor do they rule out other switching mechanisms.

Our reply: We thank the Reviewer for the insightful comment. In our work, we should distinguish between the transport mechanism (characterized by quasi-steady-state I - V characteristics) and the resistive switching mechanism (governed by dynamic ion migration and redox reactions). We have submitted new experimental evidence to support our valence-change mechanism. The purpose of transport analysis is to identify transport mechanism and the role of possible defects (primarily oxygen vacancies) in modulating carrier dynamics, rather than to serve as conclusive evidence of the switching pathway. To assess the possible transport mechanisms, we analyzed the I - V characteristics and temperature-dependent resistance. The results suggest that oxygen vacancies play a role in the transport behavior. We have revised the Supplementary Information and new figures to Supporting Information (Supplementary Fig. 15).

The I - V characteristics of Gr-bottom-electrode device is shown in Fig. R6a. As a semimetal, graphene possesses conduction and valence bands that meet at the Dirac point, exhibiting a linear dispersion relation rather than the parabolic dispersion characteristic of conventional metals (*Nat. Phys.* 2006 2(9): 595-599). This electronic structure allows the Fermi level of graphene to be modulated via external stimuli, such as electric fields or chemical doping. Unlike conventional metal electrodes, electron transfer between graphene and semiconductors mitigates pinning, enabling the Fermi level of graphene to align naturally with the semiconductor, thereby eliminating the potential barrier (*Sci. Adv.* 2023 9(29): eadh9770). Consequently, the experiment observed Ohmic contact behavior in the HRS. Furthermore, the heterogeneous electron transfer (HET) dynamics are determined not only by the driving force (potential difference) but also by electronic coupling (*Nature* 2026 653(8113): 98-103). Electronic coupling reflects the probability of electron tunneling across the interface and stems from the density of states (DOS) of the electrode

material. In contrast, upon switching to the LRS where oxygen vacancy conductive filaments penetrate the interface, localized states on the graphene surface introduce intermediate energy levels and modulate the interface barrier. These modifications cause the electron injection efficiency to vary non-linearly with voltage, leading to the sublinear transport characteristic of $I \sim V^{0.46}$ observed experimentally. This sublinear transport characteristic serves as a macroscopic manifestation of HET kinetics being modulated by localized defect states.

Conversely, for the Au-electrode devices (Fig. R6b), the double-logarithmic I - V plot reveals a clear three-regime behavior: an Ohmic region ($n \approx 1$) at low voltages, a Child's law region ($n \approx 2$) at intermediate voltages, and a trap-filled limit (TFL) region with a steep exponent of $n \approx 14$ at high voltages. This sequential transition is characteristic of space-charge-limited conduction (SCLC) mediated by an exponential distribution of bulk traps (*Nature* 1958 182(4645), 1296-1297). The high exponent in the TFL region is suggestive of rapid filling of deep-level traps by injected carriers, leading to a sudden current surge once all traps are occupied. Crucially, temperature-dependent resistance measurements for the Au-electrode devices (Fig. R6d) conducted from 300K down to 100 K show negligible variation in the HRS. This weak temperature dependence, combined with the absence of a linear regime in the $\ln(I)$ versus V plot across the entire voltage range, does not support thermally activated processes such as Schottky or Poole-Frenkel emission, and is more compatible with defect-mediated tunneling transport (*Nat. Commun.* 2024 15(1), 3492). While we acknowledge that the transport analysis alone does not uniquely prove the switching mechanism, these observations are consistent with the presence of a high density of oxygen vacancies, which are the likely candidate defects responsible for the valence-change switching (*Nat. Nano.* 2016 11(1), 67-74).

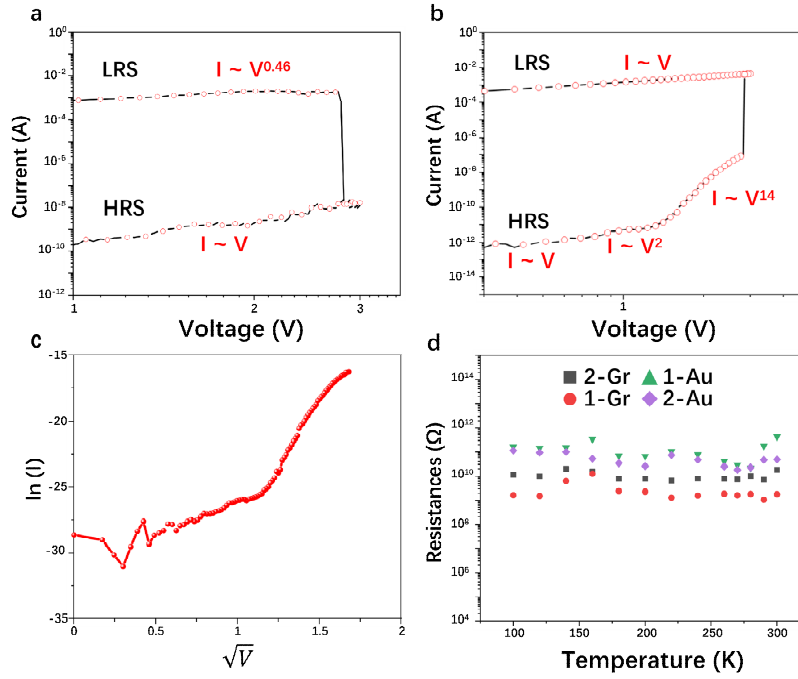


Figure R6 Transport mechanism analysis of the Ti/SmO₂/Sm₂O₃ memristor with Au and Gr bottom electrodes. (a,b) I - V characteristics of Ti/SmO₂/Sm₂O₃/Gr and Ti/SmO₂/Sm₂O₃/Au during the RESET operation. (c) The $\ln(I)$ versus $\sqrt{V}$ for the Au-device in the HRS. (d) Temperature-dependent resistance of the Gr- and Au-devices in HRS measured from 300 K to 100 K.

In high-quality crystalline SmO₂/Sm₂O₃ heterointerface system, the vertical heterointerface functions as a structurally distorted region with high defect density. Phase interfaces are widely reported to serve as preferential sites for oxygen vacancy formation when considering thermodynamic, electronic, elastic, and kinetic factors (*Sci. Adv.* 2021 7, eabe9053). Structurally, phase boundaries are characterized by under-coordinated atomic configurations and a high density of dangling bonds (*Adv. Mater. Interfaces* 2020, 7, 1901944.). The removal of an oxygen atom from such an interfacial site requires the cleavage of substantially fewer chemical bonds than from the lattice interior, leading to a marked reduction in the oxygen vacancy formation energy (*Adv. Mater.* 2019 31(52), 1906156). Simultaneously, phase interfaces serve as regions of localized stress concentration. The local lattice expansion accompanying oxygen vacancy formation can partially accommodate the elastic strain energy

accumulated from lattice mismatch (*Nat. Mater.* 2014 13, 1019-1025). By directly converting this elastic relief into a reduction in formation energy, vacancy generation becomes a thermodynamically favorable pathway for minimizing the overall free energy of the system. Kinetically, the intricate local bonding configurations and the long-range electrostatic potential gradients at the phase boundary impose a substantial energy barrier for inward vacancy migration. Once formed, oxygen vacancies therefore tend to be kinetically trapped at the interface, with limited propensity for escape into the bulk (*Nat. Electron.* 2020 3, 739-746). More critically, the band bending and the presence of low-lying unoccupied electronic states at the phase boundary provide an efficient charge-compensation channel for the excess electrons released upon vacancy formation. This “electron sponge” effect effectively screens the Coulombic repulsion that would otherwise destabilize the charged defect, thereby further stabilizing oxygen vacancies at the electronic level (*Nat. Commun.* 2020 11, 1371). These considerations suggest that the phase interface could serve as a self-consistent defect reservoir in our $\text{SmO}_2/\text{Sm}_2\text{O}_3$ system, providing a plausible explanation for the interfacial switching behavior.

Comment 4. *Device robustness and reproducibility are not at the level expected for the claims made: The graphite-based devices are tested for only 85 cycles, while the Au-based devices show endurance of only 10 cycles and substantial cycle-to-cycle variability. Moreover, the device-to-device on/off ratio spans several orders of magnitude. This degree of dispersion is difficult to reconcile with the manuscript’s repeated emphasis on a highly controlled interface-governed mechanism and undermines the claim of robust high-performance memristors.*

Our reply: We thank the Reviewer for the critical and constructive assessment regarding device robustness and reproducibility. We fully acknowledge that the endurance and variability data presented in the original manuscript were not at the level expected for the claims made. Accordingly, we have revised the relevant content to describe the device performance in a more measured tone, avoiding overstatement and reflect the actual device characteristics accurately. Specifically, we emphasize the

proof-of-concept nature of this work and the mechanistic insights gained, rather than the device performance metrics.

As shown in Fig. R7, cross-sectional TEM reveals that the Au/oxide interface suffers from poor adhesion, high roughness, and abundant defects. Recent work by Yuan et al. (*Nat. Mater.* 2026) offers direct insight into the consequences of such morphological imperfections: rough metallic surfaces induce nano-voids that increase electrode separation and suppress out-of-plane current, while simultaneously trapping environmental species that cause performance degradation and device-to-device variability. Consistent with this picture, the poor contact in our Au devices likely favors disordered oxygen-vacancy migration during electrical cycling, accounting for the unstable filament formation and the limited endurance (~ 10 cycles) observed. These findings clearly motivate the replacement of Au with an atomically smooth and chemically inert electrode, such as graphene, to eliminate these interfacial instabilities.

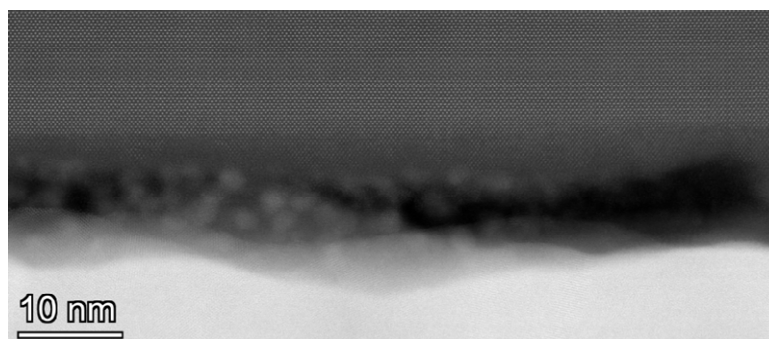


Figure R7 Cross-sectional TEM image of Au/oxide interface. Scale bar, 10nm.

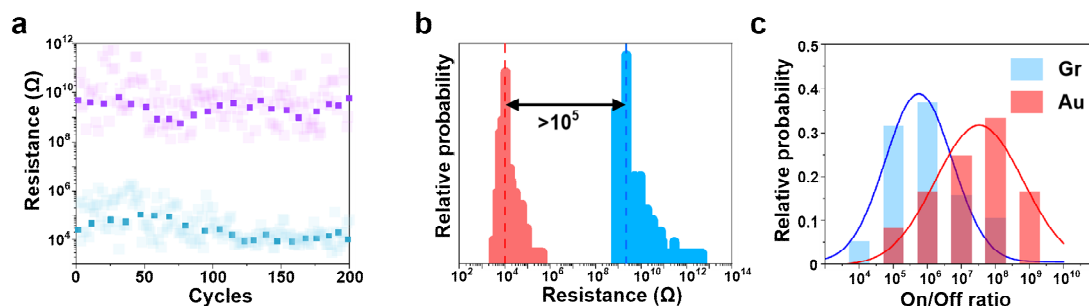


Figure R8 Statistical endurance and device-to-device variability of memristive

418 devices. (a) High/low resistance states (H/LRS) of Au/Ti/SmO₂/Sm₂O₃/Gr memristor
419 under 200 cycles (CC= 1μA). b, Relative probability of the resistance levels at the
420 LRS and HRS (CC= 1μA). (c) Statistical distribution of on/off ratio for multiple
421 devices.

422
423 In the original experiments, a compliance current of 50 μA was applied to the
424 Gr-based devices to maximize the on/off ratio. However, such a high current induces
425 excessive Joule heating, which accelerates device degradation and compromises
426 endurance. To mitigate this effect, the compliance current was reduced to 1 μA in
427 additional measurements. Under this condition, the endurance of the Gr-based devices
428 improved substantially, reaching up to 200 cycles. Fig. R8a and b exhibit the
429 statistical distributions of the HRS and LRS with the on/off ratio still exceeding five
430 orders of magnitude. In addition, the newly measured data have been incorporated
431 into the statistical analysis, and the updated distribution of on/off ratios is presented in
432 Fig. R8c. These statistics reveal a relatively broad distribution of switching ratios,
433 which likely arises from variations in the oxide layer thickness across different
434 samples, highlighting the importance of precise thickness control for achieving more
435 uniform device performance in future optimization. We have revised figures in
436 manuscript and Supporting Information(Fig. 5d, e, f and Supplementary Fig. 16).

437
438 We have added relevant content to the manuscript. *“To further improve the cyclic*
439 *On/Off ratio, endurance tests were performed on the graphene-based devices at a*
440 *compliance current (CC) of 50 μA (Supplementary Fig. 16). The experimental results*
441 *show that the cycle life was limited to only 85 cycles. Statistical analysis of the HRS*
442 *and LRS distributions reveals that, compared with devices operating at a lower CC,*
443 *the elevated current level yields an on/off ratio of at least 10⁷. However, this*
444 *enhancement was achieved at the cost of reduced cycling stability, which is consistent*
445 *with the trade-off between the on/off ratio and endurance observed in oxide-based*
446 *memristors. We attribute this degradation in device longevity to the excessive Joule*
447 *heating generated at higher current levels.”*(pages 13, lines 312)

Comment 5. *The material is introduced as a lateral heterostructure, but this is not supported by the displayed TEM measurement. The structural characterization is inherently local, and the TEM analysis does not demonstrate that the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface extends continuously across the full thickness of the nanosheet. In particular, there is no direct evidence that such an interface forms a vertically connected pathway between the top and bottom electrodes. This point is critical, as the proposed memristive mechanism relies on a vertically continuous interfacial channel for ionic and electronic transport.*

Our reply: We sincerely thank you for your critical and rigorous comment regarding the structural continuity of the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface. This is indeed a central issue for the proposed memristive mechanism, and we appreciate the opportunity to clarify it with additional experimental evidence. We have added new figure to Supporting Information (Supplementary Fig. 9).

To address this concern, we have included additional cross-sectional TEM images in which the interfacial region is delineated by white dashed lines to clearly indicate the location and orientation of the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ phase boundary. These observations suggest that in a fraction of the examined areas, the interface appears to extend continuously from the bottom to the top surface of the nanosheet, providing visual evidence for a vertically oriented pathway that can bridge the two electrodes.

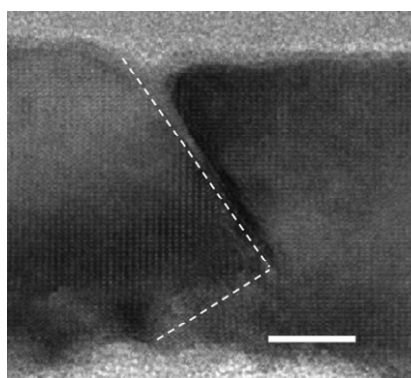


Figure R9 Cross-section TEM image of $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterostructure. Scale bar, 20nm.

Comment 6. *The manuscript contains numerous grammatical issues and awkward phrasing, including several statements in the abstract and main text that are overstated relative to the evidence. Expressions such as “unambiguous evidence,” “robust room-temperature ferroelectric polarization,” and “the switching mechanism originates from...” should be softened unless substantially stronger evidence is provided.*

Our reply: We thank the Reviewer for carefully reading the manuscript and for pointing out both the grammatical issues and the overstatements in our presentation. We have removed the words “unambiguous” and “robust”, and have revised “originate from” to “is consistent with”. In addition, we have carefully reviewed the phrasing throughout the text to ensure that it conveys scientific findings with appropriate caution and precision and revised the overstated expressions identified by the Reviewer, as well as similar phrasing elsewhere in the manuscript.

Comment 7. *Quantitative statistics for the ferroelectric measurements are missing. It would be important to know how many flakes/devices were tested and how reproducible the PFM response is.*

Our reply: We thank the Reviewer for highlighting the importance of statistical validation for the ferroelectric measurements. To address this, we have systematically characterized 16 individual flakes, all of which exhibit clear PFM signals. The observed $\sim 180^\circ$ phase reversal and butterfly-shaped amplitude responses are consistent with switchable ferroelectric polarization. We have added new figure to Supporting Information (Supplementary Fig. 11).

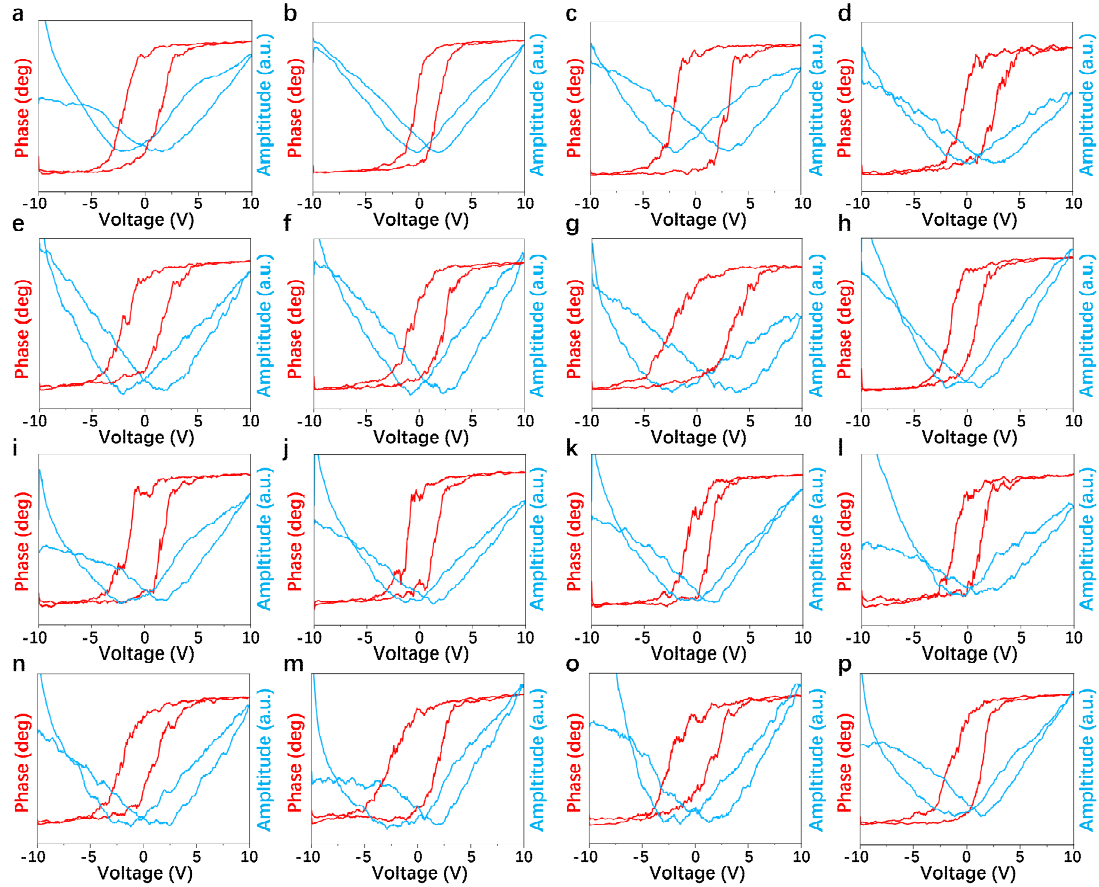


Figure R10 PFM characteristic of multiple flakes.

We have added relevant content to the manuscript. “*Reproducibility of these PFM responses was verified across multiple flakes and devices and spatially resolved pfm images demonstration that the PFM response appears to be associated with the interface(Supplementary Fig. 11, 12). Collectively, these macroscopic and local electrical measurements are consistent with the presence of switchable ferroelectric response in the SmO₂/Sm₂O₃ heterostructure.*” (pages 10, 251)

Comment 8. *The phase characterization would benefit from valence-sensitive spectroscopy and more direct mapping of phase purity and interface distribution.*

Our reply: We thank the reviewer for this insightful suggestion regarding phase characterization. We have added figures to Supporting Information(Supplementary

Fig. 3). The chemical bonding states and surface compositions were characterized by X-ray photoelectron spectroscopy (XPS), as shown in Fig. R11. The O 1s core-level spectrum collected on the SiO₂/Si substrate was deconvoluted into four components at 528.6, 531.3, 532.4, and 533.3 eV. The peak at 528.6 eV and 531.3 eV are assigned to lattice oxygen (*Nat. Mater.* 2013 12, 827-835). Owing to the relatively low sample mass, the micro-area XPS analysis inevitably captured a considerable signal from Si-O bonded species originating from the underlying substrate (*Surf. Interface Anal.* 2015 47(7): 777-784). In addition, a weak high-binding-energy feature at 533.3 eV corresponds to O₂²⁻ species (*J. Chem. Phys.* 2014 140(9): 094706).

The Sm 3d region reveals a more complex spectral feature. On the basis of spin-orbit splitting, the spectrum can be deconvoluted into two sets of characteristic peaks corresponding to Sm 3d_{5/2} and Sm 3d_{3/2}, indicating the coexistence of two distinct valence states of Sm ions. The Sm 3d region exhibits complex spectral features. Based on spin-orbit splitting, the spectrum can be deconvoluted into two sets of characteristic peaks for Sm 3d_{5/2} and Sm 3d_{3/2}, indicating the coexistence of two distinct samarium valence states. The intense doublets located at 1083.8 eV (3d_{5/2}) and 1112.5 eV (3d_{3/2}), along with those at 1081.9 eV (3d_{5/2}) and 1109.4 eV (3d_{3/2}), correspond to Sm³⁺ species in two slightly different coordination environments (*Nat. Mater.* 2025 24, 852-860). The features at 1078.8 eV (3d_{5/2}) and 1106.0 eV (3d_{3/2}) are identified as satellite peaks of Sm³⁺, while the remaining signals originate from multiplet splitting caused by the partially filled 4f shell of Sm³⁺ ions, serving as a distinctive spectroscopic fingerprint of the trivalent state. Furthermore, the doublets observed at 1075.7 eV (3d_{5/2}) and 1102.6 eV (3d_{3/2}) are assigned to Sm²⁺ species (*Nano Res.* 2024, 17(7): 5856-5862).

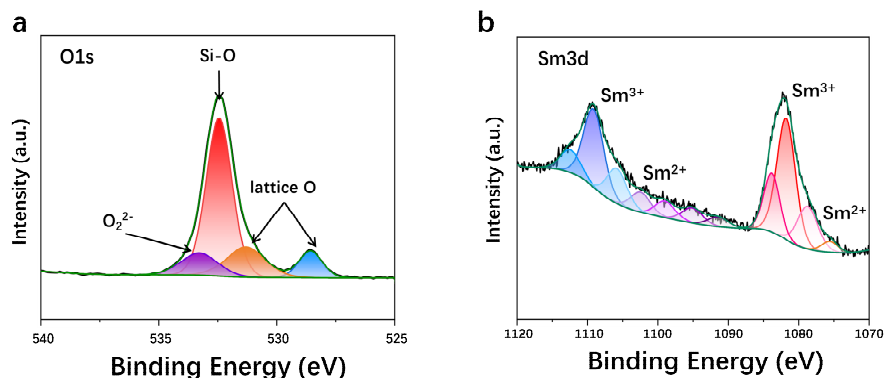


Figure R11 (a) XPS spectra of O 1s. (b) XPS spectra of Sm 3d.

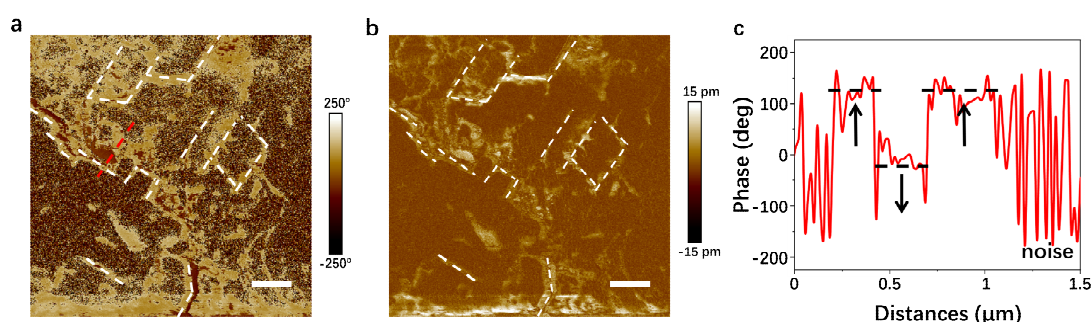


Figure R12 Phase characterization (a) PFM phase image. Scale bar, 1μm. (b) PFM amplitude image. Scale bar, 1μm. (c) The PFM phase profile along the red dash line shown in a.

As shown in Fig. R12, the PFM phase and amplitude images reveal contrast variations that are spatially correlated with the SmO_2/Sm_2O_3 heterointerface (marked by dashed lines). The phase contrast exhibits a reversal across the putative interface region, while the surrounding regions show relatively weak or negligible response. The corresponding amplitude map shows that the piezoresponse signal is primarily distributed near the interfacial region, with the signal intensity gradually diminishing away from the interface. These observations indicate a spatial correlation between the PFM response and the interface location, suggesting that the switching behavior is associated with the heterointerface rather than uniformly distributed across the oxide.

Response to Reviewer #2:

In the manuscript entitled "Symmetry breaking induces room-temperature ferroelectricity in two-dimensional metastable heterostructures" Yang et al. explore the SHG and ferroelectric properties of the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface, which displays a switchable polarization due to oxygen vacancy migration. The work is technically sound and the results are interesting. However, several clarifying edits are required before the work is suitable for publication.

Our reply: We sincerely appreciate the reviewer's valuable comments and constructive suggestions, which are crucial for improving the quality of our manuscript. Below, we provide a detailed response to the reviewer's feedback and highlight how these suggestions have been incorporated into the revised version.

Comment 1. *Figure 2(g) shows a SHG signal that completely disappears at a temperature around 700 K. Is this change reversible? If it occurs due to a phase transformation of the metastable SmO_2 to Sm_2O_3 , then it likely is not. Is the measurement shown in 2(g) taken on heating or cooling?*

Our reply: Thank the reviewer for raising this critical question regarding the reversibility of the SHG signal. We fully agree that this point is essential for understanding the nature of the observed transition. In our original manuscript, the data were collected upon heating. Following the reviewer's insightful suggestion, we have now performed additional measurements by monitoring the SHG signal intensity during both heating and cooling cycles across the same temperature range.

We have added relevant content to the manuscript and added new figure to Supporting Information(Supplementary Fig. 4). *"The SHG signal showed negligible variation upon cooling from 400 K to 300 K. In contrast, a substantial reduction in the SHG signal was detected upon cooling from 1000 K to 300 K. The signal failed to return to its initial state, which is consistent with an apparently irreversible phase transformation (Supplementary Fig. 4)."*(page 8, line 190)

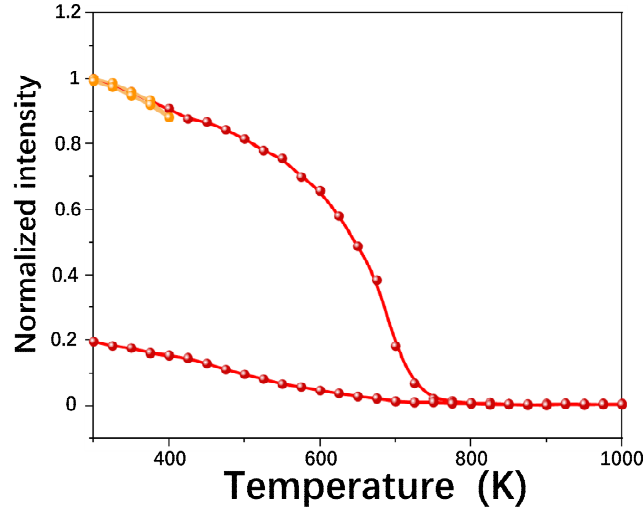


Figure R13 Temperature-dependent SHG intensity during heating-cooling cycles.

Comment 2. *How is in-plane PFM data taken? Is a nanosheet measured that is on its side? Or perhaps one with a different out-of-plane direction? Does the interface occur in one plane in a nanosheet or is the interface 3-dimensional?*

Our reply: The measurement of the in-plane piezoresponse signal fundamentally relies on detecting the torsional deformation of the probe cantilever (*Phys. Rev. B* 2012, 86(13): 134115). This detection process captures the displacements occurring parallel to the sample surface. When an electric field is applied perpendicular to the surface, it induces in-plane strain through the transverse piezoelectric coefficients d_{31} and d_{32} , which represent the strain responses along the two orthogonal axes within the sample plane (*J. Mater. Sci.* 2006, 41(1): 107-116). The strain causes a physical shift in the sample surface, which in turn exerts a lateral shear or push-pull force on the conductive probe tip in contact with it. This mechanism constitutes the source of contrast in in-plane PFM data (*New J. Phys.* 2009 11 033029).

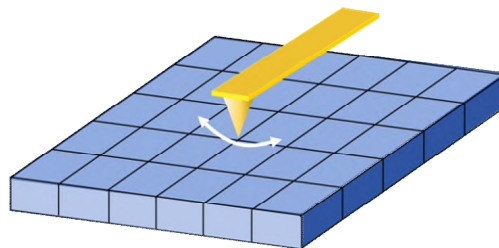


Figure R15 Schematic illustrations of cantilever deflection and torsion induced by

in-plane piezoresponse signal.

Comment 3. *SHG can be used to measure water/mica interfaces, which is essentially a mica/oxide interface as is obtained during SmO_x growth. How can one be certain that the SHG line shown in Figure 2(f) is indeed from the SmO₂/Sm₂O₃ interface, when a response may be expected from a mica/oxide interface? Was the SHG measured following exfoliation onto a different substrate*

Our reply: Thanks again for the reviewer's very constructive suggestion. In the manuscript, the SHG signal shown in Fig. 2f was measured on a Si/SiO₂ substrate following exfoliation of the material onto the mica. The substrate-oxide interface region may give rise to a detectable SHG contributionr (*Phys. Rev. B* 2002, 65(19): 193103). However, the interfacial response is fundamentally constrained by the lack of long-range structural order compared to the bulk crystal. This lack of coherent orientation leads to a randomized distribution of local nonlinear dipoles, which results in an inherently weak nonlinear susceptibility and ensures that the macroscopic response is negligible anisotropy (*J. Phys. Chem. B* 2002 106(16), 4203-4213). As shown in Fig. 2h, polarization-resolved SHG measurements shows that a well-defined two-fold symmetry should originate from the crystal lattice of the sample. In contrast, an interface-dominated signal typically yields a nearly isotropic polarization pattern. Therefore, the experimental observation of a pronounced two-fold symmetry directly demonstrates that the detected SHG response is dominated by the crystalline layer. Any interfacial contribution remains weak and essentially isotropic, thus posing no substantial interference to the identification of the intrinsic nonlinear response of the material.

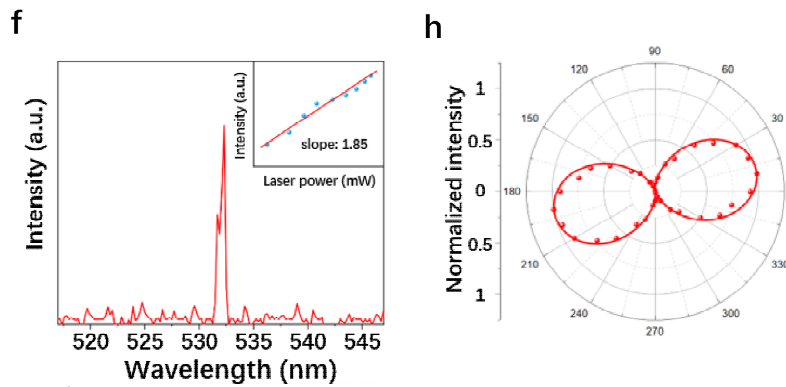


Fig. 2 | f, SHG signal of the nanosheets with a 1064 nm laser. The insert shows the SHG intensity vs laser power in logarithmic scale **h,** The polarization-resolved SHG signal of the nanosheets.

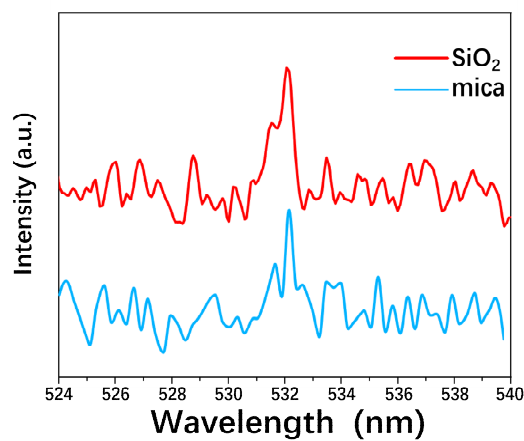


Figure R15 SHG signal of the nanosheets on the different substrates.

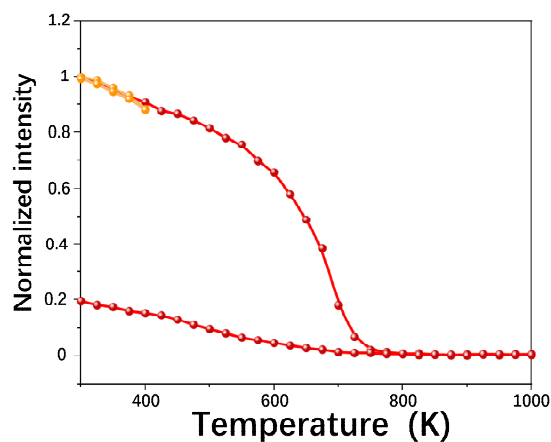


Figure R16 Temperature-dependent SHG intensity during heating-cooling cycles.

As illustrated in Fig. R15, consistent SHG signals are observed on both mica and silicon oxide substrates, demonstrating that the signal characteristics remain invariant across different substrates. Furthermore, temperature-dependent SHG measurements in Fig. R16 demonstrate a decrease in signal intensity as the temperature surpasses the phase transition temperature. Collectively, these observations indicate that the detected signals are intrinsic to the sample. We have added relevant content to the manuscript and added new figure to Supporting Information (Supplementary Fig. 5). *“Control measurements on different substrates showed similar SHG response (Supplementary Fig. 5), confirming that the observed signal originates from the heterostructure.”*(pages 8, lines 194)

Comment 4. *How are plots in Fig 4(f) and 4(g) calculated? Is DFT used in these cases.*

Our reply: We thank reviewer’s to raise this issue. In the manuscript, both figures presented here were obtained from density functional theory (DFT) calculations. The heterostructure model was constructed based on the atomic structure observed via TEM. The detailed calculation procedures are described as follows.:

The data were derived from the three-dimensional local potential output by self-consistent DFT calculations. A planar-averaged electrostatic potential curve was obtained by integrating over the in-plane coordinates at each point along the direction perpendicular to the interface. This curve was subsequently smoothed along the out-of-plane direction using a window strictly equal to the lattice period, thereby filtering out atomic-scale noise and yielding the macroscopic average electrostatic potential. The interfacial potential discontinuity ΔV , originating from interfacial charge transfer and the associated dipole layer, was then determined by extracting the difference between the flat potential values in the bulk-like regions on either side of the curve.

The energy evolution curve obtained during the optimization of the heterojunction model essentially traces the progressive decrease and eventual convergence of the total energy of the system as the iterations proceed during structural relaxation. In

each iteration, the atomic positions are first held fixed while a self-consistent DFT electronic calculation is performed to obtain the ground-state total energy of that particular configuration. The Hellmann-Feynman theorem is then employed to compute the forces acting on each atom. If these forces fail to satisfy the prescribed convergence criterion, the optimization algorithm updates the atomic positions accordingly and proceeds to the next iteration. Connecting the total energies recorded at each step yields the energy evolution curve.

Comment 5. *It is shown in Figure 4(h) that illumination with an electron beam results in a transformation to the more stable Sm₂O₃ phase due to mass transport. This implies that the SHG and ferroelectric properties are irreversibly changed during heating (see comment 1). This characteristic should be discussed, especially considering that component electronics are generally expected to heat during operation.*

Our reply: We thank reviewer's for the careful review and for the helpful suggestions. Figure R11 demonstrates that the material exhibits irreversible phase transition during the reheating process. Consequently, assessing whether the device operating temperature exceeds this phase-transition threshold is critical to ensure device reliability. We have added relevant content and new figure to Supporting Information (Supplementary Fig. 17).

As shown in Fig. R17a, the *I-V* characteristics were measured with a 1 μA compliance current to prevent excessive heating and a slow voltage sweep to ensure quasi-steady-state conditions. To preliminarily estimate the operating temperature of the device, a simplified thermal model was constructed based on the vertical structure, where the oxygen-vacancy conductive filament is approximated as a cylindrical channel bridging the two electrodes in the Fig. R17b . Under these quasi-steady-state conditions, the filament temperature is derived from the following equations:

$$P = I \times V$$
$$T = T_0 + \frac{P}{R_{th}}$$

$$R_{th} = \frac{d}{k_{th} \times A}$$

where P is the Joule heating power, I and V are the measured current and voltage respectively, T_0 is the ambient temperature of 300K, d is the oxide thickness (filament length, 35nm), R_{th} is the thermal resistance, k_{th} is the thermal conductivity, and $A = \pi r^2$ represents the filament cross-sectional area, r denotes the filament radius which is estimated from the current distribution measured by C-AFM in Fig. R18, giving $r \approx 25$ nm.

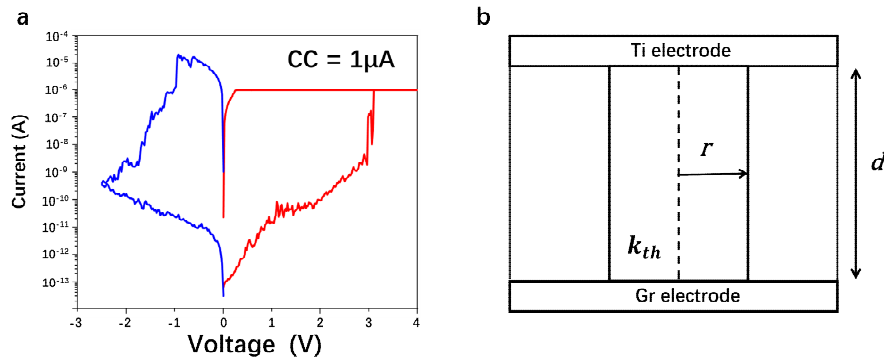


Figure R17 (a) I - V switching curve of a Ti/SmO₂/Sm₂O₃/Gr memristor at compliance current (CC) = 1μA. (b) Schematic diagram of one-dimensional simplified thermal model for memristor.

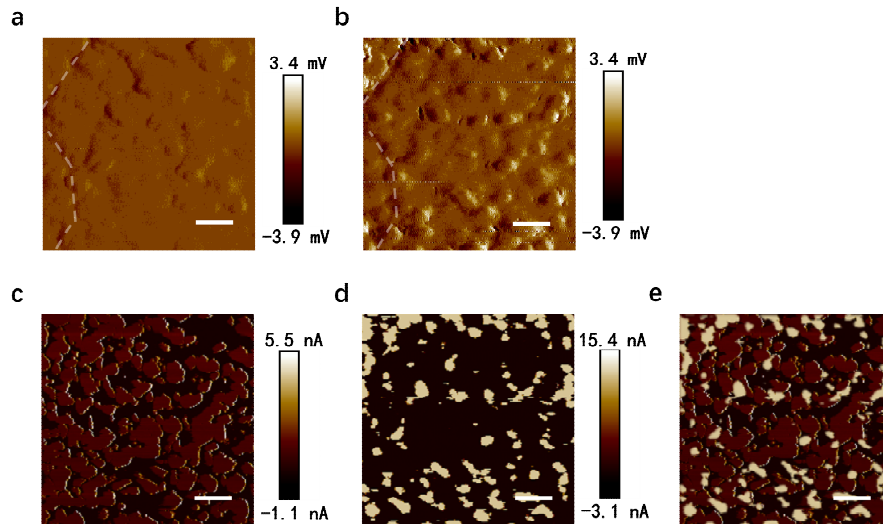


Figure R18 C-AFM characterization of the memristive device in HRS and LRS. (a) The C-AFM surface deflection at HRS. (b) The C-AFM surface deflection acquired immediately after the forming process. (c) The C-AFM current mapping images of

device at HRS. (d) The C-AFM current mapping images of device at LRS. (e) Spatially superimposed C-AFM current maps acquired from the same device region in the HRS and LRS. All scale bar, 200nm.

The thermal conductivity of epitaxially grown single-crystalline rare-earth oxide films is approximately five times that of SiO₂ (*ECS Trans.* 2011, 41 3 161). Given a SiO₂ thermal conductivity of $\sim 1.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (*Nat. Commun.* 2023 14, 8242), the conductivity is estimated at $\sim 6.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. However, in oxygen-vacancy-rich filaments, high defect concentrations induce strong phonon scattering. According to the Klemens model and prior simulations on oxide memristor filaments (*Mater. Horiz.* 2020 7(6), 1452–1456), the local thermal conductivity in such regions can decrease by at least one order of magnitude relative to the pristine lattice. To ensure a rigorous assessment, we adopt a thermal conductivity of $k_{th} = 0.65 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ as a reasonable baseline for the filament region. Regarding the power parameters used in the model, although the maximum RESET power extracted from the measured *I-V* cycles is $\sim 1.89 \mu\text{W}$, we utilize a value of $P \approx 10 \mu\text{W}$ to account for device-to-device variations.

The peak filament temperature is estimated at 574 K, representing a conservative upper bound for the actual operating temperature because the one-dimensional model neglects radial heat loss and electrode heat-sink effects. Serving as a qualitative assessment rather than an exact measurement, this estimate aims to determine whether thermal effects could trigger irreversible phase transformations. Under these assumptions, the conclusion that the peak temperature remains below the phase-transition threshold remains credible, suggesting the potential for thermally stable device operation under low-compliance-current measurement conditions. We have added the relevant content to the manuscript. “ *Preliminary thermal analysis of the conductive filament indicates that at a power of 10 μW , the conservative estimate of the peak temperature is approximately 574 K, which remains below the threshold of 672 K for irreversible phase change (Supplementary Fig. 17). This suggests that the Joule heat generated when working under the aforementioned low-current conditions exerts a acceptable thermal impact on device reliability.*”(pages 13, lines 321)

Comment 6. *It is not clear based upon the microscopy present in the manuscript - does the SmO_2 , Sm_2O_3 form a smooth interface with the Sm_2O_3 ? For example, can this be considered a bilayer? Or are there regions of SmO_2 within the Sm_2O_3 nanosheets? The image in figure 3(a) (as well as supplementary figure 6) implies the latter of these options.*

Our reply: We sincerely thank the reviewer for this keen observation and for giving us the opportunity to clarify this critical structural point. Based on our detailed analysis of the original TEM in Fig. 3a and Figure S6, the structure is not a bilayer. Instead, as the reviewer correctly deduced, the actual morphology consists of SmO_2 nanodomains that are embedded within the Sm_2O_3 nanosheet. In other words, the Sm_2O_3 forms the continuous basal framework, while the SmO_2 species are distributed as discrete "islands" within this framework, rather than forming a separate laminated overlayer.

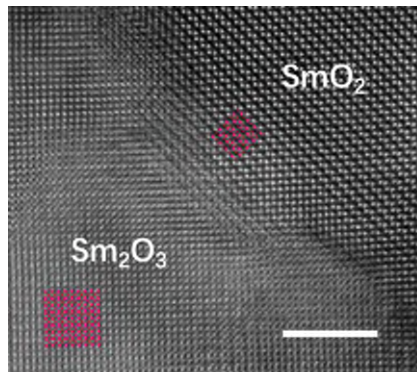


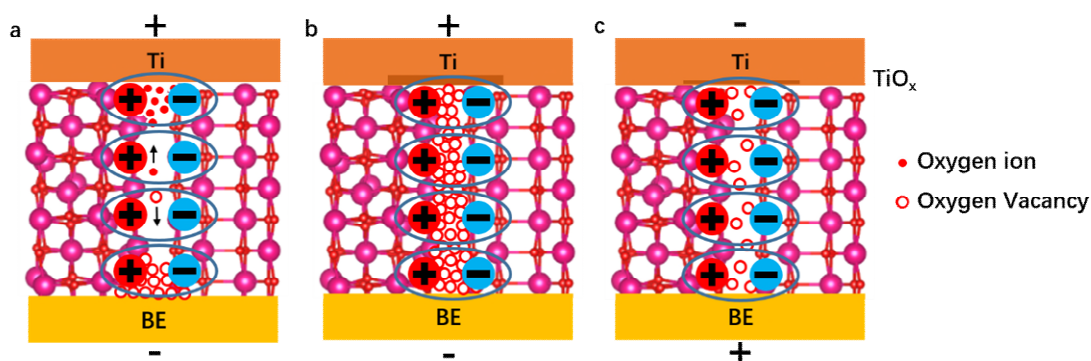
Figure R19 HAADF-STEM image of $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterostructure. Scale bar, 2.5nm.

We have revised the content in the manuscript to clearly state. “Evidence from the contrast variations and lattice fringe mismatches in the TEM images confirms that SmO_2 nanodomains do not form a continuous top layer, but are instead embedded throughout the Sm_2O_3 nanosheet matrix.” (page 12, lines 287)

Comment 7. *The analysis of the mechanism driving the difference between LHS and RHS is slightly difficult to understand. Based upon the symmetry arguments given, the*

expectation would be that the center of symmetry is broken at any $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface. However, the explanation given around lines 340 - 352 centers around the formation of conductive filaments, which should be a mechanism separate from ferroelectric switching. Do these two mechanisms coexist? This seems reasonable based upon the cyclical I-V curves, however the discussion perhaps needs more clarity in articulating this and connecting this with the I-V curves.

Our reply: We sincerely thank the reviewer for this perceptive comment. The reviewer has correctly identified a critical point where our original discussion was insufficiently articulated. It should be recognized that the two mechanisms are not separate or competing; rather, they are intimately coupled in a cause-and-effect relationship within our system.



Supplementary Fig. 22 | Schematic of the resistive switching mechanism.

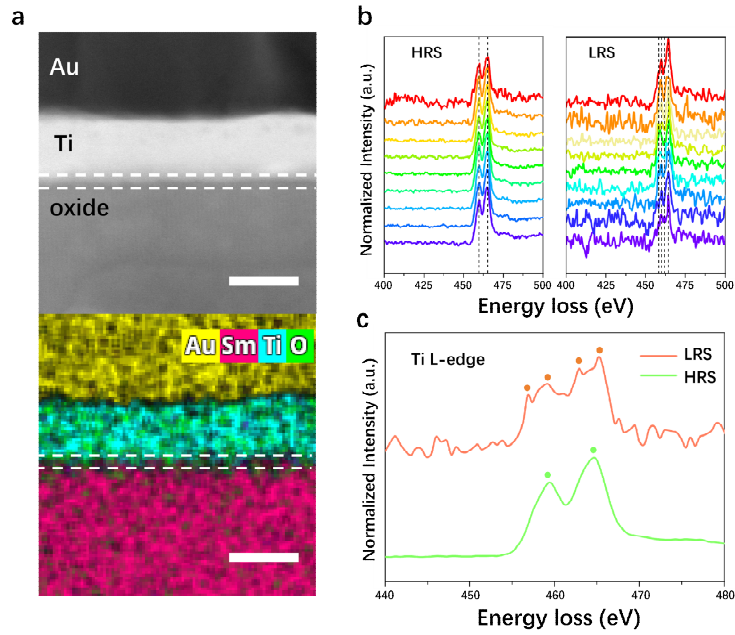


Figure R21 Cross-sectional TEM-EELS chemical analysis of Ti at the electrode interface in HRS and LRS (a) TEM image and EDS mapping of the interface. Scale bar, 10nm. (b) Ti L-edge EEL spectra as a function of position for the device in the HRS and LRS. The spectra were acquired across the Ti electrode from the bottom to the top. (c) Comparison of Ti L-edge EEL spectra between HRS and LRS. (c) O K-edge normalized intensity for the same region in the HRS and LRS.

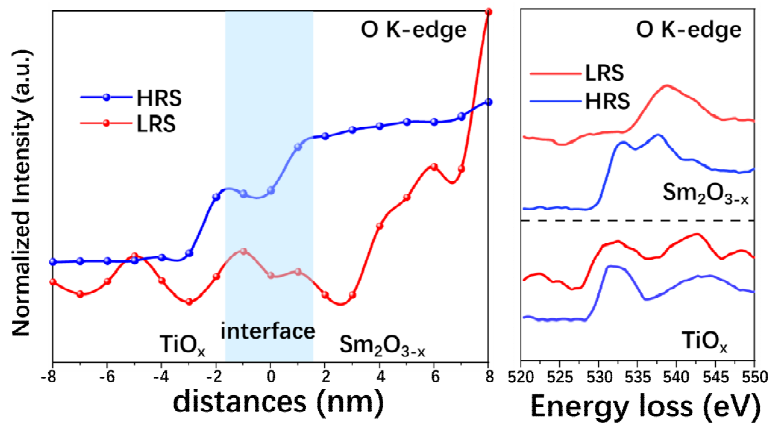


Figure R22 Cross-sectional TEM-EELS chemical analysis of O at the electrode interface in HRS and LRS

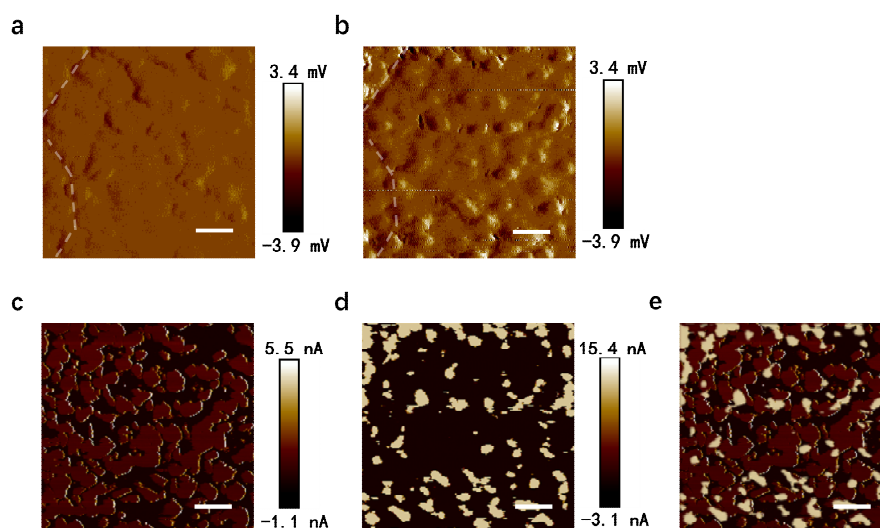


Figure R18 C-AFM characterization of the memristive device in HRS and LRS. (a) The C-AFM surface deflection at HRS. (b) The C-AFM surface deflection acquired immediately after the forming process. (c) The C-AFM current mapping images of device at HRS. (d) The C-AFM current mapping images of device at LRS. (e) Spatially superimposed C-AFM current maps acquired from the same device region in the HRS and LRS. All scale bar, 200nm.

The broken inversion symmetry inherently present at the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interfaces provides the structural prerequisite, allowing the polarization direction to modulate the local electrostatic potential and oxygen vacancy migration barriers under an applied electric field. This modulation thereby dictates the formation and rupture of conductive filaments, which are locally guided by the polarization state of the surrounding Sm_2O_3 matrix (*J. Mater. Sci. Technol.* 2024 198 36-43). In other words, the interface acts as a guiding template that determines the preferential pathways for oxygen vacancy accumulation or depletion, which in turn dictates the macroscopic resistance state (*J. Chem. Phys.* 2006 125, 074711). To make this coupling explicit, we have revised the manuscript and systematically connected each region of the I - V curve to the corresponding physical process.

We have added relevant content in the Supplementary Information. “Consequently, the difference in Fermi levels between SmO_2 to Sm_2O_3 leads to charge transfer, where

holes transfer from SmO_2 to Sm_2O_3 and electrons transfer from Sm_2O_3 to SmO_2 respectively. This process consequently induces downward energy band bending at the SmO_2 interface and upward bending at the Sm_2O_3 interface.”(pages 17, lines 377)

We have added relevant content in the manuscript. “The resistance switching in our $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterostructure arises from the coupled interplay of interfacial polarization and oxygen-vacancy dynamics.”(pages 15, lines 361)

We have added relevant content in the manuscript. “It is worth noting that the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ heterostructure constitutes the fundamental structural unit of the resistive switching mechanism. Lattice mismatch disrupts inversion symmetry, and local strain fields induced by differences in thermal expansion cause the crystal structure to distort. This process lowers the formation energy of oxygen vacancies, thereby reducing the insulation of the system. Furthermore, the difference in Fermi levels between the two phases results in charge transfer and band bending, establishing an electrostatic potential gradient and inducing interfacial polarization. Consequently, the interface serves as a preferred polar-confined channel for the accumulation and migration of oxygen vacancies. These two effects of the interface structure promote the formation of lattice defects (primarily oxygen vacancies) and facilitate their preferential transport at the interface under an electric field⁶⁹. This implies that the interface serves not only as the site for polarization but also constitutes an endogenous reservoir for oxygen vacancies, thereby establishing it as the preferred pathway for ionic transport⁷⁰.

The applied bias dictates the migration direction of these interfacial oxygen vacancies. The initial positive bias aligns the polarization, creating a localized accumulation of oxygen vacancies along the $\text{SmO}_2/\text{Sm}_2\text{O}_3$ interface toward the top electrode, progressively aggregating into a conductive filament that bridges the two electrodes. This corresponds to the SET process and the transition to the low-resistance state (LRS). Conversely, the negative bias induces polarization reversal, which destabilizes the filament and promotes oxygen vacancy redistribution.

Oxygen vacancies are driven away from the filament region, leading to its partial dissolution and the recovery of the high-resistance state (HRS) during the RESET process. Through the application of alternating bias voltages, the SET and RESET operations are iteratively performed, enabling reversible resistance switching. The resistance switching mechanism, which hinges on the migration of O^{2-} and V_O , is commonly referred to as the valence change mechanism (VCM)⁷¹. This framework unifies the two seemingly distinct mechanisms: the polarization and the filamentary switching. The polarization modulates the local electrostatic potential and migration barriers, effectively guiding the preferential pathways for oxygen vacancy movement, while the resulting filament provides the macroscopic resistive readout.” (pages15, lines 375)

Comment 8. *There are several typographical errors that require attention for readability:*

a. Line 71 - Perhaps the word 'ionic' should be removed?

b. Line 139 - 140 - Only half of a sentence.

c. Line 145 - 147 - Only half of a sentence.

d. Line 150 - Perhaps the ', is helpful.' should be removed?

e. Line 342 - 345 This sentence needs to be rewritten.

f. Supplementary figures 11 and 12 are mentioned in the main text before supplementary figure 10.

g. Figure 2(d) is poor resolution and the step height inset is not readable.

h. Figure 4(e) (and in the text) uses the phrase 'in-of-plane', where typically 'in-plane' is used.

Our reply: We sincerely thank you for your careful reading and constructive comments on our manuscript. These typographical and presentation issues are very helpful for improving the clarity and professionalism of our paper. We have carefully addressed each point as detailed below.

a. Line 71 - “ionic”

We agree that the word "ionic" is unnecessary in this context. We have removed it

880 from the revised manuscript (pages 3, Line 72).

881 b. Lines 139-140 - incomplete sentence

882 We have completed this sentence. The revised version now reads:

883 *“It is worth noting that the introduction of Fe_2O_3 could drive oxygen atom transfer*

884 *reactions and effectively enhance the oxidation process*⁵⁹*(Supplementary Fig. 2).”*

885 (pages 6, lines 141).

886 c. Lines 145-147- incomplete sentence

887 This sentence has also been rewritten and completed. The new text is:

888 *“Fig. 2b illustrates that...”* (pages 6, 146–148).

889 d. Line 150 - “, is helpful.”

890 We agree that this phrase is redundant and potentially confusing. We have removed it

891 from the sentence (pages 6, lines 152).

892 e. Lines 342-345- unclear sentence

893 We have thoroughly rewritten this sentence to improve clarity and logical flow(see

894 reply 7).

895 f. Supplementary Figures 11 and 12 mentioned before Figure 10

896 We appreciate this careful observation. We have reordered the citation sequence in the

897 main text so that Supplementary Figures now appear in numerical order

898 g. Figure 2(d) – low resolution and illegible step-height inset

899 We have replaced Figure 2(d) with a new, high-resolution image. The step-height inset

900 has been enlarged and re-labeled for better readability. We have also verified that all

901 elements are clearly visible when the figure is printed or viewed at standard zoom.

902 h. Figure 4(e) and related text – "in-of-plane"

903 We have corrected all instances of "in-of-plane" to "in-plane" in both the main text

904 and the figure caption.

1 Reviewers' Comments:

2 **Reviewer #1 (Remarks to the Author):**

3 I appreciate the authors' thorough and constructive response to the reviewers'
4 comments. The revised manuscript has been substantially strengthened through the
5 addition of macroscopic ferroelectric measurements, additional PFM characterization,
6 cross-sectional TEM-EELS analysis, and C-AFM current mapping. These new results
7 significantly reinforce the proposed physical picture and the authors have also
8 moderated several mechanistic claims, making the interpretation more balanced and
9 consistent with the available evidence.

10 While some aspects of the microscopic mechanism remain inferential—as is often
11 the case in oxide memristive systems—I consider that the conclusions are now
12 adequately supported by the experimental data presented. I therefore recommend
13 publication in its present form. Comments:

14

15 **Reviewer #2 (Remarks to the Author):**

16 The authors have addressed many of the comments provided, clarifying the structural
17 organization of the films and origin of transport signals, as well as providing
18 additional details regarding modeling and characterization. Below is provided an
19 additional comment that will be necessary to address ahead of publication:

20 1. Based upon the irreversibility observed using T-resolved SHG, it is evident that
21 there is no intrinsic ferroelectricity in this structure (i.e. a thermodynamically stable
22 unit cell with a stable field-dependent dipole switching mechanism). Instead, broken
23 symmetry and reversible, field-dependent oxygen transport at the interface between
24 the Sm oxides gives the appearance of ferroelectricity. This detail should be clarified
25 in the title, and elsewhere in the manuscript. As read, the title implies that the Sm
26 oxide interface constitutes a 2D ferroelectric, such as MoS₂/WS₂, or In₂Se₃. However,
27 in these two other cases, the polarization mechanism involves reversible movement of
28 constitutive species and not charged defects.

29

30

Response to Reviewer #1:

I appreciate the authors' thorough and constructive response to the reviewers' comments. The revised manuscript has been substantially strengthened through the addition of macroscopic ferroelectric measurements, additional PFM characterization, cross-sectional TEM-EELS analysis, and C-AFM current mapping. These new results significantly reinforce the proposed physical picture and the authors have also moderated several mechanistic claims, making the interpretation more balanced and consistent with the available evidence.

While some aspects of the microscopic mechanism remain inferential—as is often the case in oxide memristive systems—I consider that the conclusions are now adequately supported by the experimental data presented. I therefore recommend publication in its present form.

Our reply: We are truly grateful for your positive and encouraging feedback on our revised manuscript. Your recognition of the strengthened experimental evidence means a great deal to us. We also appreciate your understanding regarding the inherent limitations in fully resolving the microscopic mechanism in oxide memristive systems. Your constructive comments throughout the review process have been invaluable in improving the clarity and balance of our work. We are delighted that the current version meets the standards for publication, and we thank you sincerely for your time and expert guidance.

Response to Reviewer #2:

The authors have addressed many of the comments provided, clarifying the structural organization of the films and origin of transport signals, as well as providing additional details regarding modeling and characterization. Below is provided an additional comment that will be necessary to address ahead of publication.

Our reply: We sincerely appreciate the reviewer's acknowledgment of our efforts in addressing the previous round of comments. We also take your valuable new comment very seriously. We fully agree that this point needs to be addressed before publication, and we are committed to providing a thorough response.

Comment 1. *Based upon the irreversibility observed using T-resolved SHG, it is evident that there is no intrinsic ferroelectricity in this structure (i.e. a thermodynamically stable unit cell with a stable field-dependent dipole switching mechanism). Instead, broken symmetry and reversible, field-dependent oxygen transport at the interface between the Sm oxides gives the appearance of ferroelectricity. This detail should be clarified in the title, and elsewhere in the manuscript. As read, the title implies that the Sm oxide interface constitutes a 2D ferroelectric, such as MoS₂/WS₂, or In₂Se₃. However, in these two other cases, the polarization mechanism involves reversible movement of constitutive species and not charged defects.*

Our reply: We agree with the Reviewer that both the layers are not strictly 2-dimensional. The original title using “two-dimensional metastable heterostructures” was overly broad and could be misleading to readers. To better highlight the central theme of the article, we have revised the title: “Symmetry breaking induces room-temperature interface ferroelectricity in two-dimensional metastable mosaic-like heterostructures.” Additionally, we have updated the abstract and the manuscript accordingly to ensure consistency and clarity.

Reviewers' Comments:

Reviewer #2 (Remarks to the Author):

The authors have sufficiently addressed my comments.

Response to Reviewer #2:

The authors have sufficiently addressed my comments.

Our reply: We are deeply grateful to the reviewers for their insightful and constructive feedback, which has been invaluable in strengthening this manuscript.