nature portfolio

Peer Review File

High Piezoelectric Property with Exceptional Stability in Self-Poled Ferroelectric Films

Corresponding Author: Professor Lisha Liu

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

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The present manuscript reports on the observation of self-poling in lead zirconate titanate (PZT) films fabricated by spin coating, leading to a high and temperature-stable piezoelectric coefficient d33 even at elevated temperatures without the need for additional poling. The effect is attributed to a combination of a high degree of crystallographic texture, with the pseudocubic (001) axis oriented perpendicular to the film plane, and a compositional gradient of the PZT, introduced by successive spinning of different solutions and inducing a stress/strain gradient in the film.

The results reported here are highly interesting and potentially will have a strong impact on the field of piezoelectric films, e.g. for MEMS applications, pushing the limits of what is possible for solution-deposited materials. While there are other reports of self-poling in ferroelectric films, they typically arise entirely from effects at the film interfaces and do not make use of boundaries through the film thickness; they also certainly do not result in such good functional properties. The presentation style is very clear and easily understandable, with a good description of the literature context. The measurements seem to be carefully performed; if the results are valid (please see below), the interpretation is very plausible.

There are, however, a few points concerning the validity of the work that would be worth clarifying:

- It appears rather difficult to grow crack-free PZT films with a thickness much larger than 1 micrometer; the four micrometers reported in the present manuscript seem rather exceptional in this case. Was there no cracking observed in these films? Were any special measures taken to avoid cracking? As the cracks could strongly influence the measurement results, e.g. by creating mostly free-standing membranes that may lead to a serious over-estimation of the piezoelectric and dielectric constants, it would be relevant to show that this did not happen here. Could the authors present pictures, e.g. by optical microscopy, that show the films are crack-free on the scale of the electrodes used for the electrical measurements (200 microns) and the tip diameter for the piezoelectric measurements (2 mm)?

- The piezoelectric coefficient d33 was determined by measuring the direct piezoresponse using the Berlincourt method. How was the bottom electrode contacted for this measurement? As the loading tip diameter was much larger than the film thickness, it is difficult to assess the suitability of this measurement. Would it be possible to have a measurement of the inverse piezoelectric response with a Double Beam Laser Interferometer? This seems to be the gold standard for d33 determination in thin films.

- While both the dielectric permittivity and piezoelectric coefficient is very high for a solution-deposited PZT film, the polarization values (both remanent polarization and maximum polarization under field) shown in Supplementary Fig. 9 seem to indicate a film of good quality, but not exceptionally high poling. How can this apparent discrepancy be reconciled?

If these questions could be satisfactorily addressed, the manuscript should be well suited for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)
This paper discusses the self-poling effect of sol-gel PZT thin films and its reasons due to the introduction of buffer layers and inhomogeneous Zr/Ti ratio in one layer, as well as the realization of excellent temperature stability and high d33c. The reported findings are important in the field of piezoelectric MEMS and are expected to be applied to future devices.
On the other hand, there are several points in the detailed discussion that are inconsistent with previous reports and cannot be published if there are no clear answers to the following questions.

1. The variation of Zr/Ti ratio in sol-gel deposition has already been reported in Appl. Phys. Lett. 90, 062907 (2007). In this paper, it was shown that eliminating the Zr/Ti variation improves the piezoelectricity, which is different from the results in this study. Clarification on this point is needed.
2. Regarding the origin of self-poling, it has been explained that it is due to hierarchical heterogeneity, but whether the self-poling is upward or downward with respect to the c-axis has not been adequately discussed. The self-poling of PZT thin films has been reported for sputtered PZT thin films, but in such cases, the hysteresis curves are highly anisotropic (e.g. Sens. Actuators A, 107, 68-74 (2003)). For example, in the case of upward polarization, the positive Ec is larger than the negative Ec when a voltage is applied to the top electrode because the energy required to rotate the polarization downward is larger. However, in Fig. 9suppl, the difference of Ec between positive and negative is small, which contradicts the fact that stable self-polarization occurs in this condition?
3. In this study, the authors report a very high d33c of 520 pC/N for the PZT thin film. On the other hand, it is stated that d=2PrεQ, but the Pr is less than 10μC/cm2, which is very small compared to normal oriented films (e.g. Sens. Actuators A, 107, 68-74 (2003)). Even taking into account the large dielectric constant, a clear explanation is needed for why such a high piezoelectricity could be obtained for a PZT thin film with low Pr.
4. R. A. Wolf et al. have already reported that the piezoelectric coefficient of PZT thin films increases with temperature (J. Appl. Phys. 95, 1397-1406 (2004)). This can be understood from the simple relation of k2=d/(ε*s), since the dielectric constant and elastic compliance increase with temperature. In Figs. 4, 11suppl and 12suppl, the piezoelectric coefficients are almost constant or show a decreasing trend, even though the dielectric constant is reported to increase with temperature. This is a result that contradicts the conventional properties of piezoelectric thin films, and it is necessary to explain the reason for this in an easy-to-understand manner. Alternatively, there may be a problem with the method used to measure the temperature dependence.
5. In Fig. 3, the lattice constant of Zr-rich is c:4.08A, a:4.11A, while that of Ti-rich is c:4.22A, a:4.10. In this case, the PZT lattice volume of Zr-rich is smaller than that of Ti-rich. This is a contradictory result considering that the ionic radius of Zr is larger than that of Ti. Y. Sato et al. fabricated PZT superlattices and reported that the Zr-rich PZT layer has a longer c axis than the Ti-rich PZT layer (J. Mater. Sci. (2024) 59:8134 -8146). If there is no confirmation regarding the position of each measurement, could it be that the Ti-rich and Zr-rich are reversed?

Reviewer #3

(Remarks to the Author)
All the detail comments are included in the attachment file.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have satisfactorily addressed all points raised in my previous report, and there are no new issues arising from the modifications they have made in response to all reviewer comments. As the assessment of the potential interest and impact of the manuscript have not changed, I can now recommend publication of the manuscript in its present form.

Reviewer #2

(Remarks to the Author)
The authors answered all my questions. However, the answers are still questionable, and difficult to fully convince me. In addition, some results seem unreliable, so I don't recommend this revised manuscript for publication. The reasons are below.

Response to Comment 1: Ref 26 does not mention the elemental segregation in the PZT thin films, and the authors do not satisfactorily answer why the results are inconsistent with Ref 26.
In addition, the authors' response states that "the increase in d33 is likely attributed to the reduced substrate clamping…" which is also inconsistent with the reason of the self-polarization due to the strain gradients illustrated in Fig. 1c.

Response to Comment 2: Suppl. Fig. 5 is added to explain the asymmetry of the P-E hysteresis curves. However, the external electric field (E1~E5) in suppl. Fig. 5 g does not shown.

Response to Comment 3: The authors added the data of the converse piezoelectric effect in Suppl. Fig. 7. However, since the applied voltage was less than 4 V, the displacement generated was as small as 1 nm, and judging from the measurement conditions, it was outside the resolution of the laser Doppler vibrometer used, so the data was not reliable.

Response to Comment 3: The authors respond that the larger cell volume of Ti-rich PZT than Zr-rich PZT is due to stress relaxation and polarization alignment. However, it is difficult to be convinced of this discrepancy based on these reasons alone.

Reviewer #3

(Remarks to the Author)
I sincerely appreciate your time and effort in reviewing the manuscript. I have carefully considered all of your comments and suggestions, and I'm pleased to inform you that the necessary revisions have been made accordingly. I have no further issues to argue about in your work.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
The authors have satisfactorily answered the reviewer's comments, and I think this paper can be accepted for publication.

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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.
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We really appreciate the time and effort that the reviewers have invested in evaluating our manuscript entitled "High piezoelectric property with exceptional stability in self-poled ferroelectric films" (*NCOMMS-24-33730-T*). We have carefully read the reviewers' feedback, all the comments and suggestions are important to improve the quality of our manuscript. We have revised our manuscript accordingly, and the point-by-point response to the comments are enclosed in this response letter. In order to make the changes easily readable, we highlighted in yellow the revisions in the revised manuscript and supplementary file.

Reviewer #1:

General Comment:

The present manuscript reports on the observation of self-poling in lead zirconate titanate (PZT) films fabricated by spin coating, leading to a high and temperature-stable piezoelectric coefficient d_{33} even at elevated temperatures without the need for additional poling. The effect is attributed to a combination of a high degree of crystallographic texture, with the pseudocubic (001) axis oriented perpendicular to the film plane, and a compositional gradient of the PZT, introduced by successive spinning of different solutions and inducing a stress/strain gradient in the film.
The results reported here are highly interesting and potentially will have a strong impact on the field of piezoelectric films, e.g. for MEMS applications, pushing the limits of what is possible for solution-deposited materials. While there are other reports of self-poling in ferroelectric films, they typically arise entirely from effects at the film interfaces and do not make use of boundaries through the film thickness; they also certainly do not result in such good functional properties. The presentation style is very clear and easily understandable, with a good description of the literature context. The measurements seem to be carefully performed; if the results are valid (please see below), the interpretation is very plausible.

Response: We sincerely appreciate the positive and valuable comments from the reviewer.

Specific comments:

Comment 1: It appears rather difficult to grow crack-free PZT films with a thickness much larger than 1 micrometer; the four micrometers reported in the present manuscript seem rather exceptional in this case. Was there no cracking observed in these films? Were any special measures taken to avoid cracking? As the cracks could strongly influence the measurement results, e.g. by creating mostly

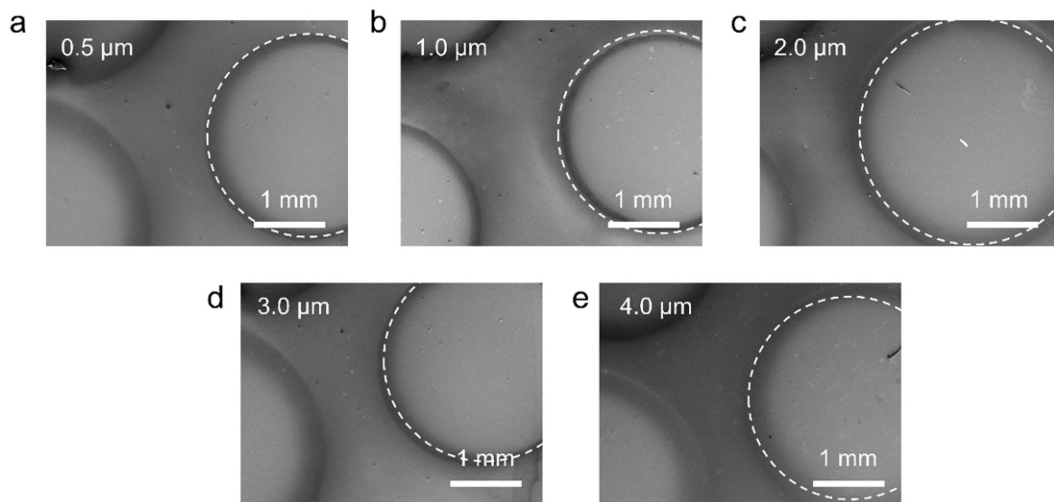
free-standing membranes that may lead to a serious over-estimation of the piezoelectric and dielectric constants, it would be relevant to show that this did not happen here. Could the authors present pictures, e.g. by optical microscopy, that show the films are crack-free on the scale of the electrodes used for the electrical measurements (200 microns) and the tip diameter for the piezoelectric measurements (2 mm)?

Response: We appreciate the reviewer's valuable comment. To address this concern, we have taken SEM images of the film surface corresponding to a large-area electrode (diameter of 2.5 mm) to confirm that the studied film is crack-free. The high-quality and crack-free characteristics are achieved by adding methanamide as an adhesive to the solution. All relevant images and experimental details have been included in the revised manuscript and supplementary files.

Revisions in the Manuscript: "….we achieved increased [001] Lotgering factors measuring at 85.8%, 93.0%, 99.8%, 98.4%, and 98.9% for high-quality crack-free PZT films with thickness ranging from 0.5 to 4 μm, respectively (Supplementary Fig. 3). " (Revised Manuscript, Page 7, Lines 165-167)

"A 1% volume proportion of methanamide is added to the solution as an adhesive to prevent micro-cracks in the film." (Revised Manuscript, Page 23, Lines 575-576)

Revisions in the Supplementary File:



"**Supplementary Fig. 3.** Scanning electron microscopy (SEM) images of high-quality, crack-free PZT films with varying thicknesses. **a,** 0.5 μm. **b,** 1 μm. **c,** 2 μm. **d,** 3 μm. **e,** 4 μm. The bright circular regions represent surface Pt electrodes with a diameter of 2.5 mm. " (Revised Supplementary File, Page S4, Supplementary Fig. 3)

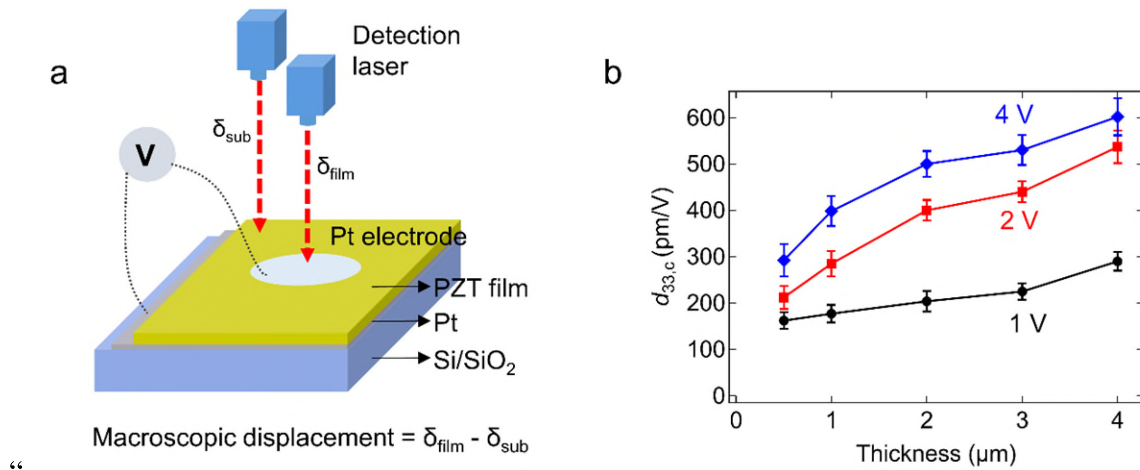
Comment 2: The piezoelectric coefficient d_{33} was determined by measuring the direct piezoresponse using the Berlincourt method. How was the bottom electrode contacted for this measurement? As the loading tip diameter was much larger than the film thickness, it is difficult to assess the suitability of this measurement. Would it be possible to have a measurement of the inverse piezoelectric response with a Double Beam Laser Interferometer? This seems to be the gold standard for d_{33} determination in thin films.

Response: We appreciate the insightful and valuable comment from the reviewer. The bottom electrode is a continuous Pt layer on the Si/Pt substrate, which is connected to the measuring circuit. A loading tip with a diameter of 2 mm was used for the measurements on the film surface electrode, which has a diameter of 2.5 mm. To address concerns regarding the suitability of $d_{33,\mathrm{d}}$ measurements, we have additionally measured the converse piezoelectric coefficient ($d_{33,\mathrm{c}}$) using a laser scanning vibrometer (LDV). The $d_{33,\mathrm{c}}$ values range from 293 to 602 pm/V for films with thicknesses between 0.5 μm and 4 μm, which is comparable to $d_{33,\mathrm{d}}$. These results have now been included in the revised manuscript and supplementary file.

Revisions in the Manuscript: "Additionally, the converse piezoelectric coefficient $d_{33,\mathrm{c}}$ measured by a laser scanning vibrometer, ranges from 293 to 602 pm/V at a 4 V bias with a frequency of 1 kHz, showing a good consistency with $d_{33,\mathrm{d}}$ (Supplementary Fig. 7)." (Revised Manuscript, Page 7, Lines 173-175)

"***Converse piezoelectricity*:** The voltage-dependent displacement of the studied films under an electric bias was measured using a laser scanning vibrometer (LSV, PSV-400, OFV-3001-SF6, PolyTech GmbH, USA). A tungsten probe pin was used to apply the bias at the edge of the electrode, which has a diameter of 2.5 mm, consistent with that used for direct piezoelectricity measurements. The bottom electrode was grounded. Notably, only AC bias at amplitudes of 1-4 V with a frequency of 1 kHz were applied since the self-poled film does not require DC poling. During the measurement, a focused laser beam was directed at two regions on the thin-film, covered and uncovered by the electrode, to measure the magnitude of the vibration. The displacement from non-electroded area (i.e., the substrate displacement, δ_{sub}) was subtracted from the displacement of the film under the electrode (δ_{film}) to obtain the effective displacement, eliminating the substrate bending effect. To further minimize the substrate bending effect and mechanical resonance, the sample was affixed to the platform with silver paste." (Revised Manuscript, Page 25, Lines 645-658)

Revisions in the Supplementary File:



“

Supplementary Fig. 7. The converse piezoelectric coefficient $d_{33,c}$ of films with different thicknesses, as measured using a laser scanning vibrometer (LSV)[4,5]. a, Schematic of the measurement setup. The electrode used has a diameter of 2.5 mm, the same as that for direct piezoelectricity measurements. To rule out the bending effect in the measurements, the sample is adhered to the platform by silver paste, and both the displacement from the non-electroded area (i.e., the substrate displacement, δ_{sub}) and the electroded area (δ_{film}) are measured, with the effective displacement being obtained by subtracting the substrate value. **b,** $d_{33,c}$ as a function of film thickness and applied bias. As anticipated, the self-poled film shows measurable displacement even without any external poling. However, the converse effect is significantly clamped by the substrate at a measuring bias of 1V with a frequency of 1 kHz. The clamping effect will be weakened with increasing bias voltage. Therefore, with slightly increasing bias to 4V, $d_{33,c}$ is greatly enhanced, reaching 293-602 pm/V for films with thicknesses ranging from 0.5 μm to 4 μm in thickness, being comparable to $d_{33,d}$. Notably, the applied bias of 1-4V are far below the coercive fields for all films.”
(Revised Supplementary File, Page S8, Supplementary Fig. 7)

Comment 3: While both the dielectric permittivity and piezoelectric coefficient is very high for a solution-deposited PZT film, the polarization values (both remanent polarization and maximum polarization under field) shown in Supplementary Fig. 9 seem to indicate a film of good quality, but not exceptionally high poling. How can this apparent discrepancy be reconciled?

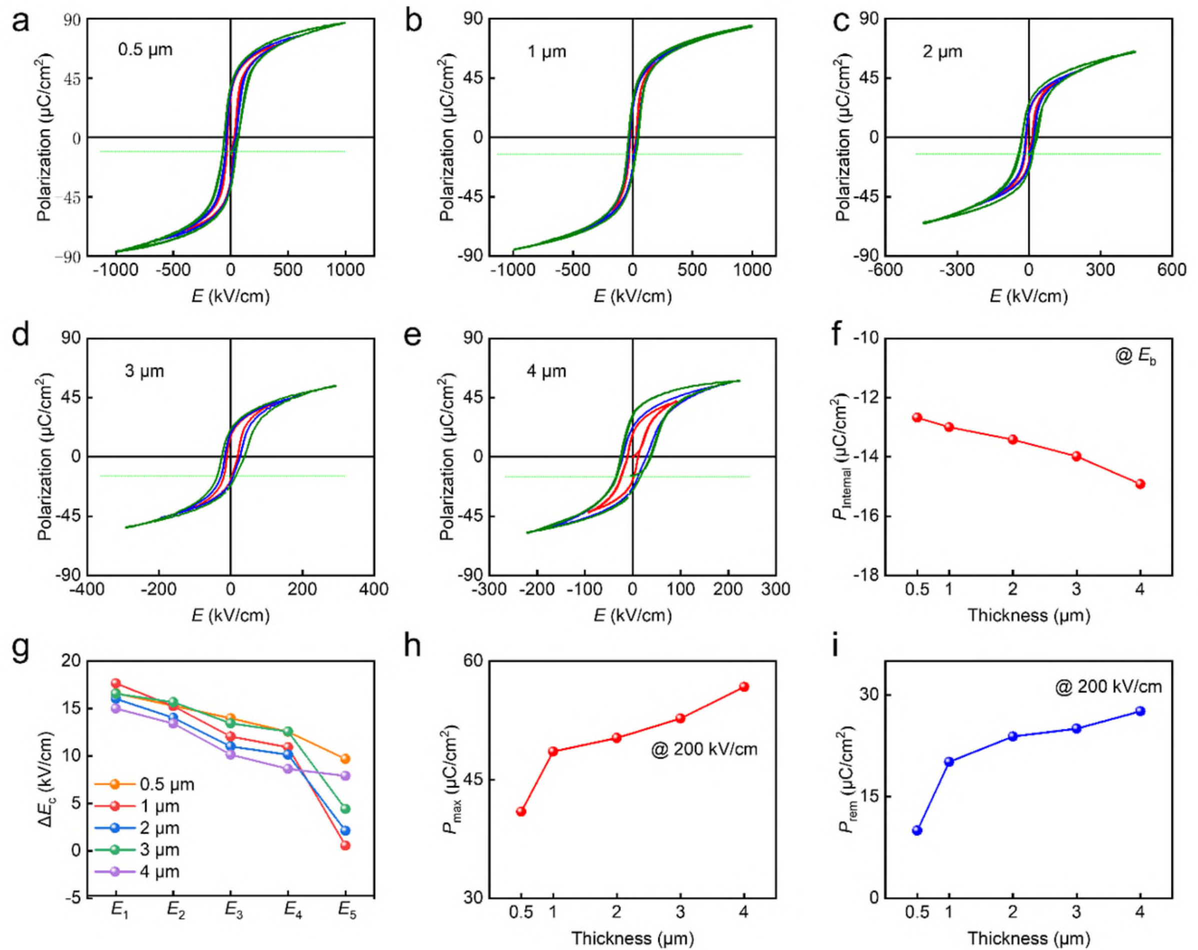
Response: We greatly appreciate the reviewer’s professional comment and question. Initially, we measured the field- and temperature-dependent *P-E* loops only for the 2 μm-thick films as a demonstration. In response to the reviewer’s concern, we have now re-measured the field-dependent *P-E* loops for all film thicknesses ranging from 0.5 to 4 μm, and compared them carefully with the

previous dataset. It appears that an earlier calibration error with the electrode mask area led to the misinterpretation of the polarization data. We have corrected these errors and included the updated datasets in the revised manuscript and supplementary file.

The remnant polarizations are 10, 20, 23, 25, and 27 μC/cm^2 for films with thicknesses of 0.5, 1, 2, 3, and 4 μm at 200 kV/cm, respectively. These values generally align with literature reports [for instance: Sens. Actuators A, 107, 68-74 (2003)]. It is evident that at the same electric field of 200 kV/cm, the remnant polarization generally increases with film thickness, which correlates well with the increasing $d_{33,d}$ values with larger thickness. The smaller P_{rem} values for thinner films (in particular, 0.5 μm film) might be attributed to its severe clamping effect.

Revisions in the Manuscript: "As the Lotgering factor approaches 100%, the $d_{33,d}$ value significantly increases from 310 to 550 pC/N, as shown in Fig. 2b. Given that $d_{33,d} = 2P_{rem}\varepsilon Q_{33}$[27], the exceptional $d_{33,d}$ values are attributed to the large remnant polarization (P_{rem}) and dielectric constant (ε). These parameters range from 10-27 μC/cm^2 at 200 kV/cm and 1610-2180 at 1 kHz (Supplementary Figs. 4-6), and are generally consistent with those reported in the literature[2,28]. Additionally, the converse piezoelectric coefficient $d_{33,c}$ measured by a laser scanning vibrometer, ranges from 293 to 602 pm/V at a 4 V bias with a frequency of 1 kHz, showing good consistency with $d_{33,d}$ (Supplementary Fig. 7). " (Revised Manuscript, Page 7, Lines 168-176)

Revisions in the Supplementary File:



"

Supplementary Fig. 5. a-e, Field-dependent *P-E* loops for films with thicknesses of 0.5, 1, 2, 3, and 4 μm. Each film set exhibits an initial polarization during the first measurement cycle, with the varying initial polarization values indicated by horizontal dashed green lines. **f,** Initial polarization values for different film sets at their breakdown fields, with the maximum value reaching –15 μC/cm^2, indicating the initial polarization alignment. **g,** Internal bias as a function of increasing applied external field (E_1 to E_5) for different film sets. Notably, a reduction of the internal bias with increasing applied external fields is observed, consistent with the PFM results, indicating a relatively easy polarization switching in the studied self-poled films. **h and i,** Maximum polarization (P_{max}) and remnant polarization (P_{rem}) at a fixed field of 200 kV/cm for films with increasing thicknesses. It is evident that at the same electric field of 200 kV/cm, remnant polarization increases with film thickness, correlating well with the increasing $d_{33,d}$ with greater thicknesses." (Revised Supplementary File, Page S6, Supplementary Fig. 5)

Reviewer #2:

General Comment:

This paper discusses the self-poling effect of sol-gel PZT thin films and its reasons due to the introduction of buffer layers and inhomogeneous Zr/Ti ratio in one layer, as well as the realization of excellent temperature stability and high d_{33c}. The reported findings are important in the field of piezoelectric MEMS and are expected to be applied to future devices.

On the other hand, there are several points in the detailed discussion that are inconsistent with previous reports and cannot be published if there are no clear answers to the following questions.

Response: We sincerely appreciate the positive and valuable comments from the reviewer and thank the reviewer for suggesting a chance of revision.

Specific comments:

Comment 1: The variation of Zr/Ti ratio in sol-gel deposition has already been reported in Appl. Phys. Lett. 90, 062907 (2007). In this paper, it was shown that eliminating the Zr/Ti variation improves the piezoelectricity, which is different from the results in this study. Clarification on this point is needed.

Response: We sincerely appreciate the reviewer's insightful comment. For films that require standard poling procedures, it is clear that elemental segregation can be detrimental to the piezoelectric response by causing compositional deviations from the desired morphotropic phase boundary (MPB). As noted in prior studies (e.g., Appl. Phys. Lett. 90, 062907 (2007)), efforts have been made to eliminate such elemental segregation. In our current work, however, we have intentionally engineered nanoscale elemental heterogeneity to facilitate self-poling. The observed increase in $d_{33,d}$ in our self-poled films, compared to the values reported in literature, is likely attributable to the reduced substrate clamping and the consequent elimination of the depoling effect. This also helps explain why traditionally poled films with the same MPB composition often exhibit significantly lower $d_{33,d}$ values than their bulk counterparts (200 vs. 500 pC/N), whereas self-poled films can achieve comparable performance. According to the reviewer's suggestion, we have added clarification regarding this discrepancy in the revised manuscript.

Revisions in the Manuscript: "It is believed that elemental segregation in PZT films is often detrimental to both film quality and piezoelectric performance, as previously reported[26]. Therefore, efforts are typically made to minimize or eliminate elemental segregation to achieve optimal

piezoelectric properties. This is particularly crucial for films requiring standard poling procedures, as elemental segregation can lead to compositional deviations from the desired MPB, which generally yields the best performance. However, even at the precise MPB, piezoelectric response is frequently constrained by substantial substrate clamping and subsequent depoling effect, explaining why poled films with the same MPB composition often exhibit much lower $d_{33,\mathrm{d}}$ values compared to their bulk counterparts (200 vs 500 pC/N). In contrast, films engineered with nanoscale elemental segregation and self-poling characteristics can significantly enhance the piezoelectric response, bringing it closer to that of bulk PZTs." (Revised Manuscript, Page 12, Lines 298-309)

Comment 2: Regarding the origin of self-poling, it has been explained that it is due to hierarchical heterogeneity, but whether the self-poling is upward or downward with respect to the c-axis has not been adequately discussed.

The self-poling of PZT thin films has been reported for sputtered PZT thin films, but in such cases, the hysteresis curves are highly anisotropic (e.g. Sens. Actuators A, 107, 68-74 (2003)). For example, in the case of upward polarization, the positive E_c is larger than the negative E_c when a voltage is applied to the top electrode because the energy required to rotate the polarization downward is larger. However, in Fig. 9suppl, the difference of E_c between positive and negative is small, which contradicts the fact that stable self-polarization occurs in this condition?

Response: We appreciate the reviewer's professional comments. The polarization with an upward direction is confirmed by additional PFM observation.

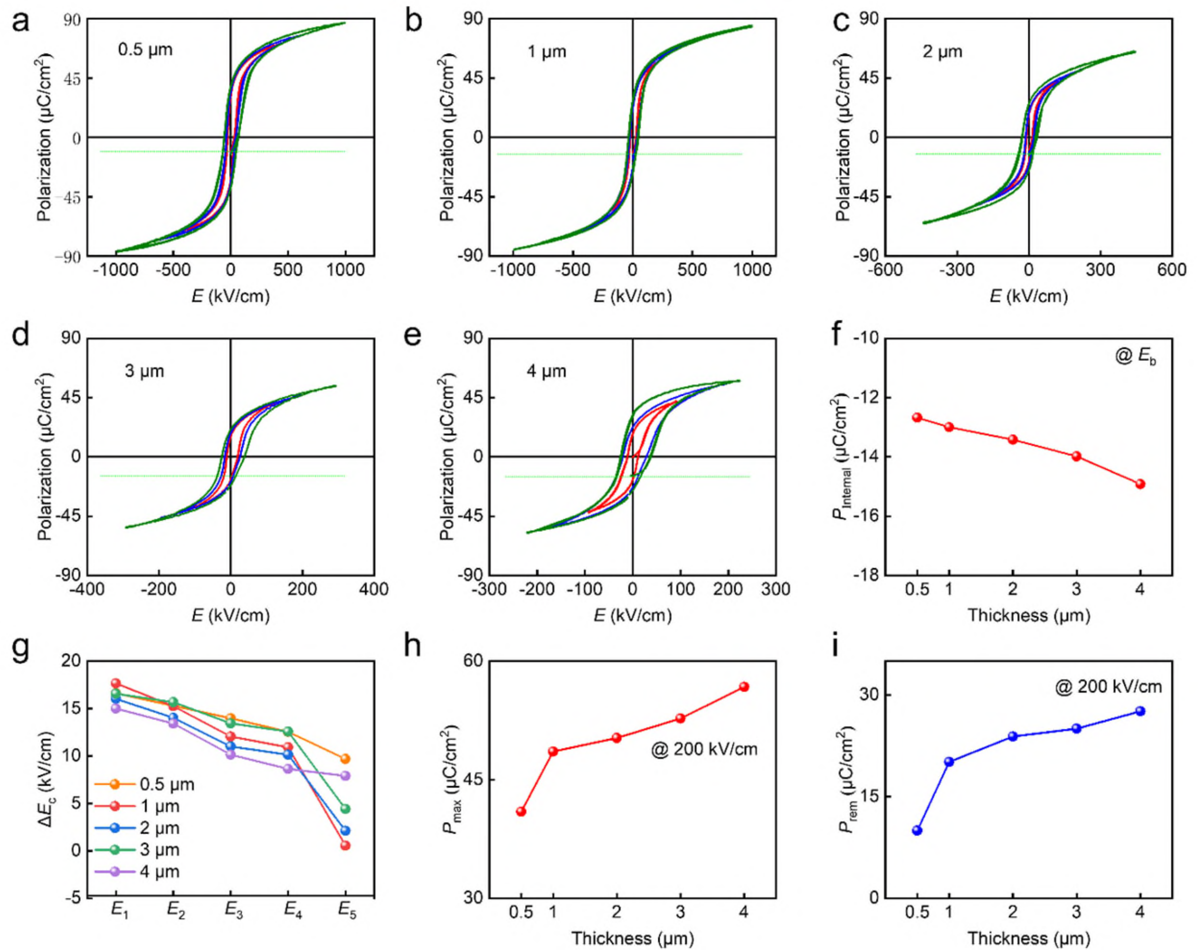
We have re-measured the field-dependent *P-E* loops for all film sets, allowing us to extract the internal bias field. It was observed that at lower fields, the *P-E* loops are asymmetric, indicating a relatively large internal bias field. However, as the applied external field increases, there is a significant reduction in the internal bias across all films, with some films showing a reduction to nearly zero. This observation is consistent with the PFM switching results. This behavior differs from previously reported fixed internal bias associated with self-polarization induced by macroscopic compositional gradient[18], interfacial pinning[30], or defect dipoles[21,31], suggesting a relative ease of polarization switching in the studied self-poled films. Nonetheless, the stabilized and significant upward self-alignment of the polarizations is reflected in the large initial polarization (offset on the polarization axis of the *P-E* loops), reaching up to –15 μC/cm² during the first measurement cycle.

These new experimental results and analyses have been included in the revised manuscript and

supplementary file.

Revisions in the Manuscript: "As shown in the polarization maps (Figs. 3 f and g, left), the polarization orientations within both Zr- and Ti-rich regions exhibit out-of-plane tendency, coinciding with the [001] driving force and texture of the film. The strong alignment of polarization along the thickness direction in its as-prepared state is further confirmed by piezoresponse force microscopy (PFM), which reveals only upward polarizations (Supplementary Fig. 12). Notably, due to the highly aligned polarizations, both the localized switching spectra through the PFM tip (SSPFM) and the macroscopic polarization-electric field (*P*-*E*) hysteresis loops exhibit visible asymmetry, resulting in positive internal fields. However, this internal field significantly reduces, and some even diminish to a negligible level with increasing applied field, as observed in both SSPFM (Supplementary Fig. 12) and *P*-*E* (Supplementary Fig. 5) curves. This behavior differs from the previously reported fixed internal bias associated with self-polarization induced by macroscopic compositional gradient[18], interfacial pinning[31], or defect dipoles[21,32], suggesting a relative ease of polarization switching in the studied self-poled films. Nevertheless, the stabilized and significant upward self-alignment of the polarizations is reflected by the very large initial polarization of up to –15 μC/cm^2, which appears as an offset on the polarization axis in the *P*-*E* loops during the first measurement cycle." (Revised Manuscript, Page 11, Lines 260-277)

Revisions in the Supplementary File:



“**Supplementary Fig. 5. a-e**, Field-dependent *P-E* loops for films with thicknesses of 0.5, 1, 2, 3, and 4 µm. Each film set exhibits an initial polarization during the first measurement cycle, with the varying initial polarization values indicated by horizontal dashed green lines. **f,** Initial polarization values for different film sets at their breakdown fields, with the maximum value reaching –15 µC/cm^2, indicating the initial polarization alignment. **g,** Internal bias as a function of increasing applied external field (E_1 to E_5) for different film sets. Notably, a reduction of the internal bias with increasing applied external fields is observed, consistent with the PFM results, indicating a relatively easy polarization switching in the studied self-poled films. **h and i,** Maximum polarization (P_{max}) and remnant polarization (P_{rem}) at a fixed field of 200 kV/cm for films with increasing thicknesses. It is evident that at the same electric field of 200 kV/cm, remnant polarization increases with film thickness, correlating well with the increasing $d_{33,d}$ with greater thicknesses.” (Revised Supplementary File, Page S6, Supplementary Fig. 5)

Comment 3: In this study, the authors report a very high d_{33c} of 520 pC/N for the PZT thin film. On the other hand, it is stated that d=2$P_r\varepsilon Q$, but the Pr is less than 10µC/cm^2, which is very small

compared to normal oriented films (e.g. Sens. Actuators A, 107, 68-74 (2003)). Even taking into account the large dielectric constant, a clear explanation is needed for why such a high piezoelectricity could be obtained for a PZT thin film with low P_r.

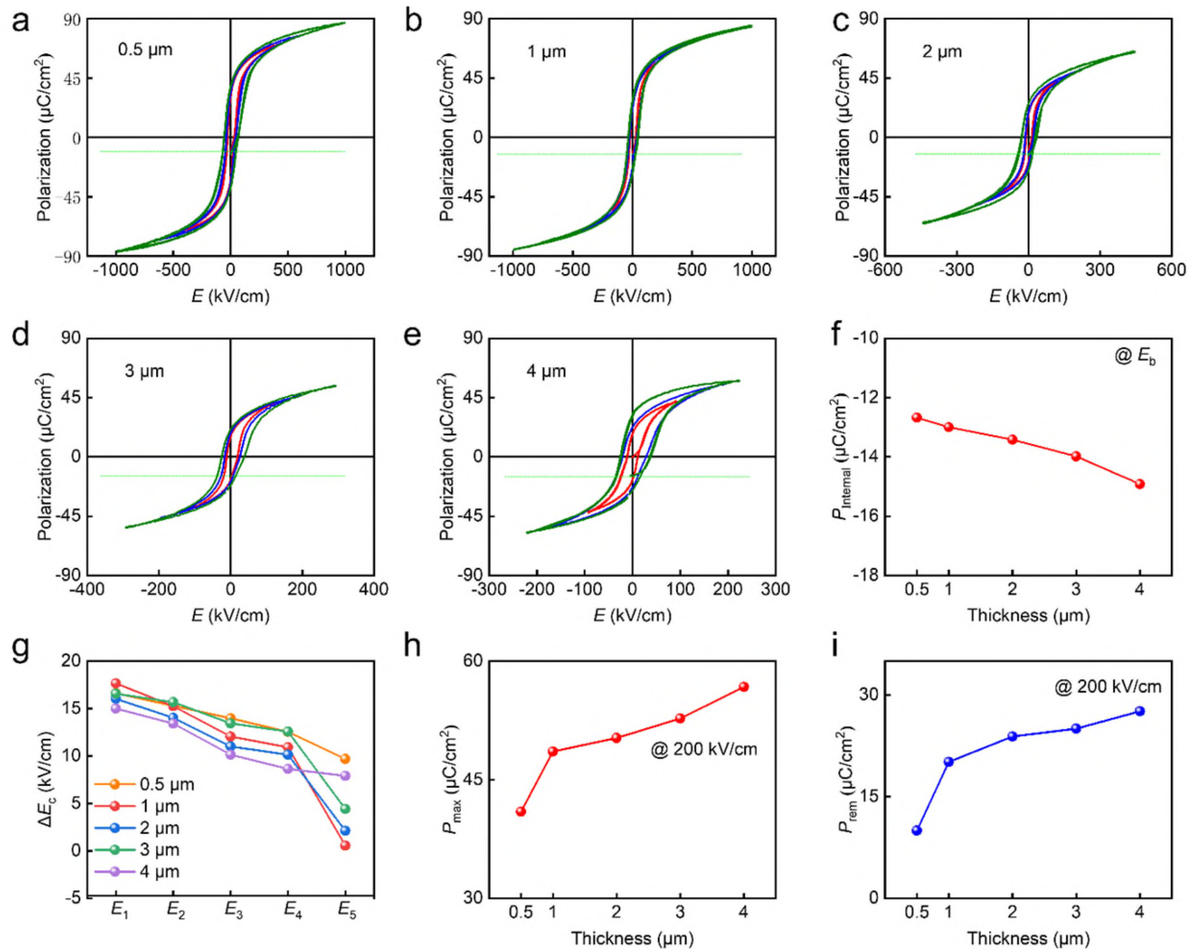
Response: We greatly appreciate the reviewer's professional comment and question. Initially, we measured the field- and temperature-dependent *P-E* loops only for the 2 μm-thick films as a demonstration. In response to the reviewer's concern, we have now re-measured the field-dependent *P-E* loops for all film thicknesses ranging from 0.5 to 4 μm, and compared them carefully with the previous dataset. It appears that an earlier calibration error with the electrode mask area led to misinterpretation of the polarization data. We have corrected these errors and included the updated datasets in the revised Supplementary File.

The remnant polarizations are 10, 20, 23, 25, and 27 $\mu C/cm^2$ for films with thicknesses of 0.5, 1, 2, 3, and 4 μm at 200 kV/cm, respectively. These values generally align with literature reports [for instance: Sens. Actuators A, 107, 68-74 (2003)]. It is evident that at the same electric field of 200 kV/cm, the remnant polarization generally increases with film thickness, which correlates well with the increasing $d_{33,d}$ values with larger thickness. The smaller P_{rem} values for thinner films (in particular, 0.5 μm film) might be attributed to its severe clamping effect.

The reference mentioned by the reviewer has also been acknowledged in the revised manuscript as reference 28 for comparison.

Revisions in the Manuscript: "As the Lotgering factor approaches 100%, the $d_{33,d}$ value significantly increases from 310 to 550 pC/N, as shown in Fig. 2b. Given that $d_{33,d} = 2P_{rem}\varepsilon Q_{33}$[27], the exceptional $d_{33,d}$ values are attributed to the large remnant polarization (P_{rem}) and dielectric constant (ε). These parameters range from 10-27 $\mu C/cm^2$ at 200 kV/cm and 1610-2180 at 1 kHz (Supplementary Figs. 4-6), and are generally consistent with those reported in the literature[2,28]. Additionally, the converse piezoelectric coefficient $d_{33,c}$ measured by a laser scanning vibrometer, ranges from 293 to 602 pm/V at a 4 V bias with a frequency of 1 kHz, showing a good consistency with $d_{33,d}$ (Supplementary Fig. 7)." (Revised Manuscript, Page 7, Lines 168-176)

Revisions in the Supplementary File:



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Supplementary Fig. 5. a-e, Field-dependent *P-E* loops for films with thicknesses of 0.5, 1, 2, 3, and 4 μm. Each film set exhibits an initial polarization during the first measurement cycle, with the varying initial polarization values indicated by horizontal dashed green lines. **f,** Initial polarization values for different film sets at their breakdown fields, with the maximum value reaching –15 μC/cm^2, indicating the initial polarization alignment. **g,** Internal bias as a function of increasing applied external field (E_1 to E_5) for different film sets. Notably, a reduction of the internal bias with increasing applied external fields is observed, consistent with the PFM results, indicating a relatively easy polarization switching in the studied self-poled films. **h and i,** Maximum polarization (P_{max}) and remnant polarization (P_{rem}) at a fixed field of 200 kV/cm for films with increasing thicknesses. It is evident that at the same electric field of 200 kV/cm, remnant polarization increases with film thickness, correlating well with the increasing $d_{33,d}$ with greater thicknesses.” (Revised Supplementary File, Page S6, Supplementary Fig. 5)

Comment 4: R. A. Wolf et al. have already reported that the piezoelectric coefficient of PZT thin films increases with temperature (J. Appl. Phys. 95, 1397-1406 (2004). This can be understood from

the simple relation of k2=d/(ε*s), since the dielectric constant and elastic compliance increase with temperature. In Figs. 4, 11suppl and 12suppl, the piezoelectric coefficients are almost constant or show a decreasing trend, even though the dielectric constant is reported to increase with temperature. This is a result that contradicts the conventional properties of piezoelectric thin films, and it is necessary to explain the reason for this in an easy-to-understand manner. Alternatively, there may be a problem with the method used to measure the temperature dependence.

Response: We sincerely appreciate the reviewer's insightful comment. To address this concern in a straightforward manner, it is worth noting that while the dielectric constant increases with temperature as anticipated, it is experimentally demonstrated that P_{rem} decreases significantly with temperature (as shown in Supplementary Fig. 6c). This behavior is responsible for the observed high thermal stability of $d_{33,\mathrm{d}}$ given that $d_{33,\mathrm{d}} = 2P_{\mathrm{rem}}\varepsilon Q_{33}$, where Q_{33} is electrostrictive coefficient, which is typically insensitive to temperature.

In addition to this straightforward explanation, we also modified the thermal stability of the PZT films by varying the annealing atmosphere (as illustrated in supplementary Fig. 15). It was observed that annealing in atmosphere with higher oxygen partial pressure significantly deteriorates thermal stability, primarily due to the reduction of oxygen vacancies, indicating *p*-type conduction in the studied PZT. Therefore, processing the films in air or nitrogen, as demonstrated in the current work, is believed to inhibit active electrical transport at elevated temperatures and stabilize the built-in fields, thereby promoting exceptional thermal stability.

Following this comment, we have added discussions in the revised manuscript, with the corresponding datasets included in the updated supplementary file.

Revisions in the Manuscript: "Notably, the piezoelectric response typically increases with increasing temperature due to the temperature dependent dielectric constant, ε. In this study, the dielectric constant and remnant polarization exhibit opposite trends as a function of temperature—ε increases, while P_{rem} decreases (Supplementary Figs. 4 and 6). This may contribute to the exceptional thermal stability of $d_{33,\mathrm{d}}$ as described by the equation $d_{33,\mathrm{d}} = 2P_{\mathrm{rem}}\varepsilon Q_{33}$ (where Q_{33} is the electrostrictive coefficient, typically insensitive to temperature). Moreover, it is observed that annealing in atmosphere with increased oxygen partial pressure significantly deteriorates thermal stability, primarily due to the reduced oxygen vacancies, indicating a *p*-type conduction in the studied PZT (Supplementary Figs. 16-17). Thus, the electrical transport behavior may alter the built-in fields in the film at elevated temperatures, thereby affecting their thermal stability." (Revised Manuscript,

Page 14, Lines 336-347)

Revisions in the Supplementary File:

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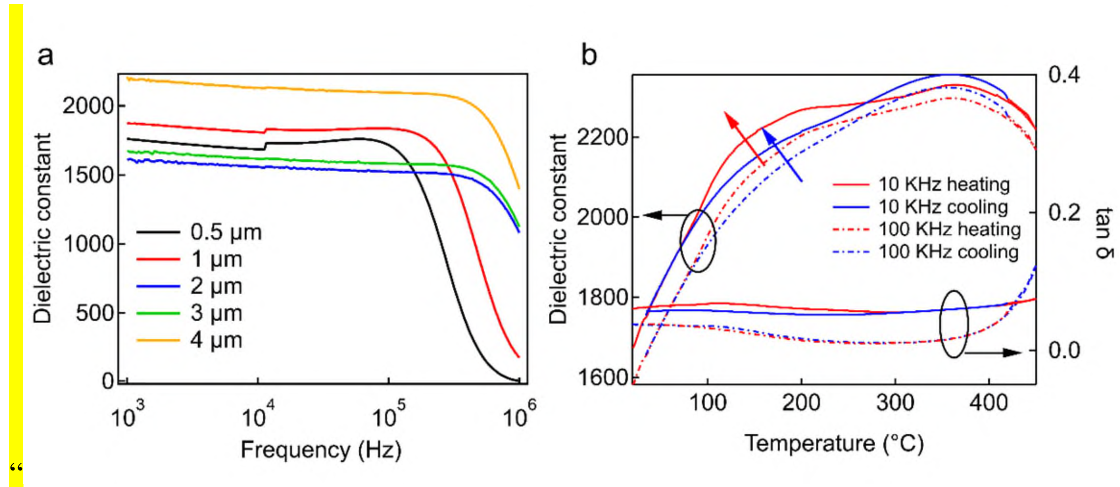

Supplementary Fig. 4. a, Frequency-dependent dielectric constant of the studied PZT film with thicknesses of 0.5, 1, 2, 3, and 4 μm. **b**, Temperature- and frequency-dependent dielectric constant and loss of the 2 μm-thick film. As shown in panel a, the dielectric constant ranges from 1610 and 2180 at a frequency of 1 kHz. These high values are attributed to the dense structure and pronounced texture of the PZT films at the morphotropic phase boundary (MPB). The dielectric constant increases with film thickness in the 2-4 μm range, contributing to the enhanced piezoelectricity observed with thicker films, as discussed in the main text. The 0.5 and 1 μm-thick films did not show smaller dielectric constants than the 2 and 3 μm-thick films and possess different trend in the frequency range above 100 kHz, likely due to their reduced texture degree or different electrical features. This discrepancy is also reflected in their *P-E* hysteresis characteristics. In panel b, for the representative 2 μm-thick film, the room temperature dielectric constant is consistent with that shown in panel a. Notably, frequency-dispersion behavior (red and blue arrows) is observed, which is a characteristic of relaxor-like ferroelectrics[1,2], and may be attributed to the reduced domain size in the nanoscale range of ~10 nm (the grain size of the studied thin film is about ~100 nm and the domain size is proportional to the square root of grain size[3]). This relaxor-like behavior may partially account for the outstanding dielectric constant." (Revised Supplementary File, Page S5, Supplementary Fig. 4)

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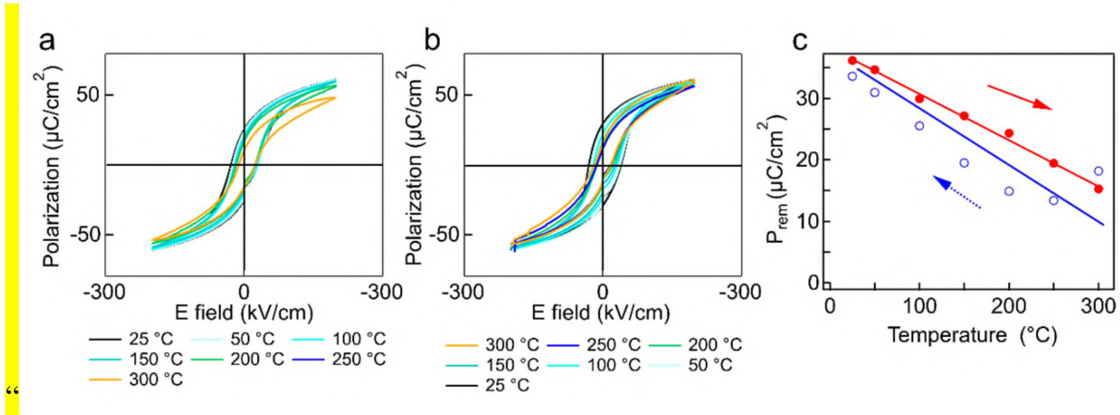


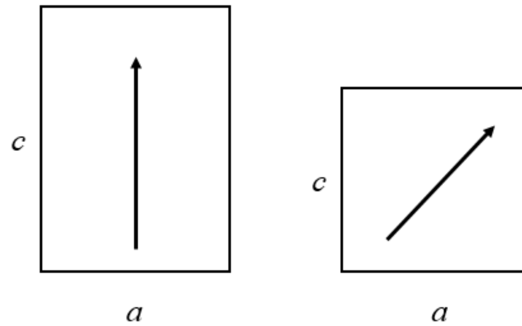
Supplementary Fig. 6. a and **b**, Temperature-dependent *P-E* loops during heating for as-prepared PZT film with 4 µm in thickness, up to its Curie temperature (i.e., 350 °C), and subsequently cooling down to room temperature. **c,** Temperature-dependent remnant polarizations (P_{rem}) extracted from the *P-E* loops measured during heating and cooling. P_{rem} decreases with increasing temperature and recovers upon cooling. At 350 °C (the Curie temperature), the loop becomes *broad*, indicating a leaky behavior induced by space charge at elevated temperature, and is therefore excluded from the figure. Notably, the heat treatment results in a difference in the *P-E* loop and the resultant P_{rem} value at the same temperature for the heating and cooling cycle.” (Revised Supplementary File, Page S7, Supplementary Fig. 6)

Comment 5: In Fig. 3, the lattice constant of Zr-rich is c:4.08A, a:4.11A, while that of Ti-rich is c:4.22A, a:4.10. In this case, the PZT lattice volume of Zr-rich is smaller than that of Ti-rich. This is a contradictory result considering that the ionic radius of Zr is larger than that of Ti. Y. Sato et al. fabricated PZT superlattices and reported that the Zr-rich PZT layer has a longer c axis than the Ti-rich PZT layer (J. Mater. Sci. (2024) 59:8134 -8146). If there is no confirmation regarding the position of each measurement, could it be that the Ti-rich and Zr-rich are reversed?

Response: We appreciate the reviewer’s professional comment. After thoroughly reviewing the original data and conducting re-measurements on the same sample, we have confirmed the accuracy of the results presented in the original manuscript.

The results can be understood as follows: (i) In-plane lattice matching leads to the same *a* parameter in both the Ti- and Zr-rich regions. (ii) The statistical out-of-plane lattice parameter *c* is likely influenced by the strong alignment of the polarizations. Specifically, the alignment of polarizations along the *c* axis could cause out-of-plane elongation or distortion of the unit cells, resulting in a larger statistical *c* in regions with highly ordered polarizations. (iii) This explains the

smaller *c* value in the Zr-rich regions, where polarizations are less ordered and aligned, in contrast to the Ti-rich regions. This difference could originate from the antiferroelectric nature of the Zr-rich regions. In these regions, localized polarizations are more likely to deviate from the out-of-plane direction (as shown in the schematic below, the right panel), leading to a smaller statistical out-of-plane lattice parameter (*c*), as expected.



The final statistical lattice constants for the Zr-rich and Ti-rich regions are 4.08 versus 4.22 Å (for the *c* lattice) and 4.11 versus 4.10 Å (for *a* lattice). On one hand, these values differ from previously reported 3.98 versus 4.10 Å (for the *c* lattice) and 4.03 versus 4.04 Å (for *a* lattice) for the respective Ti-rich and Zr-rich regions, as noted by the reviewer. This discrepancy can be attributed to the tensile stress on Ti-rich unit cells in the previously studied $PbZrO_3/PbTiO_3$ superlattice, which had a period of only 10 nm. On the other hand, the present data shows a seemingly larger lattice volume for $PbTiO_3$ compared to $PbZrO_3$. *We would like to emphasize that, the current film exhibits a $PbZrO_3/PbTiO_3$ period of 100 nm with relaxed stress, whereas the strong local polarizations alignment plays a crucial role in lattice distortion, distinguishing it from bulk $PbZrO_3$ and $PbTiO_3$ ceramics.*

Following the question, we have added more discussion in the revised manuscript.

Revisions in the Manuscript: "It is noteworthy that the lattice parameter *a* remains constant due to the lattice matching between the Ti- and Zr-rich regions. While *c* ~ 4.08 Å in the Zr-rich regions closely matches that of bulk $PbZrO_3$ (~ 4.07 Å), *c* ~ 4.22 Å in the Ti-rich regions deviates from both bulk $PbTiO_3$ (~4.15 Å) and previously reported superlattice of 5 nm $PbTiO_3$/5 nm $PbZrO_3$ under tensile stress (~3.98 Å) [29]. This discrepancy is likely attributed to (i) stress relaxation in the current micron-thick films with 100 nm periodic Ti- and Zr-rich regions, and (ii) strong polarization alignment from self-poling, as analyzed below, where cell distortion predominantly occurs along the out-of-plane direction. The pronounced polarization ordering results in a significantly elongated

statistical *c* parameter in the Ti-rich regions, as confirmed by the analysis of more than eight HAADF images." (Revised Manuscript, Page 10, Lines 247-257)

"Notably, Fig. 3f shows antiparallel nano-domains within the Zr-rich regions, likely due to the antiferroelectric nature of $PbZrO_3$ (indicated by black dashed lines). This antiferroelectric characteristic, along with the reduced polarization alignment (Fig. 3f), may also explain the smaller *c* parameter observed in the Zr-rich regions." (Revised Manuscript, Page 11, Lines 278-281)

Reviewer #3:

General Comment:

The paper addresses challenges associated with ferroelectric films, particularly their susceptibility to depolarization and degradation in piezoelectric properties at high temperatures, which are common in CMOS processing environments. Additionally, the reliance on external poling procedures can be impractical for thin films in miniaturized MEMS devices. To tackle these issues, the authors propose a two-step approach that involves texture construction and hierarchical heterogeneity engineering.

Response: We appreciate the reviewer's valuable feedback.

However, the originality of the work is questionable, as it builds on well-established concepts like self-polarization without offering significant innovation or clear differentiation from existing research.

Response: Regarding the reviewer's concerns about originality, we would like to emphasize that PZT is a commercial material that has been extensively studied for decades, with concepts of elemental segregation, self-polarization, and texture construction being recognized to some extent. However, the precise mechanisms of self-polarization, which lack clear visualization or quantification, remain unclear and are often contradictory. For instance, some studies report stronger self-polarization in thicker films, while others claim an interfacial effect that reinforces in thinner films. Some studies emphasize the significance of Pb excess for self-polarization, while most link it to texturing by using PbO as a buffer. Even so, the relationship between texture and self-polarization remains unclear; otherwise, epitaxial films (representing an extreme case of texture) would always demonstrate self-polarization, but this is not the case. Defects, lacking direct visualizations or quantifications, add to the mystery. **The ongoing controversy surrounding *self-polarization* has made the concept less practical, and yet to lead to a major breakthrough in achieving macroscopic piezoelectric performance in PZT or any other ferroelectric films.**

In response to this issue, and with the assistance of phase field simulations, we have introduced a facile two-step strategy involving texture and hierarchical heterogeneity to achieve reliable self-poling. This approach has allowed us to innovatively and clearly unveil the mysteries surrounding self-polarization by designing comprehensive comparative experiments and leveraging it to attain unprecedented macroscopic $d_{33,\mathrm{d}}$.

To the best of our knowledge, this represents an innovative approach in the field. This work is expected to open new research frontiers for ferroelectric films and attract significant attention, particularly in exploring macroscopic $d_{33,\mathrm{d}}$ in various systems with reported self-polarization.

Furthermore, the experimental validation is inadequate, with no evidence showing potential applications in CMOS or MEMS devices.

Response: We appreciate the reviewer for highlighting this issue. As our current study does not involve CMOS/MEMS device fabrications, we have revised the relevant statements to focus on the potential of the processed films in addressing limitations related to poling challenges, high-temperature packaging procedures, and high-temperature shocks in harsh environments for thickness-mode MEMS devices. The revision details addressing specific comments 1, 2, and 6 are provided below.

Some of the following details should be addressed to be published.

Response: We greatly appreciate the reviewer for suggesting an opportunity of revision. We have carefully addressed the concerns raised, as detailed in the following comments.

Specific comments:

Comment 1-1: The paper describes a two-step approach for enhancing the piezoelectric properties of thin films using a simple spin coating process. This method involves constructing textures and engineering hierarchical heterogeneity within the film by applying multiple layers via spin coating and annealing them to achieve the desired microstructure and composition gradients. However, the feasibility of achieving such complex structural and compositional control using just a spin coating process is questionable.

Response: We appreciate the reviewer's comment. The elemental heterogeneity in the studied PZT is effectively designed by leveraging the different crystallization dynamics of $PbZrO_3$ and $PbTiO_3$, the two end members of PZT solid solution. $PbTiO_3$ has a lower crystallization energy, and the addition of TiO_2 in the 83PbO-17TiO_2 buffer layer activates the faster growth of $PbTiO_3$, leading to a reliable segregation of Ti-rich and Zr-rich regions. This buffer is used every five layers throughout the micron-scale film, ensuring the reliable activation of the proposed elemental heterogeneity.

Additionally, this strategy efficiently integrates with the solution-based spin-coating method, as PbO and TiO_2 can be mixed in varying ratios in the buffer solution, ensuring the texture construction feasible.

The above two steps ensure the reliable introduction of both texture and hierarchical heterogeneity. We have now clarified these points in the revised manuscript.

Revisions in the manuscript: "(ii) Ti-rich composition nucleates and grows more easily than Zr-rich composition in PZT due to the lower crystallization energy of $PbTiO_3$[26], which could facilitate composition-based hierarchical heterogeneity." (Revised Manuscript, Page 5, Lines 120-122)

"Mixed lead oxide (PbO) and titanium oxide (TiO_2) in various ratios, which are well-suited for the solution-based spin-coating method, were employed as buffer layers to comprehensively tailor the film textures. To start with, a texture transition from [001], [111], to [011] by adjusting the PbO-TiO_2 buffer ratio from 100:0 to 0:100 (Supplementary Fig. 2) were constructed." (Revised Manuscript, Page 6, Lines 147-151)

"Of particular importance is that using sole PbO buffer (i.e., without TiO_2) yields 98.3% [001] texture in PZT films, but less reliable macroscopic piezoelectricity (i.e., only one third out of a dozen samples present $d_{33,\mathrm{d}}$). Thus, the addition of TiO_2 in the buffer—a straightforward process in solution-based method like spin-coating—is crucial for the stabilization of macroscopic piezoelectricity, i.e., the self-poling feature. This is achieved by impacting the initiation of hierarchical heterogeneity in the two-step approach, a topic that will be discussed further in the following session." (Revised Manuscript, Page 7, Lines 177-183)

"This significant composition gradient within each film layer, as shown in Fig. 3c, is caused by the addition of TiO_2 in the buffer layer, which is routinely applied every five PZT layers. This gradient is further reinforced by the easier nucleation and growth of the Ti-rich component in a perovskite structure regime." (Revised Manuscript, Page 9, Lines 225-229)

Comment 1-2: Also, the annealing process over 700 °C, as described in the paper, involves high temperatures that may not be compatible with standard CMOS or MEMS processes. Such elevated temperatures could limit the process's flexibility, making integrating these ferroelectric films into CMOS or MEMS-based devices problematic. The authors should address the compatibility of their annealing process with the standard CMOS or MEMS technology to ensure that the proposed method is viable for practical applications.

Response: We thank the reviewer for raising the concern about the high processing temperature, which exceeds the acceptable 450°C for CMOS/MEMS devices. This limitation may be partially addressed by employing a transfer procedure for MEMS devices, though it could significantly increase complexity. We have acknowledged this issue in the revised manuscript.

Additionally, as our current study does not involve CMOS/MEMS device fabrications, we have

revised the relevant statements to focus on the potential of the processed films in addressing limitations related to poling challenges, high-temperature packaging procedures, and high-temperature shocks in harsh environments for thickness-mode MEMS devices.

Revisions in the manuscript: "The high $d_{33,d}$ values and its exceptional temperature stability, combined with self-poling feature, overcomes the limitations associated with poling challenges, high-temperature packaging and high-temperature shocks in harsh environments, particularly in the ferroelectric film-based thickness-mode MEMS devices. While these properties open new research avenues for ferroelectric films, integrating the current PZT films into MEMS devices will require additional transfer procedures due to their high processing temperatures (750 °C). Reducing this temperature below 450 °C would better align with standard MEMS fabrication platforms." (Revised Manuscript, Page 16, Lines 402-410)

Comment 2: The authors mention that the material demonstrates impressive resilience to elevated temperatures up to its Curie temperature of 350 °C, with less than a 16% degradation in performance. However, there are no additional demonstrations to prove that this concept can be applied in CMOS platforms, which require not only high-temperature processes but also exposure to reactive ions, large electric fields, and RF plasma during fabrication. The authors should explore these aspects to ensure the material's compatibility with demanding process conditions.

Response: We appreciate the reviewer's professional comments regarding discussions on CMOS devices. We recognize that claiming revolutionary potential for the current film in the CMOS platform could be misleading without relevant experimental demonstrations, as standard CMOS platforms involve not only packaging but also exposure to reactive ions, large electric fields, and RF plasma, as the reviewer noted. We have revised the relevant statements to focus on the potential of the processed films in addressing limitations related to poling challenges, high-temperature packaging procedures, and high-temperature shocks in harsh environments for thickness-mode MEMS devices.

Revisions in the manuscript: "However, their tendency to depolarize and degradation in piezoelectric properties when exposed to packaging procedures at temperatures exceeding 260 °C remains a significant challenge." (Revised Manuscript, Page 2, Abstract)

"Additionally, the high-temperature treatments (usually exceeding 260 °C, Fig. 1a) required in MEMS packaging process, negatively impact the functionality of ferroelectric films." (Revised Manuscript, Page 3, Lines 59-61)

"Remarkably, we aim to attain direct piezoelectricity, $d_{33,d}$, particularly merits thickness-mode MEMS devices, reaching exceptional levels between 310 and 550 pC/N with varying film thicknesses. The high $d_{33,d}$ values and its exceptional temperature stability, combined with self-poling feature, overcomes the limitations associated with poling challenges, high-temperature packaging and high-temperature shocks in harsh environments, particularly in ferroelectric film-based thickness-mode MEMS devices. While these properties open new research avenues for ferroelectric films, integrating the current PZT films into MEMS devices will require additional transfer procedures due to their high processing temperatures (750 °C). Reducing this temperature below 450 °C would better align with standard MEMS fabrication platforms. Nevertheless, these films offer a promising prototype for evaluation of stability upon exposure to reactive ions and/or RF plasma used in MEMS platforms. Advances in simplified thickness-mode MEMS designs, self-poling and unprecedented $d_{33,d}$ hold significant potential to facilitate industry progress." (Revised Manuscript, Page 16, Lines 400-413)

Comment 3: The comparison between the PZT-based ferroelectric material and other materials presented in Fig. 4 is reasonable to demonstrate the results of this study. However, when discussing the d_{33} factor in comparison with other materials, the statement, "In addition to their prominent thermal stability, the studied PZT films exhibit small-signal d_{33},d surpassing that of the most actively researched and/or commercially available ferroelectric films," requires further clarification. Bi-based materials exhibit higher Curie temperatures (T_c) and d_{33} values than in this paper [1-3]. The paper appears to focus solely on 'self-poled' materials, and it would be more accurate and precise to define these boundaries when making such comparisons.

[1] Zhang, Shujun, Clive A. Randall, and Thomas R. Shrout. "Characterization of perovskite piezoelectric single crystals of 0.43 $BiScO_3$–0.57 $PbTiO_3$ with high Curie temperature." Journal of Applied Physics 95.8 (2004): 4291-4295.

[2] Zhang, Shujun, Clive A. Randall, and Thomas R. Shrout. "High Curie temperature piezocrystals in the $BiScO_3$-$PbTiO_3$ perovskite system." Applied Physics Letters 83.15 (2003): 3150-3152.

[3] Liu, Zenghui, et al. "Recent progress in bismuth-based high Curie temperature piezo-/ferroelectric perovskites for electromechanical transduction applications." Current Opinion in Solid State and Materials Science 26.5 (2022): 101016.

Response: We appreciate the reviewer's valuable suggestion. In the revised manuscript, we have

adjusted the contrast boundaries of Fig. 4 for better clarity.

In revised Fig. 4c, we now include only previously reported ferroelectric films with in situ heating experiments related to their direct piezoelectric properties ($d_{33,d}$, d_{31}, and/or $-e_{31}$). Corresponding claims in the text have been updated accordingly. Notably, given the main research focus of our work (i.e., films and direct piezoelectricity, $d_{33,d}$), we did not involve systems that, while potentially outstanding, only reported bulk counterparts or converse piezoelectricity ($d_{33,c}$).

In revised Fig. 4d, we have also limited the scope to the field of "ferroelectric films and $d_{33,d}$".

Revisions in the Manuscript: "In Fig. 4c, thermal instability of lead-based and lead-free inorganic films (ferroelectric film systems under *in situ* measurements are involved) as a function of temperature are compared [33-35]. Notably, the studied PZT shows prominent thermal stability, in contrast to the piezoelectricity described by d_{31}, $-e_{31}$ and/or $d_{33,d}$, since the latter is yet to be investigated in many ferroelectric films." (Revised Manuscript, Page 14, Lines 352-356)

"Within the board temperature range, the studied PZT films exhibit small-signal direct piezoelectricity, $d_{33,d}$, surpassing those of the most actively researched and/or commercially available ferroelectric films to date (Fig. 4d)[10-12,17,36-42]. The achieved value of 550 pC/N is more than double the highest value of 230 pC/N documented for PZT films on silicon or other substrates[10,43]. It should be noted that (i) previously reported self-poled ferroelectric films warrant in-depth investigation on their macroscopic $d_{33,d}$ [18,19,21,32]; (ii) the reported $d_{33,c}$ values of ~ 200 - 400 pm/V for the converse piezoelectric effect in PZT films, attributes to the substantial domain switching under electric stimuli up to 120 V [44], which is beyond the practical several volts stimulus in a MEMS device. These films may exhibit different behavior in terms of their direct piezoelectric coefficients after poling, which may experience severe depoling." (Revised Manuscript, Page 15, Lines 357-368)

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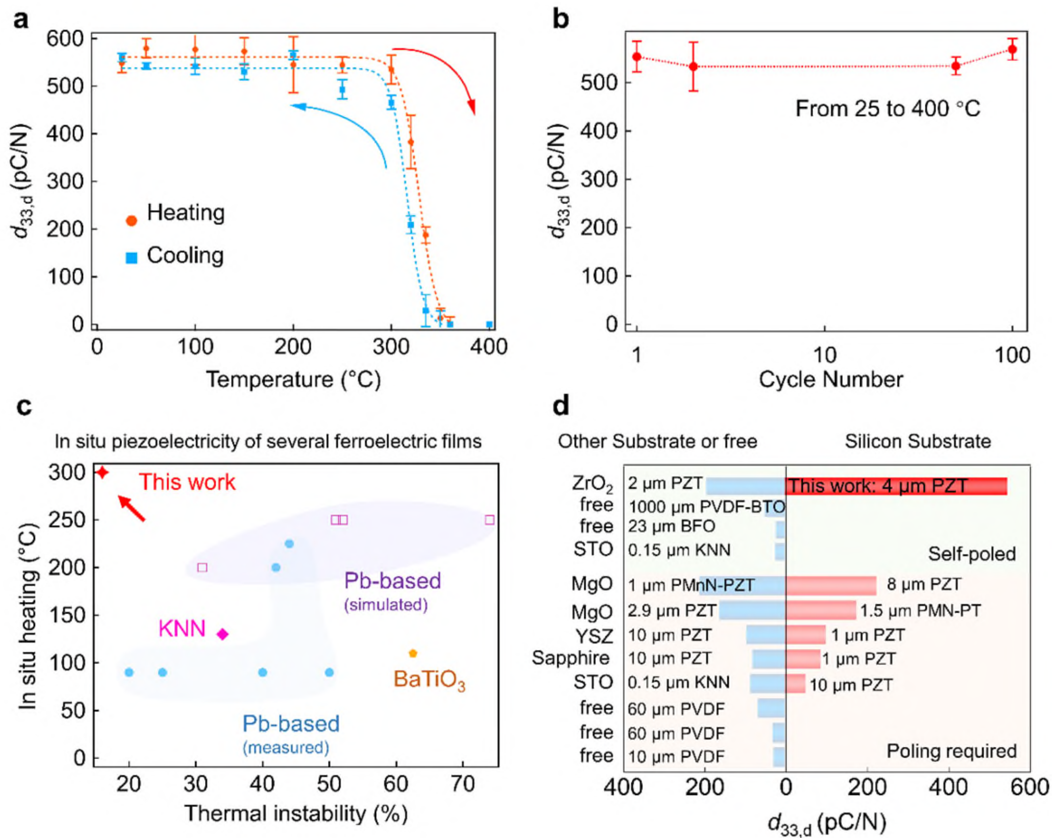

Fig. 4 | Thermal stability and service features of self-poled PZT films. a, Temperature-dependence of $d_{33,d}$ in self-poled PZT films. **b**, $d_{33,d}$ after different numbers of heating and cooling cycles above its Curie temperature of 350 °C. The data in this study are for 4 μm-thick PZT films. **c**, Thermal instability as a function of *in situ* heat treatment temperature, comparing the current film to other ferroelectric films. The comparison involves piezoelectricity described by parameters such as $d_{33,d}$, d_{31}, or $-e_{31}$, since $d_{33,d}$ is yet to be investigated in many ferroelectric thin films. **d**, $d_{33,d}$ achieved in self-poled PZT films compared to other representative ferroelectric films with or without self-poling character on different substrates. Notably, the graph exclusively features ferroelectric films and the small signal direct piezoelectric charge coefficient, $d_{33,d}$.” (Revised Manuscript, Page 15, Fig. 4)

Comment 4: While the measurement setup for quantifying the direct d_{33},d of thin films appears to provide accurate piezoelectric data, the paper lacks a detailed explanation of the thermal characterization method and the device setup, particularly concerning temperature reliability. The authors should clarify the actual in-situ temperature experienced by the piezoelectric material rather than simply stating the applied temperature to ensure that the device’s thermal stability is appropriately assessed. Furthermore, to address the first concern, the authors should provide additional details about the materials used in the thermal experimental setup, including the specifics

of the thermocouples, their thermal conductance properties, and how these components are integrated within the system. This clarification is necessary to ensure the reliability and accuracy of the experimental system.

Response: We really appreciate the reviewer for the valuable comments and suggestions. To facilitate a better evaluation of the $d_{33,\mathrm{d}}$ results, we have now detailed the experimental procedures for in situ thermal stability measurements of piezoelectricity in the revised manuscript. Please see below the additional details provided regarding the thermocouples, experimental setup, and system integration.

Revisions in the Manuscript: "***Room-temperature and high-temperature piezoelectricity measurements*:** The Pt electrode with a diameter of 2.5 mm was deposited on the PZT films by *rf* magnetron sputtering (VTC-2RF, MTI corporation, China). For room-temperature piezoelectricity measurement, the sample is placed on a 5×5 cm^2 silver platform (Supplementary Fig. 1a), which possesses a flatness of 0.1 mm. Pt in the Si/Pt/PZT wafer is wired to the silver platform as the bottom electrode. On top of the surface electrode, a metallic probe coated with Pt in a diameter of 2 mm applies small forces incrementally (such as 20 g, 40 g, 60 g, and 80 g) and measures the output voltage through the circuit, from which the piezoelectric coefficient can be fitted (Supplementary Fig. 1b). It should be noted that $d_{33,\mathrm{d}}$ values measured on PZT ceramic with our instrument closely align with the values obtained using commercial d_{33}-meter, as shown in Supplementary Movie. 1, proving the validity of the measuring instrument. Therefore, this method has recently been proven effective for quantifying piezoelectricity with fine accuracy[46].

For *in situ* high temperature measurements, the silver platform was used to heat the samples (Supplementary Fig. 1c), adopting a quarto temperature controller of LRT 001 (Gogo Instruments Technology, Shanghai, China). The heating rate can reach up to 100 °C/min, with a maximum temperature of 600 °C. Measurements are taken every 25 °C, allowing 10 minutes for stabilization at each temperature. A fixed *K*-type thermocouples is attached to the surface of the silver platform to record the operando temperature of the platform, whereas a mobile thermal-meter (AS877, *K*-type, Smart Sensor) is contacted to the sample edge to ensure the alignment of the sample surface temperature with the silver platform. The electrical resistance of the silver platform changes from 0.5 to below 0.1 Ω as temperature increases from 25 to 500 °C, measured with a multimeter, ensuring superb contact of the sample bottom electrode. The temperature, force, and signal control are achieved by the software as shown in Supplementary Fig. 1d. For the thermal fatigue measurements, a tube furnace is used to heat the Si/Pt/PZT sample to 400 °C, preserving 5 min for each cycle." (Revised

Manuscript, Page 24, Lines 605-631)

Revisions in the Supplementary File:

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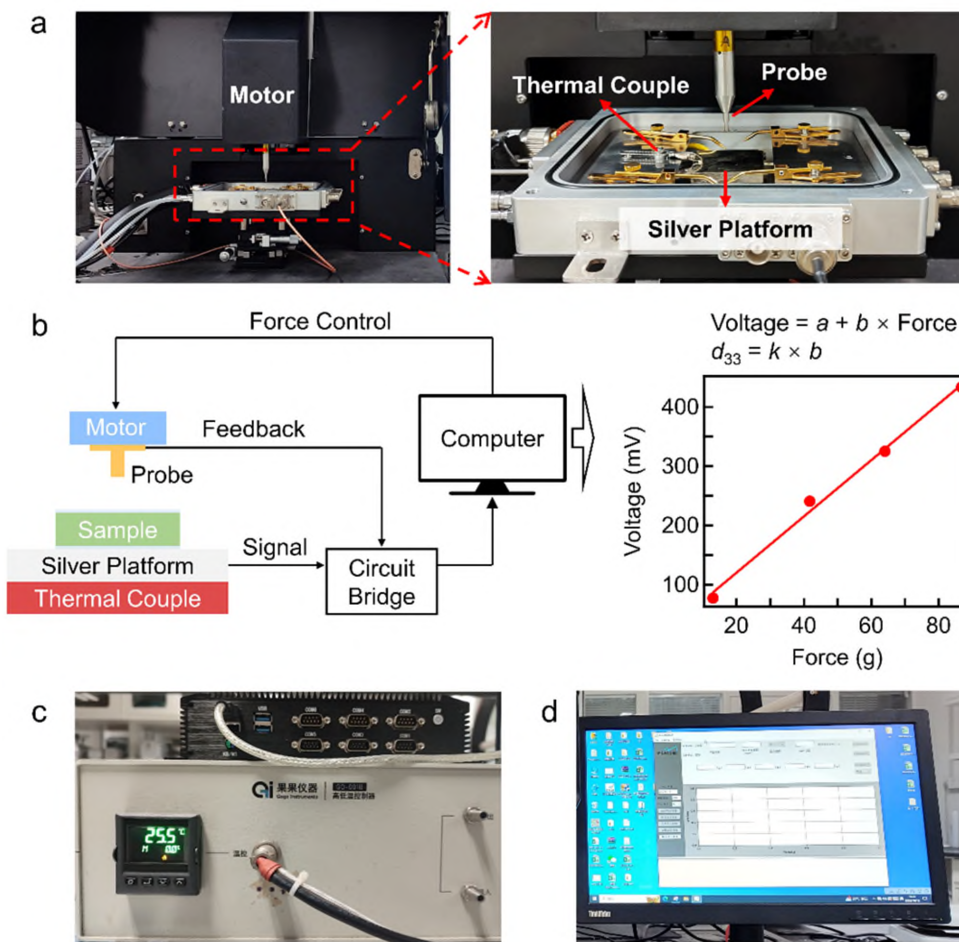


Supplementary Fig. 1. a, Experimental setup for measuring the direct $d_{33,\mathrm{d}}$ of thin films. The samples are placed on the silver platform. **b,** Schematic diagram of the measurement circuit and output voltage versus applied force for fitting the $d_{33,\mathrm{d}}$. The forces are applied in linear sequence of 20, 40, 60, and 80 g. The equations on the top-right corner provide a basic explanation of the measuring principle of the system. The constant k is calibrated by an internal standard sample at each measurement. **c,** Temperature controller LRT 001 (Gogo Instruments Technology, Shanghai, China) used for heating the silver platform for *in situ* high temperature measurements. The operando temperatures of the sample surface and the silver platform are recorded simultaneously using a K-type thermocouple (See Methods). **d,** Software for controlling the applied force and collecting the output signals." (Revised Supplementary File, Page S2, Supplementary Fig. 1)

Comment 5-1: In this study, self-poling was conducted on a silicon wafer, but comparing the self poling effects across different types of wafer substrates would be beneficial.

Response: We appreciate the reviewer's valuable suggestion. According to this suggestion, we have fabricated 1 μm-thick PZT films on Mica and ZrO_2 substrates using the same procedure described in the main text. The films exhibit [001]-texture and show measurable macroscopic $d_{33,d}$, further validating the proposed two-step approach. These additional experimental results have now been included in the revised manuscript and supplementary file.

Additionally, we also included a comparison of $d_{33,d}$ for both self-poled and non-self-poled ferroelectric films on various substrates, such as Si, MgO, sapphire, and STO, which is given in the revised Fig. 4d. Notably, we clarified in the revised manuscript that several previously studied self-poled ferroelectric films exhibit significant potential for achieving appreciable macroscopic $d_{33,d}$ and warrant further investigations. For instance, self-polarized $(1-x)Bi_{0.5}Na_{0.5}TiO_3-xBaTiO_3$ films [ACS Appl. Mater. Interfaces 2017, 9, 28716−28725; ACS Appl. Mater. Interfaces 2018, 10, 23945−23951] and self-polarized PZT heterostructures [Adv. Mater. 2013, 25, 1761–1767; Nano Energy 85 (2021) 105984; Sensors and Actuators A 107 (2003) 68–74] are examples of systems with great potential.

Revisions in the Manuscript: "Leveraging the strategy of two-step approach and its experimental validation, we unambiguously demonstrate the simple rules for designing self-poling in ferroelectric films with superior macroscopic piezoelectric performance, achieved through texture construction and hierarchical heterogeneity. This is validated not only for Si substrate, but also on a range of other substrates, including Mica and ZrO_2 (Supplementary Fig. 17)." (Revised Manuscript, Page 16, Lines 384-389)

"Within the board temperature range, the studied PZT films exhibit small-signal direct piezoelectricity, $d_{33,d}$, surpassing those of the most actively researched and/or commercially available ferroelectric films to date (Fig. 4d)[10-12,17,36-42]. The achieved value of 550 pC/N is more than double the highest value of 230 pC/N documented for PZT films on silicon or other substrates[10,43]. It should be noted that (i) previously reported self-poled ferroelectric films warrant in-depth investigation on their macroscopic $d_{33,d}$ [18,19,21,32]; (ii) the reported $d_{33,c}$ values of ~ 200 - 400 pm/V for the converse piezoelectric effect in PZT films, attributes to the substantial domain switching under electric stimuli up to 120 V [44], which is beyond the practical several volts stimulus in a MEMS device. These films may exhibit different behavior in terms of their direct piezoelectric coefficients after poling, which may experience severe depoling. " (Revised Manuscript, Page 15, Lines 357-368)

“

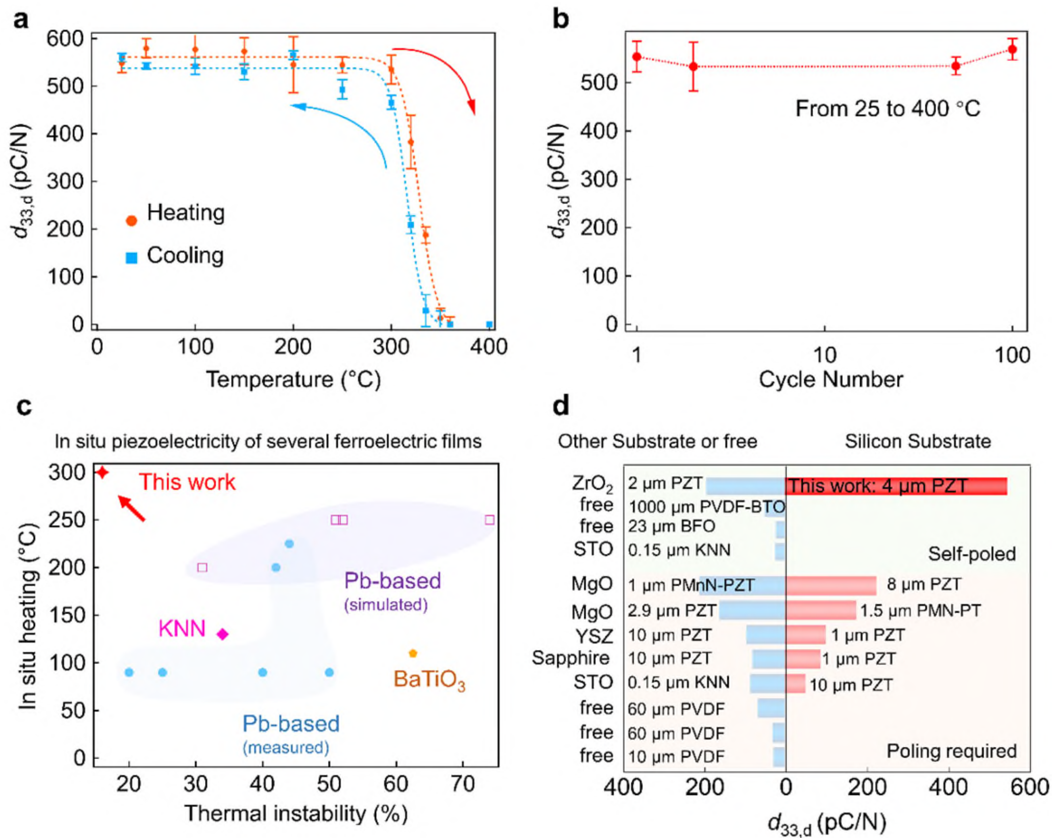
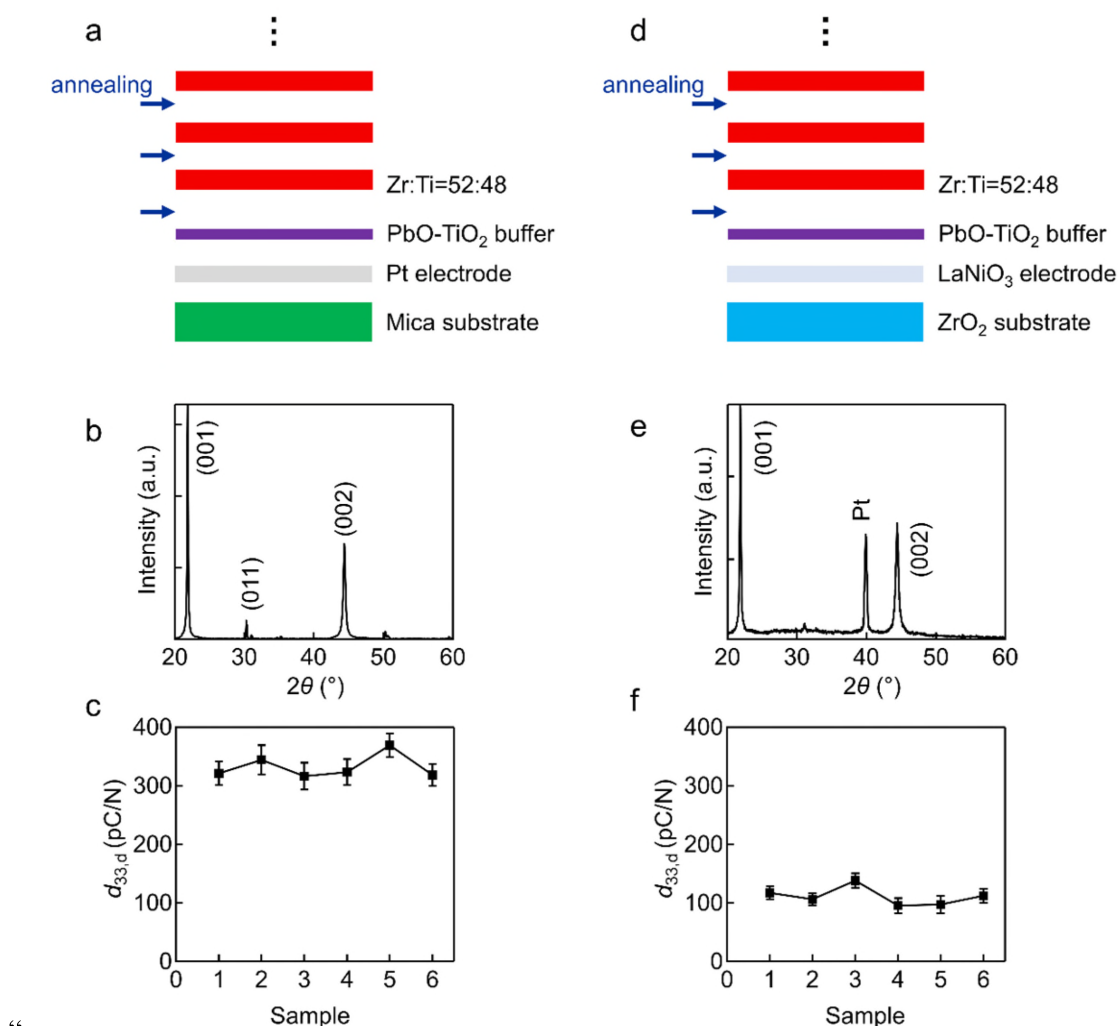


Fig. 4 | Thermal stability and service features of self-poled PZT films. a, Temperature-dependence of $d_{33,d}$ in self-poled PZT films. **b**, $d_{33,d}$ after different numbers of heating and cooling cycles above its Curie temperature of 350 °C. The data in this study are for 4 μm-thick PZT films. **c**, Thermal instability as a function of *in situ* heat treatment temperature, comparing the current film to other ferroelectric films. The comparison involves piezoelectricity described by parameters such as $d_{33,d}$, d_{31}, or $-e_{31}$, since $d_{33,d}$ is yet to be investigated for numerous ferroelectric thin films. **d**, $d_{33,d}$ achieved in self-poled PZT films compared to other representative ferroelectric films with or without self-poling character on different substrates. Notably, the graph exclusively features ferroelectric films and the small signal direct piezoelectric coefficient, $d_{33,d}$. Certain components, such as PMN-PT films, exhibit much lower piezoelectric properties compared to their single crystal or ceramic counterparts.”

(Revised Manuscript, Page 15, Fig. 4)

Revisions in the Supplementary File:

“ 

Supplementary Fig. 17. Validation of the proposed two-step approach for achieving macroscopic $d_{33,d}$ on Mica and ZrO_2 substrates. a, Schematic illustrating the deposition of [001]-textured PZT films with controlled Zr/Ti segregation using a PbO-TiO_2 buffer layer as shown in the main text on a Mica substrate. A 100 nm Pt electrode was deposited by *rf* magnetron sputtering. **b,** XRD pattern of PZT/Pt/Mica, confirming the [001] texture of the film. **c,** $d_{33,d}$ values measured across eight samples deposited on Mica substrates. **d,** Schematic of the deposition of [001]-textured PZT films with controlled Zr/Ti segregation using a PbO-TiO_2 buffer layer as shown in the main text on ZrO_2. A 100 nm $LaNiO_3$ (LNO) was deposited via sol-gel method as the bottom electrode (Note that the Pt electrode tends to peel off easily on ZrO_2). **e,** XRD pattern of PZT/LNO/ZrO_2, confirming the [001] texture of the film. **f,** $d_{33,d}$ values measured across six samples deposited on ZrO_2 substrate. The measurable macroscopic properties validate the effectiveness of the proposed two-step approach for achieving self-poling.” (Revised Supplementary File, Page S20, Supplementary Fig. 17)”

Comment 5-2: Additionally, it would be valuable to include results demonstrating whether the self-poling effect remains consistent after the samples are diced from the wafer.

Response: We appreciate the reviewer's question. In fact, the measurements were conducted on both the entire wafer and diced samples, and the differences between them are negligible. We have acknowledged this in the revised manuscript.

Revisions in the Manuscript: "Notably, wafer-sized and diced PZT samples exhibit negligible difference in $d_{33,d}$, as observed across dozens of samples." (Revised Manuscript, Page 5, Lines 130-132)

Comment 6: Generally, piezoelectric materials operate in thickness mode, but depending on the aspect ratio, they may function in other modes as well. If the developed poling technique exclusively generates a thickness mode response, the paper must articulate this claim more clearly.

Response: We appreciate the reviewer's professional suggestion. The studied self-poling primarily generates a thickness-mode response. We have revised the statement for further clarity in the revised manuscript.

Revisions in the manuscript: "Remarkably, we aim to attain direct piezoelectricity, $d_{33,d}$, particularly merits thickness-mode MEMS devices, reaching exceptional levels between 310 and 550 pC/N with varying film thicknesses. The high $d_{33,d}$ values and its exceptional temperature stability, combined with self-poling feature, overcomes the limitations associated with poling challenges, high-temperature packaging and high-temperature shocks in harsh environments, particularly in the ferroelectric film-based thickness-mode MEMS devices." (Revised Manuscript, Page 16, Lines 400-406)

Comment 7: In addition to the results obtained from the 4 μm PZT film, experiments should be conducted on films with other thicknesses to ensure the broader feasibility of the findings. Although it is mentioned that experiments were conducted on films ranging from 0.5 to 4 μm, if the 4 μm results are the only ones presented as reliable, it raises concerns about the overall trustworthiness and consistency of the data.

Response: We appreciate the reviewer's insightful comment. To address this issue, we have conducted additional measurements of temperature-dependent $d_{33,\,d}$, converse piezoelectricity $d_{33,\,c}$, field-dependent *P*-*E* loops, and SEM morphologies of the film surface for all PZT film sets with

thicknesses of 0.5, 1, 2, 3, and 4 μm.

It was observed that the temperature stability of $d_{33,\mathrm{d}}$ for all film sets is excellent and consistent with previous measurements. It is also observed that the depolarization temperature increases from 220 °C (for 0.5 - 1 μm film) to approximately 300 °C (for 2-4 μm films). This variation is likely due to the more significant thermal stress or stress gradient in thinner films, which would impact its built-in fields and the $d_{33,\mathrm{d}}$ at elevated temperatures. Additionally, the converse piezoelectricity $d_{33,\mathrm{c}}$, measured using a laser scanning vibrometer, ranges from 293 to 602 pm/V and aligns well with $d_{33,\mathrm{d}}$.

We have now included all the results in the revised manuscript and supplementary file to support a more comprehensive evaluation of the current study.

Revisions in the Manuscript: "As the Lotgering factor approaches 100%, the $d_{33,\mathrm{d}}$ value significantly increases from 310 to 550 pC/N, as shown in Fig. 2b. Given that $d_{33,\mathrm{d}} = 2P_{\mathrm{rem}}\varepsilon Q_{33}$[27], the exceptional $d_{33,\mathrm{d}}$ values are attributed to the large remnant polarization (P_{rem}) and dielectric constant (ε). These parameters range from 10-27 μC/cm^2 at 200 kV/cm and 1610-2180 at 1 kHz (Supplementary Figs. 4-6), and are generally consistent with those reported in the literature[2,28]. Additionally, the converse piezoelectric coefficient $d_{33,\mathrm{c}}$ measured by a laser scanning vibrometer, ranges from 293 to 602 pm/V at a 4 V bias with a frequency of 1 kHz, showing a good consistency with $d_{33,\mathrm{d}}$ (Supplementary Fig. 7)." (Revised Manuscript, Page 7, Lines 168-176)

"This is demonstrated for all films with thicknesses ranging from 0.5 to 4 μm, showing $\Delta d_{33,\mathrm{d}}/d_{33,\mathrm{d}}$ ranging from 10% to 16% (Supplementary Fig. 14)." (Revised Manuscript, Page 14, Lines 330-332)

Revisions in the Supplementary File:

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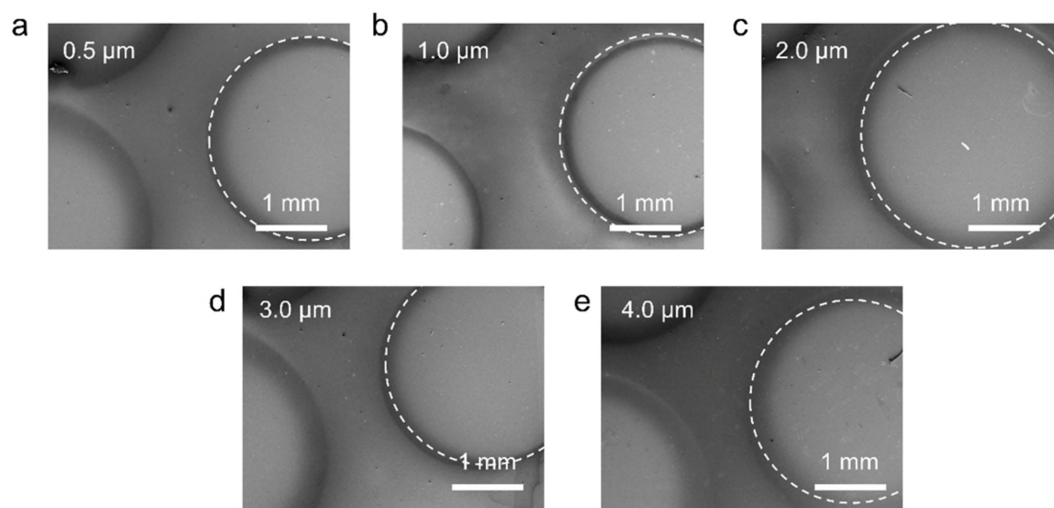
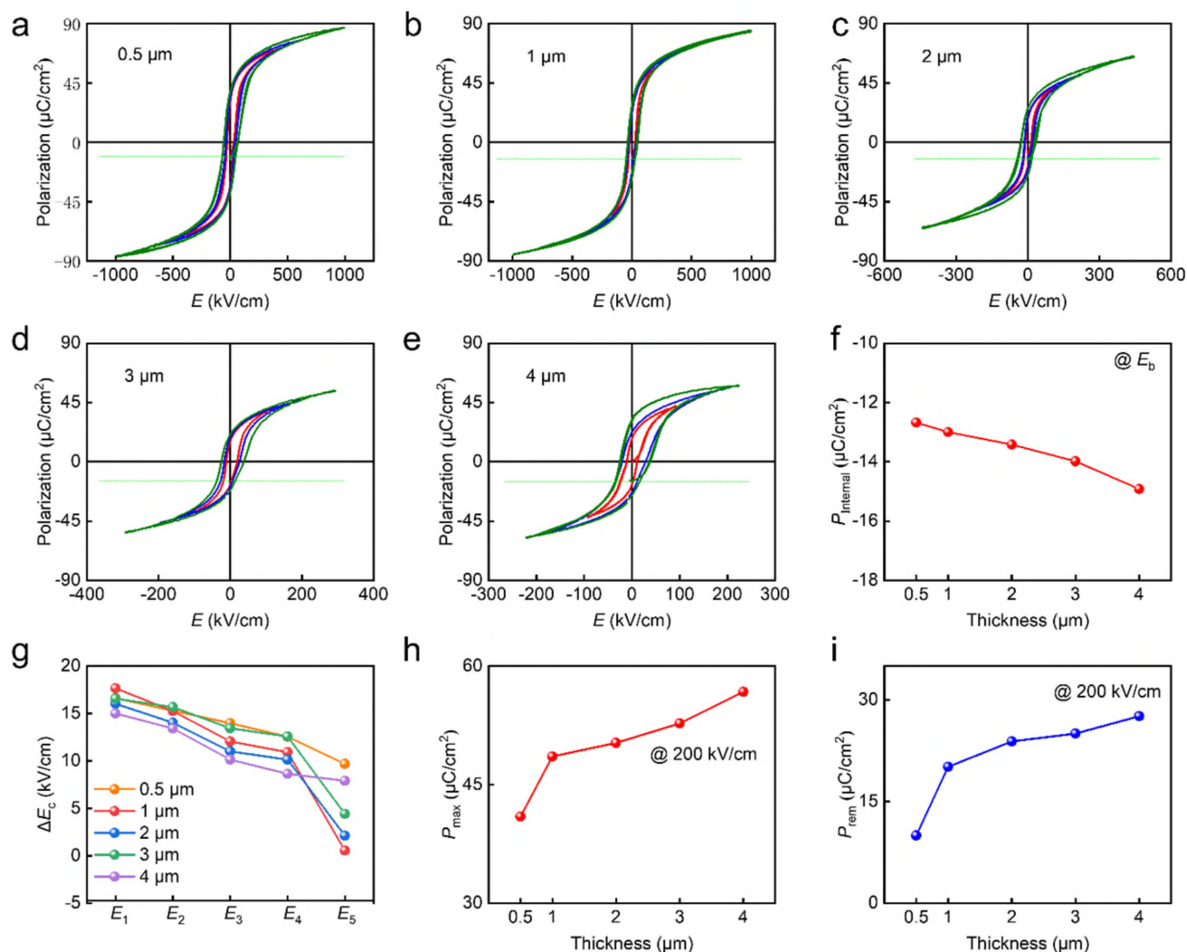


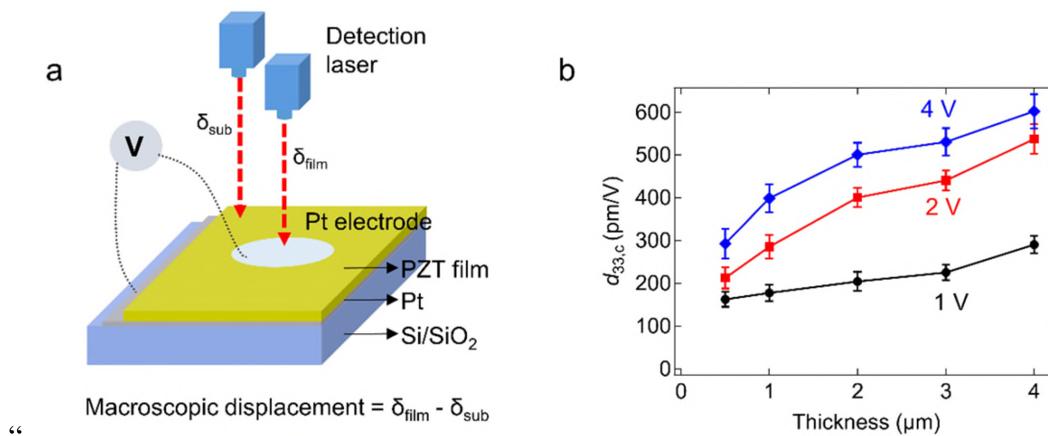
Supplementary Fig. 3. Scanning electron microscopy (SEM) images of high-quality, crack-free PZT films with varying thicknesses. **a,** 0.5 μm. **b,** 1 μm. **c,** 2 μm. **d,** 3 μm. **e,** 4 μm. The bright circular

regions represent surface Pt electrodes with a diameter of 2.5 mm." (Revised Supplementary File, Page S4, Supplementary Fig. 3)



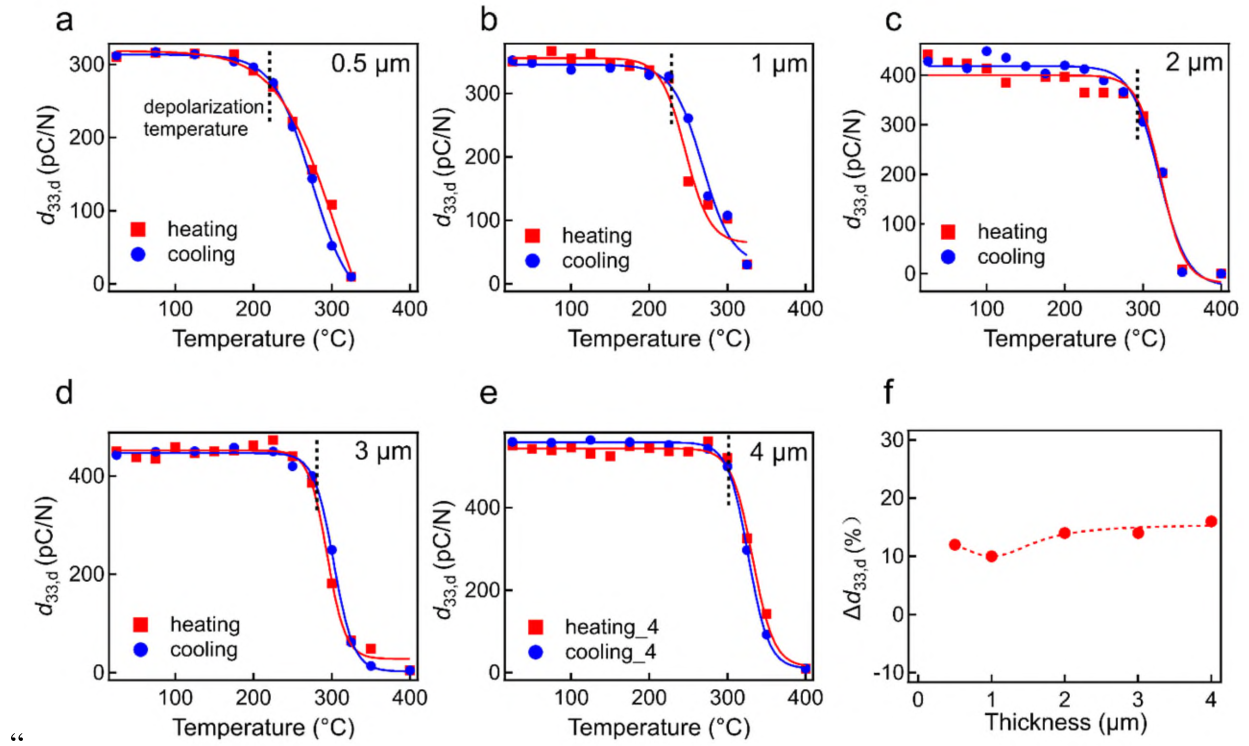
"

Supplementary Fig. 5. a-e, Field-dependent *P-E* loops for films with thicknesses of 0.5, 1, 2, 3, and 4 μm. Each film set exhibits an initial polarization during the first measurement cycle, with the varying initial polarization values indicated by horizontal dashed green lines. **f,** Initial polarization values for different film sets at their breakdown fields, with the maximum value reaching –15 μC/cm^2, indicating the initial polarization alignment. **g,** Internal bias as a function of increasing applied external field (E_1 to E_5) for different film sets. Notably, a reduction of the internal bias with increasing applied external fields is observed, consistent with the PFM results, indicating a relatively easy polarization switching in the studied self-poled films. **h and i,** Maximum polarization (P_{max}) and remnant polarization (P_{rem}) at a fixed field of 200 kV/cm for films with increasing thicknesses. It is evident that at the same electric field of 200 kV/cm, remnant polarization increases with film thickness, correlating well with the increasing $d_{33,d}$ with greater thicknesses." (Revised Supplementary File, Page S6, Supplementary Fig. 5)

“ 

Supplementary Fig. 7. The converse piezoelectric coefficient $d_{33,c}$ of films with different thicknesses, as measured using a laser scanning vibrometer (LSV)[4,5]. a, Schematic of the measurement setup. The electrode used has a diameter of 2.5 mm, the same as that for direct piezoelectricity measurements. To rule out the bending effect in the measurements, the sample is adhered to the platform by silver paste, and both the displacement from the non-electroded area (i.e., the substrate displacement, δ_{sub}) and the electroded area (δ_{film}) are measured, with the effective displacement being obtained by subtracting the substrate value. **b,** $d_{33,c}$ as a function of film thickness and applied bias. As anticipated, the self-poled film shows measurable displacement even without any external poling. However, the converse effect is significantly clamped by the substrate at a measuring bias of 1V with a frequency of 1 kHz. The clamping effect will be weakened with increasing bias voltage. Therefore, with slightly increasing bias to 4V, $d_{33,c}$ is greatly enhanced, reaching 293-602 pm/V for films with thicknesses ranging from 0.5 μm to 4 μm in thickness, being comparable to $d_{33,d}$. Notably, the applied bias of 1-4V are far below the coercive fields for all films.”

(Revised Supplementary File, Page S8, Supplementary Fig. 7)



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Supplementary Fig. 14. a-e, Thermal stability of PZT films with thicknesses of 0.5, 1, 2, 3, and 4 μm. The depolarization temperature for each film is indicated by black vertical dashed lines. **f,** Extracted piezoelectric property variation up to their depolarization temperatures as a function of film thickness. The different PZT films sets exhibit variations in piezoelectric properties ($\Delta d_{33,d}/d_{33,d}$) ranging from 10% to 16%, with negligible thermal hysteresis during both upward and downward temperature sweeps. The depolarization temperature increases from 220 °C (for 0.5 - 1 μm film) to approximately 300 °C (for 2-4 μm films). This variation is likely due to the more significant thermal stress or stress gradient in thinner films, which could impact its built-in fields and damage $d_{33,\mathrm{d}}$ at elevated temperatures." (Revised Supplementary File, Page S16, Supplementary Fig. 14)

We sincerely thank the reviewers once again for their valuable feedback. We hope these improvements will warrant further consideration for publication in Nature Communications.

We really appreciate the time and effort that the reviewers have invested in evaluating our manuscript entitled "High piezoelectric property with exceptional stability in self-poled ferroelectric films" (*NCOMMS-24-33730A*). We acknowledge reviewers 1 and 3 for their positive comments, and have carefully read reviewer #2' additional feedback. All the comments and suggestions are valuable to improve the quality of our manuscript. We have revised our manuscript accordingly, and the point-by-point response to the comments are enclosed in this response letter. In order to make the changes easily readable, we highlighted in yellow the revisions in the revised manuscript and supplementary file.

Reviewer #2:

General Comment:

The authors answered all my questions. However, the answers are still questionable, and difficult to fully convince me. In addition, some results seem unreliable, so I don't recommend this revised manuscript for publication. The reasons are below.

Response: We sincerely appreciate the Reviewer's valuable comments. We apologize for any ineffective response in our last version. Below we will further address the reviewer's concern, revise and improve the manuscript.

Specific comments:

Comment 1: Response to Comment 1: Ref 26 does not mention the elemental segregation in the PZT thin films, and the authors do not satisfactorily answer why the results are inconsistent with Ref 26. In addition, the authors' response states that "the increase in d33 is likely attributed to the reduced substrate clamping…" which is also inconsistent with the reason of the self-polarization due to the strain gradients illustrated in Fig. 1c.

Response: We appreciate the reviewer's valuable comment.

Ref 26 used the term "*Zr/Ti compositional gradient*". To precisely describe prior results, we updated related term to "*Zr/Ti compositional gradient*" in the revised manuscript.

It is noted that Ref 26 improve the piezoelectric response (d_{31} and e_{31}) by removing Zr/Ti compositional gradient and making the composition more close to the morphotropic phase boundary (MPB, which should yield the optimal performance). It is worth noting that the mentioned d_{31} and e_{31} are measured after a specific poling process — the samples were poled at high temperature of 150 °C

under 100 kV/cm for 10 min. Although ref 26 does not address the depoling effect within these films, it is widely recognized that films experience depoling due to thin thickness or silicon substrate clamping and the resultant tensile stress [Mat. Res. Soc. Symp. Proc., 493, 1998]. This effect is generally unavoidable and typically reduces piezoelectric property. Therefore, the measured d_{31} of -156 pC/N (corresponding to an approximate d_{33} of 312 pC/N) likely reflects partial depoling. This value is smaller than what we have observed for the 2 μm-thick PZT in our study (440 pC/N).

In the currently-studied films with self-poling characteristic, we do not need external poling procedure and avoids suffering from partial depoling. This would make the d_{33} approaching their intrinsic value as in the bulk counterpart, though it may show some compromise due to slight deviation from the MPB. We would like to emphasize that the build-in field and internal strain for achieving self-poling in our work is due to the compositional gradient (independent from Si substrate clamping stress as demonstrated by Supplementary Fig. 10). This does not contradict the previous discussions on depoling from substrate clamping. Since a standard poling procedure is not necessary in the current work to acquire the piezoelectric property, we avoid both poling and depoling, allowing us to achieve values approaching that of its bulk counterpart.

We have made revisions in the manuscript based on these discussions to clarify any confusion.

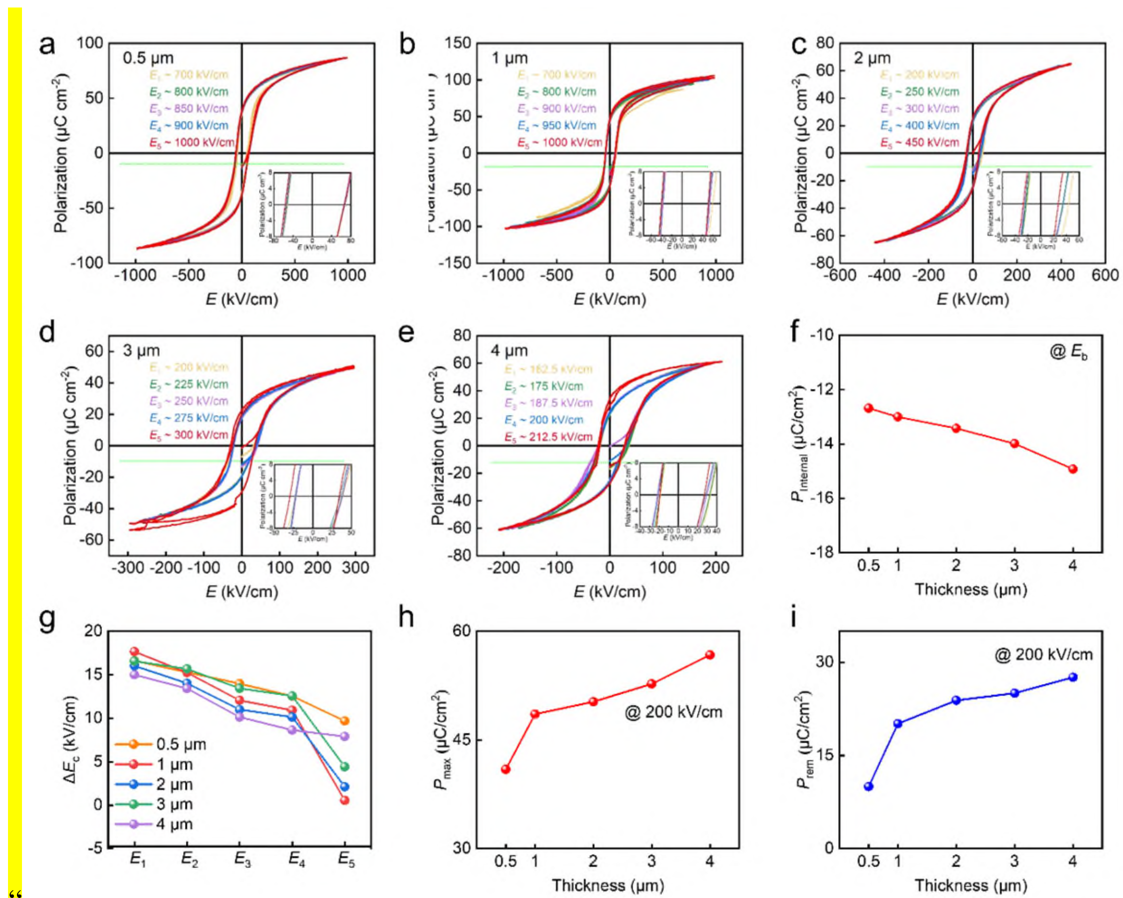
Revisions in the Manuscript: "The Zr/Ti compositional gradients, commonly observed in PZT films, are believed to negatively impact both film quality and piezoelectric performance, as previously reported[26]. These gradients lead to compositional deviations from the desired MPB, which generally yields optimal performance. Therefore, efforts are typically made to minimize or eliminate undesired changes in the Zr/Ti ratio to achieve optimal piezoelectric properties. However, even at the precise MPB, films with the same composition often exhibit much lower $d_{33,d}$ values compared to their bulk counterparts (200 vs 500 pC/N). This reduction is ascribed to partial depoling after the standard poling procedure, due to larger depolarization field in thinner films or substrate clamping, unlike bulk counterpart. In contrast, films engineered with nanoscale elemental segregation, as studied here, exhibit self-poling characteristic, allowing them to largely avoid both poling and partial depoling, resulting in piezoelectric response closer to that of bulk PZTs" (Revised Manuscript, Page 12, Lines 299-311)

Comment 2: Response to Comment 2: Suppl. Fig. 5 is added to explain the asymmetry of the P-E hysteresis curves. However, the external electric field (E1~E5) in suppl. Fig. 5 g does not shown.

Response: We greatly appreciate the comment from the reviewer. We realized that the electric fields E_1 to E_5 were not clearly specified for each film, making them difficult to interpret due to their difference. Thus, we have modified panels a-e and labeled the electric field E_1 to E_5. In addition, to better distinguish the ΔE_c, an enlarged view of each panel at the coercive field is provided as bottom-right insets. The revisions of the text and figures are referred as below.

Revisions in the Supplementary File:

“



Supplementary Fig. 5. a-e, *P-E* loops for films with thicknesses of 0.5, 1, 2, 3, and 4 μm at respective fields ranging from E_1 to E_5 as marked. Each inset at the bottom-right shows enlarged view near the $+E_c$ and $-E_c$, illustrating the internal bias, if any, at respective applied external electric field. Each film set exhibits an initial polarization during the first measurement cycle, with the varying initial polarization values indicated by horizontal dashed green lines. **f,** Initial polarization values for different film sets at their breakdown fields, with the maximum value reaching –15 μC/cm^2, indicating the initial polarization alignment. **g,** Internal bias as a function of increasing applied external field (E_1 to E_5 as shown in panels a-e) for different film sets. Notably, a reduction of the internal bias with increasing applied external fields is observed, consistent with the PFM results, indicating a relatively easy polarization switching in the studied self-poled films. **h and i,** Maximum polarization (P_{max}) and

remnant polarization (P_{rem}) at a fixed field of 200 kV/cm for films with increasing thicknesses. It is evident that at the same electric field of 200 kV/cm, remnant polarization increases with film thickness, correlating well with the increasing $d_{33,d}$ with greater thicknesses." (Revised Supplementary File, Page S6, Supplementary Fig. 5)

Comment 3: Response to Comment 3: The authors added the data of the converse piezoelectric effect in Suppl. Fig. 7. However, since the applied voltage was less than 4 V, the displacement generated was as small as 1 nm, and judging from the measurement conditions, it was outside the resolution of the laser Doppler vibrometer used, so the data was not reliable.

Response: We greatly appreciate the reviewer's comment and question.

Normally, DC bias above the coercive field is used in LSV method, to pole the films. This is not used in the current work. Here, only an AC bias to measure the displacement is used, which is constrained below 4 V (mostly below the coercive field) with a frequency of 1 kHz, since we need to demonstrate its self-poling character. To address the reviewer's concern, the actual displacement is added, with the range of 162 – 2408 pm for films with different thickness and bias.

We would kindly note that, LDV can easily reach a resolution of 10 pm as demonstrated in previous works [Liu et al., Science 369, 292–297 (2020)], thus it was widely used for measuring converse piezoelectricity of films. However, we did not push to this limit in the current work, our measured absolute displacement reaches above 100 pm, which can be clearly distinguished from any noise as shown in the below figure. In the absolute displacement range of 162 – 2408 pm in this work, LDV is widely adopted in many studies and is reckoned trustworthy.

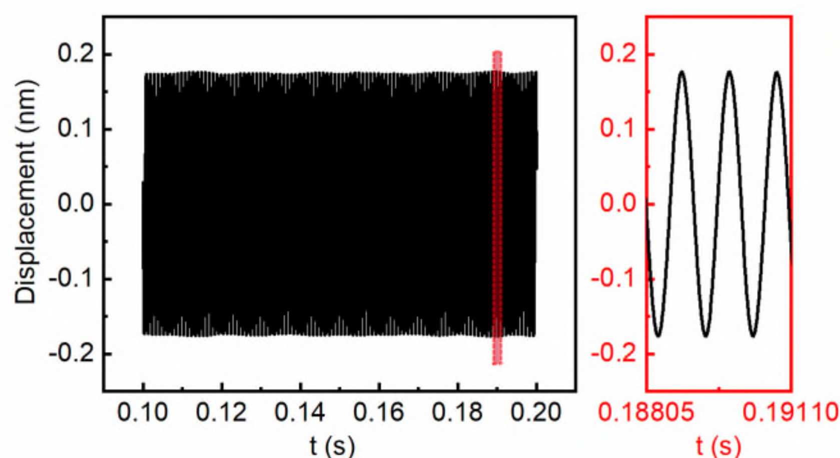
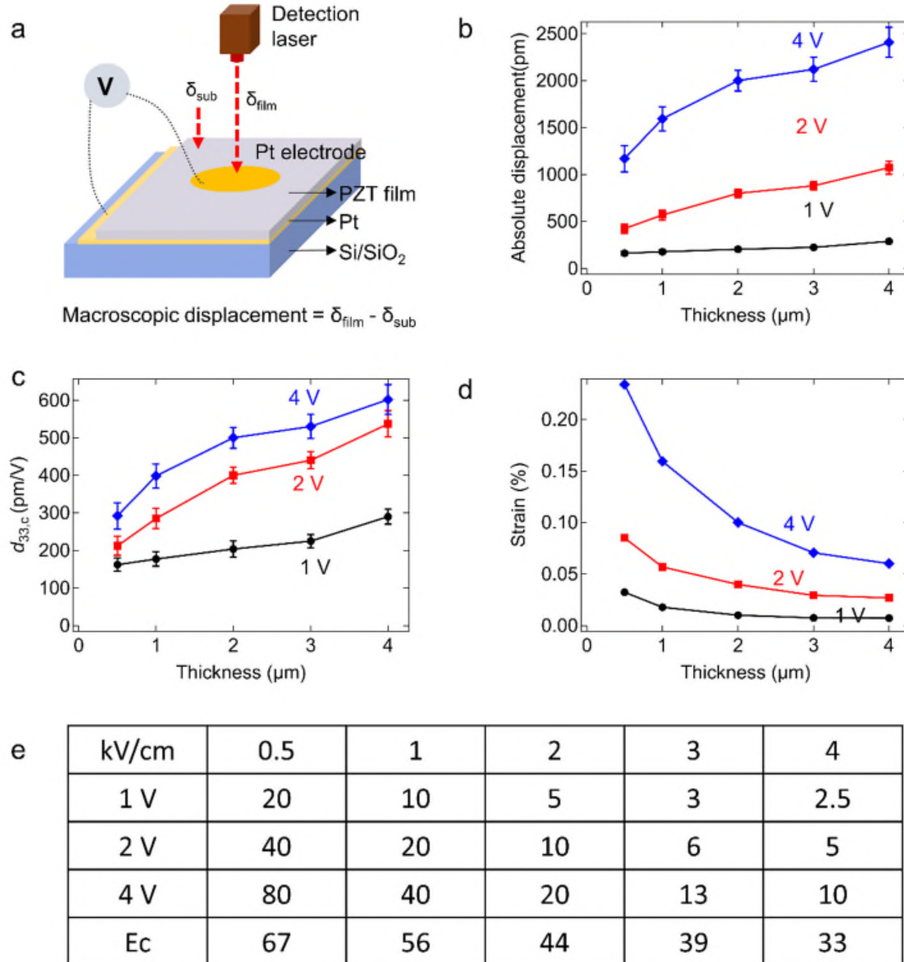


Fig. R1 The minimum LSV displacement value of ~160 pm in this study for the 0.5 μm PZT

film with measuring AC bias of 1V.

To further validate the data, we calculated the strains from the actual displacement measured at 4 V. It is in the range of 0.06 – 0.23%, which is reasonable for PZTs as reported in many thin films and bulk materials.

Revisions in the Supplementary File:



kV/cm	0.5	1	2	3	4
1 V	20	10	5	3	2.5
2 V	40	20	10	6	5
4 V	80	40	20	13	10
Ec	67	56	44	39	33

“

Supplementary Fig. 7. The converse piezoelectric coefficient $d_{33,c}$ of films with different thicknesses, as measured using a laser scanning vibrometer (LSV)[4,5]. a, Schematic of the measurement setup. The electrode used has a diameter of 2.5 mm, the same as that for direct piezoelectricity measurements. To rule out the bending effect in the measurements, the sample is adhered to the platform by silver paste, and both the displacement from the non-electroded area (i.e., the substrate displacement, δ_{sub}) and the electroded area (δ_{film}) are measured, with the effective displacement being obtained by subtracting the substrate value. **b and c,** The absolute displacement and calculated $d_{33,c}$ of the films as a function of thickness and applied AC bias. Note that normally DC bias above the coercive field is used to pole the film, while the superimposed AC bias is used to

measure the displacement through LSV method. In the current work, to demonstrate its self-poling character, only AC bias constrained below 4 V with a frequency of 1 kHz is used. As anticipated, the self-poled film shows measurable displacement even without any substantial external poling. However, the converse effect is significantly clamped by the substrate at a measuring bias of 1V. The clamping effect will be weakened with increasing bias voltage. Therefore, with slightly increasing bias to 4V, $d_{33,c}$ is greatly enhanced, reaching 293-602 pm/V for films with thicknesses ranging from 0.5 μm to 4 μm in thickness, being comparable to $d_{33,d}$. **d,** The calculated strain of the films at the bias of 4V. Notably, applying the same bias of 4V to films with increasing thickness will lead to reduced electric field and strain in the films. However, these strain values are reasonable for PZT films, considering that the applied fields are near or below their coercive fields, as compared in panel **e.** This demonstrate the validity of these measurements." (Revised Supplementary File, Page S8, Supplementary Fig. 7)

Comment 4: Response to Comment 5: The authors respond that the larger cell volume of Ti-rich PZT than Zr-rich PZT is due to stress relaxation and polarization alignment. However, it is difficult to be convinced of this discrepancy based on these reasons alone.

Response: We sincerely appreciate the reviewer's professional comment.

Please note that our film has a bulk-like thickness per layer (100 nm), and is mainly dominated by a polycrystalline characteristic with significant out-of-plane texture but in-plane grain titling. Thus, unlike epitaxial thin films, it should possess both *c* and *a* domains in each grain akin to bulk ceramics. Due to the strong polarization alignments, we originally considered each grain as a mono domain and displayed the absolute lattice parameters *c* and *a*. However, after conducting more STEM-HAADF analysis, we identified two representative Ti-rich regions:

(1) For regions with relatively strong polarization alignment, the statistical *c*/*a* ratio for Zr-rich and Ti-rich regions (with estimated Zr/Ti ratios of 70:30 and 30:70) as calculated from more than two dozens of HAADF images are 0.994 versus 1.024, showing an increase towards the $PbTiO_3$ end member. This is consistent with previously reported *c*/*a* ratios for thick $Pb(Zr_{70}Ti_{30})O_3$ and $Pb(Zr_{30}Ti_{70})O_3$ films on silicon substrate as shown below. Note that the EDX spectra shows a smooth transition of the composition from 70:30 to the nominal 52:48, and to 30:70, thus the lattice *c* and *a* also show smooth transition. The lattice *a* is not always the same for Ti-rich and Zr-rich regions as seen from all statistical data. Additionally, our intention was to demonstrate statistical *c*/*a* ratio

variation along the composition transition, we thus replace the absolute lattice parameters with statistical *c*/*a* ratios to avoid confusions. The *c*/*a* results are more robust and reliable for non-epitaxial polycrystalline materials, supporting the key conclusions of our study.

Table S1 The lattice parameter of bulk PZT ceramics and PZT films with different Zr/Ti ratio on different substrates.

	Lattice	30:70	40:60	~52:48	70:30	Ref
Bulk	***c*** **(Å)**	**4.15**	**4.14**	**4.12**	**4.10**	**Chung, C.-C, Doctoral Dissertations**
	a **(Å)**	**3.99**	**4.02**	**4.08**	**4.10**	
Film on Si (tensile stress on *a*)	***c*** **(Å)**	**4.14(T)**	**4.14(T)**	**4.14(T)**	**4.11**	***Appl. Phys. Lett.*** **121, 162907 (2022); Mater. Chem. Phys., 102 (2007) 159–164**
	a **(Å)**	**4.00(T) 4.07(R)**	**4.02(T) 4.08(R)**	**4.07(T) 4.07(R)**	**4.11**	
	c*/*a	**~1.027**	**~1.022**	**~1.017**	**~1**	
Film on STO (compressive stress on *a*)	***c*** **(Å)**	**-**	**4.18**	**4.15**	**4.15**	***J. Appl. Phys.*** **93, (2003) 4091–4096.**
	a **(Å)**	**-**	**4.03**	**4.07**	**4.09**	

(2) At Ti-rich regions with more random polarization distribution (such as that near a grain boundary), the *c*/*a* ratio can decrease from the aforementioned 1.024 to 0.996. This indicates a normal Poisson's effect as constrained by the adjacent Zr-rich unit cells. In these localized regions, this result is similar to those found in epitaxial grown thin superlattices such as 4 nm $Pb(Zr_{65}Ti_{35})O_3$/4 nm $Pb(Zr_{30}Ti_{70})O_3$, with *c*/*a* ratio from 1.016 to 0.987 at these two regions due to lattice constraint and Poisson's effect.

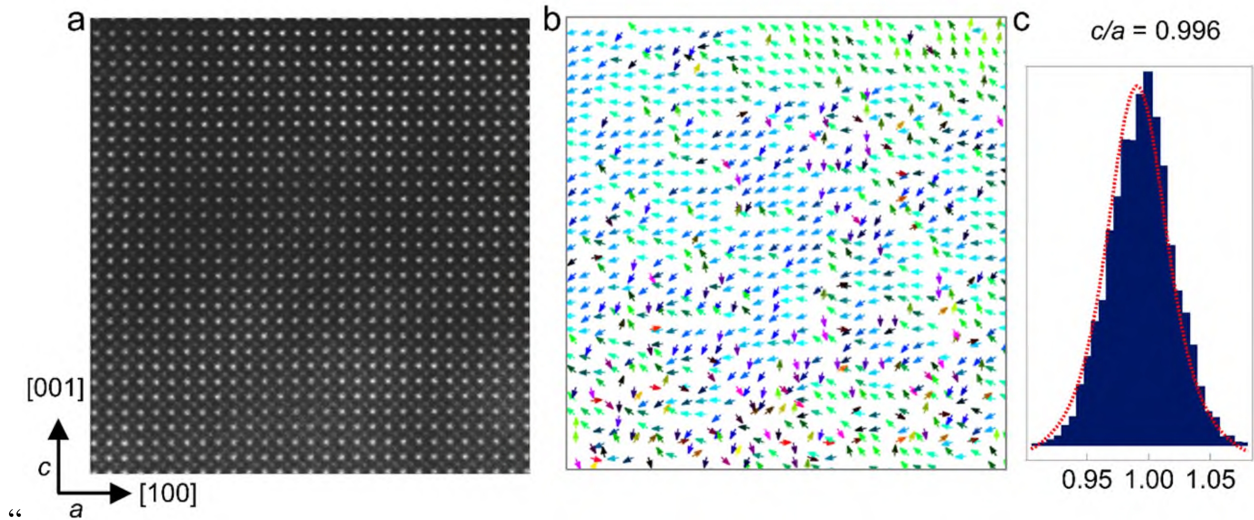
We have made revisions in the manuscript and supplementary File based on these discussions as referred below.

Revisions in the Manuscript: "Atomic-scale STEM-HAADF images of Zr-rich and Ti-rich regions in each 100 nm-thick individual layers can be obtained (Fig. 3d and e). The representative statistical *c*/*a* ratio for Zr-rich and Ti-rich regions (with estimated Zr/Ti ratios of 70:30 and 30:70, respectively), were calculated from more than two dozens of HAADF images, yielding values of 0.998 versus 1.025, showing an increase towards the $PbTiO_3$ end member. This is consistent with previously reported *c*/*a* ratios for thick $Pb(Zr_{30}Ti_{70})O_3$ and $Pb(Zr_{70}Ti_{30})O_3$ films on silicon substrate (Supplementary Table 1). As the Zr/Ti composition gradually transitions from 30:70 to the nominal 52:48 and then to 70:30, as identified from the EDXS spectra (Fig. 3b), a corresponding smooth transition in the *c*/*a* ratio within

each 100 nm layer is expected. Therefore, a strain gradient with a maximum value reaching ~ 3% can be induced by Zr/Ti segregation (i.e., the composition gradient) in each PZT layer. The magnitude of this strain aligns with that introduced in the phase field simulation, as shown in Fig. 1. ” (Revised Manuscript, Page 10, Lines 228-239)

“The discernible positions of the *A*-site (Pb) and *B*-site (Zr and Ti) atomic columns can be used to quantify the displacement of *B*-site cations relative to *A*-site cations (i.e., localized polarization). As shown in the polarization maps (Figs. 3 f and g, left), the polarization orientations within both Zr- and Ti-rich regions exhibit out-of-plane tendency, coinciding with the [001] driving force and texture of the film. However, Fig. 3f shows certain antiparallel nano-domains within the Zr-rich regions, likely due to the antiferroelectric nature of $PbZrO_3$ (indicated by black dashed lines). This antiferroelectric characteristic is observed to reduce the polarization alignment strength (Fig. 3f) in the Zr-rich regions compared to that in the Ti-rich regions. Furthermore, it is found that the strong polarization alignment is largely correlated with their localized *c*/*a* ratio, particularly in the Ti-rich regions. For instance, at Ti-rich regions with more random polarization distribution (such as those near grain boundaries), the *c*/*a* ratio decreases from the aforementioned 1.025 to 0.996. This indicates a normal Poisson’s effect as constrained by the PZ unit cells (Supplementary Fig. 11) in some localized regions, similar to what has been observed in epitaxial grown thin superlattices, such as 4 nm $Pb(Zr_{65}Ti_{35})O_3$/4 nm $Pb(Zr_{30}Ti_{70})O_3$, of which the *c*/*a* ratio shifts from 1.016 to 0.987 due to lattice constrains and Poisson’s effect[33]. These reflect complexity of localized lattice structures in polycrystalline textured films, especially those with elemental transitions and polarization alignment as observed here.” (Revised Manuscript, Page 10, Lines 248-266)

Revisions in the Supplementary File:



“**Supplementary Fig. 11. Ti-rich regions with less out-of-plane polarization alignments compared to that shown in the main text. a**, STEM-HAADF images at selected Ti-rich regions. **b**, The maps of atomic-scale polarization as calculated from the *A*- and *B*-site atomic positions in corresponding STEM-HAADF images. **c,** Histogram of the *c*/*a* ratio.” (Revised Supplementary File, Page S14, Supplementary Fig. 11)

Supplementary Table 1 The lattice parameter of bulk PZT ceramics and PZT films with different Zr/Ti ratio on different substrates. Notably, the MPB and Ti-rich compositions of films on the silicon substrates are previously reported with rhombohedral and tetragonal coexistence[6].

	Lattice	30:70	40:60	52:48	70:30	Ref
Bulk	*c* (Å)	4.15	4.14	4.12	4.10	7
	a (Å)	3.99	4.02	4.08	4.10	
Film on Si (tensile stress on *a*)	*c* (Å)	4.12(T)	4.14(T)	4.14(T)	4.11	6,8
	a (Å)	4.00(T) 4.07(R)	4.02(T) 4.08(R)	4.07(T) 4.07(R)	4.11	
	c/*a*	~1.027	~1.022	~1.017	~1	
Film on STO (compressive stress on *a*)	*c* (Å)	-	4.18	4.15	4.15	9
	a (Å)	-	4.03	4.07	4.09	

(Revised Supplementary File, Page S13, Supplementary Table 1)

We really appreciate the time and effort that the reviewers have invested in evaluating our manuscript entitled "High piezoelectric property with exceptional stability in self-poled ferroelectric films" (*NCOMMS-24-33730B*). We acknowledge reviewer 2 for the positive comments

Reviewer #2:

General Comment:

The authors have satisfactorily answered the reviewer's comments, and I think this paper can be accepted for publication.

Response: We appreciate the Reviewer's valuable feedback.

The paper addresses challenges associated with ferroelectric films, particularly their susceptibility to depolarization and degradation in piezoelectric properties at high temperatures, which are common in CMOS processing environments. Additionally, the reliance on external poling procedures can be impractical for thin films in miniaturized MEMS devices. To tackle these issues, the authors propose a two-step approach that involves texture construction and hierarchical heterogeneity engineering. However, the originality of the work is questionable, as it builds on well-established concepts like self-polarization without offering significant innovation or clear differentiation from existing research. Furthermore, the experimental validation is inadequate, with no evidence showing potential applications in CMOS or MEMS devices.

Some of the following details should be addressed to be published.

Comment #1: The paper describes a two-step approach for enhancing the piezoelectric properties of thin films using a simple spin coating process. This method involves constructing textures and engineering hierarchical heterogeneity within the film by applying multiple layers via spin coating and annealing them to achieve the desired microstructure and composition gradients. However, the feasibility of achieving such complex structural and compositional control using just a spin coating process is questionable. Also, the annealing process over 700°C, as described in the paper, involves high temperatures that may not be compatible with standard CMOS or MEMS processes. Such elevated temperatures could limit the process's flexibility, making integrating these ferroelectric films into CMOS or MEMS-based devices problematic. The authors should address the compatibility of their annealing process with the standard CMOS or MEMS technology to ensure that the proposed method is viable for practical applications.

Comment #2: The authors mention that the material demonstrates impressive resilience to elevated temperatures up to its Curie temperature of 350°C, with less than a 16% degradation in performance. However, there are no additional demonstrations to prove that this concept can be applied in CMOS platforms, which require not only high-temperature processes but also exposure to reactive ions, large electric fields, and RF plasma during fabrication. The authors should explore these aspects to ensure the material's compatibility with demanding process conditions.

Comment #3: The comparison between the PZT-based ferroelectric material and other materials presented in Fig. 4 is reasonable to demonstrate the results of this study. However, when discussing the d33 factor in comparison with other materials, the statement, "In addition to their prominent thermal stability, the studied PZT films exhibit small-signal d33,d surpassing that of the most actively researched and/or commercially available ferroelectric films," requires further clarification. Bi-based materials exhibit higher Curie temperatures (Tc) and d33 values than in this paper [1-3]. The paper appears to focus solely on ‘self-poled’ materials, and it would be more accurate and precise to define these boundaries when making such comparisons.

[1] Zhang, Shujun, Clive A. Randall, and Thomas R. Shrout. "Characterization of perovskite piezoelectric single crystals of 0.43 BiScO 3–0.57 PbTiO 3 with high Curie temperature." *Journal of Applied Physics* 95.8 (2004): 4291-4295.
[2] Zhang, Shujun, Clive A. Randall, and Thomas R. Shrout. "High Curie temperature piezocrystals in the BiScO 3-PbTiO 3 perovskite system." *Applied Physics Letters* 83.15 (2003): 3150-3152.
[3] Liu, Zenghui, et al. "Recent progress in bismuth-based high Curie temperature piezo-/ferroelectric perovskites for electromechanical transduction applications." *Current Opinion in Solid State and Materials Science* 26.5 (2022): 101016.

Comment #4: While the measurement setup for quantifying the direct d33,d of thin films appears to provide accurate piezoelectric data, the paper lacks a detailed explanation of the thermal characterization method and the device setup, particularly concerning temperature reliability. The authors should clarify the actual in-situ temperature experienced by the piezoelectric material rather than simply stating the applied temperature to ensure that the device's thermal stability is appropriately assessed. Furthermore, to address the first concern, the authors should provide additional details about the materials used in the thermal experimental setup, including the specifics of the thermocouples, their thermal conductance properties, and how these components are integrated within the system. This clarification is necessary to ensure the reliability and accuracy of the experimental system.

Comment #5: In this study, self-poling was conducted on a silicon wafer, but comparing the self-poling effects across different types of wafer substrates would be beneficial. Additionally, it would be valuable to include results demonstrating whether the self-poling effect remains consistent after the samples are diced from the wafer.

Comment #6: Generally, piezoelectric materials operate in thickness mode, but depending on the aspect ratio, they may function in other modes as well. If the developed poling technique exclusively generates a thickness mode response, the paper must articulate this claim more clearly.

Comment #7: In addition to the results obtained from the 4 μm PZT film, experiments should be conducted on films with other thicknesses to ensure the broader feasibility of the findings. Although it is mentioned that experiments were conducted on films ranging from 0.5 to 4 μm, if the 4 μm results are the only ones presented as reliable, it raises concerns about the overall trustworthiness and consistency of the data.