

Beyond Substrates: Strain Engineering of Ferroelectric Membranes

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Strain engineering in perovskite oxides provides for dramatic control over material structure, phase, and properties, but is restricted by the discrete strain states produced by available high-quality substrates. Here, using the ferroelectric BaTiO₃, production of precisely strain-engineered, substrate-released nanoscale membranes is demonstrated via an epitaxial lift-off process that allows the high crystalline quality of films grown on substrates to be replicated. In turn, fine structural tuning is achieved using interlayer stress in symmetric trilayer oxide-metal/ferroelectric/oxide-metal structures fabricated from the released membranes. In devices integrated on silicon, the interlayer stress provides deterministic control of ordering temperature (from 75 to 425 °C) and releasing the substrate clamping is shown to dramatically impact ferroelectric switching and domain dynamics (including reducing coercive fields to <10 kV cm⁻¹ and improving switching times to <5 ns for a 20 μm diameter capacitor in a 100-nm-thick film). In devices integrated on flexible polymers, enhanced room-temperature dielectric permittivity with large mechanical tunability (a 90% change upon ±0.1% strain application) is demonstrated. This approach paves the way toward the fabrication of ultrafast CMOS-compatible ferroelectric memories and ultrasensitive flexible nanosensor devices, and it may also be leveraged for the stabilization of novel phases and functionalities not achievable via direct epitaxial growth.

lattice distortions in epitaxial films or dynamically by applying stress or external fields. Integrating the diverse functionalities of complex oxides into semiconductor^[1–7] and flexible^[8–12] electronics is a major technological challenge that has motivated extensive work. But despite considerable effort, the structural, chemical, and thermal mismatches between such substrates and complex-oxide materials often yield films with considerably worse crystal quality than that attained on single-crystal perovskite substrates. Alternative strategies for hetero-integration via substrate release and transfer, mimicking the fabrication processes of van-der-Waals heterostructures,^[13–15] are just now beginning to yield single-crystal oxide films on arbitrary substrates,^[16–21] thus circumventing the constraints of epitaxial growth. Moreover, these detached films no longer experience mechanical constraint from the substrate, giving more flexibility in structural manipulation and heterostructure assembly.

Strain control over the lattice structure is particularly impactful in ferroelectrics where the polarization is directly connected to structural distortions.^[22,23] In thin films, strain can define the optimal operating temperature regime^[24–26] or domain configuration^[27–29] that will boost electro-mechanical or thermal functionalities,

Perovskite ABO₃ oxides can display an immense number of phases and functions by merely changing the A- and B-site cations. Even within a single chemistry, multiple phases can be in competition, and their stability can be tuned statically by fixing

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whose associated susceptibilities (piezo-/pyroelectricity) are enhanced at temperatures near phase transitions^[30] or when competing microstructures coexist.^[31–34] While strain is typically introduced by lattice mismatch with a substrate in epitaxial films, released films relax their lattice towards their bulk crystal structure; therefore, different approaches to manipulate properties are required. Mechanical and electric-field manipulation of micrometer-sized freestanding flakes in electron-microscopy experiments^[35,36] and straining experiments on polymer-supported ultrathin perovskite membranes (restricted to films <10 nm in thickness)^[37,38] have demonstrated their exceptional flexibility. Whereas transfer to polymers or electroactive substrates has been exploited to tune magnetic properties,^[38–40] test the resilience of ferroelectric properties,^[41–43] or induce ferroelectricity in non-polar materials,^[44] deterministic strain control of properties has not been demonstrated on single-crystal ferroelectric membranes.

Mechanical separation of a film from the substrate is also expected to facilitate polarization switching processes, either by enabling ferroelastic events limited by substrate constraint,^[45] or by reducing domain-wall pinning at the substrate/film interface.^[46] Structural inhomogeneities emerging in unclamped membranes, however, can mask the impact of the substrate release on the switching kinetics.^[47] Therefore, preserving high crystal quality in the ferroelectric membranes after the release is important to identify intrinsic changes in switching mechanisms and domain-wall mobilities with the aim of lowering switching times, as is sought after for ultra-high-speed, non-volatile memories,^[48] memristors,^[49] and neuromorphic networks.^[50]

Here, we demonstrate that high-quality nanoscale epitaxial films of the ferroelectric $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ can be transferred from single-crystal oxide substrates to silicon and polymer substrates without structural degradation. Heterostructure design, supported by simple elastic and thermodynamic modeling, provides for continuous tuning of the lattice distortion of trilayer membranes (i.e., oxide-metal electrode $\text{Ba}_{1-y}\text{Sr}_y\text{RuO}_3$ /ferroelectric $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ /oxide-metal electrode $\text{Ba}_{1-y}\text{Sr}_y\text{RuO}_3$) and deterministic control of critical temperature, polarization, and switching voltage over a wide range. The ferroelectric membranes also display faster switching kinetics upon release, resulting from modified domain-wall dynamics, with switching times of just a few nanoseconds upon application of low-voltage pulses. Finally, capacitor-based devices integrated on flexible polymer substrates are demonstrated with high room-temperature dielectric susceptibility and strain sensitivity that also exhibit large strain-induced changes of dielectric permittivity ($\approx 90\%$ with just $\pm 0.1\%$ strain) with varying substrate curvature. This work demonstrates the versatility of film transfer to integrate oxide functionalities designed ad hoc into any technological platform.

We focus on (001)-oriented films and symmetric heterostructures of the form $\text{Ba}_{1-y}\text{Sr}_y\text{RuO}_3$ ($y = 1$ or 0.5 ; oxide-metal electrode (E) with thickness $t_E = 10\text{--}40$ nm)/ $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0$ or 0.2 ; ferroelectric (FE) with thickness $t_{FE} = 100$ nm)/ $\text{Ba}_{1-y}\text{Sr}_y\text{RuO}_3$ ($y = 1$ or 0.5 ; oxide-metal electrode (E) with thickness $t_E = 10\text{--}40$ nm) grown on GdScO_3 (110) substrates buffered with 7 nm of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ produced via pulsed-laser deposition (Experimental Section). As a shorthand notation, we will refer to these symmetric trilayer heterostructures using the form (x, y, z) where x and y denote the chemistry of

the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ and $\text{Ba}_{1-y}\text{Sr}_y\text{RuO}_3$ layers and $z = 2t_E/t_{FE}$ refers to the thickness ratio of the different layers and $t_{FE} = 100$ nm for all heterostructures. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ layer serves as an epitaxial, sacrificial-release layer that maintains the quality of the heterostructure, but allows for complete release of the symmetric trilayers upon immersion in an acidic solution (Experimental Section and Figure S1, Supporting Information). This etching process is highly selective to the sacrificial layer—as proven in previous works^[17,36,51,52]—and millimeter-size membranes with few or no visible cracks could be repeatedly produced (Figure S2–S3, Supporting Information). Following growth, these membranes were then transferred to either rigid silicon or flexible poly(ethylene terephthalate) (PET) substrates (Figure 1a, Experimental Section, and Supporting Information).

The crystallinity of all the layers is maintained in the films transferred to platinum-coated silicon, as observed in the X-ray diffraction line scans (Figure 1b) and in the sharp rocking curves about the 002-diffraction condition of BaTiO_3 (Figure 1c), which show comparable full-width at half-maximum to the epitaxial films grown on GdScO_3 substrates, and demonstrate significantly improved crystallinity compared to BaTiO_3 films grown directly on SrTiO_3/Si (001)^[4–7] (dashed lines, Figure 1c). Notably, the ferroelectric layer remains strained (2θ position of the BaTiO_3 peak shifted with respect to the expected bulk value after transfer), indicating that the electrode and ferroelectric layers remain epitaxially coupled in the transferred membranes, preventing complete lattice relaxation towards their respective bulk lattice parameters.

The structural coupling of the electrode and ferroelectric layers opens-up an unexplored opportunity to control the ferroelectric layer by engineering the mechanical constraints imposed by the electrode layers. A simple model that considers the elastic balance between the two electrode and ferroelectric layers in a freestanding heterostructure^[53] (Supporting Information) shows that the elastic compliances, lattice misfit u_{misfit} , and layer thickness ratio z can be used to tailor the strain in the ferroelectric layer, ϵ_{FE} (Figure 1d), the sign of which is exclusively determined by u_{misfit} . Conversely, in epitaxial films, the strain is dictated by the substrate (Figure S4, Supporting Information). In general, this strategy will be limited by the combination of electrode and ferroelectric layers that can be epitaxially grown without significant structural relaxation, as is the case for the $\text{Ba}_{1-y}\text{Sr}_y\text{RuO}_3$ and $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ layers used herein (Figure S5, Supporting Information). Here, the stress σ imposed on the ferroelectric layer is controlled by the strontium content (x in the ferroelectric layer and y in the electrode layers, see Supporting Information)—which determines the lattice and elastic parameters of the individual layers—and the thickness ratio z . This is illustrated in X-ray diffraction scans (Figure 1b), where the position of the 002-diffraction peak of the BaTiO_3 layer ($x = 0$) lies in the bulk position for a single-layer membrane (bottom scan, Figure 1b), is only slightly shifted to lower angles when using electrode layers with a small u_{misfit} of -0.3% ($y = 0.5$) and can be further shifted by continuously increasing the thickness of the electrode layers with a larger u_{misfit} of -1.5% ($y = 1, z = 0.2\text{--}0.8$).

Consequently, the room-temperature tetragonality (c/a lattice parameter ratio) of the BaTiO_3 can be tuned, as demonstrated by the evolution of the in-plane a and out-of-plane c lattice parameters of the BaTiO_3 membranes as a function of

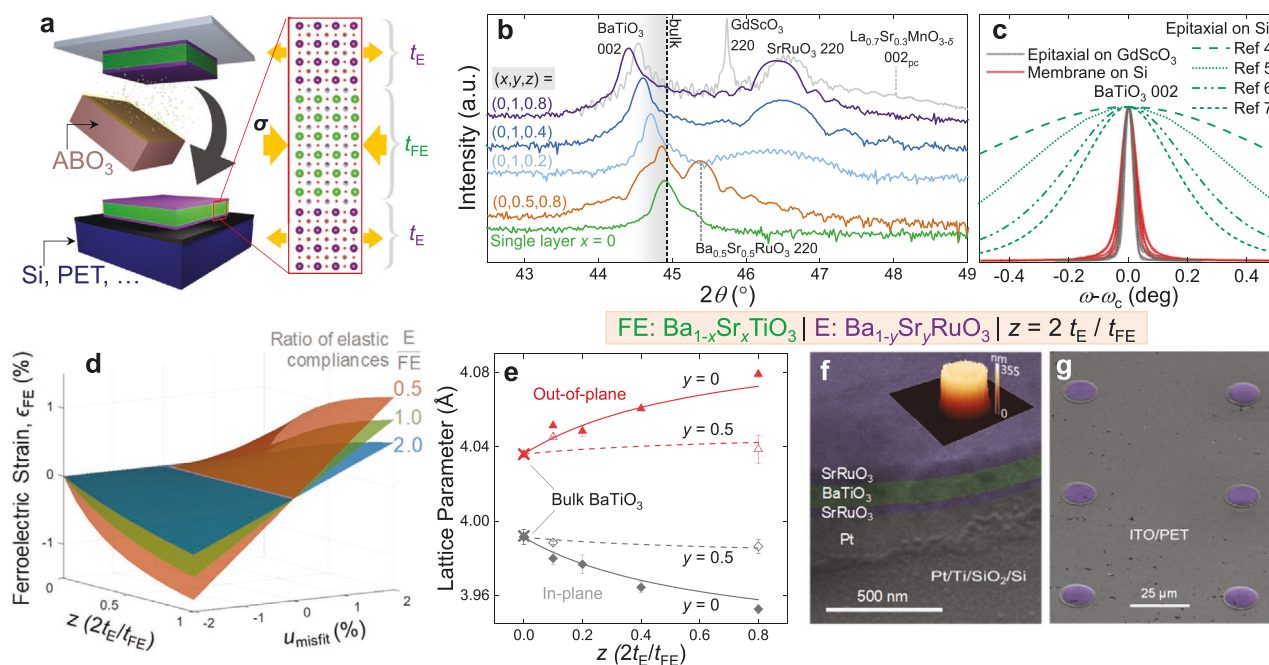


Figure 1. Fabrication and structural control of BaTiO₃ membranes and capacitor devices via elastic-boundary engineering. a) Membranes are fabricated via lift-off of an epitaxial heterostructure from a single-crystal oxide perovskite substrate by etching a sacrificial layer and subsequent transfer via polymer stamp onto an arbitrary substrate. After releasing the films from the substrate, the elastic balance between the electrode (E) and ferroelectric (FE) layers creates an internal stress σ . b) Top curves: θ - 2θ scans about the BaTiO₃ 002-diffraction condition for a $(x, y, z) = (0, 1, 0.8)$ trilayer heterostructure before lift-off (gray) and after transfer to silicon (purple); the BaTiO₃ peak is shifted with respect to the single-layer membrane (bottom curve) with increasing y and z values in the trilayer membranes on silicon. c) X-ray rocking curves about the 002-diffraction condition of all BaTiO₃ films, before lift-off (gray) and after transfer to silicon (red). Green dashed lines show different rocking curves found in the literature for BaTiO₃ films epitaxially grown on silicon. d) Calculations for the in-plane strain of a freestanding ferroelectric layer (FE) epitaxially constrained by two identical electrode layers (E) as a function of the in-plane lattice misfit (u_{misfit}), and layer-thickness ratio (z) for different ratios of elastic compliances ($S_{11} + S_{12}$) (Supporting Information). e) In-plane (gray diamonds) and out-of-plane (red triangles) lattice parameters of the BaTiO₃ layers constrained by electrode layers of SrRuO₃ (filled symbols) and Ba_{0.5}Sr_{0.5}RuO₃ (open) as a function of thickness ratio z . Cross symbols indicate the lattice parameters of bulk BaTiO₃^[25] and lines are calculations of the lattice parameters dependence with z , assuming elastic balance between layers, considering the bulk lattice parameters and elastic constants shown in Tables S1 and S2 (Supporting Information), and a BaTiO₃ Poisson's ratio of 0.35.^[69] f, g) Scanning electron microscopy images of: f) a capacitor fabricated on a trilayer membrane on a Pt/Ti/SiO₂/Si (001) substrate (wherein the inset is a 3D atomic force microscopy image of the capacitor) and g) capacitors transferred to ITO-coated PET.

the thickness ratio z for electrode compositions $y = 0.5$ and 1 (Figure 1e) as obtained from reciprocal space maps about the 103-diffraction condition of BaTiO₃ (Figure S6–S7, Supporting Information). The interlayer stress in the membranes provides finer structural control over the ferroelectric lattice than epitaxial strain on single-crystal substrates, which is limited to discrete values defined by the lattice parameters of commercially available crystals. In the following, we test the role of substrate release and interlayer stress on the evolution of the electrical properties of capacitor devices fabricated on Pt/Ti/SiO₂/Si (001) substrates after transfer (Figure 1f and Experimental Section), and the role of an external stress on capacitor devices fabricated on the growth substrate and transferred to indium-tin oxide (ITO)-coated PET (Figure 1g).

First, we use the Curie temperature (T_C) as an indicator of the influence of our heterostructure design on the ferroelectric properties of the BaTiO₃ membranes, since biaxial strain^[25] and strontium content^[26,54] are known to strongly affect T_C . Using a thermodynamic model^[55,56] we can predict the temperature dependence of the ferroelectric polarization for all membrane varieties studied herein (Figure 2a). The critical temperatures

are shown to be widely tunable by varying x , y , and z and compare well with our experimentally observed peaks in dielectric permittivity measured as a function of temperature (Figure 2b and Figure S8a, Supporting Information). This suggests that the simple models of strain in the trilayer membranes are adequate to understand the evolution of the strain state and that our understanding of how to control the strain state of the ferroelectric is accurate. We can, therefore, either increase or decrease the T_C of our BaTiO₃ epitaxial films grown on GdScO₃ (having a misfit strain of $\sim 1\%$) upon release from the substrate depending on the selection of the ferroelectric layer composition (x), electrode material (y), and thickness ratio (z) (Figure S8b, Supporting Information), with T_C values scaling linearly with the measured c/a ratio for these membranes (Figure 2c); here showing control across ≈ 350 °C.

Having observed that the strain state and, therefore, the structure of the ferroelectric layer can be tuned in a deterministic fashion, this has other implications for ferroelectric properties. For instance, the tetragonality also controls both the depth of the double-well potential and the energy barrier for polarization reversal (i.e., the larger c/a is, the more stable

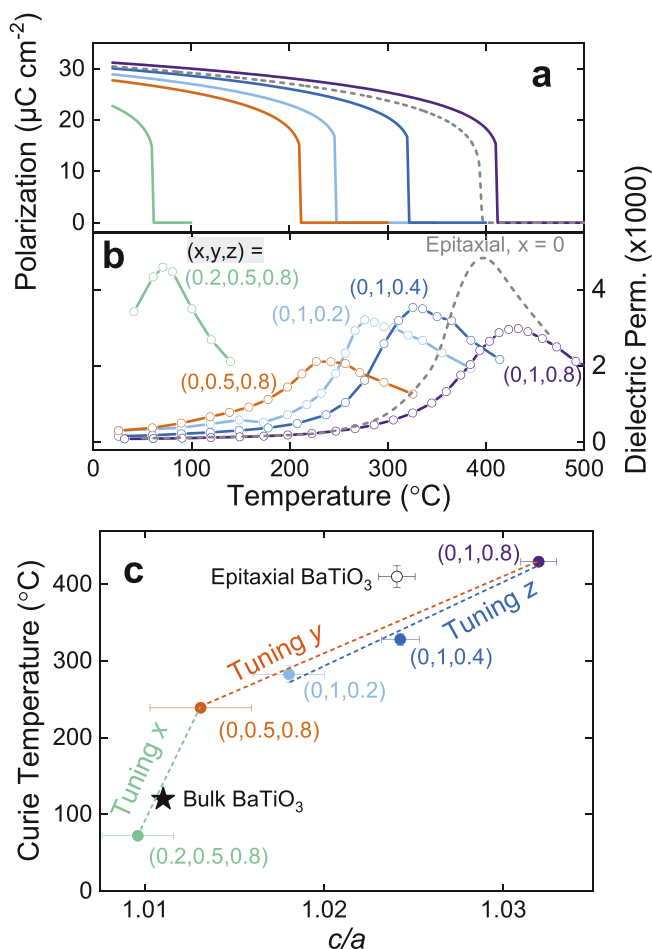


Figure 2. Engineering the Curie temperature of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ membranes on silicon. a) Simulated temperature dependence of polarization and b) measured temperature dependence of dielectric permittivity for capacitor devices of various (x, y, z) heterostructure types transferred onto silicon substrates (dashed curves correspond to epitaxial BaTiO_3 membrane grown on GdScO_3 substrate). Peak widening in the membrane samples may be caused by small strain gradients introduced by small differences in the top and bottom electrode growth conditions (see Experimental Section). c) Curie temperature obtained from the peak in permittivity in (b) (filled symbols) as a function of tetragonality in the ferroelectric layer, c/a . Dashed lines are guides to the eye, indicating the evolution of T_C when changing the tuning parameters x , y , and/or z . Transition temperatures obtained for the epitaxial BaTiO_3 samples grown on GdScO_3 (empty dot) and for bulk crystals^[25] (star) are also shown.

the polarization and the larger the coercive field should be at room temperature). The released membranes show changes of polarization and coercive field with respect to the as-grown epitaxial films (Figure S9–S10, Supporting Information) that correlate with their tetragonality: as c/a is increased, so does the polarization (Figure 3a). Furthermore, lower coercive fields for polarization reversal can be achieved by decreasing c/a (by increasing x or decreasing y and/or z), although this comes with the tradeoff of a decrease in the remanent polarization (Figure 3b). These results provide a possible strategy to target low-voltage device operation, provide access to coercive fields that approach single-crystal limits, and are some of the lowest reported for BaTiO_3 thin films. Indeed, we obtain coercive fields (voltages) as low as 12.8 kV cm^{-1} (128 mV) for BaTiO_3

membranes measured at 10 kHz (or 9 kV cm^{-1} (90 mV) when measured at 1 Hz ; Figure 3c), thus approaching the desired sub- 100 mV threshold.^[57] We note, further, that the frequency (f) dependence of the coercive field (E_c) is highly dependent on the mechanical constraints imposed on the films. From a log-log plot (Figure 3c) we identify a linear dependence that allows us to fit our data to the Ishibashi and Orihara model for domain-growth-limited switching,^[58] where $E_c \propto f^\beta$. The fitting reveals a decrease by a factor of 2 and 4 in the scaling exponent β , with respect to the epitaxial films, for membranes with $y = 1$ and 0.5 , respectively. Lower β values indicate lower frequency dispersion of coercive fields which implies higher domain-wall mobility.^[59] Faster dynamics under ac fields can be obtained by reducing the inhomogeneities caused by structural defects or surface roughness;^[60] however, these membranes show comparable structural quality and surface morphology to the epitaxial films, implying that the change of dynamics is directly related to the substrate release.

To provide further insight into domain-wall dynamics and the switching kinetics of the films, we performed pulsed-electric-field measurements (Experimental Section) on BaTiO_3 films ($x = 0$) with SrRuO_3 ($y = 1$) electrodes clamped to the substrate and in released membranes with different c/a ratios transferred to silicon substrates. From the polarization transients for an epitaxial, on-substrate film (Figure 3d) as well as released $(0, 1, 0.8)$ (Figure 3e) and $(0, 1, 0.2)$ (Figure S11, Supporting Information) membranes transferred to silicon substrates, we extract the characteristic switching times for polarization reversal t_0 obtained for the different amplitudes of the switching pulse as fit to the Kolmogorov–Avrami–Ishibashi (KAI) model^[61] (Experimental Section) (Figure 3f). The on-substrate BaTiO_3 film shows $t_0 = 17 \text{ ns}$ for a voltage pulse of 1.9 V , whereas the released $(0, 1, 0.8)$ membrane exhibits a $t_0 = 5 \text{ ns}$ and a similar value of switched polarization and for the $(0, 1, 0.2)$ membrane $t_0 = 3 \text{ ns}$, but the switched polarization is halved with respect to the epitaxial film (Figure S11, Supporting Information). While different circuit RC time constants for the three heterostructure variants can contribute to differences in the measured switching times, we find that after rescaling by RC (Experimental Section), the membranes on silicon still show faster switching times (higher switching speeds; right axis, Figure 3f), indicating that the switching times are intrinsically different and not exclusively determined by the electrode resistances. This result agrees with the observation of faster domain dynamics under ac fields shown above.

Further, we consider the energetics of the switching process: from the switching time dependence on the pulse amplitude, we obtain the activation field α from Merz's law,^[62] $t_0 \propto \exp\left(-\frac{\alpha}{E}\right)$, which results in values that are nearly 20% and 50% lower for the released $(0, 1, 0.8)$ and $(0, 1, 0.2)$ membranes, respectively (Figure 3f); implying that the domain walls require less energy to move after release from the substrate and reducing the elastic constraint (i.e., by reducing electrode thickness). This observation, together with the evidence of modified domain dynamics, points to a lower energy switching pathway upon removal of the mechanical constraint of the growth substrate. Calculations show that the energy to create 90° domain boundaries is significantly lower than that of their 180°

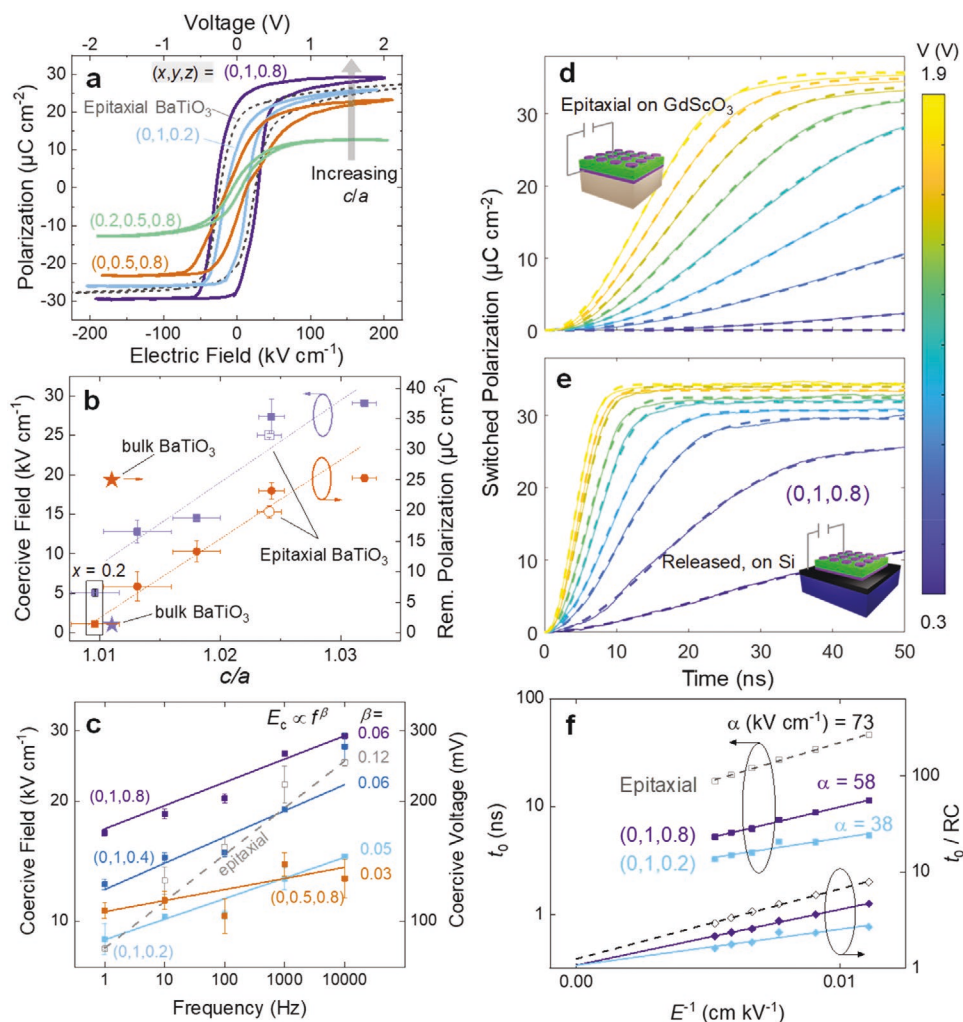


Figure 3. Controlling room temperature polarization and switching dynamics of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ membranes on silicon. a) Room-temperature ferroelectric polarization hysteresis loops measured at a frequency of 10 kHz on capacitor devices of various (x, y, z) heterostructure types transferred onto silicon substrates. Data for an epitaxial BaTiO_3 sample with SrRuO_3 electrodes are also shown (dashed). Ferroelectric hysteresis loops are corrected for bias imprint and permittivity contributions at high field. b) Coercive field (left axis) and remanent polarization (right axis) obtained from polarization hysteresis loops, as a function of c/a . Data for epitaxial samples on GdScO_3 substrates are shown as empty symbols and bulk BaTiO_3 data^[25] are shown as star symbols. Lines are guides to the eye. c) Frequency dependence of the coercive field (log-log plot) obtained for all BaTiO_3 membranes (filled symbols) and epitaxial films (open symbols). Lines are fit to the Ishibashi and Orihara model. d,e) Switched polarization obtained from the integration of the current transient after a switching voltage pulse of varying amplitude, for an as-grown BaTiO_3 epitaxial film (with 10 nm SrRuO_3 electrodes) on: d) GdScO_3 , and e) a BaTiO_3 membrane on silicon with SrRuO_3 electrodes of thickness 40 nm (data for BaTiO_3 membrane 10 nm SrRuO_3 electrodes shown in Figure S11, Supporting Information). Dashed lines are fits to the KAI model. f) Polarization switching times as a function of the inverse of electric field pulse amplitude for three BaTiO_3 films, before (left axis) and after (right axis) rescaling with the circuit RC time. Lines are fit to Merz's law.

counterparts,^[63] making it more favorable to realize the polarization reversal via two successive ferroelastic switching steps with creation of 90° domain walls, as observed experimentally in single crystals.^[64] In epitaxial films, however, substrate clamping prevents the formation and propagation of these 90° domain walls during switching due to the large elastic energy cost. The removal of this constraint in the membranes—which are only weakly bonded to the silicon substrate—likely permits the local strains generated by 90° domain walls to be readily accommodated thus facilitating a lower-energy switching process. Thus, the trilayer membrane strain engineering demonstrated herein allows one to decrease switching voltages, and the reduced mechanical constraints are shown to enable additional

switching mechanisms that improve switching speeds while maintaining high-quality interfaces and supporting long-term cycling stability ($>10^9$ cycles before breakdown; Figure S12, Supporting Information).

Lastly, we test the external stress control of our membranes by transferring capacitor devices to flexible substrates, which allows for the introduction of uniaxial tensile or compressive strains upon bending (Figure 4a). We can tune our (x, y, z) heterostructure parameters to obtain large susceptibilities at room temperature, by reducing T_C , and by searching for configurations in which multiple microstructural phases coexist such that small external stimuli (namely stress) can easily tune the phase stability. Expanding our thermodynamic

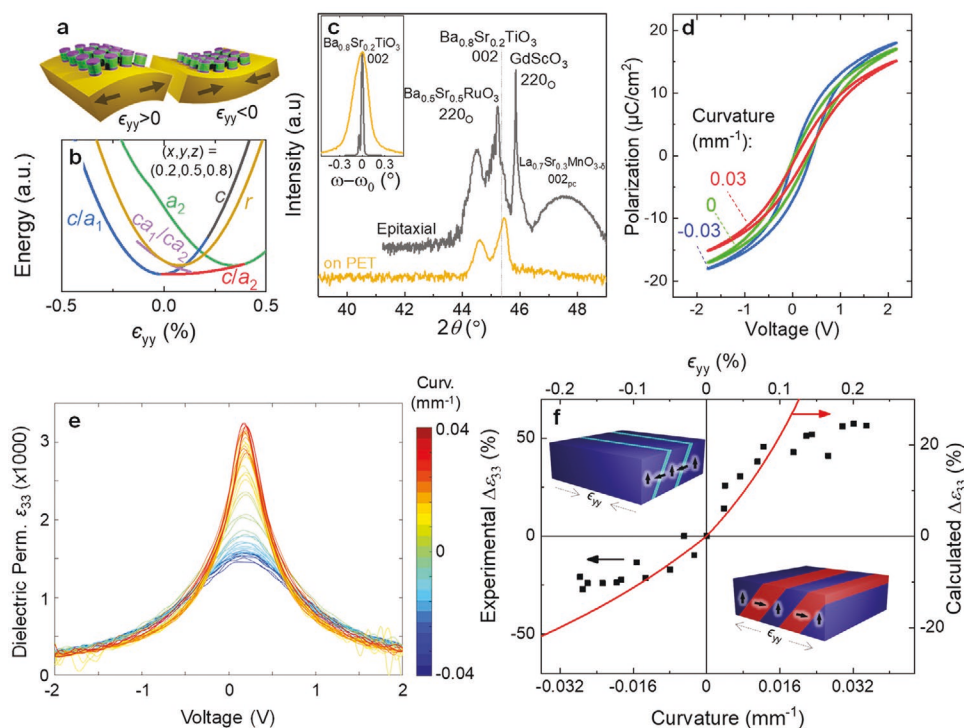


Figure 4. Strain manipulation of functional properties of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ membranes on flexible PET substrates. a) Capacitors transferred to a flexible PET substrate experience a uniaxial tensile (compressive) strain upon convex (concave) substrate bending. b) Calculated free energy density as a function of in-plane uniaxial strain for different domain configurations in a (0.2, 0.5, 0.8) membrane. c) θ - 2θ scan (main panel) and rocking curve (inset) about the 002-diffraction condition of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ grown on GdScO_3 (gray) and transferred to PET (orange). The rocking curve FWHM is increased on PET due to the larger surface roughness of the substrate. d) Ferroelectric hysteresis loops measured at 10 kHz under different bending conditions on capacitor devices transferred to PET. e) Voltage dependence of dielectric permittivity measured at 10 kHz under different substrate curvatures. f) Measured (left axis) and calculated (right axis) bending-induced dielectric tunability as a function of substrate curvature (bottom) and estimated bending strain (top). Experimental data are obtained from the peak dielectric permittivity in (e); the red line shows the strain dependence obtained from a phenomenological polydomain model; schematic drawings show the expected domain configurations from the model, for the largest strain values reached in the experiment (Figure S13, Supporting Information).

model to account for multiple single- and polydomain structures (including tetragonal, orthorhombic, and rhombohedral phases) and for a variable uniaxial strain ϵ_y (Supporting Information), we find that in a (0.2, 0.5, 0.8) heterostructure many of these structures are energetically close and the most stable phase can be tuned with a small uniaxial strain, here considered along the tetragonal [010] direction of BaTiO_3 (Figure 4b). When transferred to silicon substrates, the (0.2, 0.5, 0.8) membranes show $T_C \approx 70^\circ\text{C}$ (Figure 2a–c), resulting in a large dielectric permittivity near room temperature, as well as decreased polarization and switching voltage (Figure 3a,b). These membranes can also be transferred to flexible PET polymer substrates while maintaining high crystallinity and close-to-bulk lattice parameters (Figure 4c).

Using such PET-supported membranes, we explored the ferroelectric (Figure 4d) and dielectric (Figure 4e) response as a function of substrate bending (curvature). The uniaxial strain applied to the membranes can be estimated from the substrate curvature as $\epsilon = t_{\text{PET}}/2R$, where t_{PET} is the substrate thickness (125 μm) and R is the radius of curvature. Given that $t_{\text{PET}} \gg t_{\text{FE}}$, strain-gradient effects can be neglected. We observe that as the membranes are bent in a concave (convex) fashion, the polarization increases (decreases) and the dielectric permittivity decreases (increases) near zero bias. These results

can be qualitatively described by our thermodynamic model where polydomain c/a phases are found to be most stable in the strain range within our experimental reach (Supporting Information). At zero strain, a predominantly c -domain phase is expected and is observed. Compressive strain (convex bending) has little effect on the domain structure and favors the formation of a small fraction of a_1 domains (in-plane domains perpendicular to the strain direction) within the still predominantly c -domain matrix, whereas tensile strain (concave bending) favors a_2 domains (parallel to the strain direction) and increases their volume fraction with increasing strain (Figure 4b and Figure S13, Supporting Information). The experimentally observed bending-induced dielectric tunability ($\Delta\epsilon_{33} = (\epsilon_{33}^{\text{bent}} - \epsilon_{33}^{\text{flat}})/\epsilon_{33}^{\text{flat}}$) as a function of the substrate curvature R^{-1} , is found to change by nearly 90% and follows a trend similar to the tunability calculated from our thermodynamic model for low-strain values, within the $\pm 0.1\%$ strain range (Figure 4f). We note that the tunability values obtained experimentally (left axis, Figure 4f) exceed the calculated values (right axis, Figure 4f) by a factor of at least two, likely indicative of additional contributions from other coexisting phases or domain walls, not considered in the calculation. The measured dielectric response also shows a saturation behavior above curvature values of $\approx 0.1\%$ strain, potentially indicating sliding/slipping

of the capacitor structures under large bending curvatures, limiting the strain transmission in our experiment. While strategies for improved adhesion or clamping via microfabrication may be designed in order to increment the magnitude of the applied strain,^[65] our experiment demonstrates the high strain sensitivity of the single-crystal capacitors pre-designed to show large susceptibility at room temperature, with dielectric tunability values comparable to those obtained on Ba_{0.5}Sr_{0.5}TiO₃ and Ba_{0.67}Sr_{0.33}TiO₃ films grown on mica for curvatures 5 and 10 times larger, respectively.^[11,12]

In conclusion, we demonstrate that functionalities in heterostructured oxide nanomembranes can be designed by taking advantage of interlayer elastic interactions. In BaTiO₃-based nanomembranes, transition temperatures and coercive voltages can be manipulated via structural control and therefore adapted to the desired functionality. Likewise, in films transferred to silicon, it is possible to modify switching dynamics to reach nanosecond switching times. Ultimately, control over the membrane structure allows for the design of highly susceptible devices that display large sensitivity to external parameters, as exemplified for ferroelectric capacitors placed on flexible substrates displaying large dielectric tunability upon low-level straining induced by bending. The fabrication tools and strain-engineering strategies shown here should inspire future work transferring the well-known functionalities of perovskite oxides to semiconductor-based devices, or targeting new functions activated by strain not achievable by epitaxial growth. One could, for example, design heterostructured devices with asymmetric elastic boundary conditions, thus inducing strain gradients and enhancing flexoelectric responses on chemically homogeneous materials, fabricate freestanding devices out of suspended ferroelectric membranes with giant electromechanical performance, or apply mechanical straining methods to study unexplored elasto-/flexo-caloric effects^[66,67] in ferroelectric films.

Experimental Section

Synthesis of Epitaxial Thin Films and Single-Crystal Membranes: All films were grown using pulsed-laser deposition using a KrF excimer laser (248 nm, LPX 300, Coherent). Typical heterostructures are of the form t_E nm Ba_{1-x}Sr_xRuO₃/100 nm Ba_{1-x}Sr_xTiO₃/ t_E nm Ba_{1-x}Sr_xRuO₃/7 nm La_{0.7}Sr_{0.3}MnO₃ with t_E ranging from 0 to 40 nm, x fixed at either 0 or 0.2 and y fixed at 1 or 0.5; all heterostructures studied herein were grown on GdScO₃ (110) substrates (CrysTec GmbH). The La_{0.7}Sr_{0.3}MnO₃ and bottom Ba_{0.5}Sr_{0.5}RuO₃ growths were carried out at a heater temperature of 775 °C in a dynamic oxygen pressure of 20 mTorr with a laser fluence of 1.9 J cm⁻² and a laser repetition rate of 2 Hz. The bottom SrRuO₃ growth was deposited at 690 °C in 100 mTorr oxygen pressure with a laser fluence of 1.3 J cm⁻² and laser repetition of 15 Hz. The Ba_{1-x}Sr_xTiO₃ layers were grown at 600 °C in 40 mTorr oxygen pressure with a laser fluence of 1.5 J cm⁻² and a laser repetition rate of 2 Hz. The top electrode Ba_{1-y}Sr_yRuO₃ layers were grown at same laser conditions as the bottom-electrode layers but at a temperature of 600 °C. All layers were grown from ceramic stoichiometric targets of the same chemistry as the films (Praxair). Following growth, samples were cooled to room temperature at 10 °C min⁻¹ in a static oxygen pressure of 700 Torr.

To release the films from the GdScO₃ substrates, a polypropylene carbonate (PPC) film (Sigma Aldrich) was placed on a poly(dimethylsiloxane) (PDMS) stamp (Sylgard184 from Dow Corning) and the film surface was adhered to the PPC (Figure S1, Supporting

Information). The samples were then placed in a 1 mol L⁻¹ KI + 0.1% HCl solution and removed from it when the La_{0.7}Sr_{0.3}MnO₃ was fully dissolved, as ascertained by visual inspection. The freestanding films attached to the PPC polymer were then transferred to either 200 nm Pt/20 nm Ti/300 nm SiO₂/Si (001) or indium-tin-oxide-coated PET (Sigma Aldrich). Additional details of the transfer process are provided in the Supporting Information.

Structural and Surface Characterization: X-ray diffraction studies, including 2 θ - ω and rocking curve line scans about symmetrical reflections of the films and substrates, were collected with a Panalytical X'pert Pro3 diffractometer (copper $K_{\alpha 1}$, 1.540598 Å), using a hybrid 2-bounce primary monochromator on the incident beam side and a PIXcel3D position-sensitive detector. Pseudocubic in-plane and out-of-plane lattice parameters were obtained from reciprocal space mapping studies about asymmetrical reflections using the detector fast frame-based 1D mode. The offset angle ω for the membrane samples was obtained by averaging the peak ω value of the same reflection acquired at azimuthal angles of $\varphi = 0^\circ$ and $\varphi = 180^\circ$. Surface topography was studied using an atomic force microscope (MFP-3D, Asylum Research). Scanning electron microscopy was performed using a Quanta 3D field-emission-gun (FEG) scanning electron microscope.

Dielectric and Ferroelectric Measurements: Electrical measurements were performed on circular capacitor structures, defined on the films using dry etching via Ar-ion milling. The patterned circular electrodes studied herein were 20–40 μ m in diameter and were contacted with gold plated tungsten probe tips. For dielectric measurements, a small AC voltage (5 mV, 1–100 kHz) was applied between the microfabricated top electrode and the counter electrode and the capacitance $C = \epsilon \epsilon_0 A / t_{FE}$ was measured using an impedance analyzer (E4990A, Keysight Technologies). The capacitor area A used to extract the dielectric permittivity ϵ was measured with atomic force microscopy. Room-temperature polarization-electric field hysteresis loops were measured at frequencies from 1–10,000 Hz using a Precision Multiferroic tester (Radiant Technologies). The coercive field E_c was extracted as $(|E_c^+| + |E_c^-|)/2$, where $|E_c^+|$ and $|E_c^-|$ are the positive and negative field values for which the polarization is zero, and the remanent polarization was extracted as $(|P_r^+| + |P_r^-|)/2$, where $|P_r^+|$ and $|P_r^-|$ are the positive and negative values of polarization obtained at zero electric field after corrections of the loops for any bias field $(|E_c^+| - |E_c^-|)/2$. At least three different capacitors were measured for each sample, their hysteresis loop parameters were averaged, and the error was taken as the standard deviation. Electrical measurements under bending conditions were performed by fixing the polymer substrate to a metal foil or a polycarbonate sheet curved by a home-made three-point bending rig.

Switching-transient measurements were performed by applying a sequence of three voltage pulses with a pulse generator (Berkeley Nucleonics BN 765) across a series combination of the ferroelectric capacitor and a resistor and measuring the time dependence of the current through an oscilloscope (schematics of the measurement can be found in Ref. [68]). The first pulse (with a fixed amplitude of -2V and duration of 1 μ s) poles the ferroelectric in a well-defined state, the second pulse, of reversed polarity and duration of 0.5 μ s, switches the polarization, and the third pulse, identical to the second one and applied after a delay of 10 ns, measures the dielectric response in the absence of a switching event. The switching current transient is then revealed by subtracting the dielectric response from the switching response. RC times are extracted from the current transient (non-switching) of the third pulse. The oxide counter electrode is directly contacted in the as-grown film, while it is accessed through the less resistive platinum contact in the released films transferred to platinum-coated silicon. This yields a lower circuit RC time for the latter (≈ 2 ns versus ≈ 5 ns in the clamped film).

The polarization transients were fitted to the Kolmogorov–Avrami–Ishibashi (KAI) model for uniformly polarized ferroelectrics wherein,

$$\frac{\Delta P(t)}{2P} = 1 - \exp\left[-\left(\frac{t}{t_0}\right)^n\right] \quad (1)$$

where t_0 is the characteristic switching time and n is the effective dimensionality. Our fittings yield $n \approx 2$, consistent with a polarization reversal process with 2D domain wall propagation as the rate-limiting step.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

complex oxides on silicon, epitaxial lift-off, ferroelectric domain switching, flexible devices, strain engineering

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