Room Temperature Voltage Tunable Phonon Thermal Conductivity via Reconfigurable Interfaces in Ferroelectric Thin Films

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Supporting Information:

Synthesis of Pb(Zr$_{x}$Ti$_{1-x}$)O$_3$ bilayers

PZT bilayer films were prepared via chemical solution deposition using a hybrid chelate, inverted mixing order chemistry,$^1$ using a procedure based upon the work of Kartawidjaja, $et$ al.$^2$ 0.35 M solutions containing 70/30 and 30/70 ratios of zirconium/titanium were prepared by adding designated amounts of titanium isopropoxide to zirconium butoxide (80 wt% in butanol) under ambient conditions and stirring for approximately five minutes. Four molar equivalents of glacial acetic acid was added to the alkoxide precursors and allowed to react and stir for approximately five minutes prior to the addition of methanol. The solution was stirred for approximately five minutes. Lead (IV) acetate was added to the solutions with 27 and 20% molar excess for the 70/30 and 30/70 compositions, respectively, to account for losses to the furnace atmosphere and into the substrate electrode stack. The solution was heated to 90 °C while stirring until dissolution of the lead (IV) acetate and a clear solution resulted. The molarity of the solution was decreased through two alternating additions of methanol and four molar equivalents glacial acetic acid while stirring at room temperature. The solutions were spin cast onto substrates consisting of 100 nm platinum/40 nm ZnO/400 nm SiO$_2$/001-oriented silicon, with the metallization layers (Pt and ZnO) prepared via 30° off-axis rf magnetron sputtering as described elsewhere.$^3$ All solution layers were dispensed through a 0.2 micron PTFE filter and spun at 4000 RPM for 30 seconds. To prepare the bilayer structures, the 70/30 layer was deposited first and was placed on a 425 °C hotplate for 1 minute to pyrolyze the solvents and begin to consolidate the gel. The sample was allowed to cool and two layers of the 30/70 composition were deposited via spin casting and pyrolyzing at 300 °C for 1 minute followed by a 425 °C hotplate pyrolysis for 1 minute. The film was then fired to 700 °C for 10 minutes by directly inserting into a preheated furnace with an air atmosphere. Film layer thicknesses were 57 ± 4 nm and 142 ± 3 nm for the 70/30 and 30/70 layers, respectively. Platinum top electrodes were deposited through a shadow mask via rf magnetron sputtering to define ~500 µm × 500 µm pads. These pads were used both to
apply fields across the PZT and to act as the thermal transducer for TDTR measurements. The thicknesses of these top electrodes were measured with profilometry.

Physical Characterization

*X-ray diffraction* was performed using a Bruker Phaser D2 instrument with Cu Kα radiation. Figure S1 shows the X-ray diffraction pattern for the film studied in this work. Only peaks attributable to the PZT film layers and substrate stack are observed. There is no obvious crystallographic texture present.

![X-ray diffraction pattern](image.png)

**Figure S1.** X-ray diffraction pattern for the PbZr₀.₇Ti₀.₃O₃/ PbZr₀.₃Ti₀.₇O₃ bilayer film studied in this work.

*Scanning electron microscopy (SEM)* was performed within a Zeiss Supra 55VP SEM in in-lens imaging mode with a 3 kV accelerating voltage. Figure S2 shows a representative plan-view scanning electron micrograph of the bilayer film. Average lateral grain size was measured using the linear intercept technique and was found to be ~860 nm.
Figure S2. Plan-view scanning electron micrograph of the PZT bilayer. Levels and gamma adjustments were applied to this image to increase brightness and contrast.

Electrical property characterization was performed with a Radiant Technologies RT-66a instrument, a HP4192 LCR meter, and a Keithley 236 source measure unit at room temperature. Figure S3(a) shows nested hysteresis loops collected at the slowest measurement frequency (<200 Hz). Clear evidence of hysteretic response is observed with reasonable loop saturation. A remanent polarization value of 20.3 \( \mu \text{C/cm}^2 \) and coercive fields of -50 and 150 kV/cm can be measured from the response. Rayleigh analysis was performed for the film in the unpoled and poled states to verify that the domain structure was altered by poling.\(^4\) Figure S3(b) shows the AC field dependence (peak-to-peak amplitude) for the real component of dielectric permittivity at 3 kHz in the unpoled and remanent poled ferroelectric states. The slope of the response contains the irreversible contribution to permittivity. The increase in this irreversible contribution in the remanent poled state is consistent with a more complex domain structure, or one with more mobile domain walls.\(^5\) Likewise, the reversible contribution to the real component of permittivity, the intercept with the permittivity axis, also increases after poling, suggesting that the overall domain wall density or mobility increased.
Figure S3. (a) Polarization versus electric field for the PZT bilayer film and (b) AC field dependence of dielectric permittivity prior to and after measurement of the polarization response with maximum field of 460 kV/cm.

Leakage current through the film under a 10 V applied bias was measured to be 1 micro-amp with a 500 µm × 500 µm electrode. This corresponds to a leakage power (Joule heating) of 30 µWatts or 9.4 mW/cm². This leakage current represents approximately 5 orders of magnitude less power than the incident laser pulses during TDTR measurements and suggests that Joule heating cannot account for the decrease in thermal conductivity measured.

Transmission electron microscopic (TEM) observations of the film were conducted in a JEOL 2010F TEM operated at 200 keV and a probe corrected FEI 80-200 Titan TEM/STEM, equipped with a SuperX high throughput energy dispersive x-ray spectrometer (EDS). TEM specimens were prepared by focused ion-beam (FIB) procedures using an FEI DB235 instrument. The area of interest was first protected with a layer of electron beam and then ion beam deposited platinum. Milling of the sample to electron transparency was accomplished with a 30 kV Ga⁺ ion beam. Final polishing employed a 5 kV Ga⁺ beam at 42 and 56 degrees tilt, with one side cut free to reduce sample bowing. We confirmed the thicknesses of the films layers from EDS maps collected in the FEI Titan STEM (Figure S4). This approach allowed us to
unambiguously discern the thicknesses of the two PZT layers based on the relative zirconium and titanium x-ray signal intensities. Figure S5(b) shows selected area electron diffraction pattern obtained from the PbZr$_{0.3}$Ti$_{0.7}$O$_3$ layer in Figure 1(a). The pattern is indexed as two superimposed 90° domain variants with zone axes oriented along [021] (red) and [012] (blue) directions. The stripes in the image in (1a) are aligned with the [100] direction and are normal to the (012) (red) and (021) (blue) reflections in the diffraction pattern. This arrangement is consistent with 90° domain walls lying on (011) (red) and (011) (blue) planes, which for this grain orientation would be inclined away from an edge-on alignment with the imaging direction by 18.6°.

**Figure S4.** High Angle Annular Darkfield (HAADF) STEM image and x-ray map intensities from PZT film. The thicknesses of the lower PbZr$_{0.7}$Ti$_{0.3}$O$_3$ and upper PbZr$_{0.3}$Ti$_{0.7}$O$_3$ layers were determined from the relative change in zirconium and titanium signal intensity.
Figure S5. (a) Bright-field transmission electron micrograph of a PZT bilayer film imaged in cross-section showing a stripe pattern of 90° ferroelastic domains in the upper PbZr$_{0.3}$Ti$_{0.7}$O$_3$ layer. (b) Selected area electron diffraction pattern obtained from the PbZr$_{0.3}$Ti$_{0.7}$O$_3$ layer in Figure 1(a) of the main text. The pattern is indexed as two superimposed 90° domain variants with zone axes oriented along [021] (red) and [012] (blue) directions. The stripes in the image in (1A) are aligned with the [100] direction and are normal to the (012) (red) and (021) (blue) reflections in the diffraction pattern.

Piezoresponse force microscopy was performed on a Digital Instruments Dimension 3100 atomic force microscope using sharp <20 nm Pt coated tips (DPER-XSC11 tips from MikroMasch) with nominal resonance frequency of 12-18 kHz. PFM images were collected near the cantilever’s in-contact resonance frequency to enhance the lateral resolution. The imaging signal of 2.5 V$_{\text{peak}}$ voltage at ~58 kHz was provided by an external function generator. The out-of-plane (vertical PFM) signals were collected. All PFM data presented is the $X$ data channel ($R \times \cos \theta$ image) in uncalibrated units. The phase was adjusted to minimize the data in the $Y$ channel. Figure S6(a) shows the same PFM image as in Figure 1(c). Figure S6(b) shows the out of plane raw piezoresponse force signal collected along the black line in panel (a) showing the width of the single domains.
Figure S6. (a) PFM image shows the same piezoresponse force image as Fig. 1c in the main text. (b) shows the out-of-plane raw piezoresponse force signal collected along the black line in panel (a) showing the distance between domain walls for this particular stripe domain region.

Figure S7 shows the vertical PFM signals for a series of sequential poling experiments. Figure S7(a) shows the as-deposited domain structure. The center region (700 × 700 nm) of the area was then poled by scanning the area with a constant bias of +8 V applied to the tip at each pixel for 2.1 ms. A scan rate of 1 Hz for 512 points on a 700 nm line was used. The domain structure after poling is shown in Figure S7b.
Figure S7. PFM images showing domain switching in the bilayered thin films. (a) vertical PFM images before applying DC bias, (b) vertical PFM image after applying +8 V DC bias within the white rectangular box.

Channeling contrast scanning electron microscopy was performed within a Zeiss Supra 55VP SEM operating with a 20 kV accelerating voltage and imaged with a solid state, KE Development LTD, Four Quadrant Backscattered Electron detector Type 211. The working distance for all data shown was 4.5 mm. The use of a short working distance increases the image contrast due to changes in crystallographic orientation. To perform in operando domain switching observations, a 3 nm thick platinum film was deposited through a shadow mask via rf magnetron sputtering. The 3 nm thick electrode was deposited overlapping a previously deposited 80 nm electrode to enable visual observation of the electrodes for wire bonding. The sample was mounted to an alumina plate with silver paint and gold wires (1 mil diameter) were bonded to the electrode pads with silver epoxy (Epo-Tek H20E). The gold wires were bonded to 22 gauge copper wire to allow connection to an electrical feedthrough on the SEM chamber. Backscattered SEM images were collected viewing through the 3 nm platinum electrodes and three 3 V batteries (Energizer ECR2016 lithium) were used to supply electric fields across the sample during imaging to alter the domain structure. Domain contrast is achieved via the differential channeling of incident electrons in regions of slightly different crystallographic orientation. The finite tetragonal distortion of the PZT 30/70 layers is sufficient to allow for this contrast. Levels and gamma adjustments have been applied to the SEM images to enhance contrast. The levels were adjusted from 0-255 to 0-111 and a gamma value of 0.64 was applied to each image using Adobe Photoshop.
Time domain thermoreflectance (TDTR)

Time-domain thermoreflectance is a non-contact, optical pump-probe technique that has been used extensively over the past decade to measure the thermal properties in a wide variety of materials and nanosystems. The experiment is based on the detection of the thermoreflectance response of a thin metal film when subjected to a modulated heating event, and then relating this response to the flow of heat into the layers adjacent to the metal film. This is accomplished by splitting the femtosecond pulse train emanating from a Ti:Sapphire oscillator (Spectra Physics Tsunami emanating 800 nm center wavelength laser pulses with 10.3 nm of bandwidth at an 80 MHz repetition rate) into two paths; a pump path and a probe path. The pump path is sinusoidally modulated using an Electro-Optic Modulator (EOM, ConOptics 350-160 driven by a 25A linear amplifier) and frequency doubled via a BiB₃O₆ (BiBO) crystal (~400 nm output wavelength) to ultimately provide improved signal-to-noise via two-color filtering between pump and probe. The probe path is routed down an adjustable delay stage to control the relative time between the arrival of the pump and probe pulses. The paths are recombined and concentrically focused onto the sample surface, and the back reflection of the probe from the metal transducer is focused onto a photodiode to monitor the change in thermorelectance via a lock-in amplifier (Stanford Research Systems, SRS 844). Figure S8 depicts a diagram of the experimental setup at the University of Virginia.

Figure S8. Schematic of the TDTR system at the University of Virginia.
The data from each TDTR scan is fit to a multilayer thermal model\textsuperscript{8-10} via a least-squares fitting routine to extract values for the parameters of interest, including the thermal conductivity of different layers and the thermal boundary conductance between layers. To do so accurately, the heat capacities and thicknesses of each layer must be known as inputs for the model. The heat capacities of platinum and silicon at room temperature were taken from the literature,\textsuperscript{11,12} as are their thermal conductivities (accounting for the reduction in thermal conductivity of the platinum thin film).\textsuperscript{13-15} For the 30/70 and 70/30 PZT layers, the heat capacities were calculated as a stoichiometric average of the heat capacities of PbZrO\textsubscript{3} and PbTiO\textsubscript{3} taken from the literature.\textsuperscript{16} To validate the calculated heat capacity for PZT compositions using this method, our calculated heat capacity for 30/70 PZT is within 2\% of the value reported by Rossetti et al.\textsuperscript{17} The thickness of the platinum electrodes was measured via profilometry (Veeco Dektak 8, calibrated on a 48 nm standard to ±1 nm) and the thicknesses of the 30/70 and 70/30 PZT layers were determined from energy dispersive spectroscopy (EDS) maps collected during STEM imaging that are shown in Figure S4.

Figure S9 shows the sensitivity to various parameters for the four-layer thermal model used in this experiment, as described in Ref. 9. The sensitivities shown correspond to a modulation frequency of 2.57 MHz, which was chosen to minimize the sensitivity to the thermal boundary conductance between the top platinum electrode and the 30/70 PZT top layer ($h_{K,1}$) while providing increased sensitivity to the thermal conductivity of the 30/70 PZT top layer ($\kappa_2$) between 100-2000 ps of time delay. However, this modulation frequency results in a thermal penetration depth of approximately 260 nm, thereby causing the model to also be somewhat sensitive to the thermal conductivity of the 70/30 PZT bottom layer (trace $\kappa_3$), as well as the effective thermal conductivity of the substrate layers beneath the bottom Pt electrode (trace $\kappa_4$).

To address this, a separate “calibration” sample of 70/30 PZT was deposited via CSD on a similar platinized-silicon substrate to enable determination of the thermal conductivity of the 70/30 PZT and the backside conductance between this layer and the platinized stack below. The thickness of this separate 70/30 PZT layer was determined via cross-
sectional SEM to be 80 ± 2 nm, and the thickness of the platinum electrodes was measured to be 81 ± 2 nm via profilometry. Three TDTR scans were performed on each of three different electrodes at a modulation frequency of 8.8 MHz, resulting in a thermal penetration depth of ~160 nm. The data was fit to a four-layer model, where layer one was the platinum top electrode \((C_v = 2.84 \text{ Jm}^{-3}\text{K}^{-1}, \kappa = 33.8 \text{ Wm}^{-1}\text{K}^{-1}, d = 81 \text{ nm})\), layer two was the 70/30 PZT \((C_v = 2.616 \text{ Jm}^{-3}\text{K}^{-1}, d = 80 \text{ nm})\) and layer four was SiO\(_2\) \((C_v = 1.92 \text{ Jm}^{-3}\text{K}^{-1}, \kappa = 1.4 \text{ Wm}^{-1}\text{K}^{-1}, d = 1 \text{ m (bulk)})\). Layer three was set as an effective conductivity calculated by adding the thermal resistances of the platinum bottom electrode \((\kappa = 33.8 \text{ Wm}^{-1}\text{K}^{-1}, d = 100 \text{ nm})\), the interface resistance between the platinum and ZnO (estimated to be ~100 MWm\(^{-2}\)K\(^{-1}\)) and the resistance of the ZnO layer \((\kappa = 4.5 \text{ Wm}^{-1}\text{K}^{-1} \text{ from Ref. 18, }d = 40 \text{ nm})\) via a series resistor model. This calculation results in an effective conductivity for layer three of 6.3 Wm\(^{-1}\)K\(^{-1}\), and \(C_v\) was set to 2.85 Jm\(^{-3}\)K\(^{-1}\) as the heat capacities of platinum and ZnO are nearly equivalent at room temperature. The interface conductance between the 70/30 PZT film and the bottom platinum electrode \((h_{K,2})\) was set equal to that between the top platinum electrode and the 70/30 PZT film \((h_{K,1})\) as these interfaces are chemically equivalent. The fitted data determined the thermal conductivity of the 70/30 PZT layer to be 2.01 ± 0.057 Wm\(^{-1}\)K\(^{-1}\) and the interface conductance between the 70/30 PZT and either electrode to be ~90 MWm\(^{-2}\)K\(^{-1}\).
Figure S9. Sensitivity of the four-layer thermal model to various parameters at a modulation frequency of 2.57 MHz. $h_{k,1}$ is the Kapitza conductance between layers 1 and 2; $C_{v,2}$ is the heat capacity of layer 2 (30/70 PZT); $\kappa_2$ and $\kappa_3$ are the thermal conductivities of layer 2 and layer 3 (70/30 PZT), respectively; $h_{k,3}$ is the Kapitza conductance between layer 3 and the remaining layers beneath.

With the thermal conductivity of the 70/30 PZT bottom layer and thermal boundary conductance between this layer and the platinum electrode now known, TDTR measurements were conducted on the bilayer samples to determine the change in thermal conductivity of the 30/70 PZT top layer due to an applied electric field. Figure 1(a) in the main text is a diagram depicting the sample geometry and measurement techniques applied to each device, and Table I summarizes the fixed values used in the four-layer model when fitting the TDTR data taken on the bilayer samples while under applied electric fields.
Table I. Fixed values employed or the 4-layer model when fitting the TDTR data acquired from the PZT bilayer samples while under applied electric fields.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Description</th>
<th>(d) (nm)</th>
<th>(C_v) (Jm(^{-3}) K(^{-1}))</th>
<th>(\kappa) (Wm(^{-1})K(^{-1}))</th>
<th>(h_K) (MWm(^{-2})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Platinum top electrode</td>
<td>62 ± 2</td>
<td>2.840</td>
<td>33.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pt: PZT 30/70 Interface</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>(2)</td>
<td>PZT 30/70 Top Layer</td>
<td>142 ± 3</td>
<td>2.707</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>30/70:70/30 PZT interface</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1000</td>
</tr>
<tr>
<td>(3)</td>
<td>PZT 70/30 bottom layer</td>
<td>57 ± 4</td>
<td>2.616</td>
<td>2.01</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70/30 PZT:Pt interface</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>(4)</td>
<td>Substrate</td>
<td>Bulk</td>
<td>1.920</td>
<td>2.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Measurements were made on several different devices both before any bias fields were applied (the unpoled, or virgin domain state), as well as over a range of applied biases (max ±10 V). Five TDTR scans were performed at each applied field condition to provide an assessment of uncertainty in the measurement. For each device, the laser spot was focused onto the top surface of the platinum top electrode and was left in the same spot for all of the applied field conditions. This reduced the uncertainty due to variations in the thickness of the platinum top electrode that would need to be included had the measurement location changed on every scan. The \(1/e^2\) radii of the pump and probe beams when focused on the sample surface were measured via a beam profiler (Thorlabs, BP104-UV) and are approximately 14 \(\mu\)m and 6 \(\mu\)m, respectively. Note that this is significantly larger than the average grain size of the sample measured and therefore represents that many grains are measured at once. As mentioned previously, the pump beam was sinusoidally modulated at 2.57 MHz using an electro-optic modulator to minimize our sensitivity to \(h_{K,1}\) relative to the thermal conductivity of the 30/70 PZT top layer (See Fig. S9).

The optical power delivered to the sample by both the pump and probe beams was measured using a thermopile-based power meter (Newport 919P series), and varied between 7-14 mW for either beam on any given measurement period. There are two
separate temperature rises within the area of the laser spot due to the optical power delivered to the sample; one is a DC (or steady-state) temperature rise due to both the pump and probe, while the second is an AC temperature rise associated with the modulated pump beam. Details concerning the calculations of these temperature rises can be found in Refs. 8 and 19. As a worst-case assessment, we calculate these temperatures for pump and probe powers of 14 mW at the 1/e² spot sizes mentioned earlier, assuming an absorptivity of 15% in platinum at 800 nm and 55% at 400 nm. We calculate a maximum steady-state temperature rise of 1.75-2 K due to the absorption of DC pump and probe power. Additionally, we calculate a maximum AC temperature rise due to the 2.57 MHz sinusoidally modulated pump beam of between 1.7-2.4 K, assuming that the thermal conductivity of the 30/70 PZT top layer is somewhere between 1-2 m⁻¹ K⁻¹. Therefore, the maximum overall temperature rise in the sampled area during the measurement is between 3.45-4.4 K.

DC electric fields were applied to the bilayer devices using an LCR meter (Hewlett Packard 4284A) and a probe station (JmicroTechnology, Inc., LMS-2709) that is integrated into the TDTR system. Before making electrical contact, base-line measurements were made of each device in the unpoled, virgin domain state. Following this, contact was made and confirmed via the measurement of the capacitance of the device using the LCR meter at a measurement frequency of 1 kHz and an AC small-signal measurement amplitude of 100 mV RMS. This AC field applied across the device (~4.6 kV/cm RMS) is not expected to result in any significant electrocaloric effects in the PZT at a drive frequency of 1 kHz and at room temperature operation (far from any phase transitions in either part of the bilayer). To confirm this, different small signal values up to 1 V RMS (~46 kV/cm RMS) were also applied during measurement and no differences in the TDTR signals or calculated thermal conductivity could be observed. Bias voltages of up to ±10 V in magnitude were applied in 2.5 V increments, resulting in maximum electric fields of ~460 kV/cm. The loss tangent was monitored during the application of the bias to the film and did not exceed 0.03 during the test, indicating that the sample was stable during the measurement and no breakdown events occurred. Additionally, measurements were made with the DC bias set to 0 V after applying
maximum field with both polarities to compare the thermal conductivities of the 30/70 PZT top layer in both the unpoled, virgin states and the poled, remanant states.

The TDTR data collected under the applied electric fields were then fit to the aforementioned multilayer thermal model to determine the thermal conductivity of the 30/70 PZT top layer ($\kappa_2$). Based on the measurements made on the 70/30 PZT calibration sample, the thermal conductivity of layer three is set to 2.01 Wm$^{-2}$K$^{-1}$ for 70/30 PZT and the interface conductances between the platinum electrodes and adjacent PZT layers ($h_{K,1}$, $h_{K,1}$) are both set to 90 MWm$^{-2}$K$^{-1}$. Additionally, we assume that the thermal boundary conductance between the 30/70 top and 70/30 bottom PZT layers ($h_{K,2}$) is essentially infinite ($>1 \times 10^9$ Wm$^{-2}$K$^{-1}$). While we expect that this is not the case in actuality, this assumption is made because we are unable to definitively characterize domain structure across the interface between the PZT layers via the techniques available. As a result, any possible effects localized near the interface specifically are lumped into the overall conductivity of the 30/70 PZT top layer ($\kappa_2$). The thermal conductivity of the 30/70 PZT top layer ($\kappa_2$) and the thermal conductivity of the substrate ($\kappa_4$) are treated as free parameters when fitting the data with the least-squares algorithm. The thermal conductivity of the substrate must be fit in order to gain agreement between the data and the model and consistently yielded a value of 2.3 ± 0.2 Wm$^{-1}$K$^{-1}$ for all fits of the TDTR data. At our modulation frequency, the TDTR measurements do not probe below the SiO$_2$ layer, so in effect, this SiO$_2$ can be treated as a semi-infinite substrate. Therefore, the effective value for $\kappa_4$ determined during the fit represents the total thermal resistance measured from the substrate stack comprised of 100 nm platinum on 40 nm ZnO on an effectively semi-infinite substrate of SiO$_2$, and the Pt/ZnO and ZnO/SiO$_2$ interface resistances. We assume the heat capacity of this final layer to be equal to that of the SiO$_2$ substrate since this effectively semi-infinite layer provides the most thermal mass that is probed in our substrate stack, and our out-of-phase signal is more affected by this layer compared to the other layers in the substrate.
Figure S1. Dependence of thermal conductivity on applied DC electric field for a PZT bilayer sample at room temperature.

Figure S10 shows the results for $\kappa_2$ from a different electrode on the same sample than presented in the main manuscript. Increasing the magnitude of the electric field across the device decreases the thermal conductivity of the 30/70 PZT. PFM and SEM analyses of the 30/70 PZT top layer showed that the domain wall density increases when this film is subjected to an applied electric field. Additionally, we have shown in previous work$^{21}$ that increased domain wall density reduces the thermal conductivity in single crystalline BiFeO$_3$ films with different numbers of domain-variants. Therefore, the decrease in the thermal conductivity is attributed to an increase in the rate of phonon scattering at domain boundaries when the density of domain walls increases in the presence of an electric field. Furthermore, we see that there is a clear relationship between film thermal conductivity and applied electric field, highlighting the tunable nature of these devices.

It should be noted that the black data point corresponds to the thermal conductivity of the 30/70 PZT top layer in the unpoled, virgin domain state, while the blue and green data points at zero field represent the thermal conductivity when the DC fields were removed following either positive or negative poling at maximum field ($\pm 460$ kV/cm), which represent the remanent ferroelectric polarization states. The difference between the
thermal conductivities in the unpoled versus poled states is believed to be due to the domain configuration that persists when the electric field is removed.

To further demonstrate the functionality of the thermal device, we monitored the thermoreflectance of the platinum top electrode in real-time as bias was applied and removed (see Figure 2(b) in the main manuscript). In this measurement, the probe delay relative to the pump pulse was fixed at 150 ps to minimize the sensitivity of the model to changes in the thermal boundary conductance between the top platinum electrode and the 30/70 PZT top layer relative to the sensitivity of the 30/70 PZT top layer while allowing nearly full diffusion of deposited layer energy through the platinum electrode (i.e., reducing the sensitivity to the thermal conductivity of the platinum). The thermoreflectance of the platinum electrode is directly related to the temperature of the metal. Therefore, for a fixed power deposited on the sample by the laser and resulting heat flux through the sample structure, any changes in the temperature of the top electrode are indicative of changes in the thermal resistance of the multilayer structure beneath it when bias is applied or removed. This allowed for real time observation of the dynamic switching of the thermal conductivity of the 30/70 PZT top layer.

As a final check, we performed the same measurements on a metal-insulator-metal structure with amorphous alumina \((a{-}\text{Al}_2\text{O}_3, 135 \text{ nm thick})\) as the insulating layer; a structure in which we do not expect to see any affect on the thermal conductivity under applied electric fields due to the absence of any microstructure in such a disordered film. Figure S11 plots the thermoreflectance response of the platinum top electrode in real time at a fixed delay of 150 ps. As in the case of the bilayer sample (Figure 2b), the DC field across the sample was switched between 0 kV/cm and ± 370 kV/cm and held across the structure for approximately 2 min. Unlike the bilayer sample, no change in the thermoreflectance was observed in response to an applied electric field, indicating that the thermal properties of the \(a{-}\text{Al}_2\text{O}_3\) remain constant under an applied field. This result lends further evidence that the tunability of the domain structure within the PZT bilayer under applied electric fields is the cause of the observed change in the thermal conductivity in our reported results.
Figure S11. Real-time thermoreflectance signal measured via TDTR at a fixed delay of 150 ps for a platinum/$a$-Al$_2$O$_3$/platinum metal-insulator-metal structure as the applied electric field is cycled between 0V (0 kV/cm) and ±5 V (± 370 kV/cm). No changes are observed in the thermoreflectance signal, indicating that the response exhibited by the PZT bilayer films is unique to that structure.

Image analysis and domain perimeter detection

The domain perimeters were found using an intensity based edge detection algorithm, the Laplacian of Gaussian (LoG) Method, implemented in MATLAB Image Processing Toolbox. This method finds edges by identifying zero crossings after filtering the image with a LoG filter. The algorithm has two variables, a threshold, specified as 0 to create closed continuous contours, and a sigma value, the standard deviation of the LoG filter that determines the amount of smoothing. Sigma was varied from 3 to 7 pixels corresponding to a range where detected edges aligned to visually recognizable domain features. Prior to edge detection, all images were first normalized and converted to grayscale.
An example of domain perimeter detection on the vertical PFM signal is shown in Figure S12. The normalized PFM image is shown in Figure S12(a). The edges detected at the bounding ends of the sigma values (3 and 7) are shown in Figs. S12(b) and S12(c), respectively. One can notice that the domain perimeter is over-counted at $\sigma = 3$ and undercounted at $\sigma = 7$, indicating a $\sigma$ value somewhere between is closer to the actual perimeter.

**Figure S12.** (a) shows normalized grayscale image, (b) edge detection with $\sigma = 3$ pixels of the same image shown in (a), (c) edge detection with $\sigma = 7$ pixels of the same image shown in (a). All images are 1040 nm on a side. Note that the identified line edge length for (b) is significantly higher than for (c) and that noise is included in the edge identification of image (b). This results in over counting of domain length for a $\sigma$ value of 3 and undercounting for a $\sigma$ value of 7.

For every set of images processed with the edge detection algorithm, the perimeter was calculated as a function of $\sigma$ to remove visual bias, as shown in Figure S13. It was found that the perimeter was usually higher for all $\sigma$ values for the poled image for most of the sets of PFM images, but not all. This may be expected as differing grain orientations may be expected to have differing domain structure responses to the poling process. The perimeter values extracted for all PFM images were evaluated at $\sigma = 4.68$, which was intermediate to the clear over and under detection extremes. Figure S14 shows the percentage change of domain boundary length/unit area for six measured regions on the PZT bilayer film. To provide some detail on the sensitivity of the edge detection algorithm, the error bars on Fig. S14 represent the edge lengths measured for $\sigma$-values of
3.63 and 5.53. We observe a decrease in domain boundary length for two of the scanned regions, but increases for four others. Since these films possess randomly oriented grains, it may be anticipated that some grain orientations will realize a strain minimization by decreasing their domain wall densities, which may explain the measured decreases in some regions compared to the increases measured in other regions.

**Figure S13.** Measured perimeter as function of Gaussian $\sigma$ for the image shown in Figure 3(a) and (b) in the main manuscript.
Figure S14. Quantified percentage change in domain wall density from the unpoled state for PFM-poled regions.

The same domain perimeter detection algorithm was applied to the channeling contrast SEM images. Individual grains were extracted from the larger image from the series of 4 domain states. The grains chosen were those for which we could clearly identify domain structure in each of the 4 conditions. The individual grains were registered to each other using topographic features (boundaries and pores) and sharpened as necessary. The domain perimeter was then found for the extracted grains as a function of $\sigma$ ranging from 5 to 15. An example of an extracted grain as well as the domain perimeters for $\sigma=5$ and $\sigma=15$ are shown in Figure S15. Similar to the PFM images the variation of $\sigma$ removed visual bias from the analysis and shown in Figure S16. The ideal $\sigma$ used to extract the domain perimeter was chosen as 6.58. This value was chosen as it appeared to best identify the domain boundary edges without overcounting pixel noise in the images. The edge identification results for four different grains and their quantified percentage changes in surface domain wall length are shown in Figure S17. Here we see that some grains had increases in domain boundary length of $\sim 1\%$, while others increased by $\sim 10\%$. Again, to show the sensitivity of the edge detection algorithm to the chosen $\sigma$ value, the error bars on Figure S17(e) (also shown Figure 3(k)) show the calculated perimeter percentage change using $\sigma$ values of 5.00 and 8.68. As can be seen there is some
sensitivity to the value chosen, however, all quantifications of domain perimeter change result in increases from the negative poled state while the electric field is applied. Overall, each of the grains where domain structure could be unambiguously resolved in the experiment showed increases in domain wall length while the electric field was applied.

Figure S15. (a) extracted grain image, (b) edge detection with $\sigma = 5$ pixels, (c) edge detection with $\sigma = 15$ pixels. Similar to the PFM images, it can be seen that the $\sigma = 5$ value in (b) over counts the domain length by including noise and that the $\sigma = 15$ value in (c) under counts the domain length. This guided the selection of a $\sigma = 6.58$ value for counting domain wall length in the SEM images.
Figure S16. Measured perimeter as function of Gaussian $\sigma$ for the grain shown in Figure S13 and Figure 3 in the main text.

Figure S17. (a)-(d) Channeling contrast SEM images of a PZT bilayer film with edge identification applied to four specific grains. (e) shows the quantified changes in domain wall density relative to the negative poled state for the grains identified in panel (a).

Heat capacity dependence on applied field

The constant electric field heat capacity in ferroelectrics can differ from the constant pressure value according to the following equation: $^{23}$
\[ C_E = C_p - \alpha PT \left( \frac{dP}{dT} \right)_E, \]

where \( \alpha \) is a constant related to the Curie Constant, \( T \) is absolute temperature, and \( P \) is polarization. If the ferroelectric material is measured at a temperature where large changes in the temperature dependence of polarization \((dP/dT)\) occur \(i.e., \) near a phase transition), then there will be difference in the constant field heat capacity. However, it is known that for first order phase transition ferroelectrics, such as PZT, far from the phase transition that \( dP/dT \) is negligible. To show this, Figure S18 shows the measured polarization response of the PZT bilayer film at 24 °C and 50 °C. It is found that both the zero field and high field polarization values do not change with temperature. This results in \( dP/dT \) being zero for both zero field (remanent) and applied field conditions. Therefore the second term on the right side of the equation is zero and the heat capacity under constant applied field, both at zero field and applied fields of 460 kV/cm, equals the heat capacity under constant pressure: \( C_{E,0V} = C_{E,460kV/cm} = C_p \).

Figure S18. Polarization versus electric field for the PZT bilayer film at 24 °C and 50 °C.
References:


